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Procedures Used at the National Bureau of Standards To Determine Selected Trace Elements in Biological and Botanical Materials

Procedures Used at the National Bureau of Standards To Determine Selected Trace Elements in Biological and Botanical Materials

Edited by:

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FOREWORD

In the act of Congress which provides the basic authority of the National Bureau of Standards (NBS), an essential function of the Bureau is the "preparation and distribution of standard samples such as those used in chemical analysis . . ." and "the development of methods of chemical analysis . . .".

At the Bureau these two functions are closely joined in the Standard Reference Materials (SRM's) program. In this program the desired characteristics of a quantity of material, sufficiently large to make it available to a large number of users over a reasonably long time, is determined. By using these SRM's to calibrate instruments, to test the accuracy of newly developed methods, or in a routine program to monitor laboratory results, the quality of analytical data can be assured. More than nine hundred and fifty SRM's are available now from NBS for use in science and industry. These SRM's cover a large variety of applications and include inorganic and organic compounds certified for their chemical composition (major, minor, and/or trace elements), or for physical properties such as, for example, their optical, thermal, electrical, or radioactive characteristics.

A significant number of these SRM's are certified through the measurements performed in the Analytical Chemistry Division of the NBS Institute for Materials Research. These measurements require that the systematic and random errors of the procedures used to determine the particular element or compound desired be sufficiently well known to state the concentration of that analyte on the certificate within a required uncertainty level. It is one of the major responsibilities of the Division to select suitable procedures from the literature or, if necessary, to develop new or modified procedures to insure that the necessary accuracy is obtained during the certification process.

This publication contains a detailed description of the procedures used at NBS to determine twenty-five trace elements in biological and botanical matrices. They were used to determine the trace element content of spinach, orchard leaves, pine needles, tomato leaves, bovine liver, blood serum, etc. The dissemination of these procedures, and their careful use, should permit other analysts to perform measurements with an accuracy comparable to those obtained at NBS.

This volume was prepared at the request of the U. S. Environmental Protection Agency who also partially supported the development of the procedures and/or SRM's. The U. S. Energy Research and Development Administration also supported a portion of the work described in this report. This support is gratefully acknowledged.

Philip D. LaFleur, Chief
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July 1977

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SECTION II

PROCEDURES USED AT THE NATIONAL BUREAU OF STANDARDS TO DETERMINE SELECTED TRACE ELEMENTS IN BIOLOGICAL AND BOTANICAL MATERIALS

R. Mavrodineanu, Editor

Abstract

This volume consists of thirteen papers describing the analytical procedures selected at the National Bureau of Standards (NBS) for the determination of Ag, Al, As, Be, Bi, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Pt, Sb, Se, Te, Tl, V, and Zn in biological and botanical materials. These procedures are used at the present time for the certification of various substances issued by NBS as Standard Reference Materials, and belong to the following analytical disciplines: sample preparation, neutron activation analysis, spark source mass spectrometric isotope dilution, atomic absorption and flame emission spectrometry, molecular absorption spectrometry, fluorescence spectrometry, and polarography. Further details on the analytical methods including sample preparation, purity of reagents, and problems associated with blanks are given in sixteen additional papers which are reproduced in the Appendix to this volume.

Key Words: Analytical disciplines; analytical procedures; atomic absorption spectrometry; biological materials: blanks; botanical materials; chemical species; flame emission spectrometry; fluorescence spectrometry; molecular absorption spectrometry; neutron activation analysis; polarography; pure reagents; sample preparation; spark source mass spectrometric isotope dilution; tissues.

INTRODUCTION

This work consists of a collection of analytical procedures used in the Analytical Chemistry Division, Institute for Materials Research, of the National Bureau of Standards (NBS), for the determination of trace levels of Ag, Al, As, Be, Bi, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Pt, Sb, Se, Te, Tl, V, and Zn in biological and botanical materials. These procedures were critically selected or adapted, and often specially developed, by the scientific staff members of the Analytical Chemistry Division to provide measurements with the best obtainable accuracy. They were considered to be most appropriate for the analysis and certification of various Standard Reference Materials (SRM's) issued by NBS such as SRM 1570, Trace Elements in Spinach; SRM 1571, Orchard Leaves; and SRM 1577, Bovine Liver.

The description of these procedures is given here with sufficient detail to permit the analyst to use them as a protocol for routine analyses in his laboratory.

They are assembled according to the analytical disciplines involved in the measuring process:

I- Sample Preparation
II- Neutron Activation Analysis
III- Spark Source Mass Spectrometric Isotope Dilution
IV- Atomic Absorption and Flame Emission Spectrometry
V- Molecular Absorption Spectrometry
VI- Fluorescence Spectrometry
VII- Polarography

As a general rule, and unless otherwise indicated, all the acids and distilled water used in the measurements are of high-purity and were prepared at NBS. A detailed description of the methods and instrumentation used to produce these reagents, including the analytical techniques used to test their purity, is given in a paper reproduced as Appendix 1.

The important subject of blanks, a determining factor common to all analytical measurements, is examined in Appendix 2, which also includes a detailed description of the environmental conditions necessary to control this essential factor, and to insure a maximum protection against contamination.

An evaluation of the lyophilization method for preconcentration and drying of various analytical samples is presented in Appendix 3.

Also included in the Appendix are reprints of thirteen papers which provide further relevant and more detailed information on the analytical procedures included in this publication.

In order to describe adequately materials and experimental procedures discussed in this work, it was occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by NBS or that the particular product or equipment are necessarily the best available for that purpose.

The analytical procedures assembled in this publication are believed to provide the best measuring capabilities available at this time. They are, however, continuously being revised, improved, or replaced by more accurate ones.

Hence, it is recommended that the analyst who desires to be informed of these advancements maintain a contact with the scientific staff of the Analytical Chemistry Division at NBS.

January, 1977 R. Mavrodineanu

SECTION I

Sample Preparation

T. J. Murphy

1. Drying

All analytical results for the tissue Standard Reference Materials should be expressed on a dry weight basis. For non-volatile elements, drying may be performed on the sample to be analyzed, but for volatile elements, such as mercury and selenium, drying should be done on separate samples other than the samples for analysis.

The only animal tissue certified to date as a Standard Reference Material is SRM 1577, Bovine Liver. This material was lyophilized during preparation, so freeze-drying is the recommended drying method.[1] The material should be dried by lyophilization for at least 24 hours using a cold trap at or below-50 °C and at a pressure not greater than 30 Pa (0.2 mm Hg). Even though this material has been previously lyophilized, drying should be done on separate samples for volatile elements such as mercury and selenium.

To date, we have worked on four botanical SRM's, spinach, pine needles, tomato leaves, and orchard leaves. All contain varying amounts of water. The removal of this water is not a simple problem since additional volatiles can also be lost.

Desiccator drying over P_2O_5 or $Mg(ClO_4)_2$ is not satisfactory as the rate of moisture loss is too slow. Oven drying at 105 °C and vacuum oven drying at 75 °C are also unsatisfactory since both methods cause large losses of volatiles other than water.

Oven drying for two hours at 75 °C, vacuum drying for 24 hours at room temperature, and freeze-drying (lyophiliza-

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[1] An evaluation of the lyophilization procedure is given in Appendix 3.

tion) for 24 hours are all acceptable methods. The loss of drying by these different methods showed that all three methods agreed to about 0.2 percent. For volatile elements, drying should be performed on separate samples and results corrected to a dry basis.

In general, the samples were dried in the following manner: a suitable sample (usually about 2 g) was placed in a weighing bottle (with cover). The bottle and contents were weighed and transferred uncovered to an oven, vacuum oven or freeze-drier as desired. After leaving the samples for the desired time under the desired conditions, the bottles and contents were placed in a desiccator and covered. After equilibration, the weighing bottles and contents were again weighed and the moisture loss calculated. For the non-volatile elements the samples were used directly for analyses. For the volatile elements (Hg, Se, As, etc.) separate samples were taken for analysis and corrected to dry weight from the calculated moisture loss.

2. Wet Ashing

The basic wet ashing system employed in the decomposition of tissue samples involved the use of nitric-hydrofluoric-perchloric acids. The acids and water used in these dissolutions were prepared by sub-boiling distillation. The preparation and analyses of these acids and water are described in a paper included as Appendix 1. Covered beaker chemistry was used for all elements except the volatile elements such as Hg, As, Se, and Cr.

For the non-volatile elements such as Pb, Cu, Ni, and Cd the following procedure was used.

A suitable sample (usually 1 g) was transferred to a Teflon FEP beaker and treated with 5 ml nitric acid, 1 ml hydrofluoric acid and 2 ml perchloric acid. The beaker was covered with a Teflon cover and placed on a hot plate at low heat. After the action of nitric acid slowed, the temperature was raised to about 110 °C and the beaker and contents were heated overnight. The cover was then removed and washed with water. The solution was heated to fumes of perchloric acid and the heating was continued until fumes of perchloric acid were no longer noted.

After removing the beaker from the hot plate and allowing it to cool, the sides of the beaker were washed with water and the resulting solution was again heated until fumes of perchloric acid were no longer noted.

For the analysis of samples where perchloric acid could not be used (Cr, for example), sulfuric acid was substituted and quartz instead of Teflon beakers were used. A suitable sample (usually 1 g) was transferred to a quartz beaker and treated with 5 ml of H_2O and 10 ml HNO_3. The beaker was covered with a quartz watch glass and the solution was digested overnight on a hot plate. Five ml of sulfuric acid were added and the solution was evaporated to fumes of sulfuric acid. The beaker was then covered and nitric acid was added dropwise to the hot solution to destroy the residual organic matter. The solution was then transferred to a Teflon FEP beaker and any remaining siliceous material was washed into the Teflon beaker. To remove silica, 1 ml of hydrofluoric acid was added and the solution was evaporated to fumes of sulfuric acid.

For the volatile elements, dissolution was effected under reflux conditions. The system consisted of a 125 ml quartz flask fitted with a quartz condenser having a 24/40 standard taper joint. The condenser was filled with quartz beads.

A suitable sample (usually about 1 g) was transferred to the flask and the sides washed with a few ml of water. The condenser was then attached and cold water (∿10 °C) was circulated through the condenser jacket. Ten grams of HNO_3 were then added through the top of the condenser and the solution was allowed to digest for about four hours while the temperature was gradually increased. Nine grams of sulfuric acid (or perchloric acid) were then slowly added through the top of the condenser and the temperature was increased.

The water was drained from the condenser jacket and the solution was allowed to concentrate and reflux overnight. This treatment results in a clear solution, except for undissolved siliceous matter. When possible, this was dissolved by transferring the solution to a Teflon beaker and adding a small amount of hydrofluoric acid.

All operations involving sample preparation were performed in Class 100 environmental conditions to reduce environmental contamination. Whenever possible all analytical operations were carried-out in the same controlled conditions. A thorough discussion of these conditions, indispensable to minimize sample contamination, and to insure the production of accurate measurements, will be found in Appendix 2.

NOTE: The symbol for milliliters used throughout this manuscript was ml instead of mL.

SECTION II

NEUTRON ACTIVATION ANALYSIS

Determination of Arsenic, Antimony, Chromium, Copper, Manganese, Mercury, Platinum, Selenium, and Vanadium

A. Determination of Arsenic, Antimony and Copper in Biological and Botanical Materials Using Neutron Activation Analysis

T. E. Gills

1. Objective

The object is to provide an effective procedure for isolating and determining arsenic, antimony and copper using neutron activation analysis, in biological and botanical materials.

2. Principle

This procedure involved the neutron irradiation of a biological or botanical sample and subsequent solubilization of the radioactive material by nitric and perchloric acids. After obtaining the irradiated material in a soluble form, the radioactive solutions were made to 6M $HClO_4$ and passed through 6M $HClO_4$ equilibrated inorganic ion exchange columns of cuprous chloride and tin dioxide. Copper and antimony were absorbed on the cuprous chloride while arsenic was absorbed on the tin dioxide. Sodium, the major interference in the analysis of biological materials, was eliminated by passing through to the eluate fraction.

3. Instrumentation

Pneumatic tube RT-3 of the NBS Reactor (NBSR) and a Ge(Li) detector system coupled to a multichannel analyzer were used. For further details see Appendices 4 and 5.

4. Reagents

Cu standard:	100 mg Cu metal (99.99% pure) dissolved in high purity HNO_3 and diluted to 100 ml with high purity H_2O.
As standard:	150 mg As_2O_3 (99.95% pure) dissolved in high purity HCl and diluted to 100 ml with high purity H_2O.
Sb standard:	278 mg antimony potassium tartrate (reagent grade) dissolved in a minimum amount of high purity $HCl\text{-}HNO_3$ and diluted to 100 ml with high purity H_2O.
Carriers:	Cu, As, Sb - 1.0 mg/ml (reagent grade oxides and chlorides).
Na carrier:	1 mg/ml (reagent grade chloride).
Acids:	$HClO_4$, HNO_3, HF (ACS reagent grade).
Inorganic Ion Exchangers:	Cuprous chloride, tin dioxide.[2]
NBS SRM's:	Orchard Leaves (1571), Bovine Liver (1577).

5. Sample Preparation and Analysis

Sample sizes of approximately 250 mg are placed in clean polyethylene microcentrifuge tubes and heat sealed. Standards consisting of solutions of copper, arsenic, antimony and $\sim$250 mg of SRM 1571 Orchard Leaves are treated in the same manner. Standards and samples are irradiated for 30 minutes in the pneumatic tube RT-3 of the NBSR in a flux of $\sim 6x10^{13} n\cdot cm^{-2}s^{-1}$. After 24 hours decay, samples and standards are post-weighed and/or pipetted into 125 ml boiling flasks which have been fitted with air condensers. The irradiated materials are then dissolved in 1:3 mixtures of $HClO_4 - HNO_3$.

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[2] These inorganic ion exchangers were obtained from Carlo Erba, Division of Industrial Chemicals. Via C. Imbonati, 24, Milano, 20159, Italy.

If silica containing material is present, 3 to 4 drops of HF may be added. After dissolution, 10 ml of 6M $HClO_4$ is added and the solution is passed through 3-cm columns of cuprous chloride and tin dioxide respectively. Copper and antimony are absorbed on the cuprous chloride column while arsenic is absorbed on the tin dioxide column. After the columns are washed, the contents are transferred separately into 45 mm petri dishes and counted.

6. Procedure

Weigh the irradiated samples into 125 ml boiling flasks. Add 2 ml of Cu, As, Sb and Na carriers. Add 15 ml of the $HClO_4$-HNO_3 mixture (1:3) and heat until the sample is dissolved. Continue heating until the volume is reduced to ∿1 ml. Allow sample to cool.

Place each inorganic exchanger in a polyethylene exchange column; a height of 3 cm is sufficient for sample sizes of 1 gram. Mount the columns in series with the cuprous chloride column at the top. Wash each column three times with 5 ml of 6M $HClO_4$. Discard wash.

Add 5 ml of 6M $HClO_4$ to the cooled sample and transfer to the cuprous chloride column. Allow the sample solution to pass through both columns.

Wash both columns three times with 5 ml portions of 6M $HClO_4$. Discard all washings.

Transfer separately the cuprous chloride and tin dioxide columns into 45 mm petri dishes and count each fraction.

Remarks

The use of the inorganic ion exchangers as outlined in the above procedure provides a rapid and efficient separation for trace amounts of copper, arsenic and antimony from the matrix radioactivities. The technique also allows the analyst to process a series of samples simultaneously.

Calculation

If the induced activities are measured in an identical manner, comparing counting rates in the sample and standard will give the weight of the desired element in the sample by the following simple relation:

$$\frac{\text{Total cts/min Standard}}{\text{Total cts/min Sample}} = \frac{\text{wt }(\mu g)\text{ Standard}}{\text{wt }(\mu g)\text{ Sample}}$$

Example:

$$\begin{array}{l}\text{Sample} \\ (\mu g\text{ element})\end{array} = \frac{(\text{Total cts/min Sample})(\text{wt }(\mu g)\text{ Standard})}{\text{Total cts/min Standard}}$$

$$\begin{array}{l}\text{Sample} \\ (\mu g\text{ element})\end{array} = \frac{(5\text{x}10^4\text{cpm})(10\ \mu g)}{(2.5\text{x}10^4\text{cpm})} = 20\ \mu g$$

B. Determination of Platinum in Biological and Botanical Materials Using Neutron Activation Analysis.

D. A. Becker and T. E. Gills

1. Objective

To provide a simple and selective separation procedure for determining trace quantities of platinum in tissues, sediments and waters by neutron activation analysis (NAA).

2. Principle

The most sensitive and useful nuclear reactions for quantitation of platinum involves isotopes of low gamma energies which are difficult to detect in an activated tissue, sediment or sometimes aqueous matrix. This procedure is based on the electro-chemical theory of spontaneous deposition of an element onto a less noble element. The nuclear reaction used is $^{198}\text{Pt}(n,\gamma)\ ^{199}\text{Pt}\xrightarrow{\beta}\ ^{199}\text{Au}$. The end product of the reaction,

^{199}Au, has a 3.15 day half-life and γ-ray energies of 158 keV (37 percent abundant) and 208 keV (8 percent abundant) which are more suitable parameters for the detection.

3. Instrumentation

Pneumatic tube RT-3 of the NBS Reactor, large volume Ge(Li) detector coupled to a multi-channel analyzer (see Appendices 4 and 5).

4. Reagents

Pt standard: NBS SRM 680 - 1 mg is dissolved in a minimum volume of high purity aqua regia (hot)

Aqua regia: 1+4+1-HNO_3:HCl:H_2O
Pt carrier: 5 mg Pt/ml
Na carrier: 1 mg Na/ml
Ca carrier: 1 mg Ca/ml
Silver: metal powder

5. Sample Preparation and Analysis

Approximately 250 mg of the sample is weighed into a clean polyethylene micro vial and heat sealed. The platinum standard solution is treated in the same manner. Sample and standard are placed in an irradiation "rabbit" and irradiated for one hour in the NBS Reactor in a thermal neutron flux of $\sim 6 \times 10^{13} n \cdot cm^{-2} \cdot s^{-1}$. After a 24 hour decay period to reduce short half-life matrix radioactivities, the samples are opened and transferred to 100 ml beakers containing carriers of elements of interest, and dissolved in aqua regia. After dissolution and evaporation to 2 ml the samples are washed into a 50 ml centrifuge tube with 24 ml of H_2O which contains finely divided silver powder. The mixture is shaken to allow for spontaneous reduction of the platinum. The mixture is filtered through a glass fiber-filter pad to retain the silver metal powder upon which the platinum had been deposited. The filter pad is mounted and counted in a standard geometry. The platinum standard solution is treated in the same manner as the sample.

6. Procedure

Transfer each irradiated material to a 100 ml beaker. Add 1 ml of Pt, Na, and Ca carriers. Add 10 ml of aqua regia and heat until the sample has dissolved and the volume has been reduced to 2 ml.

Let the sample cool. Place 50 mg of finely divided silver powder into a 50 ml round bottom centrifuge tube (with polyethylene-lined cap) and add 24 ml of H_2O.

Transfer the sample solution to the centrifuge tube and shake for 10 minutes.

Filter the mixture through a 25 mm glass-fiber filter pad. The silver metal powder containing the platinum is retained on the filter pad. Discard the solution.

Place the filter pad in a 45 mm petri dish and count on a Ge(Li) detection system.

Remarks

This procedure is rapid, quantitative and selective for platinum. The sodium and calcium carriers are needed as hold-back carriers for the decontamination of the Pt from the matrix. Both photopeaks of ^{199}Au (158 keV and 208 keV) can be used individually for quantitation.

Calculation

If the induced activities are measured in an identical manner, comparing counting rates in the sample and standard will give the weight of the desired element in the sample by the following simple relation:

$$\frac{\text{Total cts/min Standard}}{\text{Total cts/min Sample}} = \frac{\text{wt (µg) Standard}}{\text{wt (µg) Sample}}$$

$$\frac{2.5\text{x}10^4 \text{ cpm}}{5\text{x}10^4 \text{ cpm}} = \frac{1 \text{ µg}}{\text{X}}$$

$$\underset{\text{(µg element)}}{\text{X}} = 2 \text{ µg}$$

C. Determination of Vanadium and Manganese in Biological and Botanical Materials by Neutron Activation Analysis.

S. H. Harrison

1. Objective

Determination of vanadium and manganese at µg/g levels in biological and botanical materials using Instrumental Neutron Activation Analysis (INAA).

2. Principle

Instrumental Neutron Activation Analysis is applied to samples for vanadium and manganese determinations utilizing the thermal neutron reactions $^{51}V(n,\gamma)^{52}V$ and $^{55}Mn(n,\gamma)^{56}Mn$. Measurement of the radiation emitted and comparison to a known standard made radioactive under the same conditions enable quantitative determination of the vanadium and manganese in the sample.

3. Instrumentation

For instrumental analysis of complex matrices such as biological or botanical materials, a high resolution Ge(Li) semiconductor detector, preferably a resolution less than 2.2 keV for the 1332 keV gamma of ^{60}Co is used in conjunction with a multichannel analyzer of at least 2048 channels.

4. Reagents

The standard solutions are made of high purity metals or oxides dissolved in purified reagents (see Appendix 1).

Distilled Water

Nitric acid, diluted 50 percent for dissolution of standards (V).

Acetic acid, reagent grade, diluted 50 percent for dissolution of standards (Mn).

5. Sample Preparation and Analysis

For this INAA procedure, careful sample preparation is important. Precleaned plastic containers and instruments are used whenever possible for sample handling, but nickel spatulas and stainless steel knives are acceptable.

A sample size of about 300 mg of dried tissue is adequate for analyses. For irradiation, the sample is pelletized to provide a small uniform sample. This pellet is then sealed in a small precleaned polyethylene bag, and the sample is sealed in a second bag for double encapsulation.

Primary standards for vanadium and manganese analyses are made by dissolving pure metals in a suitable acid medium. Solution standards are prepared to approximate the tissue sample sizes.

Tissues are irradiated for about five minutes in a flux of $1\text{x}10^{13}\text{n}\cdot\text{cm}^{-2}\text{s}^{-1}$. After irradiation, the tissue samples are transferred to new containers for counting.

After decay times of from 2 to 12 minutes the samples are counted for five minutes live time (e.g. for a matrix such as sediment it may be necessary to wait longer for some of the ^{28}Al activity to decay). Since ^{52}V decays with a half-life of 3.75 minutes, it is helpful if the total activity and decay rate of the standard approximate that of the sample.

Manganese can be determined in the same count as vanadium, however, a lower uncertainty may be obtained if a second count is taken after short-lived isotopes have decayed away. Thirty minutes to two hours is a reasonable decay time for this second count.

6. Procedure

The sample-standard comparator technique is used for quantitative determination of vanadium and manganese. The predominante γ-ray emitted by ^{52}V has an energy of 1434 keV. There are no commonly observed interferences at this energy. The predominante γ-ray for ^{56}Mn has an energy of 847 keV. The half-life of ^{56}Mn is 154.6 minutes. There is a commonly observed γ-ray interference with the 847 keV peak. This interference is caused by the 843 keV γ-ray of ^{27}Mg, which has a half-life of 9.46 minutes. Two choices are available for avoiding this interference: The second most prominent γ (1811 keV) of ^{56}Mn may be used for quantification or one can wait until the 9.46-minute ^{27}Mg has decayed. In using the second alternative, it would be impossible to determine V and Mn in the same count.

7. Calculation of V in Tissue

Vanadium was chosen for the calculation example because of the special problems in measuring short-lived isotopes. The commonly used activation analysis equation is:

$$A = A_o e^{-\lambda t} \tag{1}$$

where λ = the decay constant,

t = the decay time,

A = the activity of the isotope at that decay time and

A_o = the activity of the isotope when $t = o$.

When using this equation, A is assumed to be equal to $\bar{A}$, the average activity of the isotope during the live time counting interval, Δt_ℓ. This is a valid assumption only when $\frac{\Delta t_\ell}{T_{\frac{1}{2}}} < 0.5$ ($T_{\frac{1}{2}}$ is the half-life of the isotope of interest). In the case of vanadium, $\Delta t_\ell = 5$ min. $T_{\frac{1}{2}} = 3.75$ min, and $\frac{\Delta t_\ell}{T_{\frac{1}{2}}} = 1.33$ not less than 0.5. Therefore, for the calculation of vanadium, it is necessary to use the following equation:

$$A_o = \frac{\lambda \bar{A} \Delta t_c}{e^{-\lambda t_1} - e^{-\lambda t_2}} \qquad (2)$$

where t_1 = the decay time at the start of the count,
t_2 = the decay time at the end of the count and
Δt_c = the clock time counting interval.

Example:

Sample wt = 297.7 mg sample
Standard wt = 0.4022 mg V/g soln x 0.1000 g soln = 0.04022 mgV

$\bar{A}$ (sample) = 1965 cts/min
t_1 (sample) = 12.00 min
t_2 (sample) = 17.80 min
Δt_c (sample) = 5.80 min = clock time counting interval,
$\bar{A}$ (sample)/mg sediment = 6.601 cts/mg sediment min

$\bar{A}$ (standard) = 12,867 cts/min
t_1 (standard) = 12.00 min
t_2 (standard) = 17.77 min
Δt_c (standard) = 5.77 min = clock time counting interval.
$\bar{A}$ (standard)/mg V = 3.199×10^5 cts/mg V min

$$T_{\frac{1}{2}}\ ({}^{52}V) = 3.75 \text{ min}$$

$\frac{\Delta t_c}{T_{\frac{1}{2}}\ ({}^{52}V)} > 0.5$, therefore equation 2 is used to calculate A_o.

$$A_o = \frac{\lambda \bar{A} \Delta t_c}{e^{-\lambda t_1} - e^{-\lambda t_2}} \text{ where } \lambda = \frac{.693}{3.75 \text{ min}}$$

After substituting the time and activity parameters in equation 2 for the sample and then the standard, the fol-flowing values for A_o are obtained:

A_o (sample)/mg sample = 98.82

A_o (standard)/mg V = 4.777×10^6

$$\frac{A_o \text{ (sample)}}{A_o \text{ (standard)}} = \frac{98.82 \text{ cts/mg sed.}}{4.777 \times 10^6 \text{ cts/mg V}} = 2.068 \times 10^{-5} \text{ mg V/mg}$$

sample or conc. = 20.68 μg V/g sample.

D. Radiochemical Separation for the Determination of Mercury and Selenium in Biological and Botanical Materials Using Neutron Activation Analysis.

H. L. Rook, T. E. Gills and G. J. Lutz

1. Objective

The objective is to determine mercury and selenium at concentration levels as low as 10 ppb using neutron activation coupled to a selective radiochemical separation procedure.

2. Principle

The principle of the procedure is the irradiation of an unknown sample along with standards in an intense thermal neutron flux for a period of several hours inducing the reaction $^{196}\text{Hg}(n,\gamma)^{197}\text{Hg}$ and $^{74}\text{Se}(n,\gamma)^{75}\text{Se}$. The mercury and selenium activities are subsequently separated from the matrix radioactivities by combusting the sample in a stream of oxygen and trapping the volatile elements in a liquid nitrogen cooled trap.

3. Instrumentation Apparatus and Reagents

Instrumentation and apparatus required include: a tube combustion furnace, a quartz tube combustion assembly, a high resolution gamma-ray detector, a pulse height analyzer, precipitation and filtering equipment. For further details see Appendix 4 and 5.

Reagents required are tank oxygen, mercury oxide, concentrated nitric acid, ammonium hydroxide, liquid nitrogen, and thioacetamide. The chemicals are of reagent grade.

4. Procedure

The samples are weighed and encapsulated in quartz tubes for irradiation. If expected levels of mercury are very low, encapsulation is done in a Class 100 clean room.[3] The quartz encapsulated samples are subsequently packaged along with encapsulations of mercury solution standards in polyethylene rabbits and irradiated in the NBS Reactor in a flux of $6x10^{13}n/cm^2$ s for approximately six hours. After irradiation, the individual quartz ampoules are rinsed with conc. HNO_3 and water. The samples are then immersed in liquid nitrogen for a few minutes and opened by scoring the vial with a file and pressing at the scratch mark. The samples are then transferred along with approximately ten milligrams of HgO carrier into porcelain combustion boats (1x10 cm). The combustion boat is then inserted into the combustion assembly. An oxygen stream of 20 cm^3/min is allowed to flow over the sample. If the sample is a biological material, it is allowed to burn freely after igniting with a torch. After combustion, the tube is heated to about 800 °C for 20 minutes. Portions of the tube not covered by the furnace are flamed down with a gas oxygen torch to further distill mercury into a liquid nitrogen cooled condenser. The assembly is then allowed to cool and the distilled mercury in the condenser is transferred with nitric acid and water into a 4-oz polyethylene bottle. The solution containing the mercury and selenium is diluted to a selected standard volume and shaken to homogenize the solution. Standards can be carried through the procedure or an aliquot can be transferred to a 4-oz bottle and diluted.

All samples and standard solutions are counted on a Ge(Li) detector in conjunction with a multichannel pulse height analyzer. The 68 and 77 keV peaks of ^{197}Hg and the 265 keV line of ^{75}Se are used in the evaluation.

An improvement in sensitivity can be achieved by reducing the volume of the counting sample by precipitating the mercury as a sulfide. Selenium coprecipitates with the HgS.

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[3] See Appendix 2.

Bromine-82 can be removed during the combustion step with a heated silver wool trap. Silver wool also removes selenium so the procedure is applicable when only mercury is to be determined. Bromine-82 can also be removed during the precipitation step by the addition of hold-back carrier.

5. Calculation

The concentration of mercury and selenium is calculated using the standard-comparator method:

$$\frac{\text{Total cts/min Standard}}{\text{Total cts/min Sample}} = \frac{\text{Wt } (\mu g) \text{ Standard}}{\text{Wt } (\mu g) \text{ Sample}}$$

Example:

Standard: Counts per min = 9068

Wt (μg) = 1.53

Sample: Counts per min = 1831

Wt (μg) = X

$$\frac{9068 \text{ cts/min}}{1831 \text{ cts/min}} = \frac{1.53}{X}$$

$$X = .31\ \mu g$$

Note: For further information see Appendix 6.

E. Determination of Chromium in Biological and Botanical Materials Using Neutron Activation Analysis.

L. T. McClendon

1. Objective

The objective is to provide a simple and accurate procedure for determining chromium in biological and botanical materials using neutron activation analysis.

2. Principle

This procedure is designed for a rapid, selective determination of trace quantities of chromium in tissues, by separating it from the matrix activity produced when these materials have been irradiated in a nuclear reactor. Experiments have shown that a volatile form of chromium is present in some tissues so that dissolution of the sample in a closed system and entrapment of the vapor fumes in a HNO_3 or HCl solution is recommended.

3. Instrumentation

Pneumatic tube RT-3 or RT-4 of the NBS Reactor, Ge(Li) detector system or NaI detector system. Further details will be found in Appendices 4 and 5.

4. Reagents

Cr standard:	0.5000 g Cr metal (99.9% pure) dissolved in high purity HCl and diluted to 1000 ml with high purity H_2O.
Cr carrier:	1 mg Cr/ml, ($CrCl_3 \cdot 10\ H_2O$ reagent grade) dissolved in HCl, 1.5M.
H_2O:	High Purity
HNO_3:	Conc., 6M
$HClO_4$:	70-72%
$Ce_2(SO_4)_3$:	10% (w/v) in 3M H_2SO_4

Tribenzylamine: 1% (w/v) in $CHCl_3$

NBS SRM: Orchard Leaves (1571).

5. Sample Preparation and Analysis

Approximately 250 mg of the sample is placed in a clean quartz vial or polyethylene tubing and sealed. The chromium standard solution and Orchard Leaves (∿250 mg) are treated similarly. Samples and standards are placed in an irradiation "rabbit" and irradiated for an appropriate period of time (1 to 6 h) in RT-3 or RT-4 of the NBS Reactor. After a sufficient decay period is allowed to minimize some of the matrix activity, the sample container is washed with 1:1 HNO_3 to remove any exterior contamination. If Cr is ≥ 2 μg, the Cr concentration can be determined instrumentally without chemical treatment. If the concentration is below 1 ppm a radiochemical separation may be needed. Thus the sample is transferred to a 50-ml Erlenmeyer flask for "open" or "closed" flask dissolution. The chromium standard solution and comparative standards (Orchard Leaves, Coal, etc.) are treated in the same manner as samples.

6. Procedures

a. Instrumental Analysis

If the sample and standards were preweighed into a container that was suitable for both irradiation and counting, the following operation may be omitted. Weigh the sample into a suitable counting vessel. Calibrate the detection system for assaying the 320 keV gamma ray emitted by Cr-51 and count sample for a suitable time period.

b. Radiochemical Separation

Weigh the sample into a 50 ml boiling or distilling flask. Add 1 ml of Cr carrier, 5 ml conc. HNO_3 and 3 ml of conc. $HClO_4$. Place on hot plate and heat using a medium temperature setting until sample has dissolved and Cr^{+3} has been oxidized to Cr^{+6}. To the hot solution add 4 ml of hot ceric sulfate solution and heat for five minutes. Let sample cool. Transfer the sample to a 50-ml extraction tube equipped with a polyethylene-lined top using 15 ml of 1.5M HCl. Mix well. Add 10 ml of tribenzylamine solution to the extraction vessel. Agitate for five minutes. Let stand until phases have separated, take a 5-ml aliquot of the organic phase and count on a gamma detection system. Transfer the trap solution to a suitable counting vessel and count if a "closed system dissolution" was used.

Remarks

This solvent extraction procedure is selective for Cr VI which makes it advantageous to dissolve the sample in an oxidizing media. Ceric sulfate is added to the dissolved sample to maintain the chromium in solution as Cr VI. If gold, antimony, or mercury are present in large quantities, they may also extract under the conditions described. The gamma-ray energies of these three elements are sufficiently different from the 320 keV gamma ray emitted by Cr-51 so that no interference will occur.

Calculation

The amount of chromium in a sample is calculated using the comparator technique, since the measured counting rate using a standard measuring set-up is proportional to the total activity:

$$\frac{\text{Wt } (\mu g/g) \text{ of Cr in Sample}}{\text{Wt } (\mu g/g) \text{ of Cr in Standard}} = \frac{\text{Counts/min of Cr in Sample}}{\text{Counts/min of Cr in Standard}}$$

Example:

Cr in Orchard Leaves (O.L.)
1 μg of Cr standard yields 10.4×10^3 cpm;
count rate of Cr in 1 g of O.L. yields 26.8×10^3 cpm.

$$\frac{\text{Cr in 1 g O.L.}}{1\ \mu\text{g}} = \frac{26.8 \times 10^3\ \text{cpm}}{10.4 \times 10^3\ \text{cpm}}$$

$$\mu\text{g Cr in O.L.} = \frac{26.8 \times 10^3\ \text{cpm}}{10.4 \times 10^3\ \text{cpm}}$$

$$\text{Cr in O.L.} = 2.577\ \mu\text{g/g sample.}$$

F. Rapid, Quantitative Separation for the Determination of Selenium Using Neutron Activation Analysis.[4]

H. L. Rook

1. Objective

The analytical procedure described in this section was developed to permit the quantitative determination of selenium in biological and botanical materials, at the part per million and sub-part per million levels, using neutron activation analysis (NAA) and with a minimum of chemical manipulations. The physical separation method used minimizes the errors associated with chemical separations, and, in addition, permits the simultaneous determination of mercury.

2. Principle

The method is based on the irradiation of the analytical sample in a nuclear reactor followed by the separation of

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[4] The material used in this section was taken from a work published by the author in Analytical Chemistry, Vol. 44, No. 7, p. 1276 to 1278 (1972).

selenium by thermal volatilization in an oxygen stream. The selenium separated in this manner is transferred quantitatively to an adequate container, and the activity of the sample is determined by counting with a Ge(Li) detector and 2048-channel pulse-height analyzer.

3. Procedure

Apparatus. The sample combustion train (Figure 1) was made from an outer 19/38 standard taper Vycor[5] joint which had been extended to a total length of 30 cm. The condenser was made from an inner 19/38 standard taper Vycor joint, extended to 25 cm, which was inserted through a liquid nitrogen cold trap made from a small polyurethane acid shipping container.

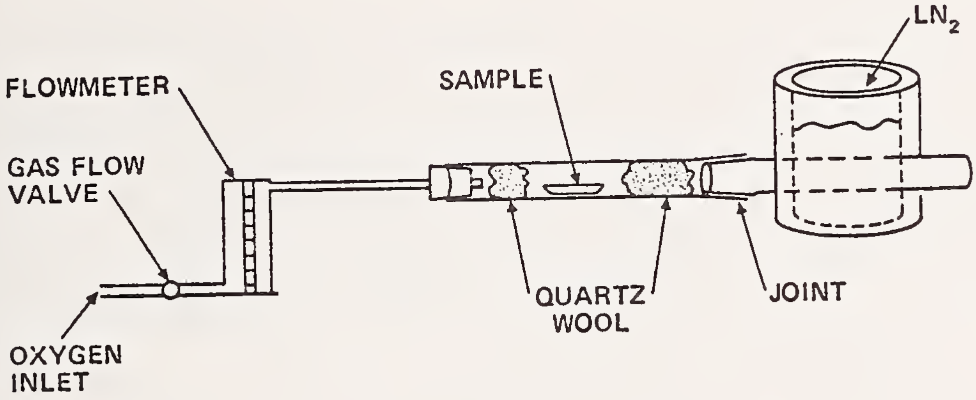

Figure 1. Sample Combustion Tube and Mercury Trap.

Reagents. Standard solutions were made by dissolving a weighed quantity of high purity elemental selenium in concentrated high purity nitric acid and diluting to volume with

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[5] In order to specify procedures adequately, it has been necessary to identify commercial materials in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material identified is necessarily the best available for the purpose.

distilled water. The selenium concentration used was 0.5910 mg/ml, which was dilute enough to prevent any significant neutron self-adsorption, but large enough to negate loss due to wall adsorption of selenium in the storage container.

Procedure. For analysis, 0.5-gram samples were encapsulated in cleaned quartz tubes. Standard solutions were encapsulated in a like manner. Five sample tubes were arranged in a concentric ring with a standard in the center in a polyethylene rabbit and irradiated in pneumatic transfer facility RT-3 of the National Bureau of Standards Reactor [1] for two to six hours at a thermal neutron flux of approximately $6x10^{13}n \cdot cm^{-2} \cdot s^{-1}$. Flux monitors were not used, as the radial flux variation is less than ±2 percent in RT-3. The samples were allowed to decay 5 days to minimize personnel radiation exposures.

The quartz tubes were washed in 1:1 nitric acid, cooled to liquid nitrogen temperature, and broken ∿5 mm from the top. The samples were weighed into a ceramic combustion boat, and 2.5-mg of mercuric oxide carrier added. Since selenium oxides are difficult to dissolve in mineral acids, inactive selenium carrier was not used. Mercury carrier was adequate to eliminate adsorption of selenium on the walls of the Vycor condenser and polyethylene counting bottle through the formation of mercury selenide. This was readily soluble in nitric acid, enabling the dissolution procedure developed for the mercury separation to be used. The boat was inserted into the combustion chamber, an oxygen flow of ∿30 cc/min was passed over the sample and the sample was then ignited with an oxygen-gas torch. The sample was allowed to burn freely with the downstream quartz wool plug heated to red heat to ensure complete combustion of volatile hydrocarbons and carbon produced during the sample burn. After combustion ceased, the ash was heated to approximately 1000 °C for five minutes and the entire combustion tube heated down to the standard taper joint to drive all volatile compounds of the sample into the condenser.

The combustion tube was allowed to cool for five minutes, the liquid nitrogen cold trap was removed, and the condenser was placed joint-end down into a 4-oz polyethylene bottle. The condenser was warmed to room temperature, and the selenium and mercury carrier washed into the bottle with 10 ml of concentrated nitric acid and three 10-ml portions of distilled water. The total volume of solution was adjusted to 50 ml and the sample was counted using a 60-cc Ge(Li) detector in conjunction with a 2048-channel pulse-height analyzer. The 265 keV gamma ray of selenium-75 was used for the determination, as the 136 keV gamma ray suffers from interferences from mercury-197m.

After irradiation, the standard was frozen in liquid nitrogen, broken in a beaker, allowed to melt, and decanted into a 4-oz polyethylene bottle. The broken quartz vial and beaker were washed with six 5-ml portions of distilled water and the final volume was adjusted to 50 ml. The specific activity at the end of the irradiation was compared to that of the sample for quantitative results.

4. Discussion

In this work, the method for the separation of volatile elements, originally developed for the determination of mercury, was studied and adapted to the selenium problem [2]. Four significant improvements over currently used procedures have been attained: the procedure has a minimum of chemical manipulations, thereby minimizing technique related errors; the radio-selenium separation is quantitative, thus eliminating errors involved in the determination of chemical yields; the procedure is based on a physical, rather than a chemical separation allowing the same technique to be used on a wide variety of matrices; and the determination of mercury may be conducted simultaneously using this separation procedure.

The method was tested using radiotracer experiments and excellent agreement was obtained by independent analysis using isotope-dilution spark-source mass spectrometry. The procedure has been subsequently used to determine the selenium concentrations of three new Standard Reference Materials being issued by the National Bureau of Standards.

Results

The method was tested for complete recovery of selenium by burning non-irradiated samples of biological material with known quantities of selenium-75 nitrate solutions added. The recovery selenium-75 was brought to 50-ml volume and compared to the activity of a like quantity of tracer diluted directly to 50-ml volume and counted in a standard configuration. The results of these tests indicated a complete recovery of selenium-75 tracer. A total of five separations was carried out with a mean recovery of 99.1 percent and a relative standard deviation of 1.1 percent.

Using the analytical procedure developed, the selenium concentration in three new Standard Reference Materials (SRM) being issued by the National Bureau of Standards was determined. These materials are:

SRM 1630	Mercury in Coal
SRM 1577	Bovine Liver
SRM 1571	Orchard Leaves

The method described was used to determine the selenium contents in these materials with an accuracy in the mean results of better than ±10 percent relative at the 95 percent confidence level. The results were in excellent agreement with independent analyses using isotope-dilution spark-source mass spectrometry. The individual results are given in Table I.

Table I. Selenium contents of Standard Reference Materials, ppm.

Results Obtained by Neutron Activation Analysis Using the Combustion Technique

	SRM 1571 Orchard Leaves	SRM 1577 Bovine Liver	SRM 1630 Mercury in Coal
	0.079	1.08	2.16
	0.084	1.05	2.03
	0.083	1.16	2.14
	0.075	1.13	2.08
	0.074	1.12	2.08
	0.069	1.16	2.05
	0.085	1.17	2.14
	0.075	1.11	--
	0.087	--	--
Mean	0.079	1.12	2.11
2s	±0.012	±0.08	0.09

Results Obtained by Isotope-Dilution Spark-Source Mass Spectrometry

SRM 1571 Orchard Leaves	SRM 1577 Bovine Liver	SRM 1630 Mercury in Coal
0.08 ± 0.02	1.11 ± 0.04	N.D.[a]

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[a] Not determined.

The results indicate that the described separation affords a degree of confidence in the final results not obtainable using the nondestructive activation analysis technique. Yet with the simple one-step combustion separation, samples may be processed in a minimum of time (approximately 15 minutes each), maintaining the process-time advantage of nondestructive activation analysis when large numbers of samples must be analyzed. The technique has the added advantage that the mercury content, which is often of great interest in biological materials, may be determined simultaneously.

5. References

[1] LaFleur, P. D. and Becker, D. A., Eds., NBS (U.S.) Tech Note 548, 10 (1970).

[2] Rook, H. L., Gills, T. E., and LaFleur, P. D., Anal. Chem. 44, 1114 (1972).

SECTION III

SPARK SOURCE MASS SPECTROMETRIC ISOTOPE DILUTION

Determination of Cadmium, Copper, Iron, Lead, Mercury, Molybdenum, Nickel, Selenium, Silver, Tellurium, Thallium, and Zinc.

P. J. Paulsen

1. Introduction

The spark source mass spectrometer (SSMS) can detect all elements in the periodic table at detection limits down to a few ng/g. In actual samples there will be interferences between elements, however all elements are inherently detectable with similar sensitivity. Quantitative results will require concentrations significantly higher than these "detection limit" values.

Isotope dilution (ID) analysis can, in theory, be applied to any element having two or more stable isotopes. If one considers the various practical aspects of SSMS analysis, approximately 50 elements are amenable to isotope dilution SSMS analysis. Our laboratory has had occasion to perform SSMS ID analysis on a total of 36 different elements and a wide variety of matrices during the last 10 years.

Isotope dilution SSMS has multi-element capabilities. As many as 28 elements have been measured simultaneously by isotope dilution in a single sample while doing a survey type analysis (designed for low detection limits in pure materials, but not designed for the best precision). In a precise quantitative analysis of a NBS SRM for certification, up to 11 elements have been determined simultaneously from a single sample.

Using the element copper as an example, the general procedure for mass spectrometric isotope dilution analysis is as follows:

1. A known amount of ^{65}Cu isotope (spike) is added to a weighed amount of sample to be analyzed.
2. The ^{65}Cu spike is equilibrated (mixed) physically and chemically with the natural copper in the sample. Equilibration is usually obtained by dissolution of the sample in the appropriate acids.
3. The equilibrated copper is separated from the sample in a form suitable for mass spectrometric measurements.
4. The altered ^{63}Cu/^{65}Cu isotopic ratio is measured mass spectrometrically.

The concentration of copper is then calculated using the formula:

$$\text{ppm (by weight)} = \frac{WK}{M} \frac{(A_{sp} - B_{sp}R)}{(BR - A)}$$

where:

W = Spike weight in μg; M = sample weight in grams

K = Ratio of natural atomic weight to atomic weight of spike

R = Measured altered isotopic ratio a/b

A_{sp} and B_{sp} = Abundances of isotopes a and b in spike

A and B = Abundances of isotopes a and b in <u>natural</u>

From this equation it is seen that it is the ratio (R) of the two Cu isotopes that is required to calculate the copper concentration. The total amount of copper is not measured. It is therefore not necessary to either recover 100 percent of the copper in the sample or know recovery efficiency in order to obtain quantitative results. Therein lies the biggest advantage of using isotope dilution analysis.

Once equilibrium is obtained between the "spike" and "natural" isotopes of an element, procedures for separation can be adopted which optimize such factors as group separations, low blanks, clean separations, etc., without the restraint of having a controlled, known recovery. Efficient recovery methods are, of course, desirable since the sensitivity of the method is dependent on recovery.

2. General Considerations for Multi-Element SSMS Isotope Dilution

a. Concentration Range Covered

Quantitative analysis good to about ±5 percent can be obtained if from $1x10^{-6}$ to $1x10^{-7}$ g of an element can be loaded into the instrument for sparking. Smaller amounts have been measured on occasion, however, the precision suffers proportionally as the concentration is lowered. For a 1-g sample this gives quantitative values at the 1 to 0.1 ppm level. Lower concentrations can be determined at this precision if the sample size is increased, however, in any system there is a limit to either the sample available or the amount of the sample that can be effectively handled. For some of the more common elements the system blank may be the limiting factor and it may increase with the sample size depending on its source. There is no upper concentration limit on the use of isotope dilution SSMS, however at high concentrations there are usually other techniques of analysis which are more cost effective and more precise than the ±5 percent obtained with SSMS photoplate detection. Because of the value of the separated isotopes ($1 to $10/mg + time involved in preparation), spikes are held to less than 1 mg. Samples with high concentrations are dissolved, aliquoted and then spiked in order to conserve spikes.

b. Spike Levels

A given amount of spike will cover only a limited range of concentrations, the range will depend on the natural isotopic ratio, the purity of the separated "spike" isotope and the precision and accuracy with which the altered isotopic ratio can be measured. A valid analysis cannot be performed when the measured altered isotopic ratio differs from either the natural or "spike" ratio by only the measurement uncertainty (± percent standard deviation or ± accuracy). With photographic plate detection the plate uniformity limits precisions to ±5 percent and accuracy (for ratios $\neq 1$) depends on obtaining a good plate calibration curve.

The best accuracy with the photoplate is usually obtained if the amount of spike added is adjusted to give a measured isotopic ratio of 1 ($R=2$ if the natural ratio $=1$). This procedure minimizes the errors associated with photoplate calibration and also gives the maximum number of measurable ratios for a given situation. If electronic detection SSMS is used, the accuracy is not dependent on having $R=1$ and a wider concentration range can be covered with a given spike. The effective range is still limited by the measurement precision and the isotopic ratio of the spike and natural element.

c. Preconcentration

The need for obtaining physical and chemical mixing of the "spike" and natural isotopes for a solid sample is met by dissolving the sample in acids. This step both dilutes the sample and adds extraneous anions. The high absolute sensitivity of the SSMS makes it impractical to consume more than a total of about 10 mg of material in a normal analysis. Some form of preconcentration is therefore usually necessary in order to reach this consumable size and hence obtain maximum sensitivity. The ideal preconcentration procedure would yield only those elements to be analyzed and no others. This would give the best analytical sensitivity while minimizing interference problems. The presence of a large excess of an element not being analyzed in the SSMS sample can cause interference problems. This is especially true if it is an unwanted cation which carries along an equivalent anion from the acids used in dissolution - double trouble.

Isotope dilution SSMS is a practical method mainly because a number of elements can be determined simultaneously. This means that any preconcentration method used needs to provide group separations. In some types of samples this can be obtained simply by excluding the major components of the sample. A number of preconcentration procedures have been used for SSMS isotope dilution. These include ion exchange, solvent extraction, electrodeposition, precipitation with and without carriers, and high temperature volatilization. Electrodeposition onto high purity gold wires (photoplate detection) is an especially attractive method since it has a very high rejection factor for organics and anions originating from the acids used in sample dissolution.

The SSMS readily detects organic molecules. If organic material from either the sample or the reagents used in preconcentration is present in the sample loaded into the SSMS, interferences can result.

d. Interferences

As in all analytical methods it is the identification of interferences that enables the proper action to be taken which avoids errors in analysis. There are three general types of interferences in SSMS ID analysis.

1. Isobars - adjacent Z elements with isotopes having the same nominal masses: Interferences of this type can always be identified and it occurs with only a few elements. In some cases proper selection of the isotopes measured may minimize the magnitude of the interference,

and/or allow correction for the interference. Chemical preconcentration procedures could also be used to remove the undesired element. In any case, this type of interference could not go undetected.

2. Multicharged ions of high mass falling at the same nominal mass as the singly charged ion of the desired element: The SSMS disperses ions according to their mass to charge ratio (m/e). The energy available for ionization in the spark is so high that all elements can be multiply ionized. This can result in interferences when two elements of different masses and different charge states have the same nominal mass to charge ratio. The relative intensities of the +1, +2, +3, etc., ions of an element follows a predictable pattern (intensity drops off by a factor of ∿3 for each additional charge). This type of interference is therefore readily recognized by a visual examination of the photoplate. Again, in many instances, interferences can be avoided or corrected for by measuring the proper isotopes of both elements. In some cases the interference can be further minimized or avoided if a multiply charged ion of the desired element can be measured. Again this type of interference would not go undetected.

3. Interference by compounds of the same nominal mass as the element being analyzed: Hydrocarbons fit this classification. The resolution of any SSMS using photoplate detection is adequate to resolve and identify the presence of a hydrocarbon line with the same nominal mass as an element line. Quantitative measurements can be made on the resolved element lines providing the hydrocarbon line is not too intense. In this case the sample preconcentration method could be modified to lower hydrocarbons or in some situations (explained later) the interference can be avoided by measuring a multiply charged ion of the element.

Other types of compound lines will usually not have a large enough mass difference from an element of the same nominal mass to be resolved into separate lines. The major difficulty with this type of interference is that the intensity of compound interferences cannot be as easily predicted from other information on the photographic plate. However, since the SSMS can detect *all* elements there is good information on what elements are available as starting material to form the compounds. The stability of a compound in the form of a positive ion (the species being detected) under the conditions that exist in the spark source is very small. It is only the extremely high sensitivity of the SSMS combined with the presence of elements at high concentrations that allows the detection of such ions. Under most conditions these interferences occur only for elements being determined in the low ppm range.

When checking for potential interferences a list of possible compounds can be obtained by following these general rules:

1. Consider only the major elements (as detected by SSMS).
2. All samples, regardless of source, have adequate O, H, (and possibly carbon) available for forming compounds.
3. Anions of the acid used in sample dissolution can appear in all possible forms, *i.e.*, ClO_4^- gives Cl^+, ClO^+, ClO_2^+, ClO_3^+, plus "cation" combinations thereof.
4. Group 1a, 1b, 2a, and 2b elements have a tendency to form dimers, trimers, etc., and these can also pick up oxygen and hydrogen, or anion fragments.
5. The compounds that cause interferences need to exist as ions for less than 1 µs; during their lifetime (as a detected ion) no collisions occur with other ions, molecules, or any surface. The combinations that will occur therefore may appear to be strange when viewed from a classical chemical background.

The presence of compounds can be detected by their generation of abnormal isotopic ratios and of lines which do not correspond to any element lines. If the compound has an element with more than one isotope it may allow corrections to be made. Abnormal lines that can be identified give good clues to the possibility of a related compound. For instance, if a sample (with high $NaClO_4$ content) shows lines which are identified as $NaClO_2^+$ then the spectrum should also be checked for $NaClO_3^+$, $NaClO^+$, ClO_3^+, ClO_2^+, etc. One approach to this type of interference problem is to measure the isotopic ratios for all elements being analyzed in an unspiked sample. If the ratios found are the natural ratios of the elements it can be assumed that no interferences exist. This approach requires good control over the sample preconcentration process.

There is a simple method of avoiding errors of analysis from compound interference that will apply to most but not all elements. The method is to measure the isotopic ratios for elements on a +2, +3, or +4 ion instead of the +1 ion. The stability of a compound with a +2 or +3 charge on it is so low that such species cannot be detected. The +2 and +3 ions of an element on the other hand are only a factor of ∿3 and ∿10 times less intense than the +1 ion.

There will be a loss in sensitivity in such an analysis and the method cannot be used much below 1 μg. The precision of isotope ratio measurements using the photoplate is the same for all charge states (limited only by plate uniformity) so the precision does not suffer. There is one major qualification that prevents use of multiply charged ions for all elements. Both measured isotopes of the multiply charged ion of the element must fall at fractional mass/charge (m/e) values if that charge state is to be usable. This is necessary since the unit m/e positions are very likely to have either a +1 element line or possibly a compound line. This is especially true at the lower m/e region of the plate where most of these types of measurements would be made.

Interference by compound lines is usually only significant in the analysis of low ppm concentration elements. The interference can be minimized by keeping elements not being analyzed out of the sample, and interference can be eliminated if a multiply charged ion can be measured. The major problem is being able to spot the existence of this type of interference.

3. Analysis of Organic Materials Using SSMS Isotope Dilution

Most of the SSMS ID analysis at NBS has been for the certification of Standard Reference Materials (SRM's). The procedures adopted have emphasized accuracy and precision over other factors such as speed and turn around time. Since a wide range of analytical techniques are applied to a SRM certification, the SSMS ID analysis stressed only those elements where it would be most effective. In general, most elements above 100 to 500 ppm would be analyzed by other methods to a better precision than the ±5 percent obtained by SSMS photoplate detection. More elements could have been analyzed by SSMS ID than were reported if it had been necessary.

The organic materials (not all SRM's) that have been analyzed by SSMS ID are: orchard leaves, beef liver, coal, tomato leaves, pine needles, spinach, tuna fish, urine, wheat, rice, fuel oil, and river bottom extract. The elements determined for NBS organic SRM certification are: Pb, Tl, Hg, Te, Cd, Ag, Mo, Se, Zn, Cu, Ni, and Fe. A total of 35 elements have been analyzed for SRM certification if other types of SRM's are included.

The chemical preconcentration methods used in the analysis of the organic materials include: electrodeposition onto high purity gold wires, ion exchange, vaporization of volatile elements, and co-precipitation.

Our analysis of coal, beef liver, and spinach SRM's will be used as examples for SSMS ID analysis.

A detailed description of the instrumentation and techniques used to perform the actual analysis by SSMS ID will be found in the four papers reproduced in the Appendices 7 through 10. Although the chemical species discussed in those papers are contained in a metallic matrix, the same analytical procedures are applicable to organic matrices.

4. Preliminary Analysis

The preliminary analysis serves two functions in a SRM analysis. First, several group separation techniques can be tested to see which system recovers the greatest number of elements of interest. Second, the concentration levels of the different elements needs to be determined in order to adjust the spike level for each element for optimum precision and accuracy in the actual analysis. If no information is available on the sample, it is spiked with 100 ppm, 10 ppm, and 1 ppm of a master spike solution containing "spikes" of 28 elements. This range of spike levels can be obtained by changing both sample and spike amounts, but it is best to keep the spike above 1 μg. Analysis of these three samples would give reasonably accurate results over a concentration range from ∿500 ppm down to ∿0.1 ppm.

If an element not in the spike is detected, its concentration can be estimated by using one of 28 spiked elements as an internal standard. In all of the SSMS ID analyses performed to date the preconcentration procedure has been selected to give the maximum number of desired elements from a single sample processing. Two independent procedures (two SSMS samples) would have doubled both the chemical and the

SSMS workload but would not have doubled the number of elements determined.

What has been just referred to as a preliminary analysis for our NBS SRM SSMS ID analysis would, in fact, provide adequate accuracy and precision for "final" analysis of many types of analyses. Such a system would be much more efficient than the one we feel obligated to use on NBS SRM's.

5. Procedure Used for Analysis of Coal, Beef Liver, and Spinach Spiking

Weighed samples of the organic material were spiked with proper amounts of each element's "spike" in order to obtain an equilibrated ratio (R) of 1. Silver has a natural ratio of 1, it is spiked to give a ratio of 2.

The amounts of spike required were computed using the results of the preliminary analysis. The spike elements can be added one element at a time, however, our preferred method is to mix all the spikes together in the proper proportion and then make just one addition. In either case, spike calibration samples are prepared at the same time using the same pipet setting and spike solutions as used on the samples. Known amounts of the pure natural elements are also added to these spike calibration samples. The natural solutions are obtained by quantitative dilutions of a solution prepared from a known amount of the pure natural element. SSMS analysis of the spike calibration sample gives an accurate determination of the amount of spike actually added to the samples.

"Blanks" are also spiked at the same time as the samples using only 5 to 10 percent as much spike as was used on the sample (but not less than 0.1 μg). This level of spiking can safely measure the blanks down to less than 1 percent of the value being determined in the analysis. The blank samples are then treated in an identical manner as the real samples.

Spike Equilibration

Equilibration is obtained by the acid dissolution of the samples. These samples were dissolved by a stepwise treatment with HNO_3, $HClO_4$, and HF (no HF for beef liver). The amounts of reagents required were determined during the preliminary analysis.

A detailed discussion of the procedures used for the dissolution of samples contained in an organic matrix is given in Section I, "Sample Preparation" by T. J. Murphy of this work. The analyst should refer to this section when such matrices are under consideration.

6. Preconcentration

All three samples were separated-preconcentrated by electrodeposition onto high purity gold wire cathodes. This technique is used often since it has a number of advantages. The method is simple and uses no reagents beyond those needed for sample dissolution. This results in low analysis blanks. The gold wires are loaded directly into the SSMS for analysis and give high elemental sensitivity with photoplate detection. Electrodeposition gives good rejection of the alkalies and alkaline earths (high in these samples) which are seldom analyzed by SSMS ID. The elements are recovered in a reduced form and therefore no extraneous anions or cations are added to the sample being sparked.

Following dissolution (equilibration) the samples were evaporated to dryness and redissolved in 10 ml of distilled water. They were plated for three hours or more at voltages from 2.5 to 3.0 V. The elements recovered depended on both the plating voltage and the acid content of the plating solution. Zinc recovery is very sensitive to the presence of small amounts of acid in the plating solution. Unless the sample is dried carefully, zinc will not plate. The six-nines pure gold wire used for electrodeposition is about

1/2 mm diameter. The wire is plated only on the tip for a distance of about 2 mm.

7. Sample Sparking

Two cathode wires are plated during deposition. These are loaded so that their 2 mm of plating overlap and that the sparking will occur along this 2 mm length. Two photoplates are exposed using 1/2 of the plated surface for each. A graded series of 20 exposures are made on each plate starting from 1×10^{-12} coulombs and going up to 1×10^{-8} coulombs. The electrodes are moved so as to spark new sample on each exposure. The gold wire becomes warm while making the 10^{-8} exposures on the first plate. This outgasses the sample appreciably and the second plate exposed has significantly lower hydrocarbon content (interference). Some elements (Cd, Se) may also be volatilized and show lower intensities on the second plate.

8. Photoplate Analysis

The plates are carefully examined for any of the types of interferences discussed previously. Based on this information, appropriate lines and charge states are selected for each element for the densitometric measurement of the altered isotopic ratio. Even though electrodeposition gives the "cleanest" possible spectrum, significant amounts of the sample's major cations and anions (from acid) are retained in the plated sample by occlusion, adsorption and absorption. The procedures used on these samples result in perchlorate being the major anion in the final solutions. Perchlorate fragments showed up in all three organic SRM's. The SSMS spectrum show lines for Cl^+, ClO^+, ClO_2^+, and ClO_3^+. The ClO^+ gives lines at m/e 51 and 53, these would interfere with SSMS ID analysis of V and Cr respectively if they had been determined in any of the samples (they were not). The

ClO_2^+ gives lines at m/e of 67 and 69 (two lines are due to the fact that Cl has two isotopes). Zinc is spiked with ^{67}Zn and therefore ClO_2^+ can interfere with the analysis of Zn. Fortunately, the amount of ClO_2^+ interference can be determined by measuring the line at 69. Also the measurement of the $^{67}Zn/^{64}Zn$ ratio can be made at Zn^{+3} (if enough Zn is recovered to give a measurable +3 zinc line) where zinc is free from ClO_2^+ interference.

Even if interferences are not detected, as many different charge states of an element are measured as is practical. This gives the maximum number of ratios (we stop at $\overline{<}20$/element) and improves the accuracy of the analysis. (A multiply charged ion is used only if both isotopes fall off unit mass and have no other type of interference). The +1 data for an element is calculated separately to determine if it gives significantly different results than that from the multiply charged ions. If it is different, it is assumed to be caused by an undetected interference and the +1 data are discarded.

Results

The results of the analysis of coal, beef liver and spinach are given in tables 1, 2, and 3.

Table 1. Trace elements (μg/g) in Coal, SRM 1632, by spark source mass spectrometry isotope dilution.

	Pb	Ag	Cd	Se	Zn	Cu	Tl
Bottle 358							
1	22.6	0.041	0.15	3.02	32	17.7	0.642
2	31.6	0.065	0.14	2.88	36	20.1	0.648
Bottle 292							
1	27.1	0.057	0.17	3.02	--	18.4	--
2	--	--	--	--	41	17.6	0.603
3	30.8	--	0.22	--	36	19.3	0.532
4	28.7	0.12	--	3.03	44	17.2	0.532
Average	28	0.07[a]	0.17	3.0	38	18	0.59

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[a] Recommended value ≤ 0.1.

Table 2. Trace elements (μg/g) in Beef Liver, SRM 1577, by spark source mass spectrometry isotope dilution.

	Pb	Cd	Ag	Mo	Se	Zn	Cu	Tl
1	0.41	0.32	0.058	3.25	1.13	126	181	0.048
1	0.41	0.29	--	--	1.12	128	183	0.046
2	0.38	0.26	0.060	3.08	1.12	131	184	0.050
2	0.33	0.27	0.081	--	1.07	--	182	0.051
3	0.36	0.27	0.054	3.34	1.12	130	184	0.047
3	0.33	0.27	0.077	3.24	1.12	130	197	0.050
4	0.33	0.28	0.061	3.24	1.10	121	183	0.045
6	0.34	0.26	0.067	--	1.12	120	181	0.043
Average	0.36	0.28	0.06	3.23	1.11	126	184	0.047

Table 3. Trace elements (µg/g) in Spinach, SRM 1570, by spark source mass spectrometry isotope dilution.

Sample No.	Lot No.	Pb	Tl	Cd	Cu	Zn
304	6-2	1.15	0.028	2.11	12.18	49.0
305-1	13-2	1.09	0.037	1.54	11.13	50.0
305-2	13-2	1.10	---[a]	1.53	11.25	50.2
306	9-1	1.15	0.029	1.50	11.36	48.7
Average		1.12	0.031	1.67	11.5	49.5

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[a] Insufficient data obtained for sample 305-2.

Table 3b. Cd and Cu in spinach (Lot 6-2)[a], additional sampling.

Element	µg/g
Cd	2.32[b]
Cu	12.54

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[a] Original sample depleted; additional material of the same lot was analyzed.

[b] The close agreement for the two independent runs on Lot 6-2 for Cd and Cu indicates that the Cd is inhomogeneous in the sample and should not be certified.

SECTION IV

ATOMIC ABSORPTION AND FLAME EMISSION SPECTROMETRY

A. Determination of Beryllium, Cadmium, Copper, Magnesium, Manganese, Mercury, Nickel, and Zinc by Atomic Absorption, and of Calcium, Potassium, Rubidium, and Sodium by Flame Emission Spectrometry in Biological and Botanical Materials.

T. C. Rains

1. Objective

The procedures described in this section were developed and applied to the quantitative determination of traces of beryllium, cadmium, copper, magnesium, manganese, mercury, nickel, and zinc, using atomic absorption spectrometry (AAS), and calcium, potassium, rubidium and sodium, using flame emission spectrometry (FES), in a variety of biological and botanical materials.

The uncertainty of these methods are 2 to 10 percent, and improvements in the accuracy of the measurements can be attained if a number of precautions are taken. Instrumental parameters must be optimized for each element; standard solutions should be prepared to contain the same chemical species as are present in the unknown sample. Also, the optimum precision and accuracy are attained by AES and FES when the technique of bracketing is used [1-4].

2. Principle

The absorption of radiant energy by ground state atoms in the gaseous state is the basis of AAS. When radiation of proper wavelength passes through a vapor containing ground state atoms, some of this radiation will be absorbed by excitation of particular atoms (3).

The magnitude of the absorption signal is directly related to the number of these ground state atoms found in the optical path. Ground state atoms necessary for the measurements are produced from the sample material, by vaporization of the material introduced in an adequate excitation source followed by dissociation of the molecular species into neutral atoms. Normally these steps are carried out by a nebulizer associated with a flame or by a nonflame excitation device [5,6].

In flame emission spectrometry a combustion flame is used to provide the energy necessary to atomize and to excite the atoms introduced into the flame. The solution containing the element of concern is converted into small droplets by a nebulization process. The small droplets enter the flame where they are dried, vaporized, and dissociated. The dissociated species are then excited to emit characteristic radiation having an intensity proportional to the number of excited particles. The emission spectra produced by various chemical species excited in combustion flames is relatively simple, and the discrete monochromatic radiations can be easily separated by a monochromator and measured by a photoelectric device with a minimum of radiation interferences [1]. In certain circumstances, the concomitant or flame gases can produce atomic lines or overlapping band structures which may interfere with the measurements. To overcome these difficulties in FES, it is recommended that repetitive optical scanning in the derivative mode be used. This technique was described by Snelleman et al. [7]. Further discussions on the principles of AAS and FES will be found in references 1 to 6.

3. Procedure

1. Instrumentation

A number of commercial instruments are available to perform measurements by AAS and FES, and it is assumed that the analyst is familiar with his particular instrument. It is not possible in this section to give detailed instructions concerning specific instrumental parameters to assure stability, linearity, adequate flame conditions, etc. for all the available commercial instruments. For AAS, the Perkin Elmer Models 403 and 603 were used in this work.[1] For FES, the instrumentation described by Snellman et al. (7) was used.

2. Reagents

All standard stock solutions were prepared from high purity metals or salts[2] as described in reference 2, Chapter 13 reproduced in Appendix 14. All other solutions were prepared from ACS reagent grade chemicals. All acids were NBS purified [8].

3. Sample Preparation and Analysis

It is difficult to cover the many problems associated with sampling the variety of plant and animal tissues. The sample, of course, must be representative, and it must be protected from contamination and deterioration prior to analysis [9, see also Appendix 2]. It must be determined at the start if the analysis is to be reported on the "as received" basis or after drying to a constant weight by one of several methods [1,9].

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[1] In order to describe adequately the materials and experimental procedures, it was occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Bureau of Standards, nor does it imply that the particular product or equipment is necessarily the best available for that purpose.

[2] Editor's Note - The weights given in this reference were calculated on the assumption that the compounds are 100 percent pure.

a. Sample Preparation and Analysis for Na, K, Rb, and Ca by Flame Emission Spectrometry.

The following procedure is applicable for the dissolution of a variety of tissues such as NBS Orchard Leaves, SRM 1571, and Bovine Liver, SRM 1577, for the determination of the elements mentioned above:

> Transfer a 2 to 5-g sample of tissue to a 100 ml Teflon beaker and add 25 ml of dilute nitric acid 1:1. Digest on a hot plate for one hour, and cool and rinse the sides of the beaker with water. Add 10 ml of HNO_3 and 5 ml of HF and evaporate to approximately 10 ml. If the sample contains black particles of unreacted carbon, repeat the addition of 10 ml of HNO_3. Add 10 ml of $HClO_4$, heat to strong fumes of perchloric acid, cool and wash the sides of the beaker and continue the digestion until the sample volume is reduced to approximately 2 ml. In some analyses where the concentration of the analyte is less than 1 µg/g, separation and preconcentration are required, therefore, the volume of samples should be evaporated to near dryness to remove excess acid. Transfer the solution to a 100-ml volumetric flask and dilute to volume with water.

Proceed with the FES determination as described for each individual element.

4. Determination of Sodium by FES

Prepare a standard stock solution of sodium from NBS SRM 919, Sodium Chloride, as described in reference [2] (see Appendix 14). Prepare a series of standard working solutions from the standard stock solution containing 1.0, 2.0, 3.0, 4.0 and 5.0 µg Na/ml in 0.1N $HClO_4$. Transfer duplicate test portions of the sample to 100-ml volumetric flasks. The aliquot taken will depend upon the concentration of sodium in the sample. The final concentration should be 2.0 to 3.0 µg Na/ml in the final volume of 100 ml.

To one volumetric flask, add 100 µg of Na and dilute the solution to volume. Label this sample as spiked with 1.0 µg Na/ml. Start the FES instrument [7], set the wavelength control to 589.0 nm, and, install an oxy-hydrogen burner (total consumption) in the instrument. Set the tank regulators and flow rates for the oxygen and hydrogen as recommended by the burner manufacturer. Light the oxy-hydrogen burner and allow the burner and the spectrometer to stabilize for 15 minutes while aspirating water. Nebulize the 5.0 µg Na/ml or higher standard into the flame and adjust the amplifier gain until the emission signal is reading 90 percent transmission or 90 divisions on the strip chart recorder. Nebulize water after each sample or standard and record the percent transmission. Nebulize the 1.0, 2.0, 3.0, 4.0 and 5.0 µg Na/ml into the flame and record the percent transmissions. Repeat the measurements until the percent transmissions of the standards do not deviate by more than ±0.5 percent. Nebulize the unknown solutions and record the percent transmissions. Repeat the nebulization of water between all samples. Nebulize a standard solution after each 3 to 5 unknown solutions. (Note: If the FES instrument drifts, the standard solutions should be repeated more often.) Determine the net percent transmission for the standards and unknowns by substracting the background and water readings from each standard and unknown. Calculate the concentration of the unknown sample as follows:

Calculation

Set up a calibration curve using a least square fit on a hand calculator. (Note: If a hand calculator or computer is not available, plot on rectilinear graph paper the percent transmission corrected for the background, as the ordinate, and the concentration of the standards, expressed in micrograms of analyte per milliliter, as the abscissa. The calibration curve should pass through the origin). Determine the concentration of the unknowns from the calibration curve. If the recovery of the standard addition is not 100 percent, correct the concentration by the following equation:[3]

$$C = x \cdot \frac{s}{y-x}$$

where: x = µg/ml of analyte in the unknown as determined from the calibration curve.

s = amount of standard added, µg/ml in final volume.

y = µg/ml of analyte found in unknown with standard added as determined from the calibration curve.

C = concentration µg/ml.

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[3] The calculation procedure used here is also applied to the succeeding determinations described in this section.

Calculate the analyte concentration of the original sample as follows:

let W = weight of solid sample, g,

Vs = volume of liquid in which W is dissolved, ml,

V = test portion of liquid sample or aliquot of Vs, ml,

Z = dilution factor $= \dfrac{V_1 \, V_2 \cdot \cdot \cdot V_n \, V_f}{a_1 \, a_2 \cdot \cdot \cdot a_n}$

where: V_1 = volume to which V is first diluted, ml,

a_1 = aliquot of V_1, ml,

V_2 = volume to which a_1 is diluted, ml,

a_2 = aliquot of V_2, ml, etc. to V_n and a_n,

V_f = final volume on which measurement is made, ml.

C = analyte concentration of V_f, µg/ml; then analyte in the original sample,

$$\mu g/g = \frac{C \cdot Z \cdot V_s}{V \cdot W}$$

5. Determination of Potassium by FES

Prepare a standard stock solution of potassium as described in reference [2], and prepare a series of standard working solutions from the standard stock solution containing 1.0, 2.0, 3.0, 4.0 and 5.0 µg K/ml in 0.1N $HClO_4$. Proceed as directed in paragraph 4 (page 52) except set the wavelength control to 766.5 nm.

Calculations

Proceed as directed in Calculations, page 54.

6. Determination of Rubidium by FES

Prepare a standard stock solution of rubidium as described in reference [2], and prepare a series of standard working solutions from the standard stock solution containing 0.1, 0.2, 0.3, 0.4, and 0.5 μg Rb/ml in 0.1N $HClO_4$ which also contains 100 μg K/ml. Transfer duplicate test portions of the sample to 10-ml volumetric flasks. (Note: Select an aliquot of the sample that will provide a final concentration of 0.2 μg Rb/ml.) To one volumetric flask, add 1.0 μg of Rb and dilute the solution to volume. Start the FES instrument [7], set the wavelength control to 780.0 nm and proceed as directed in item 4 (page 52).

Calculation

Proceed as directed in Calculations, page 54.

7. Determination of Calcium by FES

Prepare a standard stock solution of calcium as described in reference [2] using NBS SRM 915, Calcium Carbonate. Prepare a series of working solutions of calcium containing each 1000 μg K/ml in 0.1 N $HClO_4$. The concentration of the standards will depend upon the type of tissue to be analyzed. (Note: For NBS-Bovine Liver, standard solutions containing 0.2, 0.4, 0.6, 0.8 and 1.0 μg Ca/ml were prepared. For NBS-Orchard Leaves, standard solutions containing 2.0, 4.0, 0.6, 0.8 and 10.0 μg Ca/ml were prepared.) Select an aliquot of the unknown and spike with an appropriate concentration of calcium as described in item 4 (page 52). (Note: A solution of K must be added to the unknown to provide a final concentration of 1000 μg K/ml.) Start the FES instrument [7], set the wavelength control to 422.7 nm and install a premix laminar flow burner with a 5-cm slot burner head. Set the tank regulator and flow rates for air, nitrous oxide, and acetylene as recommended by the manufacturer and light the air-acetylene flame. Switch to nitrous oxide-acetylene, while observing all safety precautions recommended by the manufacturer for nitrous oxide-acetylene flame. Proceed as directed in paragraph 4 (page 52).

Calculations

Proceed as directed in Calculations, page 54.

b. Sample Preparation and Analysis for Be, Cd, Cu, Mg, Ni, Mn, and Zn by Atomic Absorption Spectrometry.

The sample preparation procedure described in paragraph 3, page 51, is used for the dissolution of a variety of tissues such as orchard leaves (SRM 1571), and bovine liver (SRM 1577) for the determination by AAS of the elements mentioned above.

8. Determination of Beryllium by Nonflame AAS

Prepare a standard stock solution of beryllium as described in reference [2], and prepare a series of standard working solutions from the standard stock solution containing 0.005, 0.010, 0.015, 0.020 and 0.025 μg Be/ml in 0.1N HNO_3. If the unknown solutions contain more than 10 μg Ca/ml, add an equal amount of calcium to the beryllium standard working solutions. Transfer duplicate test portions of sample to 100 ml Teflon beakers, evaporate to near dryness. Add 4 ml of 0.2N HNO_3, and transfer to 10-ml volumetric flasks. Select an aliquot that will provide a final concentration of Be in the range of 0.010 to 0.015 µg Be/ml. To one volumetric flask, add 0.05 µg of Be and dilute the unknown solution to volume. Start the instrument (Perkin-Elmer Model 603 equipped with the HGA-2100 graphite furnace) as described in the instruction manual [12]. Turn on the beryllium hollow cathode lamp, adjust the lamp current to 14 mA, and set the wavelength to 234.9 nm using a slit width of 0.7 nm. Turn on the D_2 arc lamp, and allow the hollow cathode and D_2 arc lamps to warm for 15 minutes, then balance the two beams. Set the HGA-2100 furnace at the following instrumental conditions: dry for 30 seconds at 100 °C; char for 40 seconds at 700 °C; atomize for 7 seconds at 2800 °C. Set the instrumental condition as follows: peak height integration time for 5 seconds; scale expansion for 1.0. Using an Eppendorf pipette, transfer 0.005 to 0.025 µg Be/ml, establish a calibration curve and repeat the calibration curve until the absorbances are within ±5 percent. Determine the net absorbances of the unknown and standard solutions. (Note: to increase the precision of the analysis, analyze each sample in triplicate.)

Calculation

Proceed as directed in Calculations, page 54, except plot absorbance instead of transmission *versus* concentration.

9. Determination of Cadmium by Nonflame AAS

Prepare a standard stock solution of cadmium as described in reference [2] and prepare a series of standard working solutions containing 0.002, 0.004, 0.006, 0.008 and 0.010 µg Cd/ml in 0.1N HNO_3. Proceed as directed in paragraph 8 (page 57) except for the following instrumental conditions: for the

Perkin Elmer 603 instrument set the cadmium hollow cathode lamp at 8 mA and wavelength at 228.8 nm; set the HGA-2100 furnace: dry for 30 seconds at 100 °C; char for 40 seconds at 250 °C; atomize for 7 seconds at 2100 °C.

Calculations

Proceed as directed in Calculations, page 54, except plot absorbance instead of transmission versus concentration.

10. Determination of Copper by AAS

Prepare a standard stock solution of copper as described in reference [2], and prepare a series of working solutions of 0.5, 1.0, 2.0, 3.0 and 4.0 μg Cu/ml in 0.1N $HClO_4$ that contain 500 μg Na/ml. (Note: For plant material, potassium should be substituted for sodium.) Transfer duplicate test portions of the sample to 25-ml volumetric flasks. Select an aliquot of the sample that will provide a final concentration of 1.0 to 2.0 μg Cu/ml. To one volumetric flask add 25 μg of Cu and dilute the unknown solution to volume. Attach a premixed air-acetylene burner having a three slot burner head to the Perkin-Elmer 603 AAS unit as described in the instruction manual [12], and turn on the unit containing a copper hollow cathode lamp. Set the hollow cathode lamp current at 15 mA, set wavelength to 324.7 nm, and use a slit width of 0.2 nm. Turn on the D_2 arc lamp, allow the lamp to warm for 10 minutes, and balance the two beams. Set the instrumental conditions as follows: mode-concentration, integration time for 5 seconds, scale expansion 2.0. Turn on the air-acetylene flame and allow the burner to warm for 15 minutes while nebulizing water. Construct a calibration curve by nebulizing the series of analyte standards and measuring their absorbance. Always nebulize water before and after taking a measurement of the standards or unknown solutions. Obtain a net absorbance by subtracting any reading obtained for the water from the readings of the standard solutions. Repeat the calibration curve until the absorbances are within ±2 percent. Measure the absorbance of the unknown including a reagent blank. (Note: To increase the precision and accuracy of the analysis, measure a low standard, unknown, and then a higher standard.) Obtain the net absorbance by substracting any reagent blank and/or readings obtained for the water from the readings of the standard solution.

Calculations

Proceed as directed in Calculations, page 54, except plot absorbance instead of percent transmission *versus* concentration.

11. Determination of Magnesium by AAS

Prepare a standard stock solution of magnesium as described in reference [2], and prepare a series of working solutions of 0.1, 0.2, 0.3, 0.4, and 0.5 μg Mg/ml in 0.1N $HClO_4$ that contains 0.1 percent lanthanum solution. (Note: Magnesium concentrations of 0.5 to 2.5 μg/ml can be used for many types of plant tissues, but due to the nonlinearity of the calibration curve, the unknown samples must be closely bracketed with standard solutions.) Transfer duplicate test portions of the sample to 25- or 100-ml volumetric flasks and select an aliquot of the sample that will provide a final concentration of 0.2 μg Mg/ml. Add 0.1 percent lanthanum solution to all samples. To one volumetric flask, add a concentration of magnesium that will provide a final concentration of 0.1 μg Mg/ml. Proceed as directed in paragraph 10, (page 59), except set the wavelength to 285.2 nm and the magnesium hollow cathode lamp at 15 mA.

Calculations

Proceed as directed in Calculations, page 54, except plot absorbance instead of percent transmission *versus* concentration.

12. Determination of Manganese by AAS

Prepare a standard stock solution of manganese as described in reference [2], and prepare a series of working solutions of 0.5, 1.0, 1.5, 2.0 and 2.5 μg Mn/ml in 0.1 N $HClO_4$ that contain 300 μg K/ml and 20 μg Ca/ml. (Note: For some animal tissues, the manganese concentration may be a factor of 10 lower. In this case the analyst should use the nonflame technique with Mn standard solutions of 0.005 to 0.025 μg/ml.) Transfer duplicate test portions of the sample to 25-ml volumetric flasks and select an aliquot of the sample that will provide a final concentration of 1.0 to 1.5 μg Mn/ml. Add a known concentration of manganese to one of the samples as described previously. Proceed as directed in paragraph 10 (page 59) except set the wavelength to 279.5 nm and the manganese hollow cathode lamp at 18 mA.

Calculations

Proceed as directed in Calculations, page 54, except plot absorbance instead of percent transmission *versus* concentration.

13. Determination of Zinc by AAS

Prepare a standard stock solution of zinc as described in reference [2], and prepare a series of working solutions of 0.1, 0.2, 0.3, 0.4 and 0.5 μg Zn/ml in 0.1N $HClO_4$ that contain 300 μg K/ml and 200 μg Ca/ml. Transfer duplicate test portions of samples to 25-ml volumetric flasks and select an aliquot of the sample that will provide a final concentration of 0.2 to 0.3 μg Zn/ml. Add a known concentration of zinc to one of the samples as described previously, and proceed as directed in paragraph 10 (page 59) except set the wavelength to 213.8 nm and the zinc hollow cathode lamp at 10 mA.

Calculations

Proceed as directed in Calculations, page 54, except plot absorbance instead of percent transmission *versus* concentration.

14. Determination of Mercury by Cold Vapor AAS Sample Preparation

The following procedure is applicable for the dissolution of a variety of tissue samples such as NBS-SRM Orchard Leaves and Bovine Liver for the determination of mercury. The equipment used in this procedure is described by Rains and Menis [11].

Transfer a 2 to 3-g sample to a digestion flask, add 25 ml of 18N H_2SO_4 and 20 ml of 7N HNO_3 and connect the Allihn condenser. Using a heating mantle, gently heat the flask for one hour at 150 °C. Cool the flask, rinse the inside of the Allihn condenser and add 20 ml of HNO_3 - $HClO_4$ (1+1) through the condenser. Drain the water from the condenser and continue heating the flask until dense fumes of perchloric acid appear. Cool the flask and rinse the inside of the Allihn condenser with 5 ml of water. If the sample shows a tendency to char, add an additional 10 ml of HNO_3 and reheat to fumes of perchloric acid. Continue heating the flask until dense fumes of H_2SO_4 appear, cool, and rinse the condenser with 1:10 HNO_3. Heat to boiling, cool, and rinse the condenser again. Transfer the solution to a 100-ml volumetric flask, add 5 drops of one percent solution of $K_2Cr_2O_7$ and dilute to volume. Proceed with the determination of mercury by the cold vapor method as described in the next paragraph.

Determination

Prepare a standard stock solution of mercury as described in reference [2], and prepare a series of standard working solutions that contain 0.005, 0.010, 0.015 and 0.020 μg Hg/ml in 0.1M HNO_3. Add five drops of one percent $K_2Cr_2O_7$ and dilute to volume. Allow samples and standards to digest one hour after the addition of $K_2Cr_2O_7$ before proceeding with the analysis. Prepare "reducing" and "diluting" solutions as described in Appendix 15. Turn on the Perkin-Elmer 403 AAS unit as described in reference [12], insert the mercury hollow cathode lamp, and set the current at 10 mA. (Note: Any commercial hollow cathode lamp will give adequate sensitivity; however, vapor discharge lamps are not recommended due to severe line broadening.) Attach a quartz absorption cell (10 cm x 0.8 cm) to the burner head. This absorption cell can be constructed from a 0.8 cm internal diameter and 10 cm long Vycor tubing with gas inlet and outlet ports and quartz windows. The quartz windows are secured to the Vycor tubing with epoxy cement. The cell is wrapped with a heating tape and attached to the burner head. Turn on the

D_2 arc lamp and allow it to warm up for 15 minutes, then balance the hollow cathode and D_2 arc lamps as recommended in the instruction manual. Heat the absorption cell to 200 °C with the aid of a variable autotransformer as directed in Appendix 15. Attach the reducing cell and set argon gas flow at 0.3 l/min. Transfer an aliquot of standard mercury working solution to the reducing cell. (Note: A mercury concentration of 0.2 µg will give an absorbance of 0.800.) Dilute to 25 ml with diluting solution, and turn on recorder. Add 20 ml of reducing solution and immediately close the system. Record maximum absorbance. (See comments under calibration in Appendix 15.) Obtain a net absorbance by substracting the value obtained for the reagent blank from the standard solution. Repeat the calibration curve until the absorbance values are within ±2 percent. Transfer an aliquot of unknown sample that has a mercury concentration of 0.01 to 0.1 µg into the absorption cell. Proceed as directed above. Bracket the unknown sample with standard samples since the mercury calibration curve is nonlinear.

Calculation

Proceed as directed in Calculations, page 54, except plot absorbance instead of percent transmission *versus* concentration.

4. References

[1] Dean, J. A., and Rains, T. C., eds., Flame Emission and Atomic Absorption Spectrometry, Vol. 3, Elements and Matrices, (Marcel Dekker, New York, 1975).

[2] Dean, J. A., and Rains, T. C., eds., Flame Emission and Atomic Absorption Spectrometry, Vol. 2, Components and Techniques, (Marcel Dekker, New York, 1971). Chap-

ter 13, Standard Solutions for Flame Spectrometry is reproduced as Appendix 14.

[3] Dean, J. A., and Rains, T. C., eds., Flame Emission and Atomic Absorption Spectrometry, Vol. 1, Theory, (Marcel Dekker, New York, 1969).

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B. Determination of Calcium, Potassium, and Sodium in Flour by Emission Flame Spectrometry.

J. R. Baldwin and R. Mavrodineanu

1. Objective

The purpose of the procedure described in this paper is to determine calcium, potassium, and sodium in flour using emission flame spectrometry.

2. Principle

Emission flame spectrometry is based on the well known principle that chemical species, when properly energized, may re-emit the absorbed energy as radiations.

These radiations are specific for every emitting species and their intensities are proportional to the number of particles, atoms, ions, molecules, or free radicals, participating in the radiation process. These two properties are at the foundation of qualitative and quantitative spectral analyses [1]

In the present case, the excitation energy is supplied by a pre-mixed acetylene-air combustion flame into which the analytical sample is introduced, in a constant and reproducible manner, as a suspension of fine droplets using compressed air and a pneumatic sprayer.

3. Procedure

Instrumentation

The equipment needed to perform the analysis consists in principle of the analytical flame, with its sample supplying system, an adequate spectrometer followed by a photodetector, and a data acquisition and presentation system. A detailed description of the equipment assembled and used for this purpose at NBS, is given in reference [3], which is reproduced in Appendix 16. A pre-mixed acetylene-air flame with pneumatic sprayer was used in this work. Further information on the instrumentation and methodology used in general for Na, K, and Ca determinations by emission flame spectroscopy will be found in reference [2].

4. Reagents

Distilled water
Nitric acid
Perchloric acid
Lanthanum perchlorate, 10 mg La/ml, made by dissolving 11.727 g La_2O_3, reagent grade, in 83 ml of perchloric acid, diluted to 1 liter with distilled water.
Sodium, potassium and calcium stock standard solutions, each containing 1000 µg/ml. These solutions were made by dissolving for:

Sodium: 2.5447 g sodium chloride 99.9 percent pure, SRM 919, in 1000 ml distilled water to which 5-ml nitric acid were added; Potassium: 1.9087 g potassium chloride 99.9 percent pure, SRM 918, in 1000 ml distilled water to which 5-ml nitric acid were added; Calcium: 2.4997 g calcium carbonate 99.9 percent pure, SRM 915, in 1000 ml distilled water to which 5 ml nitric acid has been added.

This basic standard solution as well as the composite diluted solutions were kept in polyethylene bottles.

Composite Standard Solutions:

Suitable dilutions of the above stock solutions are made with distilled water as indicated below to produce the standards needed to calibrate the emission flame spectrometer:

Composite Solution	µg/ml Na	K	Ca
1	0.35	50	8
2	0.50	80	10
3	0.70	100	16
4	1.00	120	24

These composite standard solutions were used in the determination of Na and K.

For the determination of Ca, a lanthanum solution was added to the same concentrations of Na, K, and Ca, to produce solutions containing a final concentration of 1000 µg/ml La each.

5. Sample Preparation

The weight loss at 85 °C is determined in separate 1-g flour samples taken in duplicate. Each sample is weighed separately into a glass weighing bottle provided with a cover. The bottles are placed uncovered in an oven at 85 °C for 20 hours, then placed in a desiccator. After cooling, they are weighed with the cover on.

For the analysis, 5 g of flour sample is weighed in five replications at the same time the samples for weight loss are taken. The weighing is made to the nearest 0.1 mg. Each sample is transferred to a 250-ml Teflon beaker provided with a Teflon cover, and 10 ml of distilled water is added to each sample. The samples are treated with a mixture of 30 ml of HNO_3 and 5 ml of $HClO_4$ on a hot plate until all organic matter is destroyed. During this time, HNO_3 is added, periodically, in 5 ml portions, as needed to remove all organic matter, and the walls of the beaker are washed periodically with a minimum of water. Finally, the walls of the beaker are washed for the last time, and the contents of the beaker is evaporated to about 1 ml. This operation can take approximately one day, and depends on the type of the flour.

To this residue, 10 ml of water are added, the solution is transferred in a 50-ml polypropylene volumetric flask, and diluted to mark with water. This solution is used for the determination of Na and K. Calcium is determined in a similar solution to which lanthanum was added to minimize the interfering action of phosphorous. Thus, 5 ml of the lanthanum stock solution are added to the sample to provide a final concentration of 1000 μg/ml La. A corresponding amount of lanthanum stock solution is added to each standard solution to provide a final concentration of 1000 μg/ml La.

The spectrometer is calibrated in the usual manner, before and after measuring the sample solutions, and the measurements are made at 5889.9 Å for sodium; 7664.9 Å for potassium; and 6214 Å for calcium (CaOH molecular band maximum). The samples are measured each in six replications and their content of Na, K, and Ca is found by interpolation on the standard calibration curves which are prepared by plotting as the abscissa the concentrations of the standard solutions (μg/ml) and the corresponding photocurrent values (volts on the digital voltmeter) as the ordinate.

Calculation and Results

The amount of element contained by the flour is expressed as μg/g and is referred to the material on an "as received" basis. An example is given in Table 1 for a wheat flour sample and in Table 2 for a rice flour including the percent loss at 85 °C.

Table 1. Determination of sodium, potassium, and calcium (µg/g) in a wheat flour sample on an "as received" basis.

Sample No.	Sodium	Potassium	Calcium
1	0.695	116	16.44
2	0.695	115	16.33
3	0.658	109	16.22
4	0.650	105	16.77
5	0.670	108	15.34
Average µg/g in Aliquot	0.674	110.6	16.22
Standard Error (SE)	0.01	2.1	0.24
Percent SE	1.4	1.9	1.5
Average µg/g in Sample	6.71	1102.0	161.6

Loss: Twenty hours at 85 °C; 8.6 percent.

Table 2. Determination of sodium, potassium, and calcium (µg/g) in a rice flour sample on an "as received" basis.

Sample No.	Sodium	Potassium	Calcium
1	0.430	91	11.55
2	0.425	92	11.10
3	0.420	86	10.45
4	0.465	92	11.10
5	---	94	11.78
Average µg/g in Aliquot	0.435	91	11.20
Standard Error (SE)	0.01	1.3	0.23
Average µg/g in Sample	4.32	905.0	111.6

Loss: Twenty hours at 85 °C; 8.3 percent.

6. References

[1] Mavrodineanu, R., and Boiteux, H., Flame Spectroscopy, (John Wiley, New York, 1965).

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SECTION V

MOLECULAR ABSORPTION SPECTROMETRY

Procedures for the Determination of Arsenic, Copper, and Nickel by Molecular Absorption Spectrometry

R. W. Burke and B. I. Diamondstone

1. Objective

The procedures to be described have been used in the Analytical Chemistry Division for several years for the routine determination of trace concentrations of arsenic, copper, and nickel in a variety of tissue samples. Through appropriate selection of experimental conditions, analyses for these three elements can be readily performed at the 0.01 part-per-million (ppm) level.

Immediately following are detailed descriptions of the procedures currently used and recommended for the determination of these trace elements in biological matrices. To demonstrate the broad applicability of these methods, typical results are given for the analyses of some recently issued and pending Standard Reference Materials (SRM's).

2. Principle

The determination of arsenic is based on the formation of a deep red color when arsine is reacted with a pyridine solution of silver diethyldithiocarbamate; copper is determined as the yellow complex of Cu(II) - dibenzyldithiocarbamate; and nickel is determined as α-furildioxime chelate.

3. Spectrophotometric Procedure for Arsenic

Samples are wet-ashed in a mixture of high purity nitric and perchloric acids prepared at NBS (Appendix 1). To eliminate volatilization losses all dissolutions are performed under reflux in a Bethge apparatus. The arsenic(V) formed is reduced to arsine (AsH_3) in a special generator flask and the latter is absorbed in a pyridine solution of silver diethyldithiocarbamate. The deep red color which develops, and whose exact nature is not completely understood, is measured spectrophotometrically and compared to a series of known arsenic standards.

4. Apparatus

Bethge Dissolution Apparatus. Available from G. Frederick Smith Chemical Company, Columbus, Ohio.[1]

Arsine Generator/Absorption Tube. Commercially available from Arthur H. Thomas or Fisher Scientific.

Spectrophotometer. Any stable single or double beam instrument having reproducible cuvette positioning and a thermostatable sample compartment which will accept 10 mm rectangular cuvettes. Readability and reproducibility should be 0.001 absorbance or better.

Cuvettes. Rectangular, semi-micro, thick-walled, of glass or quartz construction fitted with Teflon stoppers and having a light path of 10 mm and an internal width of 4 mm.

Shaker-Water Bath. A Dubnoff type or its equivalent.

5. Reagents

Silver Diethyldithiocarbamate, 0.5 percent. Dissolve 1 g of silver diethyldithiocarbamate in 200 ml of pyridine. Store in an amber bottle.

Potassium Iodide, 15 percent. Dissolve 15 g of KI in 100 ml of distilled water and store in an amber bottle.

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[1] In order to describe materials and experimental procedures adequately it was occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Bureau of Standards, nor does it imply that the particular product or equipment is necessarily the best available for that purpose.

Stannous Chloride, 21 percent. Dissolve 25 g of $SnCl_2 \cdot 2H_2O$ in 100 ml of concentrated hydrochloric acid.

Arsenic(V) Standard Stock Solution, 100 ppm. Dissolve 0.1320 g of As_2O_3 in 10 ml of water containing 1 g of NaOH. Oxidize As(III) to As(V) by addition of 2 ml of saturated bromine water. Warm on a hot plate or steam bath to remove excess bromine. Cool and dilute to 1 liter with distilled water. This solution contains 100 μg As(V)/ml.

Arsenic(V) Working Standard, 1 ppm. Prepare 1 μg As(V)/ml working standard by diluting 10 ml of the standard stock solution to 1 liter with distilled water. Prepare fresh weekly.

Zinc. Use granulated zinc that is 20 mesh or less and whose arsenic content does not exceed 0.02 ppm.

6. Analysis Procedure

Dissolution. Depending upon the expected arsenic content, weigh a 1 to 5 g sample of dried[2] tissue and transfer to the round bottom flask of the Bethge apparatus. Add 30 ml of a 1:1 mixture of high purity nitric and perchloric acid and connect the flask to the reflux condenser. With cold tap water running through the condenser, gradually raise the temperature of the flask and contents to 120 °C by use of a variable transformer to control the power supplied to the heating mantle. The stopcock should remain open and the temperature maintained near 120 °C until all of the sample has dissolved. Close the stopcock and complete the oxidation by slowly raising the temperature to 210 °C. Initially no increase in transformer power will be necessary since the temperature will rise as the nitric acid distills up the side arm and condenses above the stopcock. Additional heat may be needed near the end of the oxidation to attain

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[2] See Section 1, Sample Preparation, page 5 for recommended drying procedures.

the 210 °C reading. Normally, 15 to 20 minutes are required to go from the 120 °C setting to 210 °C. At the latter temperature, the sample should be clear and exhibit a yellow or pale orange color. Lower the heating mantle, allow the flask and contents to cool and drain the nitric acid back into the sample solution. Wash down the inside of the Bethge apparatus with distilled water and transfer the contents of the flask to a 100-ml Teflon beaker. If silica is present add 0.5 to 1 ml of hydrofluoric acid. Evaporate to strong fumes of perchloric acid. Cool, add 5 ml of distilled water and evaporate to approximately 2 ml. If aliquots are to be taken for arsenic analysis, transfer the sample to a 25-ml volumetric flask and dilute to volume with distilled water.

Arsine Generation and Collection. Transfer the entire sample or a suitable aliquot (As $\geq$ 0.1 µg) to the generator flask and add sufficient concentrated HCl to give a total acid volume of 10 ml. Add 35 ml of water, 2 ml of 15 percent KI solution and 1 ml of 21 percent $SnCl_2$ solution. Mix and allow to stand at room temperature for 15 minutes in order to reduce As(V) to As(III). Cool the assembled generator in an ice bath for 30 minutes and transfer to a 25 °C shaker bath. Add 4.00 ml (Note A) of the pyridine solution of silver diethyldithiocarbamate to the collection tube. Disconnect the collector tube and add 2.5 g of zinc to the generator flask, using a wide-mouth funnel to keep zinc off the walls of the ground glass joint. Immediately connect the collection tube to the flask by clamping the ball joint together. Allow one hour for the evolution of

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Note A. For determining arsenic in the range of 0.1 to 0.5 µg, the amount of absorber solution used is reduced from 4.00 to 2.00 ml. In the latter instance, glass beads approximately 1 mm in diameter are used to produce the same length of column of absorber solution as was present in the normal run.

arsine to be completed. To avoid leaks, both the standard taper joint of the flask and the ball joint should be lubricated. "Nonaq" stopcock grease, available from Fisher Scientific, has proven satisfactory for this purpose. Disconnect the collection tube and, through either a rocking motion or by use of a disposable Pasteur-type pipette, rinse the walls of the tube with the absorber solution. Any residue must be redissolved and the pyridine solution thoroughly mixed. Transfer an aliquot to the 10-mm cuvette and measure the absorbance at 535 nm against a reagent blank prepared in the same way as the sample. Determine the amount of arsenic present by comparing the measured absorbance with the absorbances of a series of arsenic standards (0.5, 1, 2, 4, and 6 μg As/4.00 ml pyridine reagent or 0.1, 0.2, 0.3, 0.4 and 0.5 μg As/2.00 ml pyridine reagent - see Note A). Both systems obey Beer's law and the slopes of the two calibration curves are in the exact ratio of 1:2. The amount of arsenic present in the tissue sample is given by the relationship:

$$\text{Arsenic, ppm} = \frac{\mu\text{g Arsenic Found}}{\text{Sample Wt., g}}$$

$$\text{Arsenic, ppm} = \frac{\text{Sample Absorbance, } A_s}{\text{Slope of Calibration Curve } (A_s/\mu\text{g}) \text{ x Sample Wt., g}}$$

7. Results

The spectrophotometric arsine-silver diethyldithiocarbamate procedure for arsenic has been applied to the analysis of a number of NBS SRM's. Some typical results are given in Table 1.

Table 1. Spectrophotometric determination of arsenic in tissue samples by the arsine-silver diethyldithiocarbamate procedure.

Sample[a]	NBS SRM No.	Sample Wt., g	Arsenic, ppm
Orchard Leaves	1571	0.5	10.2; 10.3; 9.9; 10.1
Wheat Flour[b]	1567	5.0	0.03; 0.02; 0.03; 0.03; 0.03; 0.02
Rice Flour[b]	1861	5.0	0.09; 0.10; 0.10; 0.08; 0.08; 0.09
Spinach	1570	2.0	0.17; 0.18; 0.16; 0.18
Pine Needles	1575	2.0	0.22; 0.20; 0.20; 0.22
Tomato Leaves	1573	2.0	0.30; 0.29; 0.28; 0.29

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[a] Currently available from the NBS Office of Standard Reference Materials.

[b] In preparation.

Remarks

Antimony is the only potential interference in the spectrophotometric determination of arsenic in tissue by the arsine-silver diethyldithiocarbamate procedure. Upon reduction with zinc, stibene (SbH_3) is evolved which reacts similarly to arsine (AsH_3) when absorbed in a pyridine solution of silver diethyldithiocarbamate. Fortunately, the absorbance maxima of the two products are sufficiently different (λ_{max} for Sb = 505 nm; λ_{max} for As = 535 nm) and the presence of antimony can be checked by measurement of the 505/535 absorbance ratio. If only arsenic is present, this ratio should not exceed 0.80. If this ratio is exceeded, simultaneous equations can be used to correct for antimony interference since the absorbance of the colored arsenic and antimony products are additive at these two wavelengths. No corrections were necessary for any of the tissue samples analyzed to date.

8. Spectrophotometric Procedure for Copper

This procedure is based on the spectrophotometric measurement of the yellow complex formed in moderately strong acidic media between copper(II) and dibenzyldithiocarbamate after its isolation and preconcentration by extraction into a non-polar organic solvent. The selectivity and acid stability of the carbamate reagent is enhanced by using it in the form of its zinc chelate which is dissolved directly in the carbon tetrachloride extracting solvent. When this solution is equilibrated with an aqueous solution containing copper(II), the corresponding copper complex is formed and extracted almost instantaneously as a result of its chelate exchange reaction with zinc.

9. Apparatus

Spectrophotometer. Any stable single or double beam instrument having reproducible cuvette positioning and a sample compartment provided with temperature control which will accept 10 mm rectangular cuvettes. Readability and reproducibility should be 0.001 absorbance or better.

Cuvettes. Rectangular, semi-micro, thick-walled, of glass or quartz construction, fitted with Teflon stoppers and having a light path of 10 mm and an internal width of 4 mm.

Separatory Funnels. 60-ml capacity with Teflon stoppers and stopcocks. Stems are shortened to approximately 10 mm and the ends fire-polished.

10. Reagents

Zinc Dibenzyldithiocarbamate, 0.01 percent. Dissolve 20 mg of zinc dibenzyldithiocarbamate in 200 ml of carbon tetrachloride. Store in an amber bottle.

Copper Standard Stock Solution, 100 ppm. Dissolve 0.100 g of copper metal in 5 ml of 1:1 nitric acid. Evaporate to dryness and dissolve residue in 1N hydrochloric acid. Transfer to a 1 liter volumetric flask and dilute to the mark with 1N hydrochloric acid.

Copper Working Standard, 2 ppm. Dilute 5.00 ml of the standard copper stock solution to the mark with 0.1N hydrochloric acid in a calibrated 250-ml volumetric flask.

11. Analysis Procedure

Wet-ash 1 to 5 g of dried tissue in a 1:1 mixture of nitric and perchloric acids. Use 15 ml of the mixed acids for a 1-g sample and increase proportionately to 30 ml for 1 to 5-g of tissue. Dissolution may be carried out in a Bethge apparatus, using the conditions previously described for arsenic, or in a Teflon beaker. If a beaker is used, it should be covered with a Teflon lid until all reaction with the nitric acid has ceased. The cover is removed and rinsed with distilled water and the solution is heated to fumes of perchloric acid. Fuming is continued until approximately one-half of the perchloric acid is removed. The sample is cooled, the walls of the beaker are rinsed with distilled water and the fuming is repeated. When the sample volume has been reduced to 1 to 2 ml the beaker is removed from heat, cooled and reserved for copper analysis. If the total sample is to be used, it is transferred directly to a 60 ml separatory funnel and diluted to 25 ml with distilled water. If an aliquot is taken, the sample is first transferred to a 25-ml volumetric flask. In either instance the sample weight or aliquot size should be chosen so as to contain 1 to 10 μg of copper and a final acid concentration of 0.1 to 1N. Add 5.00 ml of the carbon tetrachloride solution of zinc dibenzyldithiocarbamate and extract the copper by shaking vigorously for one minute. While the phases are clearing, insert a loosely-fitting paper plug in the stem of the separatory funnel. Drain a portion of the carbon tetrachloride solution containing the yellow copper complex into a 10-mm cuvette and measure the absorbance of this solution at 435 nm against a reagent blank carried through the entire procedure. Determine the amount of copper present by comparing the net absorbance with the absorbances of known amounts of copper taken through the extraction procedure. Beer's law is obeyed over the range 1 to 10 μg of copper. When absorbance is plotted as a function of micrograms of copper added, the slope of the resulting calibration curve should be approximately 0.051 absorbance units per microgram of copper.

12. Results

The results obtained for copper in a series of new NBS botanical SRM's are summarized in Table 2. All values are reported on a dried basis, i.e., samples were heated in an air oven for one hour at 85 °C. Typical weight losses were of the order of five percent.

Remarks

Bismuth and thallium(III) are potential interferences in the spectrophotometric zinc dibenzyldithiocarbamate procedure for copper. However, neither of these elements has been found in sufficiently high concentrations to cause difficulty in any of the tissue samples analyzed.

Table 2. Spectrophotometric determination of copper in three new NBS botanical SRM's.

Sample[a]	NBS SRM No.	Sample Wt., g	Copper, ppm
Spinach	1570	0.5	12.03; 12.08; 12.07
Pine Needles	1575	1.0	2.94; 2.93; 2.95
Tomato Leaves	1573	0.5	10.81; 10.79; 10.83

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[a] Available from the NBS Office of Standard Reference Materials.

13. Spectrophotometric Procedure for Nickel

The preferred reagent for the spectrophotometric determination of nickel in tissues is α-furildioxime. It is superior to dimethylglyoxime because the wavelength of maximum absorbance of its nickel chelate lies in the visible region of the spectrum.

Nickel forms, with an excess of α-furildioxime, an insoluble chelate which can be quantitatively extracted [1] from aqueous media into chloroform in the pH range of 8.5 to 9.4. This extraction can be made very selective because the interference of cobalt and copper can be eliminated by backwashing the chloroform extract with ammonia. Citrate or tartrate is used to prevent the hydrolysis and subsequent interference of such common elements as iron and aluminum.

14. Apparatus

Spectrophotometer. Any stable single or double beam instrument having a sample compartment provided with temperature control which will accept 50-mm cuvettes. Readability and reproducibility should be 0.001 absorbance or better.

Cuvettes. 50-mm cylindrical or rectangular cuvettes having a maximum volume of 15 ml and equipped with snugly-fitting Teflon stoppers or covers.

Separatory Funnels. 60-ml capacity and fitted with Teflon stoppers and stopcocks. Stems are shortened to approximately 10 mm and fire-polished.

pH Meter. Equipped with individual or a combination glass-calomel electrode.

15. Reagents

α-Furildioxime, 1 percent. Dissolve 1 g of α-furildioxime in 100 ml of ethanol.

Nickel Standard Stock Solution, 100 ppm. Dissolve 0.100 g of nickel metal in 5 ml of 1:1 nitric acid. Evaporate to dryness and dissolve residue in 0.1N hydrochloric acid. Transfer to a 1-liter volumetric flask and dilute to the mark with 0.1N hydrochloric acid.

Nickel Working Standard, 1 ppm. Dilute 2.00 ml of the standard nickel stock solution to the mark with 0.1N hydrochloric acid in a calibrated 200-ml volumetric flask.

Ammonium Citrate, 10 g/100 ml. Dissolve 10 g of ammonium citrate in distilled water and dilute to 100 ml.

16. Analysis Procedure

Wet-ash, in a mixture of nitric and perchloric acids, a sufficiently large sample to give a minimum nickel content of 0.5 μg (see copper procedure for details). Dilute the acidic sample, or an appropriate aliquot, to 20 ml with distilled water and add, with mixing, 10 ml of ammonium citrate solution and 1.0 ml of alcoholic 0.1 percent α-furildioxime reagent. Adjust pH to 9.0 ± 0.3 with 1:1 NH_4OH and extract with 10.00 ml of chloroform. Repeat the extraction with a second 10.00 ml portion of chloroform and backwash the combined extracts with 10 ml of 1:40 NH_4OH. Place a loosely-fitting paper plug in the shortened stem of the separatory funnel and drain the chloroform extract into a 50-mm cuvette. Measure its absorbance at 435 nm against a reagent blank carried through the entire dissolution and extraction procedures. Determine the micrograms of nickel present from a calibration curve prepared from 0.50, 1.00, 2.00, 3.00 and 4.00 μg nickel standards.

17. Results

Table 3 shows some typical results for the determination of nickel in Orchard Leaves, NBS SRM 1571.

Table 3. Spectrophotometric determination of nickel in Orchard Leaves, NBS SRM 1571.

Sample Wt., g	Nickel, ppm
2	1.35; 1.41; 1.37; 1.33

Remarks

The use of the backwash step in the extraction procedure effectively removes the interference of copper and cobalt. Tests show that at least 50 μg of copper and 2 μg of cobalt can be tolerated in the determination of 1 μg of nickel.

18. Reference

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SECTION VI

FLUORESCENCE SPECTROMETRY

Determination of Beryllium by Fluorescence Spectrometry

S. A. Wicks and R. W. Burke

1. Objective

The procedure described in this section is used in the Analytical Chemistry Division to determine beryllium in tissue samples at the submicrogram level by fluorescence spectrometry.

2. Principle

The classical procedure for the determination of beryllium by fluorescence spectrometry is based on its reaction with morin. This method enjoys considerable popularity because of its high sensitivity. However, it suffers from two disadvantages: (a) the reagent is unstable, being particularly prone to oxidation even by atmospheric oxygen, and (b) the method lacks selectivity. These disadvantages necessitate the use of a carefully controlled, and hence tedious, procedure in order to obtain satisfactory results. In our experience, a more useful method for determining submicrogram amounts of beryllium, especially in tissue samples, utilizes the fluorescence of the beryllium 2-hydroxy-3-naphthoic acid complex in water near pH 7.5. This method has been described by Kirkbright, West and Woodward [1]. We have examined this method in detail and have subsequently made three modifications which significantly improve its practicality. (a) The need for silicone-coating the flasks to prevent absorption losses of beryllium has been eliminated by developing the complex under weakly acidic media (pH 2 to 3). The pH is then increased to 7.5 and the fluorescence measured at the end of five minutes.

(b) Phenol Red is used as an internal visual indicator for adjusting pH and (c) Preseparation of beryllium by extraction with acetylacetone [2] is used to improve selectivity and sensitivity.

3. Apparatus

Spectrofluorometer. Equipped with stabilized xenon source, variable slits and excitation and emission monochromators.

4. Reagents

Beryllium Stock Solution, 100 ppm. Dissolve 0.100 g of beryllium metal in 10 ml of 1:2 hydrochloric acid. Add 10 ml of perchloric acid and evaporate to $HClO_4$ fumes. Cool, transfer to a 1-liter volumetric flask and dilute to the mark with distilled water.

Beryllium Working Standard A, 1 ppm. To 10 ml of the beryllium stock solution, add 10 ml of perchloric acid and dilute to the mark in a 1-liter volumetric flask with distilled water. Prepare fresh daily.

Beryllium Working Standard B, 0.1 ppm. Dilute 10 ml of beryllium standard A and 1 ml of perchloric acid to the mark, in a 100 ml volumetric, with distilled water. Prepare fresh daily.

2-Hydroxy-3-Naphthoic Acid, $2 \times 10^{-4}M$. Dissolve 38 mg of 2-hydroxy-3-naphthoic acid in 5 ml of 1:10 ammonium hydroxide, transfer to a 1-liter volumetric flask and dilute to the mark with distilled water.

Masking Agent, Calcium-CDTA (cyclohexanediaminetetraacetic acid). Prepare the following solutions:

A. $CaCl_2$, 0.1M. Dissolve 7.35 g of $CaCl_2 \cdot 2H_2O$ in 500 ml of distilled water.

B. CDTA, 0.1M. Dissolve 3.46 g CDTA in 90 ml of distilled water by addition of 1:10 ammonium hydroxide. Adjust to pH 7.5 and dilute to 100 ml with distilled water.

Combine 25 ml of 0.1M calcium solution and 6 ml of 0.1M CDTA in a 100-ml volumetric flask and dilute to volume with distilled water.

Buffer Solution, pH 7.5. Dilute 50 ml of concentrated ammonium hydroxide to 300 ml with distilled water. Add sufficient glacial acetic acid to adjust pH to 7.5 and dilute to 1 liter with distilled water.

Ethylenediaminetetraacetic Acid, Disodium Salt Solution (EDTA), 10 Percent. Dissolve 10 g of the disodium salt in 100 ml of distilled water.

Acetylacetone, 5 Percent. Transfer 5 ml of acetylacetone to a 100 ml volumetric flask and dilute to the mark with distilled water.

Phenol Red Indicator, 0.1 Percent. Dissolve 100 mg of Phenol Red in 100 ml of distilled water.

Quinine Sulfate Standard, 5 ppm. Dissolve 5 mg of quinine sulfate dihydrate in 1 liter of 0.5M sulfuric acid.

5. Analysis Procedure

Wet-ash 1 to 5 g of dried tissue in a 1:1 mixture of nitric and perchloric acid in a platinum dish. Use 10 ml of the acid mixture for a 1-g sample and increase proportionately to 30 ml for sample weights in the range 1 to 5 g. If silica is present, add 1 ml of hydrofluoric acid. Cover the dish with a platinum lid and digest on a hot plate until oxides of nitrogen are no longer evolved. Cool, remove and wash the cover and the sides of the dish with 10 ml of distilled water. Heat to fumes of perchloric acid and continue fuming until volume has been reduced to approximately 1 ml. Dilute to 50 ml and add 2.0 ml of 10 percent EDTA solution. Add 2 to 3 drops of Phenol Red and adjust pH to 7 to 8 with 1:10 NH_4OH (until indicator just turns pink). Add 5 ml of five percent acetylacetone and readjust pH to 7 to 8. Allow the solution to stand for five minutes and then extract it with three 5-ml portions of chloroform. Combine the extracts in a platinum dish and cover with 10 ml of water, 2 ml of concentrated nitric acid and 2 ml of concentrated perchloric acid. Evaporate off the chloroform on a steam or water bath, transfer the dish to a hotplate and continue the evaporation to dryness. Add 2 ml each of nitric and perchloric acid and repeat evaporation to dryness. Dissolve the residue in 10 ml of 0.1N perchloric acid and transfer to a 100-ml volumetric flask. Dilute to approximately 70 ml with distilled water and add 5.0 ml of the calcium CDTA solution and 2 to 3 drops of Phenol Red solution. Adjust to pH 7 to 8 with 6N NH_4OH. Add 5.0 ml of pH 7.5 buffer and 5.0 ml of 2-hydroxy-3-naphthoic acid reagent. Dilute to volume with distilled water and mix. Transfer to a 10-mm cuvette and, after exactly five minutes, excite the beryllium complex at 373 nm and measure its fluorescence at 460 nm. Use a 0.5 ppm quinine sulfate solution in 0.1N sulfuric acid to correct for short term fluctuations in instrument sensitivity. This solution should be prepared fresh daily by ten-fold dilution of the stock quinine sulfate with distilled water. Determine the amount of beryllium present by comparing the measured fluorescence with that of a series of beryllium standards covering the range 0.05-0.5 μg Be.

6. Results

Table 1 summarizes the results obtained for beryllium in three SRM's which are currently available through the NBS Office of Standard Reference Materials.

Table 1. Beryllium content of three SRM's as determined by the acetylacetone extraction-2-hydroxy-3-naphthoic acid spectrofluorometric method.

Sample	SRM No.	Beryllium, ppm
Orchard Leaves	1571	0.026; 0.025; 0.025; 0.026
Bovine Liver	1577	0.021; 0.013; 0.020; 0.015
Coal	1632	1.52; 1.46; 1.50

Remarks

Some preliminary experiments carried out during the analysis of the orchard leaves suggest strongly that the preparative wet oxidation should be performed in platinum rather than Teflon. When 100-ng spike additions were made to 1-g samples of orchard leaves and the dissolution subsequently performed in 100 ml Teflon beakers, the recovery of the added beryllium was low and non-reproducible, usually in the range of 10 to 40 percent. The reason for this behavior is not understood at present. Recoveries from borosilicate glass container and platinum, however, were much superior to those observed from Teflon. Spike recoveries from platinum through the entire analysis procedure were 95 percent or better.

7. References

[1] Kirkbright, G. F., West, T. S. and Woodward, C., Spectrofluorometric Determination of Submicrogram Amounts of Aluminum and Beryllium with 2-Hydroxy-3-Naphthoic Acid, Anal. Chem. 37, 137-143 (1965).

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SECTION VII

POLAROGRAPHY

Determination of Aluminum, Bismuth, Cadmium, Copper, Iron, Lead, and Nickel.

Analysis of Botanical Standard Reference Materials by Cathode Ray Polarography[1]

E. June Maienthal

1. Objective

The procedure described in this section was developed and applied to the quantitative determination of traces of aluminum, bismuth, cadmium, copper, iron, lead, and nickel in botanical material by cathode ray polarography.

2. Principle

The principle of polarography is based on the unique characterization of the voltage - current curves, or polarograms, produced when a microelectrode is immersed in an electrochemically active solution. The abscissa, or voltage parameter, of the polarogram identifies the reducible or oxidizable chemical element present in a complex solution. The ordinate, or current parameter of the polarogram gives an information on the quantity of a particular element present in the solution.

The method is specific and sensitive, and requires only small volumes of solution for the analysis.

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[1] The material used in this section was taken from a work published by the author in the Journal of the Association of Official Analytical Chemistry, Vol. 55, No. 5, p. 1109 to 1113 (1972).

3. Procedure

Instrumentation: The Davis Differential Cathode Ray polarograph was used in performing the measurements described in this section.

Reagents: All solution are aqueous unless otherwise specified.

(a) Cupferron solution — 6 percent.
(b) Sodium acetate solution — 2M.
(c) Sodium acetate (2M) + EDTA (disodium salt) solution (0.1M).
(d) Solochrome Violet RS solution — 0.1 percent.
(e) Sodium tartrate solution — 20 percent.
(f) Potassium cyanide solution — 20 percent.
(g) Sodium diethyldithiocarbamate solution — 0.1 percent.
(h) Sodium citrate solution — 10 percent.
(i) Hydroxylamine HCl solution — 20 percent.
(j) Dimethylglyoxime solution — one percent in alcohol.

Iron and Aluminum, Acid-Soluble. Transfer 250 mg sample which has been dried 24 hours at 90 °C to 50 ml Erlenmeyer flask. Add 5 ml HNO_3, 1 ml HCl, and 1 ml perchloric acid; cover and heat cautiously until vigorous frothing ceases. Treat blank and standard solutions for the calibration curve similarly. Digest and fume to perchloric fumes, adding more HNO_3 if some organic material remains, and evaporate to dryness. Dissolve residue in 1 ml HCl and evaporate to dryness at <100 °C. Dissolve residue in 1 ml perchloric acid (1+1), transfer to 125 ml separatory funnel and dilute to ca 20-25 ml. Add 1 ml of six percent cupferron solution which has been filtered and cooled in ice and extract with four 10 ml portions of cold $CHCl_3$, adding a few drops of cupferron before each extraction. (If a reddish brown precipitate is formed more cupferron is needed.) Reserve combined organic extracts for determination of iron. Add 10 ml 2M sodium acetate solution to aqueous layer, add

1 ml six percent cupferron solution, wait 1-2 minutes and extract with 15, 10, and 5 ml portions of $CHCl_3$. Reserve combined organic extracts for determination of aluminum.

(a) Iron. Let $CHCl_3$ extract evaporate to dryness in stream of filtered air and destroy residual organic material by evaporation to dryness with a few ml HNO_3 and 1 ml perchloric acid. Add 1 ml HCl and evaporate to dryness at <100 °C. Dissolve residue in 0.4 ml H_2SO_4 (1+1); then add 5 ml 2M sodium acetate +0.1M EDTA (disodium salt) solution and adjust pH to ca 4 with NH_4OH. Dilute to 10.0 ml. Transfer portion of solution to polarographic cell, deaerate with nitrogen, and measure iron reduction peak subtractively with differential cathode ray polarograph at ca −0.2V vs. mercury pool anode, using background blank in second cell.

(b) Aluminum. Remove $CHCl_3$, destroy organic material, and evaporate with HCl as described above for iron. Dissolve residue in 1 ml perchloric acid (1+1) and 5 ml of 2M sodium acetate solution. Add 5 ml 0.1 percent Solochrome Violet RS solution. Dilute to 50.0 ml and transfer to polyethylene bottle fitted with cap. Heat in water bath five minutes at 55-70 °C, cool, transfer to polarographic cell, deaerate, and measure aluminum-dye complex reduction peak with cathode ray polarograph at ca -0.65V vs mercury pool anode. For aluminum, better peak resolution is obtained if blank signal is measured separately and then subtracted from that of sample.

Iron and Aluminum—Total. Proceed as above except filter the solution remaining after sample dissolution through Whatman No. 42 paper. Wash with HCl (1+9). Transfer residue to platinum crucible, dry, and ignite over burner. Add two drops perchloric acid and 10 drops hydrofluoric acid, and evaporate to dryness. Fuse residue in small amount of sodium carbonate. Add water and then HCl dropwise to neutralize sodium carbonate and transfer solution to reserved filtrate which has been evaporated to dryness. Proceed as described above for determination of iron and aluminum.

Lead and Bismuth. Wet-ash 1 g samples of dried material and evaporate as already described, except that ca 5-10 ml more of HNO_3 may be necessary to destroy all organic material. Treat blank and standard solutions for calibration curve similarly. Dissolve residue in 10 drops HCl and ca 10 ml water. Add ca 100 mg ascorbic acid to reduce iron and transfer solution to 125 ml separatory funnel. Add 10 ml 20 percent sodium tartrate solution, 30 ml HN_4OH, 10 ml 20 percent potassium cyanide solution, and 10 ml 0.1 percent sodium diethyldithiocarbamate. Extract lead and bismuth complexes with 15, 10, and 5 ml portions of $CHCl_3$. Evaporate $CHCl_3$ extracts and destroy organic material as already described. Dissolve residues in 0.5 ml HNO_3 (5+95) and 2.0 ml 20 percent sodium tartrate solution. Deaerate solution and measure polarographically as already described. The bismuth reduction peak occurs at ca -0.5V and lead at ca -0.7V vs. mercury pool anode.

Nickel. Wet-ash 1 g samples of dried material and evaporate as described for lead and bismuth. Treat blank and standard solutions for calibration curve similarly. Transfer solution to 30 ml separatory funnel with water, keeping final volume <10 ml. Add 1 ml 10 percent sodium citrate solution, 2 ml 20 percent hydroxylamine HCl, and 1 ml one percent dimethylglyoxime in alcohol. Make solution ammoniacal to methyl red plus three drops excess. Extract nickel complex with 15, 10, and 5 ml portions of $CHCl_3$. Evaporate $CHCl_3$ and destroy organic material as already described. Dissolve residue in 0.2 ml H_2SO_4 (1+1) and a small amount of water. Add 1 ml pyridine, dilute solution to 5.0 ml, and measure nickel polarographically as already described at ca -0.9V vs. mercury pool anode.

4. Discussion

The need for certified botanical standards both in research and in industrial and field applications is leading to the development and production of a number of new types of Standard Reference Materials by the National Bureau of Standards. Workers in the botanical and agricultural areas have long needed standards to assist in trace element determinations in leaves and plants. These standards would also be useful in the analysis of environmental samples such as air particulates and contaminated vegetation, and for calibration of much of the automated equipment now being used in these fields. Efforts have first been directed toward orchard, alfalfa, citrus, and tomato leaves, aspen chips, and pine needles.

The first of these botanical standards to be prepared, analyzed, and certified was Orchard Leaves SRM 1571 [1]. This standard was prepared from fruit leaves, mostly peach, with some apple and cherry leaves, gathered from an orchard near Lansing, Michigan.

In order to certify any given element in a Standard Reference Material, two completely independent methods or an accepted referee type method by two different laboratories must be used. The methods must be both sensitive and accurate.

The most frequently used methods of analysis by workers in botanical areas have included spectrophotometry, atomic absorption, emission spectroscopy, and classical wet chemical methods. Polarography has been utilized very little. Some of the polarographic methods have been described by Nangniot [2,3].

It is difficult to understand why polarography has not been more widely used when the sensitivity, accuracy, and resolution of the technique are considered. Differential cathode ray polarography has been applied successfully in this laboratory for the past few years for the determination of about 30 elements in many different matrices such as steels and alloys [4-10], food [9,10], environmental samples [5,7,9-11], and high purity reagents [6,7,9,10] covering concentration ranges from 3 x 10^{-9} to 100 percent. The reliability of these polarographic determinations has been verified through interlaboratory comparisons with many other techniques.

The proposed scheme was first to determine polarographically iron and aluminum in the orchard leaves; later lead, bismuth, copper, nickel, and cadmium were included.

Typical fruit leaf compositions range from about 100 to 300 ppm for both iron and aluminum, so sensitivity would be no problem. Previous work here has resulted in the determinations of as little as 0.1 μg iron or aluminum. In these cases the limitation on sensitivity was not instrumental but rather due to the blank coming from the reagents and the environment. For the iron and aluminum levels in the orchard leaves, the blank would probably be low enough with respect to the samples to be of no consequence.

Iron could be determined polarographically with no separations, but aluminum would have to be separated. Cupferron extraction at pH 4.5 has been used often here for separation of aluminum from the matrix [6]. This involves a preliminary extraction of iron cupferrate from an acid solution, so it seemed advantageous to reserve the extracted iron for its subsequent polarographic determination.

The best supporting electrolyte for the polarographic determination of aluminum is obtained by forming an aluminum-dye complex with Superchrome Garnet Y [8,12] or Solochrome Violet RS [12-15]. Iron could be determined with fewest interferences in an EDTA-sodium acetate supporting electrolyte.

Prior to the extractions, the organic material must first be removed by wet ashing. After this step a small amount of insoluble siliceous residue, which undoubtedly contained iron and aluminum, was always present; bismuth, cadmium, copper, lead, and nickel are not present in measurable amounts in this type of residue. This was probably the result of external sand or soil contamination of the fruit leaves and its content would have no relation to the actual leaf composition. Some nondestructive techniques, however, would only determine the total iron or aluminum, so it seemed advisable to determine separately the acid-soluble portion and then the total iron and aluminum on a separate sample by treating the residue with hydrofluoric acid, fusing it with sodium carbonate, and adding the fused residue to the original solution.

For lead and bismuth, a simplification of a procedure for their simultaneous determination, used in this laboratory for steels and cast iron [5,16], appeared feasible, since the orchard leaf matrix is much simpler for polarography than that of steels.

For the determination of nickel, a polarographic method developed for its determination as a trace element in Glass SRM 614 [1,10] appeared to be equally feasible, since the nickel in the orchard leaves was expected to be at about the 1 ppm level. The procedure described in this section was also used to determine iron, nickel, lead, and cadmium in tomato leaves and spinach Standard Reference Materials.

5. Results

The results for acid-soluble iron are shown in Table 1. The results for iron on the first set were not reported because of the extreme variation. The values on this set ranged from 195 to 359 ppm which is a far greater variation than has ever occurred before in this laboratory and could only be ascribed to gross and erratic environmental contamination or sample inhomogeneity. The normal blank for this procedure was in the vicinity of 0.3 ppm. The overall average value of 262 ppm is in good agreement with a value of 278 ppm later obtained by isotope-dilution, spark-source mass spectrometry [R. Alvarez, P. J. Paulsen, and C. W. Mueller (1970)], and the recommended value which appears on the provisional certificate [1] is 270 ppm.

Table 1. Polarographic determination of iron (acid soluble)[a] in orchard leaves.

Sample	Fe, ppm Set II	Fe, ppm Set III
2	260	258
9	257	282
10	263	272
11	257	259
12	257	255
13	254	253
15	258	282
19	262	267
Average	259	256
s, ppm	3.0	11.7
Pooled average	262	
Average s	9.1	

---

[a] $HCl-HNO_3-HClO_4$.

The results obtained for aluminum on the same samples are shown in Table 2. No other values for acid-soluble aluminum have been reported, hence this value has not been certified.

Table 2. Polarographic determination of aluminum (acid-soluble)[a] in orchard leaves.

Sample	Al, ppm		
	Set I	Set II	Set III
2	226	lost	218
9	226	222	211
10	228	241	224
11	225	223	225
12	220	226	204
13	225	229	222
15	223	226	222
19	230	228	225
Average	225	228	219
s, ppm	3.0	6.3	7.6
Pooled average		224	
Average s		6.7	

---

[a] $HCl-HNO_3-HClO_4$.

The results for total iron determined on new samples are shown in Table 3. From comparison with the acid-soluble iron value, it is seen that the residue contains about 50 ppm of the total sample equivalent of iron. Although isotope-dilution spark-source mass spectrometry analysis was not used for total iron, the insoluble residue was examined by semiquantitative emission spectroscopy [V. C. Stewart (1970)] and was found to contain iron in the 0.1-1 percent range (estimated to be about 0.5%). This corresponds to about 25 ppm in the total sample, which, added to the mass spectrometric value of 278 ppm, gives a total iron value of 303 ppm, in good agreement with the polarographic value of 312 ppm.

Table 3. Polarographic determination of iron (total)[a] in orchard leaves.

	- - - Fe, ppm - - -	
Sample	Set II	Set III
2	322	297
9	323	314
10	336	295
11	317	310
12	320	310
13	305	295
15	318	317
19	316	300
Average	320	305
s, ppm	8.7	9.0
Pooled average	312	
Average s	11.4	

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[a] $HCl-HNO_3-HClO_4-HF$, Na_2CO_3 fusion.

The total aluminum was then measured and the results are shown in Table 4. From comparison with the acid-soluble aluminum value of 224 ppm (Table 2), it is seen that the residue contains 123 ppm of the total sample equivalent of aluminum. The results obtained so far are not in good agreement and aluminum has not been certified. A value of 420 ppm was obtained by activation analysis [T. E. Gills (1970)]. In a round-robin study [P. D. LaFleur and T. W. Mears (1971)], values ranging from 99 to 401 ppm were reported by 11 non-NBS optical emission spectroscopy laboratories.

Table 4. Polarographic determination of aluminum (total)[a] in orchard leaves.

	- - - Al, ppm - - -	
Sample	Set II	Set III
2	359	344
9	340	349
10	340	341
11	340	348
12	345	348
13	341	350
15	346	350
19	350	368
Average	345	350
s, ppm	6.7	8.0
Pooled average	347	
Average s	7.5	

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[a] $HCl-HNO_3-HClO_4-HF$, Na_2CO_3.

The results for lead and bismuth are shown in Table 5. The lead average of 44.6 ppm was considerably higher than the anticipated value of about 5 to 10 ppm; however these results were later confirmed by two other techniques. A value of 43 ppm was obtained, using isotope-dilution, spark-source mass spectrometry, and a value of 45 ppm, using photon activation analysis [G. J. Lutz (1971)]. Another set was analyzed by the polarographic procedure, utilizing the hydrofluoric acid treatment, in order to verify that no lead was in the siliceous residue. An average of 44 ppm was obtained, thus the residue contained an insignificant amount of lead.

Table 5. Polarographic determination of bismuth and lead in orchard leaves.

Sample	Bi, ppm	Pb, ppm
2	0.11, 0.10	44.2, 41.8
9	0.10	46.3
10	0.13, 0.15	44.2, 44.8
11	0.11	44.2
12	0.11, 0.11	43.6, 44.2
13	0.12	43.0
15	0.09, 0.10	47.9, 47.9
19	0.09, 0.10	43.6, 44.2
Average	0.11	44.6
s, ppm	0.02	1.7

Each sample from bottle 15 gave significantly higher lead values than did those from the other bottles; this indicated that some lead inhomogeneity might exist.

Lead has now been certified at 45 ppm, but no other values have been reported for bismuth, hence it is not certified.

The results for nickel are shown in Table 6. The average of 1.4 ppm is in good agreement with an average of 1.2 ppm obtained by isotope-dilution, spark-source mass spectrometry. Nickel has not been certified at 1.3 ppm [1].

Table 6. Polarographic determination of nickel in orchard leaves.

Sample	Ni, ppm
2	1.4
9	1.5
10	1.2
11	1.5
12	1.3
15	1.5
19	1.5
Average	1.4
s, ppm	0.1

The investigation was extended to determine cadmium. Cadmium is also extracted by carbamate along with lead and bismuth. The peaks were very small and poorly defined for a 1 g sample but gave approximate values of 0.1 ppm. It was decided to take larger samples and try to determine cadmium, copper, lead, and bismuth simultaneously. By omitting the potassium cyanide during the extraction, copper would also be extracted. Five gram samples were taken through the procedure and bismuth, copper, lead, and cadmium were measured simultaneously in a 10 percent hydroxylamine hydrochloride supporting electrolyte.

An average value of 0.11 ppm was obtained for bismuth which is in perfect agreement with the 0.11 obtained earlier. A value of 11.5 ppm copper was obtained which agrees with the 12 ppm value by neutron activation analysis [D. A. Becker (1971)] and isotope-dilution, spark-source mass spectrometry, and copper has been certified at 12 ppm. A value of 44.5 ppm lead was found which is also in good agreement with the previous values. The cadmium content was found to be

0.10 ppm which is in good agreement with the 0.11 ppm obtained by atomic absorption [T. A. Rains (1971)].

Both the polarographic methods described here and the new Standard Reference Material which has now been certified for 18 elements with information given for nine others should be very useful in many kinds of analytical problems, particularly those concerned with trace metals in foods, plants, and other environmental samples.

6. References

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APPENDIX

This Appendix contains sixteen reproductions from papers describing various phases of the analytical procedures assembled in this volume.

It was intended to provide, in a convenient manner, additional relevant scientific information which could not be included in the main body of this work.

It is hoped that this information will be useful to the analyst.

The titles and names of the authors of the papers contained in this Appendix are listed below:

1. Production and Analysis of Special High-Purity Acids Purified by Sub-Boiling Distillation, by E. C. Kuehner, R. Alvarez, P. J. Paulsen, and T. J. Murphy.
2. The Role of the Analytical Blank in Accurate Trace Analysis, by T. J. Murphy.
3. Evaluation of Lyophilization for the Preconcentration of Natural Water Samples Prior to Neutron Activation Analysis, by S. H. Harrison and P. D. LaFleur.
4. Activation Analysis with the Nuclear Reactor, by P. D. LaFleur and D. A. Becker.
5. Characterization of a Nuclear Reactor for Neutron Activation Analysis, by D. A. Becker and P. D. LaFleur.
6. Method for Determination of Mercury in Biological Materials by Neutron Activation Analysis, by H. L. Rook, T. E. Gills, and P. D. LaFleur.
7. Simultaneous Determination of Trace Elements in Platinum by Isotope Dilution and Spark Source Mass Spectrometry, by R. Alvarez, P. J. Paulsen, and D. E. Kelleher.
8. Determination of Trace Elements in Zinc by Isotope Dilution Spark Source Mass Spectrometry, by P. J. Paulsen, R. Alvarez, and D. E. Kelleher.

9. Spark Source Mass Spectrographic Analysis of Ingot Iron for Silver, Copper, Molybdenum, and Nickel by Isotope Dilution and for Cobalt by an Internal Standard Technique, by P. J. Paulsen, R. Alvarez, and C. W. Mueller.
10. Trace Element Determinations in a Low-Alloy Steel Standard Reference Material by Isotope Dilution, Spark Source Mass Spectrometry, by P. J. Paulsen, R. Alvarez, and C. W. Mueller.
11. Chemical Aspects of Atomic Absorption, by T. C. Rains.
12. Atomic Absorption Spectrometry - General Considerations for the Application of Experimental Techniques, by T. C. Rains.
13. Flame Emission Spectrometry with Repetitive Optical Scanning in the Derivative Mode, by W. Snelleman, T. C. Rains, K. W. Yee, H. D. Cook, and O. Menis.
14. Standard Solutions for Flame Spectrometry, by J. A. Dean and T. C. Rains.
15. Determination of Submicrogram Amounts of Mercury in Standard Reference Materials by Flameless Atomic Absorption Spectrometry, by T. C. Rains and O. Menis.
16. Discussion of Some Experimental and Fundamental Conditions in Analytical Flame Spectroscopy, by R. Mavrodineanu.

APPENDIX I

Production and Analysis of Special High-Purity Acids Purified by Sub-Boiling Distillation

Edwin C. Kuehner, Robert Alvarez, Paul J. Paulsen, and Thomas J. Murphy

Analytical Chemistry Division, Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

Sub-boiling distillation from pure quartz or Teflon (Du Pont) stills has been investigated for the production of high-purity inorganic acids and water. Nitric, hydrochloric, hydrofluoric, perchloric, and sulfuric acids produced by this method contained significantly lower cationic impurities than high-purity acids from commercial sources. A complete system, including the Class 100 environment, production, and storage of these high-purity reagents is described. A method based on spark source mass spectrographic isotope dilution analysis has been developed for the simultaneous determination of 17 elements in these materials. Results of the analyses of both the acids purified by sub-boiling distillation and the ACS reagent grade acids used as starting materials are reported. The sum of the common impurity elements determined in the purified acids ranged from 2.3 ppb in nitric acid to 27 ppb in sulfuric acid. No element in any of the purified acids exceeded 10 ppb and most were well below the 1-ppb level.

THE ANALYTICAL CHEMISTRY DIVISION at the National Bureau of Standards has become increasingly involved with the analysis of samples and Standard Reference Materials (SRM's) requiring the determination of elements at the low parts per million (ppm, 10^{-6} g/g) to the parts per billion (ppb, 10^{-9} g/g) concentration range. This is illustrated by recent analyses which include lead at 3.31 ppm in lunar samples (*1*), uranium at 72.1 ppb in Trace Elements in Glass (SRM 616) (*2*), nickel at 1.3 ppm in Orchard Leaves (SRM 1571) (*2*), and strontium at 0.14 ppm in Bovine Liver (SRM 1577) (*2*). The low level of these elements puts stringent requirements on the purity of reagents used in the analytical procedure.

Inorganic acid purity is of particular importance because of the relatively large amount of these acids required for sample dissolution and other chemical operations. These procedures can require quantities of acids in excess of ten times the sample weight. To take full advantage of the sensitivity and accuracy of an analytical technique, the reagent blank should be held to no more than a few per cent of the amount being determined. Therefore, the accurate determination of an element near the 1-ppm level will depend on the availability of acids containing no more than 1 ppb of the element.

High-purity inorganic acids have been available for some time from commercial sources. Although these acids are satisfactory for many trace element determinations, they are not always adequate for low level trace work either through a lack of purity or high upper limit specifications. [Emission spectrography (*3*), the technique usually applied to the analyses of high-purity acids, lacks sensitivity causing upper limits to be set at 1 ppb or higher.] The determination of the isotopic composition and concentration of lead in lunar samples can be cited as a recent example. A reagent blank of 340 ng Pb was calculated from the producer's values for lead in commercial high-purity acids and the volume of these acids required to dissolve one gram of lunar rock and separate the lead from other constituents. Since the expected Pb concentration was only a few ppm, the introduction of this quantity of external lead (of a different isotopic composition) would have precluded a reliable determination of the Pb present either as to amount or isotopic composition. Using acids purified by sub-boiling distillation, the total blank was determined to be 5 ng for the actual analysis. Consequently, because of this experience and other problems associated with the determinations of trace metals in a variety of materials, the Analytical Chemistry Division at NBS recently set up facilities for the "in-house" purification, analyses, and distribution of inorganic acids.

Sub-boiling distillation was selected as the method of purification for the inorganic acids. No single purification procedure is capable of removing all classes of impurities from these acids. Since the trace element program at NBS is mainly concerned with trace metals, the technique which appeared to be most efficient in removing metallic or cationic impurities, sub-boiling distillation, was studied. In sub-boiling distillation, infrared radiators vaporize the surface without boiling the liquid in the vaporizer compartment. The vapor is condensed on a tapered cold finger and the distillate is collected in a suitable container. Sub-boiling distillation was selected over conventional or boiling distillation since studies have shown that in the latter method significant contamination of the distillate occurs from creeping of the unrectified liquid and entrainment of particulates in the vapor stream formed during bubble rupture (*4*). Sub-boiling distillation completely eliminates the entrainment problem since no bubbles are formed. Creeping of unrectified liquid from the vaporizer is minimized by the position of the cold finger type condenser. It should be pointed out that while this is an extremely efficient still for the separation of impurities of low vapor pressure such as metal ions, it offers little purification from impurities of high vapor pressure such as organic matter or many of the anions.

Commercial quartz sub-boiling stills which were designed for the production of high-purity water have been used for the production of high-purity mineral acids of low-level lead content at the Carnegie Institution of Washington (*5*). Similar sub-boiling quartz stills (Quartz Products Corp., Plainfield, N.J.) were installed at NBS for the production of

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(1) I. L. Barnes, B. S. Carpenter, E. L. Garner, J. W. Gramlich, E. C. Kuehner, L. A. Machlan, E. J. Maienthal, J. R. Moody, L. J. Moore, T. J. Murphy, P. J. Paulsen, K. M. Sappenfield, and W. R. Shields, "Isotopic Abundance Ratios and Concentrations of Selected Elements in Apollo 14 Samples," Proc. Apollo 14 Lunar Sci. Conf., *Geochim. Cosmochim. Acta Suppl. 3*, **2**, MIT Press, Cambridge, Mass., in press.

(2) Office of Standard Reference Materials, *NBS Spec. Publ.* **260** (1970).

(3) N. A. Kershner, E. F. Joy, and A. J. Barnard, Jr., *Appl. Spectrosc.*, **25**, 542 (1971).

(4) R. C. Hughes, P. C. Mürau, and G. Gundersen, ANAL. CHEM., **43**, 691 (1971), and references cited therein.

(5) K. D. Burrhus and S. R. Hart, *ibid.*. **44**, 432 (1972).

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hydrochloric, nitric, perchloric, and sulfuric acids as well as water. An all Teflon (Du Pont) sub-boiling still was designed and constructed at NBS for the production of high-purity hydrofluoric acid.

Efficient purification by the still only partially solves the problem of producing and distributing pure acids. Airborne particulate contamination and container contamination must also be minimized to ensure a high quality product. Airborne particulate contamination can be virtually eliminated by enclosing the still and distillate containers in a Class 100 clean air chamber. Teflon FEP bottles which have been vigorously cleaned with nitric and hydrochloric acids are used as containers for the purified acids and high-purity quartz is used for water.

To evaluate the purity of the acids and water produced by this process, an analytical method based on isotope dilution–spark source mass spectrometry (SSMS) was developed. This method has limits of detection as low as 0.01 ppb for common impurity elements. Seventeen elements were determined simultaneously in each of the high-purity acids and water produced by sub-boiling distillation and the ACS grade acids used as starting materials.

APPARATUS FOR THE SUB-BOILING DISTILLATION OF HIGH-PURITY ACIDS AND WATER

Quartz Sub-Boiling Still. The commercially available sub-boiling still shown in Figure 1 is made of quartz. This type still is used for the production of HCl, HNO_3, $HClO_4$, H_2SO_4, and H_2O. Heating of the liquid being distilled is done by a pair of infrared radiators positioned on both sides of the condenser. These elements, inside quartz tubes, heat the surface of the liquid and evaporate it without causing it to boil. This positioning also serves to heat the walls above the liquid tending to keep them dry which minimizes creep of liquid along the walls between the liquid reservoir and the condensing cold finger. The condenser is tilted downward toward the distillate outlet to allow the condensed liquid to flow to the tip above the outlet. The still is fed by a 6–8 pound bottle of ACS reagent grade acid through a liquid level control which maintains the liquid to just below the overflow height. Approximately 400 to 500 ml of liquid are thus maintained inside the still at all times. A three-way stopcock on the liquid level control is used to drain the still after the consumption of each bottle of ACS reagent grade feed acid. All parts of the liquid feed system are made of Teflon.

Teflon Sub-Boiling Still. An all-Teflon (Du Pont) sub-boiling still having all the essential features of the quartz still was designed and constructed for the production of hydrofluoric acid. This still, shown in Figure 2, was fabricated starting with a commercial 2-liter Teflon bottle. The heaters, condenser, acid inlet, and the overflow were inserted into what was originally the bottom of the bottle and the distillate outlet was inserted at the bottle cap. For the heaters, Teflon rods are machined to form 19-mm o.d. closed-end tubes. Heating coils inside glass tubes are then inserted into the heater tubes. The maximum operating temperature of the still is limited by the softening point of the Teflon around the heater. The glass tubing serves to support the heating tube. The cold finger condenser is similarily machined into a 25-mm o.d. tube from solid rod. Both the condenser and heater tubes are threaded at the open ends to fit into conversion fittings which are in turn threaded into tapped holes in the bottom of the bottle. The tapped hole in the condenser fitting is machined at an angle such that the condenser is tilted downward toward the distillate outlet. Because HF and other liquids do not adhere readily to Teflon, the distillate drips off instead of flowing down along the condenser. Therefore, a trough is secured under the condenser to catch the HF and direct it to the distillate outlet. A piece of tubing inserted through the bottle cap using commercial Teflon fittings serves as a collector for the distillate. The tube is provided with an umbrella at the end to protect the collection bottle from possible fall-out contamination. The acid feed and overflow tubes are attached with Teflon fittings threaded into the bottle bottom. Teflon tape is used when necessary on the threads of the fittings to ensure a liquid tight seal.

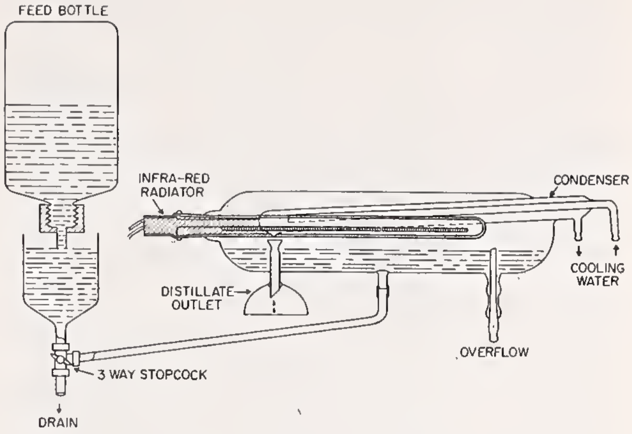

Figure 1. Pure quartz sub-boiling still

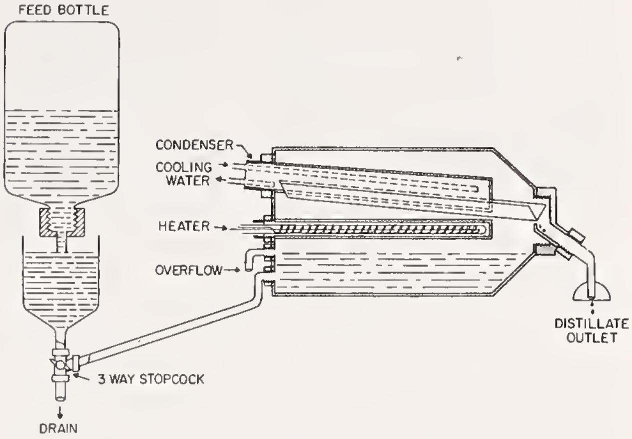

Figure 2. All-Teflon sub-boiling still

Clean Air Chamber. Each sub-boiling still is housed in a clean air chamber (Environmental Air Control, Inc., Annandale, Va.) to protect the distillation process from external particulate contamination. All parts on the clean air side of the chamber including the HEPA filter frame and diffuser are constructed of aluminum or plastic. The chambers meet Class 100 specifications—that is, they remove 99.97% of all particulate matter larger than 0.3 μm. The air flow through the chamber is adjusted to match the exhaust rate through a plenum assembly at the back-bottom of the unit. By this means, the acid purification operation is protected from room contaminates and at the same time, acid fumes are minimized in the room.

Containers for Reagent Storage. Acid distillates are collected and stored in Teflon-FEP bottles. These bottles are cleaned by soaking for 24 hours first in hot $8M$ HNO_3 and then in hot $6M$ HCl for 24 hours. They are then rinsed with sub-boiling distilled water and finally with the acid being stored. The containers are reused for the same acid after first being rinsed with distilled water and then rinsed with the acid. Water from the sub-boiling still is stored in quartz containers which are cleaned in the same manner as the Teflon bottles.

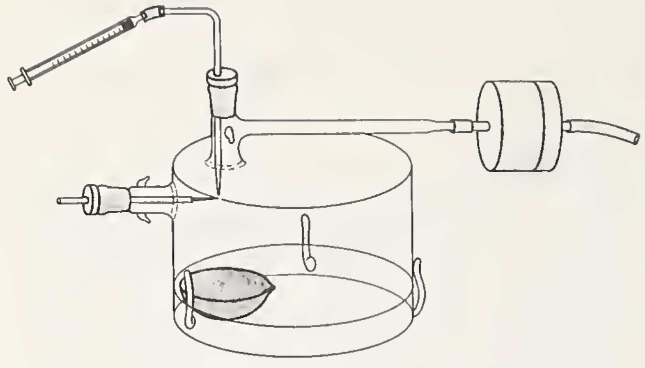

Figure 3. Clean environment evaporator and transfer system

APPARATUS AND REAGENTS FOR ANALYSIS OF ACIDS AND WATER

Enriched Isotope Spike Solutions. The individual isotopic spikes for the elements being determined were on hand as 1 mg/ml solutions. Compatible spiking elements were combined to give 50 μg/ml concentrations of each element in a pair of master spiking solutions. One solution contained the HCl soluble elements, the other solution the HNO_3 soluble elements.

Clean Air Exhaust Hood. In the analysis of the acids, evaporations were performed on a hot plate in a Class 100 exhausted fume hood. The basic unit is similar to the clean chamber except that the air is exhausted down through a grill of Teflon that serves as a "floor" for the hood and then out through a standard acid fume exhaust system. Teflon is used extensively throughout those parts of the hood exposed to acid fumes.

Evaporator and Liquid Transfer System. The apparatus, shown in Figure 3, provides a clean environment for evaporating a spiked sample and transferring the residual volume onto high-purity gold wires. Nitrogen flowing through a 0.1-μm cellulose filter provides a clean atmosphere, sweeps out evaporating acid, and prevents entry of particulate contamination. A pure quartz pipet inserted off center in a Teflon stopper at the top is used to transfer the last few drops of evaporating acid onto pure gold wires positioned from the side joint.

PROCEDURE FOR ANALYSIS OF ACIDS AND WATER BY ISOTOPE DILUTION SSMS

The isotope dilution analyses were performed on the acids and water produced by sub-boiling distillation and on the ACS reagent grade acids used as starting materials. In addition, we have also included results obtained in previous analyses of commercial high-purity acids. This variety in the type and source of acids analyzed has resulted in some changes of the procedures used.

Hydrofluoric Acid. Due to its reactivity with quartz and glassware, HF was handled exclusively in Teflon-FEP containers, otherwise it was treated the same as the other acids from a similar source.

Water from the Sub-Boiling Still. Because the purity of the sub-boiling distilled water was higher than that of the acids, the water was preconcentrated before spiking. Two liters of water were evaporated to approximately 100 ml in the original storage container before being removed and spiked. The water was not spiked in the storage container because of our reluctance to contaminate the container with the enriched spike isotopes. The spiked 100-ml water sample was then handled in the same manner as the acids purified by sub-boiling distillation.

Sample Spiking. All samples were spiked using 1 μg/ml solutions freshly diluted from the 50 μg/ml master spike solutions. Acids purified by sub-boiling distillation were all spiked for a nominal concentration of 1 ppb; nitric and hydrochloric acids were also spiked for 0.1 ppb. The nominal 1-ppb spike contained 100 ng of each spike element in 100 grams of acid (1 ng/g); the 0.1 ppb spike had 30 ng/300 grams of acid. The 1 ng/g spike gives an altered isotopic ratio of approximately one at a concentration of 1 ppb for most of the impurity elements. Concentrations up to ten times higher and more than ten times lower than the spiked for value can be determined from the measured ratios, but with greater uncertainty.

The ACS reagent grade acids used as starting materials for the sub-boiling distillation were spiked at 1 ppb, 10 ppb, and 100 ppb in order to cover the expected concentration range for the different impurity elements. An element was only measured for the sample where the spike came closest to the actual concentration. One half of the spiked sample was used for each analysis.

The commercial high-purity acids analyzed previously were spiked for many but not all of the elements surveyed in the ACS reagent grade and sub-boiling still acids. One hundred-gram samples were spiked for concentrations in the 1- to 100-ppb range. Because of the higher level of impurities only 20 grams of the 100-gram sample were required for the analyses.

Sample Evaporation and Transfer to Pure Gold Wires. The clean environment evaporator shown in Figure 3 was used to vaporize commercial high-purity acids in a standard laboratory fume hood prior to our obtaining a Class 100 clean air fume hood. A single sample at a time was evaporated to a few tenths of a milliliter and then transferred with the pure quartz pipet to the tip of "six nines grade" gold wires and dried.

The ACS reagent grade acids and the acids purified by sub-boiling distillation were evaporated in the Class 100 fume hood in open quartz and/or Teflon beakers on a hot plate. The clean environment evaporation dish was used however to transfer the last few drops of the spiked sample to the gold wires for drying. The gold wires were then heated to 425 °C for 15 minutes to drive off hydrocarbons and occluded acid. At this point partial loss due to incomplete transfer or loss on heating can be ignored inasmuch as the quantitative analytical data are a function of the altered isotopic ratio and the only requirement is that enough of each element be retained for an adequate measurement.

Spark Source Mass Spectrographic Determination of Altered Isotopic Ratios. The pair of gold wires was mounted in the spark source such that several millimeters of the wire ends, which were coated with the spiked sample residue, would be overlapping and parallel to each other. When a source vacuum of 1×10^{-7} Torr was reached, a graded series of exposures was made. The electrodes were moved relative to each other during sparking in order to spark new spiked sample residue on each exposure. One half of the surface of each electrode was sampled during this first graded series of exposures. A second identical series of graded exposures was then made on the remainder of the sample. A single photographic plate was used for each sample.

The photographic plates were processed using the bleach and internal image developer for reducing plate fog developed by Cavard (*6*).

The photoplates were examined visually to select exposures which would give optimum sensitivity for each element determined and for evidence of interferences at the same nominal mass such as unresolved doublets, abnormally wide lines, or isotopic ratios which varied from one exposure to the next. If an interference was indicated for the +1 lines of an element, the less sensitive +2 or +3 lines were considered for measurement. The selected exposures for each element were then densitometered measuring both the spike and natural isotopes on each exposure. From four to six exposures were measured for each element if available.

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(6) A. Cavard in "Advances in Mass Spectrometry," E. Kendrick, Ed., The Institute of Petroleum, London, 1968, pp 419–29.

Calculation of Impurity Concentrations. The amounts of impurities present in each acid were computed from the sample weight, the weight of each spike added, and the measured altered isotopic ratios using the usual formula for isotopic dilution analysis as described in earlier papers (*7*, *8*). Impurity concentrations were calculated for each isotopic ratio measured for an element. These values were then averaged. This system gives a more realistic evaluation of the uncertainty in the results than using an averaged ratio to calculate one concentration value. This is especially critical when the measured (altered) isotopic ratio is close to that of either the spike or natural element.

When only the spike isotope for an element was detected, an upper limit of concentration was computed by substituting twice the noise level of the photographic plate at the position of the natural isotope for the intensity of the natural isotope. The concentration of mononuclidic sodium was estimated by assuming it has the same sensitivity as potassium and measuring intensity-areas of the ^{23}Na compared to that of either the ^{39}K or the ^{41}K isotope of the same exposure.

The results of these analyses of the acids and water are presented in a later section describing the operating procedure used for the production of each of the acids by sub-boiling distillation.

DISCUSSION OF ANALYSIS PROCEDURE

The acids purified in the sub-boiling still and the ACS reagent grade starting materials were analyzed for 17 elements simultaneously by the spark source. The elements measured represent elements found as impurities in reagents, elements commonly determined in many types of analytical samples, and elements from different groups of the periodic table. It was felt that this selection of elements would give a representative view of the overall reagent purity.

The analysis technique itself is subject to blank problems which cannot be properly evaluated. Care was taken during the analysis to prevent contamination of the samples from containers and the external environment. Based upon the lowest values found in repeated analysis of the acids produced by sub-boiling distillation, estimates can be made of the probable blank contributions. In general any element reported near the 0.1-ppb level or below may have a considerable blank contribution and the value should therefore be considered as an upper limit. Concentrations significantly above this level represent actual reagent impurities with uncertainties ranging from ± 10 to 30% depending on the value of the altered ratio.

Interfering lines having the same nominal mass as either the spike or natural abundance isotope of an element being determined were sometimes encountered during these analyses. These interferences are normally most prevalent for the lower mass elements and for the more impure acids. The three major sources of these lines are hydrocarbons, anions, and anion fragments, and various molecular combinations of the major impurities with themselves and the acid anion. Heating of the sample to 425 °C before sparking and the heating that occurs during sparking greatly reduced interference from the hydrocarbon and anion lines.

Examples of anion fragment interferences are $^{37}Cl^{16}O^+$ with the $^{53}Cr^+$ spike and $^{35}Cl^{16}O_2^+$ with the $^{67}Zn^+$ spike in perchloric acid analysis, and $^{32}S^{16}O_2$ with natural $^{64}Zn^+$ in sulfuric acid. The perchloric acid interferences can be evaluated by monitoring the line from the other chlorine isotope.

Figure 4. Laboratory for production of high-purity acids

ACS reagent grade $HClO_4$ with high levels of Na and K showed lines for: NaO^+, NaK^+, Na_2^+, K_2^+, Na_2Cl^+, K_2Cl^+, Na_2ClO^+, K_2ClO^+, $Na_2ClO_2^+$, etc. Some of these lines represented potential interferences; however, this type of interference was not significant for the acids purified by sub-boiling distillation since their cationic impurities were always at a very low level.

Measurement of the isotopic ratio of an element at the +2 or +3 charge state will eliminate all three types of interfering lines since these molecular species fragment rather than form a multiply-charged ion. When such interferences existed, Ag, Cu, and K isotope ratios were measured on +2 ions and Zn, Ni, Cr, and Ca isotope ratios were measured on +3 ions.

PRODUCTION AND ANALYSIS OF HIGH-PURITY ACIDS AND WATER

Figure 4 shows the laboratory setup for the production of high-purity acids. Each quartz sub-boiling still and distillate container is housed in a separate Class 100 clean air unit to prevent particulate contamination during distillation. Any extraneous acid vapor produced is exhausted through the balanced plenum assembly which serves four clean air units. The Teflon sub-boiling still is housed in a separate clean air chamber and extraneous acid vapors are exhausted by a standard laboratory hood. The ACS reagent grade acid to be purified is fed to each still from a container just outside the clean air chamber through a liquid level control which maintains the pre-set liquid level. In this manner, acid is constantly fed to the still as distillate is removed. Since impurities are concentrated in the pot liquid, the still is drained after the consumption of each 6- to 8-pound feed bottle.

After distillation, each acid was allowed to stand in its Teflon-FEP container for at least two weeks before analysis to allow for any impurities in or on the container walls to react with the acid.

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(7) R. Alvarez, P. J. Paulsen, and D. E. Kelleher, Anal. Chem., **41,** 955 (1969).

(8) P. J. Paulsen, R. Alvarez, and D. E. Kelleher, *Spectrochim. Acta*, **24B,** 535 (1969).

Table I. Hydrochloric Acid

Impurity concentrations ppb by wt (ng/g)

	Acid from sub-boiling still	ACS reagent grade	Commercial high purity
Pb	0.07	0.5	<1
Tl	0.01	0.1	...
Ba	0.04	2	...
Te	0.01	0.1	...
Sn	0.05	0.07	<6
In	0.01	...	...
Cd	0.02	0.03	0.5
Ag	0.03	0.05	0.2
Sr	0.01	0.05	...
Zn	0.2	2	4
Cu	0.1	4	1
Ni	0.2	6	3
Fe	3	20	7
Cr	0.3	2	0.3
Ca	0.06	70	24
K	0.5	200	10
Mg	0.6	10	20
Na	1	500	...
	Σ 6.2 ppb	Σ 820 ppb	Σ 70 ppb

Table II. Nitric Acid

Impurity concentrations ppb by wt (ng/g)

	Acid from sub-boiling still	ACS reagent grade acid	Commercial high purity
Pb	0.02	0.2	0.3
Tl	...	0.2	...
Ba	0.01	8	...
Te	0.01	0.1	...
Sn	0.01	0.1	1
In	0.01	...	...
Cd	0.01	0.1	0.2
Ag	0.1	0.03	0.1
Sr	0.01	2	...
Se	0.09	0.2	...
Zn	0.04	4	8
Cu	0.04	20	4
Ni	0.05	20	3
Fe	0.3	24	55
Cr	0.05	6	130
Ca	0.2	30	30
K	0.2	10	11
Mg	0.1	13	...
Na	1	80	...
	Σ 2.3 ppb	Σ 220 ppb	Σ 240 ppb

Table III. Perchloric Acid

Impurity concentrations ppb by wt (ng/g)

	Acid from sub-boiling still	ACS reagent grade acid	Commercial pure acid
Pb	0.2	2	16
Tl	0.1	0.1	...
Ba	0.1	>1000	10
Te	0.05	0.05	...
Sn	0.3	0.3	<1
Cd	0.05	0.1	4
Ag	0.1	0.1	0.5
Sr	0.02	14	...
Zn	0.1	7	17
Cu	0.1	11	3
Ni	0.5	8	0.5
Fe	2	330	10
Cr	9	10	18
Ca	0.2	760	7
K	0.6	200	9
Mg	0.2	500	4
Na	2	600	...
	Σ 16 ppb	Σ >3400 ppb	Σ 100 ppb

The purified acids were then analyzed by the isotope dilution mass spectrometric method described previously. These analyses characterize the acid as delivered to the user rather than as produced, since this is what is of interest to the analyst.

The Teflon-FEP bottles will be used repeatedly over again to contain the same high-purity acid. It is reasoned that the container should become cleaner with use and cause less contamination to future lots of acids. Any acid not used within a few months will be replaced with freshly distilled reagent.

Hydrochloric Acid. Hydrochloric acid and water form a constant boiling mixture at 6*N* hydrochloric acid. Initial experiments were with starting acid of this concentration. Further experiments showed that the starting concentration could be increased to 10*N* HCl without causing bubble formation and that the distilled product was also 10*N*. However, concentrated 12*N* acid could not be used because of bubble formation on heating. Apparently, acid of higher concentration than constant boiling 6*N* can be produced because the azeotropic mixture that condenses on the cold finger absorbs HCl from the HCl-rich vapor to reach the concentration of the acid in the pot.

ACS reagent grade hydrochloric acid diluted to 10*N* or 31 weight per cent with high-purity water was used as the feed acid. The still heaters were adjusted to 225 W of power. About 2 liters of 10*N* high-purity hydrochloric acid were produced per day under these conditions.

Table I shows the analysis of the high-purity acid produced by sub-boiling distillation, the starting ACS reagent grade acid, and a lot of commercial high-purity acid. A summation of these impurity elements shows that the sub-boiling distilled acid contained 6.2 ppb, the ACS reagent grade contained 820 ppb, and commercial high-purity 70 ppb. The only element found in the sub-boiling distilled acid at levels higher than 1 ppb was iron at 3 ppb. The other elements were at the sub-ppb level, generally lower than 0.1 ppb.

Nitric Acid. The sub-boiling distillation of concentrated 70% ACS reagent grade nitric acid required a low heater temperature to prevent the HNO_3 vapor in the proximity of the heater from disproportionating to form nitrogen dioxide with resulting discoloration of the distillate. Experiments showed that at a heater power setting of 107 W, little or no discoloration of the distillate took place. As a result, only about 500 ml per day of nitric acid was produced. Titration showed the distillate to be 70% HNO_3, the same concentration as the starting acid.

Table II shows the results of the analysis of the sub-boiling distilled acid, ACS grade starting acid, and a lot of commercial high-purity acid. The totals of the impurity elements determined were 2.3 ppb for the sub-boiling distilled acid, 220 ppb for the ACS starting acid, and 240 ppb for the commercial high-purity acid. The sub-boiling distilled nitric acid was the purest of the acids produced. No element was found at a concentration greater than 1 ppb and only sodium was detected at that level, and this accounts for almost half of the total impurities found. Most elements were in the 0.05- to 0.01-ppb range.

Perchloric Acid. Initial experiments on the sub-boiling distillation of concentrated 70% perchloric ($HClO_4 \cdot 2H_2O$) showed that high heater temperatures caused the perchloric

Table IV. Sulfuric Acid

Impurity concentrations ppb by wt (ng/g)

	Acid from sub-boiling still	ACS reagent grade acid
Pb	0.6	0.5
Tl	0.1	0.1
Ba	0.3	0.2
Te	0.1	0.1
Sn	0.2	0.6
Cd	0.3	0.2
Ag	0.3	0.6
Sr	0.3	0.4
Zn	0.5	2
Cu	0.2	6
Ni	0.2	0.5
Fe	7	6
Cr	0.2	0.2
Ca	2	123
K	4	9
Mg	2	4
Na	9	50
	Σ 27 ppb	Σ 200 ppb

Table V. Hydrofluoric Acid

Impurity concentration ppb by wt (ng/g)

	Acid from sub-boiling still	ACS reagent grade acid
Pb	0.05	0.8
Tl	0.1	0.2
Ba	0.1	0.5
Te	0.05	0.1
Sn	0.05	11
Cd	0.03	2
Ag	0.05	0.1
Sr	0.1	0.5
Zn	0.2	4
Cu	0.2	3
Ni	0.3	12
Fe	0.6	110
Cr	5	20
Ca	5	14
K	1	28
Mg	2	10
Na	2	100
	Σ 17 ppb	Σ 320 ppb

Table VI. Water

Impurity concentrations ppb by wt (ng/g)

	Water from sub-boiling still
Pb	0.008
Tl	0.01
Ba	0.01
Te	0.004
Sn	0.02
Cd	0.005
Ag	0.002
Sr	0.002
Zn	0.04
Cu	0.01
Ni	0.02
Fe	0.05
Cr	0.02
Ca	0.08
K	0.09
Mg	0.09
Na	0.06
	Σ 0.5 ppb

acid in the still to turn bright yellow, probably because of the formation of chlorine dioxide. At lower power settings, little or no color was noted and the distillate was colorless. Another problem with this distillation was that in the earlier work, crystals would occasionally build up on the cold finger condenser. This material was probably perchloric acid monohydrate ($HClO_4 \cdot H_2O$) which has a melting point of 50 °C. Crystal formation could be controlled by changing either the flow rate of the condenser water or the heater temperature. However, this problem was noted only in the earlier work. For the last six months, no crystal formation on the cold finger has been noted even when the still is operated continuously for weeks. The power setting used for the production of purified perchloric acid was 240 W, and the production rate was about 600 ml of perchloric acid per day. Titration has shown that the distillate is 70 wt % of $HClO_4$, the same as the starting ACS grade acid.

Table III shows the results of the analyses of the sub-boiling distilled acid, the starting ACS grade acid, and a lot of commercial high-purity acid. The total of the impurity elements found was 16 ppb for the sub-boiling distilled acid, 3400 ppb for the starting acid, and 100 ppb for the commercial high-purity acid. These analyses demonstrate the efficiency of sub-boiling distillation when the concentration of impurity elements in the purified product is compared to the starting acid. The concentration of barium which was greater than 1000 ppb was reduced to 0.1 ppb, a purification factor of greater than 10,000. Another example is calcium which was reduced to 0.2 ppb in the purified acid from 760 ppb in the starting acid, a factor of 3,800. It should also be noted that chromium which was present at 10 ppb in the starting acid was not significantly changed in the purified acid. This is probably due to the fact that chromium can be volatilized from hot perchloric acid solutions as chromyl chloride, CrO_2Cl_2, so little, if any, purification can be expected by sub-boiling distillation. Chromium accounts for over half of the total impurities found in the purified acid.

Sulfuric Acid. Initial experiments with the sub-boiling distillation of sulfuric acid showed that, because of the density of H_2SO_4, the acid that condensed on the cold finger tended to drop off before reaching the collection tube. Another problem was that even at the highest power setting, the distillation rate was extremely slow. Modification of the still by increasing the angle of incline of the cold finger condenser solved the condensate problem, and the rate of distillation was increased by using a platinum foil reflector around the still. At the maximum power setting of 427 W, the rate of distillation is now about 300 ml per day. Titration has shown that the purified acid is 96 wt % H_2SO_4, the same as the starting ACS grade acid.

Table IV shows the results of the analyses of the sub-boiling distilled acid and the starting sulfuric acid. The total of the impurities found in the starting acid was 200 ppb, the lowest of any of the ACS grade acids, and the purified acid contained 27 ppb, the highest of the purified acids. Sodium was the principal contaminant in the high-purity acid at 9 ppb with iron right behind it at 7 ppb. These two elements account for over half the total impurities found in the purified sulfuric acid.

Hydrofluoric Acid. Hydrofluoric acid was purified in the all-Teflon sub-boiling still shown in Figure 2 which was designed and built at NBS. Hydrofluoric acid and water form a constant boiling mixture at 36% HF. Because of the previous experience with hydrochloric acid, the sub-boiling distillation of concentrated 48% HF was attempted. Titration showed that the distilled product was also 48% HF. Ap-

Table VII. Summary of Experimental Conditions for Producing High-Purity Acids and Water by Sub-Boiling Distillation

Reagent	Concentration of still feed acid, % by wt	Still heater power, W	Concentration of distillate, % by wt	Production rate, ml/24 hr
HCl	31	225	31	2,000
HNO_3	70	107	70	500
$HClO_4$	70	240	70	600
H_2SO_4	96	427	96	300
HF	48	164	48	300
H_2O	...	200	...	4,000

parently, as in the case of hydrochloric acid, the azeotropic mixture that condenses on the cold finger absorbs HF from the HF rich vapor to reach the same concentration as the acid in the still.

Since the heaters of the Teflon still for the purification of hydrofluoric acid are enclosed in Teflon tubes, the temperature of the heater had to be kept below the softening point of Teflon. As a result the maximum power setting for this still was 164 W which produced a distillation rate of 300 ml per 24 hour day.

Table V shows the results of the analyses of the starting ACS grade HF and the purified product. The total of the impurities in the purified acid is 17 ppb compared to 320 ppb in the starting ACS grade acid. The two principal impurities in the purified acid are Ca and Cr, both at 5 ppb, and they account for over half the total impurity found. The only other elements found at a concentration of greater than 1 ppb are K at 1 ppb, Mg at 2 ppb, and Na at 2 ppb.

Water. Water has been included in this study because it is the most commonly used chemical reagent and because sub-boiling distillation has been used to produce high-purity water both here at NBS and elsewhere. Initially, water of higher purity than the distilled water from the laboratory distribution system was obtained by re-distillation in a commercial, continuous-feed still. This still had a tin-coated evaporator and baffle and was equipped with a quartz condenser. This unit was designed to disengage CO_2 and other gases from the distillate and vent them off. Water produced by this still was used as the feed water to the sub-boiling still. The entire assembly of feed apparatus, quartz sub-boiling still, and quartz collector was contained in a Class 100 clean air chamber. The distillation rate at a power setting of 200 W was 4 liters per day.

The analysis of the sub-boiling purified water is given in Table VI. This water contained a maximum of 0.5 ppb total of the 17 elements determined. No element was detected at a concentration of greater than 0.1 ppb. Since no correction for an analysis blank could be made, the values must be regarded as upper limits for the purity of the water. The water may in fact be more pure than the analysis indicates.

The optimum conditions for the production of each high-purity acid and water by sub-boiling distillation described above are summarized in Table VII.

The impurity elements determined in the acids and water (Tables I–VI) are tabulated in order of decreasing mass. This reveals that the major impurities for the acids purified by sub-boiling distillation are all low mass elements. None of the NBS purified acids have an impurity level as high as 1 ppb for elements above iron in mass. Elements from iron on down sometimes exceed 1 ppb but none exceeded 10 ppb.

A number of the major impurities found in the ACS reagent grade and commercial high-purity acids are elements common to their glass storage containers. It would appear that the means of storing the acids are as responsible for the acid purity as the purification method. It should be noted that of all the acids analyzed, only the ACS grade perchloric acid showed an element (Ba) that exceeded the 1-ppm level.

RECEIVED for review March 27, 1972. Accepted May 30, 1972. Certain commercial instruments or chemicals are mentioned in this paper; this does not imply recommendation or endorsement by the National Bureau of Standards.

APPENDIX II

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THE ROLE OF THE ANALYTICAL BLANK IN ACCURATE TRACE ANALYSIS

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The inability to control the analytical blank, *i.e.*, contamination from all sources external to the sample, has seriously affected the accuracy of low level trace determinations. Most of the sources of the blank are variable and it is this variability that determines the uncertainty of the blank correction and, therefore, the lower limit of trace element concentration that can be determined with reliability. To improve both the accuracy and lower limit of trace determinations, it is imperative to control the variability of the analytical blank. The only practical way to accomplish this is to reduce the size of the blank itself by controlling the sources of the blank.

The analytical blank is composed of contamination from four principal sources, namely: the environment the analysis is performed in, the reagents used in the analysis, the apparatus used, and the analyst performing the analysis.

Environmental contamination is caused by particulates and gaseous compounds in the ambient air. Methods for reducing the blank from this source by the use of isolation chambers or "absolute" filters are described.

While commercially available high-purity reagents have helped the analyst to control the blank from reagents, they are frequently not low enough in trace element concentration and must be purified before use. Methods for the preparation of high-purity reagents, especially water and the mineral acids, are reviewed.

Contamination from beakers, containers, mortars and other apparatus can seriously affect the blank. Techniques for controlling this type of contamination are described with emphasis on the purity of materials.

The last source of contamination is that caused by the analyst during the analysis due to carelessness or poor technique. Suggestions are given to aid the analyst in this regard.

Keywords: Accuracy; analysts; apparatus; blank; contamination; environment; purity; reagents.

I. Introduction

The analytical blank may be considered the "Achilles' heel" of trace analysis. As the Greek warrior of Homer's Iliad had his vulnerable point, so also does trace analysis in that the size and variability of the analytical blank may render useless the information from the analysis. First, let me define what is meant by the analytical blank. The analytical blank is simply the contamination by the element or compound being determined from all sources external to the sample. I am not including in this definition the so-called instrumental blank or noise level which really refers to the sensitivity or level of detection of the analytical method. Also not included in this definition is the so-called negative blank, that is loss of an element during analysis by physical processes such as adsorption. This is really a separate subject unto itself. Obviously, this definition includes both inorganic and organic contamination, but my remarks will deal mainly with trace inorganic cation contamination.

Modern methods of analysis have lowered the threshold of determining trace elements to the low parts per billion (ng/g) for many elements but the inability to control the analytical blank has seriously affected the accuracy of these methods. The blank is a problem common to all trace element techniques with the exception of certain nuclear techniques such as neutron activation analysis and fission track analysis.

Let's look at the effect of the blank on the accuracy of a trace analysis. During the analysis, the analyst normally carries "blanks" thru all the steps of the analysis and makes a "blank-correction" of the analysis based on the estimation of the contamination from these blank determinations.

Figure 1 shows the effect on accuracy of a 10 ng blank that exhibits a variability of ±5 ng. This represents a very low blank with a reasonable uncertainty. It is not uncommon, even in very careful work to have blanks an order of magnitude higher. Notice that at the microgram level, the effect on accuracy of a blank of this size is small, but that it increases rapidly until at the 0.01 μg or 10 ng level, a 50 percent uncertainty would be introduced by the blank. If the blank were an order of magnitude higher with the same percentage variability, a determination at the 0.1 μg level would have a 50 percent uncertainty due to the blank alone.

It is the variability or the uncertainty in the blank correction [1] and not the absolute value of the blank that affects the accuracy of the analysis. As the variability becomes a significant percentage of the sample amount, more and more determinations of the blank are necessary so that the variability can be estimated with some degree of reliability. It is a common mistake of analysts to base the blank correction on a single

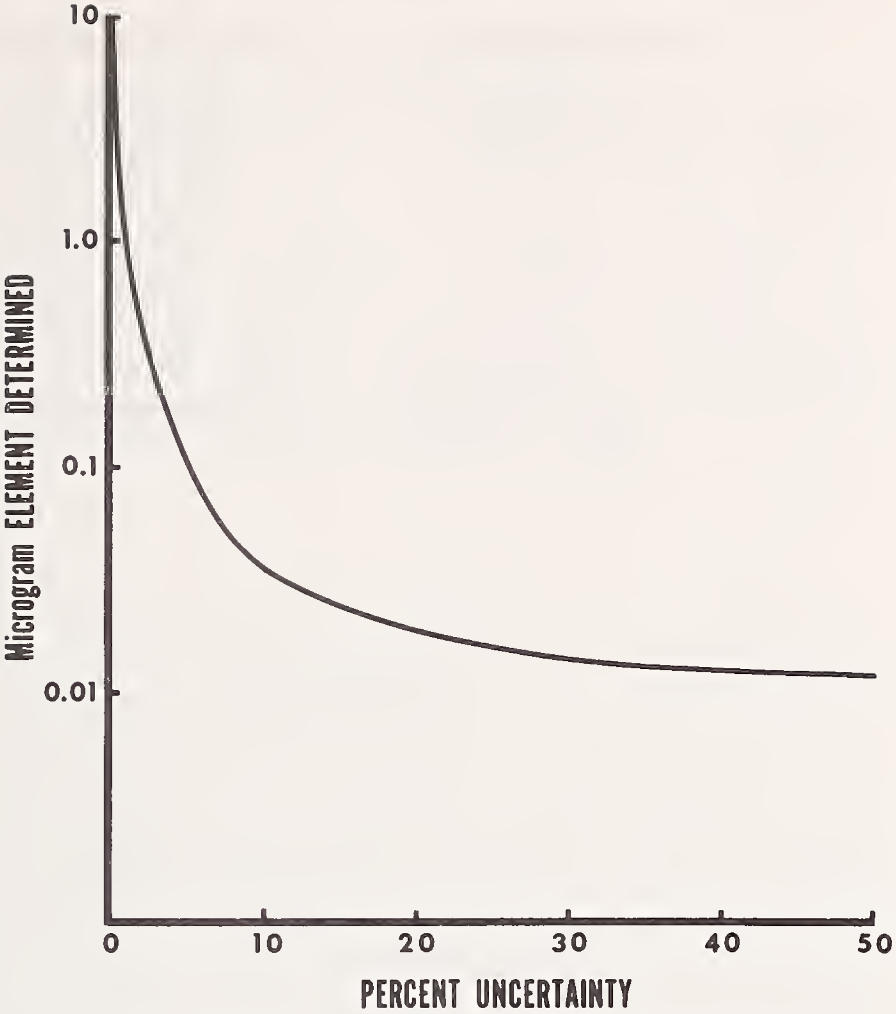

Figure 1. Effect of a 10 ± 5 ng blank on accuracy of analysis.

determination and have no information on the approximate variability or effect on accuracy.

One might argue that, since it is the variability and not the absolute value of the blank that affects accuracy, the way to increase accuracy is to have large blanks but with reduced variability. This is certainly not true in the real world of trace analysis. Firstly, it is inherently inaccurate to base a result on the difference between two signals or numbers of relatively the same size. But secondly, and more importantly, real blanks, large as well as small, do exhibit marked variability since most of the sources of the blank are not constant. The only practical way to lower the variability and increase the accuracy of the blank correction is to reduce the size of the blank. It is obvious from figure 1 that as one goes to lower levels of trace concentrations the blank becomes more and more of a factor. Figure 2

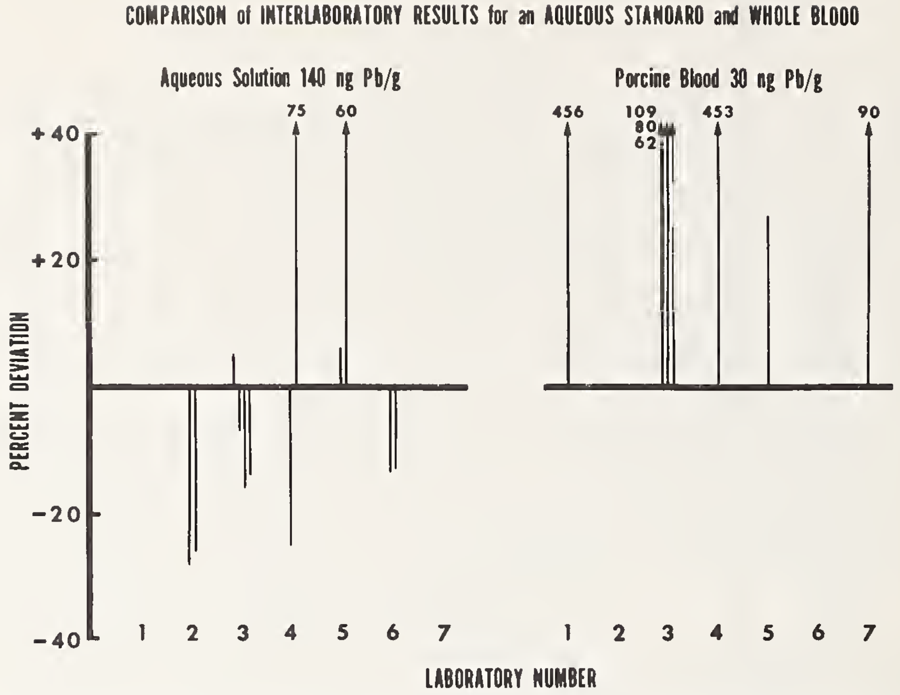

Figure 2. Comparison of interlaboratory results for an aqueous standard and whole blood.

represents two parts of a study to develop a referee method for lead in blood by atomic absorption spectrophotometry. The left portion represents the results from different laboratories for the analysis of an acidified aqueous standard. No chemistry was necessary and the results fluctuate, not very accurately, around the "base-line" value. But notice what happens when the same laboratories analyze a real blood sample as shown on the right portion.[1] The level of lead was a factor of five lower than the standard and some chemistry was necessary. The results varied from 30 to 450 percent high, in all probability due to lack of control of the analytical blank.

This is but one example of the fact that as one goes to lower trace concentrations, the blank becomes the dominant factor on accuracy and determines the lower limit of trace element concentration that can be determined with reliability. It is imperative to control and reduce the analytical blank if improvements in precision and accuracy of trace determinations are to be made.

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[1] This is for porcine blood which contains much lower lead than human blood.

II. Sources of Contamination

How does one go about lowering a blank? The sources of the blank must be considered and steps taken to reduce the contamination from each source.

The analytical blank is composed of contamination from four principal sources, namely, the environment the analysis is performed in, the reagents used in the analysis, the apparatus used, and the analyst performing the analysis. Of these factors only the contamination from reagents is relatively constant while the contamination from the other factors is variable and determines the variability of the analytical blank.

A. ENVIRONMENT

Let us consider environmental contamination. Fall-out or absorption of particulates or gases from the laboratory air can cause significant and variable amounts of contamination of the sample or a solution of the sample. As much as 200 μg of particulates per m^3 of air have been reported in the air of an analytical laboratory [2] and it was shown to contain large amounts of calcium, silicon, iron, aluminum, sodium, magnesium potassium, thallium, copper, manganese and lesser amounts of several other elements. Analysts in Dortmund, Germany, were not able to lower iron blanks lower than 0.04 μg/ml because 20 tons of ferric oxide were dispersed into the air from nearby plants [3]. Table 1 shows the lead particulate concentrations from three different locations. The lead concentration from downtown St. Louis, 18.84 μg/m^3, was much higher than rural Missouri, 0.77 μg/m^3, [4] due to automotive exhaust pollution. Our

TABLE 1. *Examples of lead concentration in air*

Site	Lead concentration μg/m^3
Downtown, St. Louis, Missouri[a]	18.84
Rural Park, Southeastern, Missouri[a]	0.77
Laboratory air, NBS, Gaithersburg, Maryland[b]	0.4

[a] See reference [4].
[b] See reference [5].

laboratory air at NBS, Gaithersburg, Maryland [5] compares favorably to rural air but still contains too much lead for low level work. Wide variations in the particulate content of air is to be expected. Useller [6] has stated that in a typical rural area airborne particulate counts larger than 0.5 μm of $1{,}400{,}000/\mathrm{m}^3$ are not unusual and that in metropolitan areas counts of $53{,}300{,}000/\mathrm{m}^3$ are normal.

The use of evaporation chambers has been one approach to reducing airborne contamination. Evaporations are performed in a closed system under filtered air or nitrogen. Figure 3 shows some different evaporation chambers from the literature. Chamber *(a)* was designed by Thiers [7,8]. Filtered air is passed over the solution and out the bottom while the sample is heated from below with a hot-plate and above with a heat lamp. Chamber *(b)* is a German design by Koch [9] in which filtered air or nitrogen is passed over the sample solution. A heated quartz dome

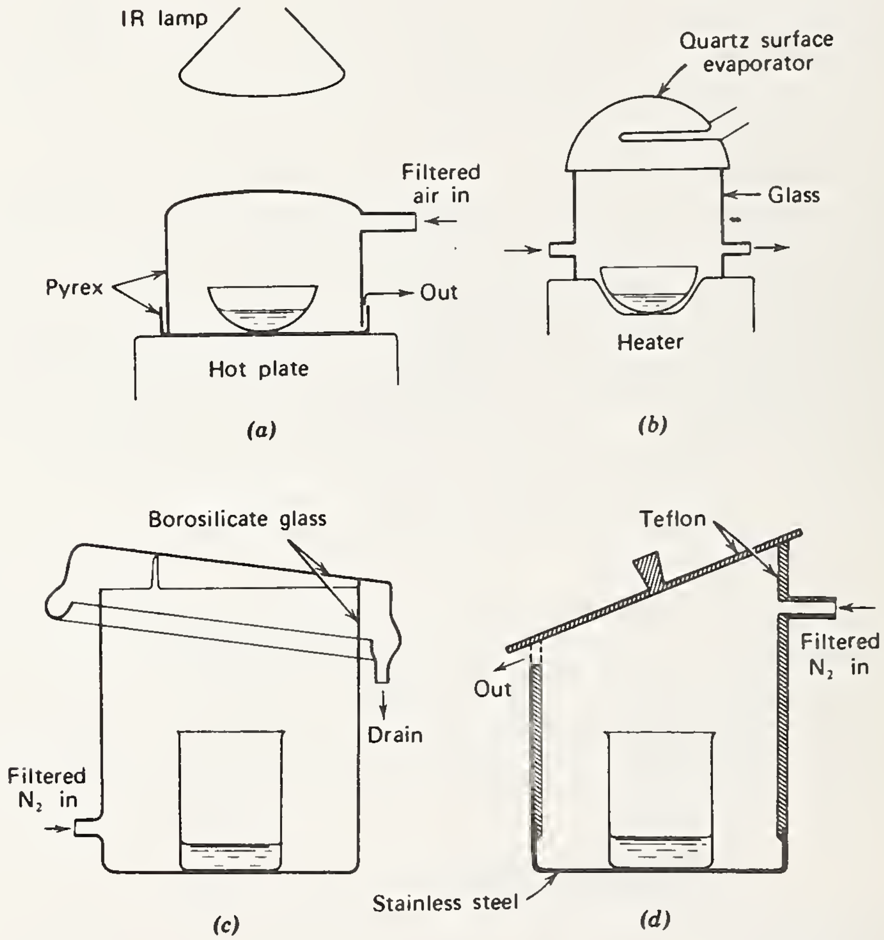

Figure 3. Evaporation chambers from the literature, reference 35. Reprinted with permission of John Wiley & Sons, Inc.

prevents condensation of liquids. The last two chambers, *(c)* and *(d)*, were used by Chow and McKinney [10] for the analysis of high-purity HCl (Glass) and HF (Teflon).

Figure 4 is a drawing of an evaporation chamber that has been used by Alvarez at NBS [11]. The solution is evaporated by heating from above and below the chamber while filtered nitrogen passes over the solution until only a drop remains. The drop is then drawn up into the capillary and loaded onto gold wire for analysis by spark source mass spectrometry.

Table 2 shows the results of Chow and McKinney [10] for the analysis of 500 ml samples of high-purity hydrochloric acid which was evaporated

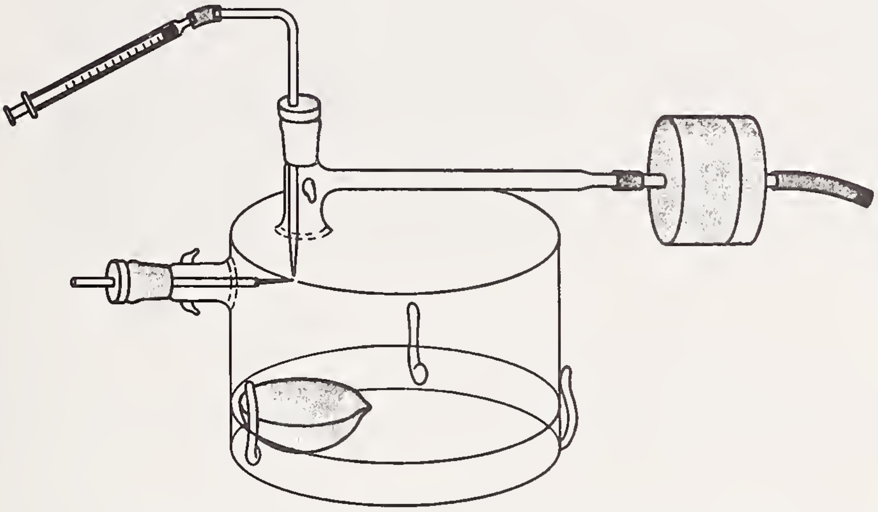

Figure 4. Clean environment evaporator and transfer system.

Table 2. *Lead contamination of labware after exposure to air*[a]

Beaker	Condition	Laboratory	Time (days)	Lead μ(g)
Teflon	Open	Ordinary	8	4.07 2.32
	Nitrogen-flushed container	Ordinary	8	1.13
	Open	Pure air	8	0.44
	Nitrogen-flushed container	Pure air	8	0.18 .13
	Nitrogen-flushed container	Pure air	1	0.02
Borosilicate glass	Nitrogen-flushed container	Pure air	1	.03

[a] See reference [10].

slowly under different conditions. When the HCl was evaporated over a period of 8 days from an open Teflon beaker, the lead contamination was high and variable. Using a clean air chamber under nitrogen reduced the lead contamination only by a factor of about three. Both of these evaporations were performed in a normal fume hood. (Since the volume of air moving across an area in a fume hood is many times greater than the air moving across the same area in the laboratory, the contamination is greater in the hood than elsewhere in the laboratory.) When the same evaporations were performed in a clean air laboratory in which dusts and aerosols were removed by electrostatic precipitation and filtration, the lead contamination was reduced by a factor of 10 when the HCl was evaporated open and by a factor of 20 when it was evaporated in an evaporation chamber flushed with nitrogen.

The major development to date for providing particulate free air is the high efficiency particulate air filter, better known as the HEPA filter [12]. This filter was developed during World War II for the Manhattan Project to remove fissionable particulates from air and to this date remains the most efficient means of air filtration. The HEPA filter has an efficiency of 99.97 percent for 0.3 μm particles and are routinely employed for supplying air that meets the Class 100 specification [13], that is less than 100 particles per cubic foot of air larger than 0.5 μm. These filters, coupled with the laminar airflow principle [14] in which the "clean" air is moved unidirectionally, have been used for the last decade to provide clean particle-free work areas.

Figure 5 is a view of the clean room located in the Analytical Chemistry Division at the National Bureau of Standards. The HEPA filters are located on the far wall. In fact the entire wall is composed of HEPA filters causing a wall of clean air to pass unidirectionally down the room. This room is really a particulate-free room and cannot be used as a clean laboratory since it was not designed for acid vapor.

Figure 6 is a cut-away view of the clean laboratory also located in the Analytical Chemistry Division at NBS. This room was designed for trace inorganic analysis and can be used for chemical operations such as acid dissolutions and evaporations. All of the air entering the room is passed thru prefilters and then thru the HEPA filters located over the center work-bench of the room. The Class 100 clean air is directed unidirectionally down and out across the bench to prevent particles from entering the area. Plexiglas dividers prevent cross-contamination. The air is recirculated thru the filters by drawing air at the base of the outside walls. In addition to the "clean" area under the center bench, there are several Class 100 hoods that provide clean work areas on the outside bench. Acid dissolutions and evaporations are performed in the two

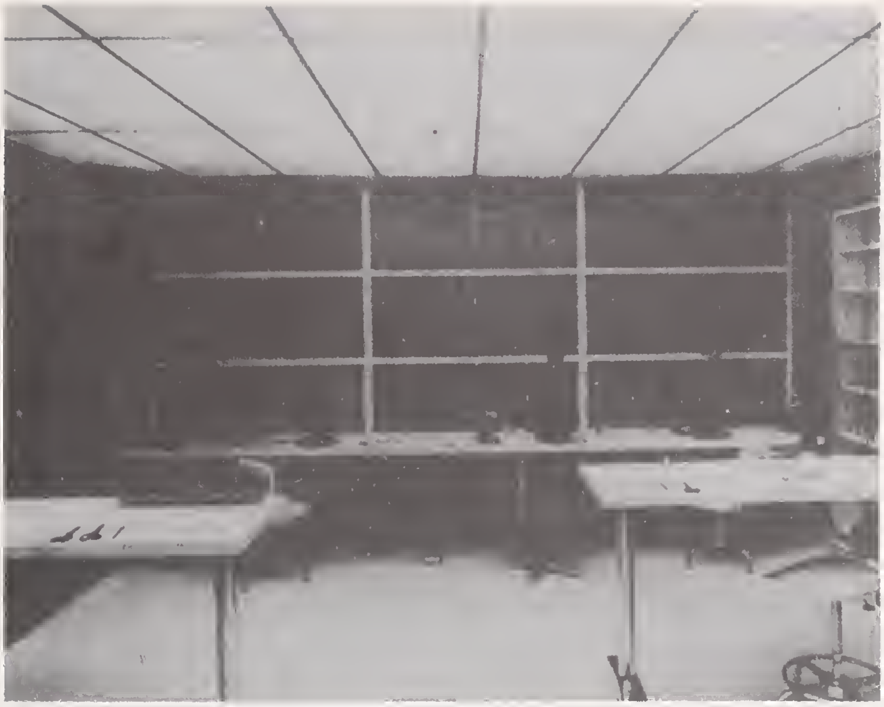

Figure 5. Particulate free clean room – National Bureau of Standards.

hoods at the rear of the room. These are Class 100 clean air hoods lined with sheet Teflon and are so designed that all air 12 cm from the front is exhausted while a curtain of air moves out the front to prevent particulates from entering the hood.

Figure 7 is a schematic of a laboratory used at Bell Telephone Laboratories for trace analysis [15]. The inlet air to the room is non-laminar flow clean air which has been filtered thru HEPA filters. The air to the clean hood is further purified by recirculation thru HEPA filters and the room is kept under positive pressure. Using this room, no significant contamination of water samples could be detected by spark source mass spectrometry or activation anaysis.

Table 3 shows a comparison of particulates in the air of an ordinary laboratory, a clean room, and a Class 100 hood, all at NBS [5]. Both the clean room and Class 100 hood air showed a dramatic reduction in contamination. Lead concentrations were reduced by a factor of over 1000, iron by a factor of 200 and the other elements, which were low to start with, by a factor of 10.

While HEPA filters are a powerful tool in reducing particulate contamination, they are not the complete answer to environmental con-

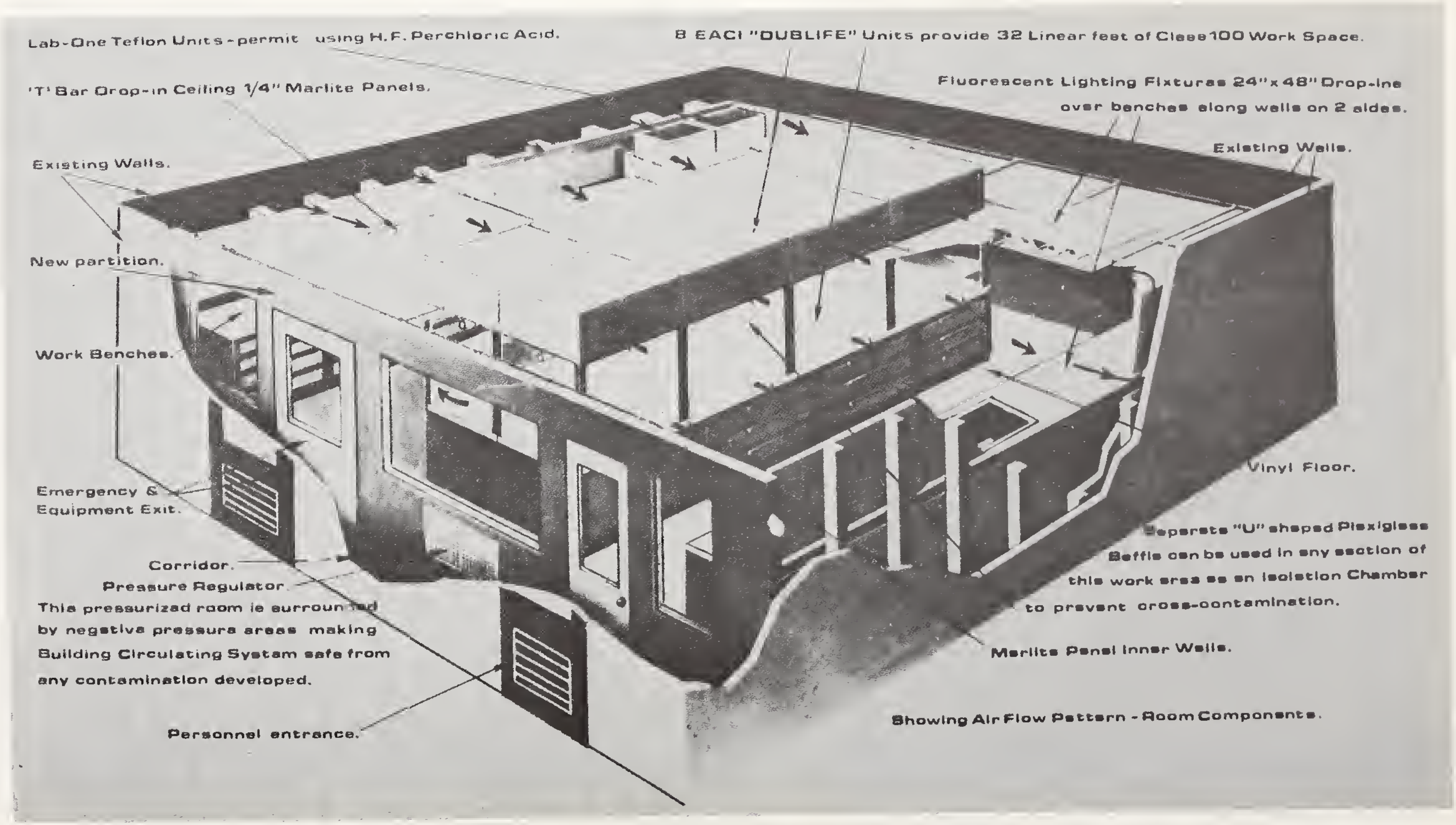

Figure 6. Cut-away of clean laboratory facility for trace level sample preparation.

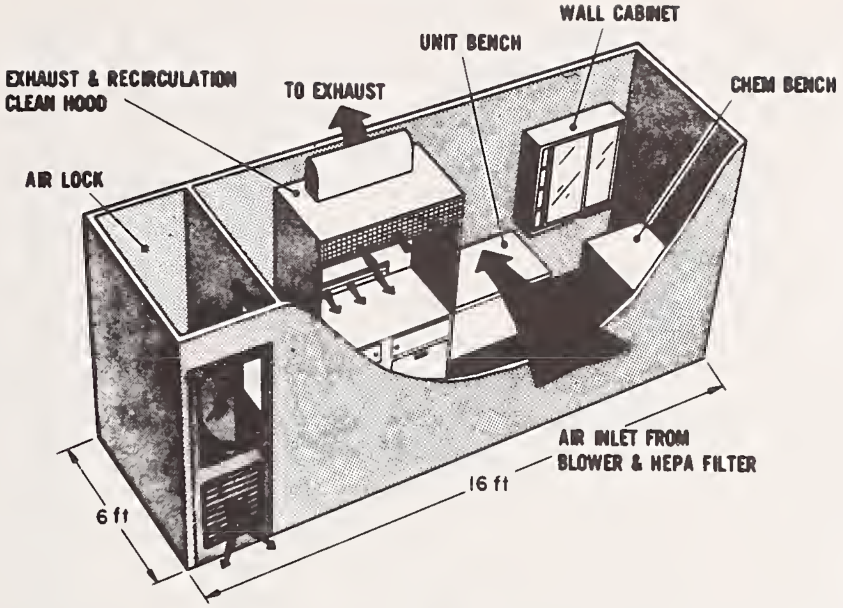

Figure 7. Schematic of clean laboratory—Bell Telephone Laboratories, reference 22. Reprinted with permission of Analytical Chemistry.

TABLE 3. *Particulate concentration in laboratory air*[a]

	Concentration, $\mu g/m^3$			
	Iron	Copper	Lead	Cadmium
Ordinary Laboratory	0.2	0.02	0.4	0.002
Clean Room	.001	.002	.0002	n.d.
Clean Hood	.0009	.007	.0003	0.0002

[a] See reference [5].

tamination. Figure 8 shows the particle size of some common contaminants. Since HEPA filters are efficient for the removal of particles 0.3 μm or larger, particles as small as bacteria are removed, but some common particulates such as tobacco smoke are not efficiently removed since they are smaller than 0.3 μm. Obviously gases, both organic and inorganic, are not removed. To remove these contaminants, the air must be passed thru absorbants and scrubbed, which is an expensive operation. Most laboratories either live with the small amount of contamination that results from clean room operation or resort to the evaporation chamber technique in the clean room to further reduce environmental blanks.

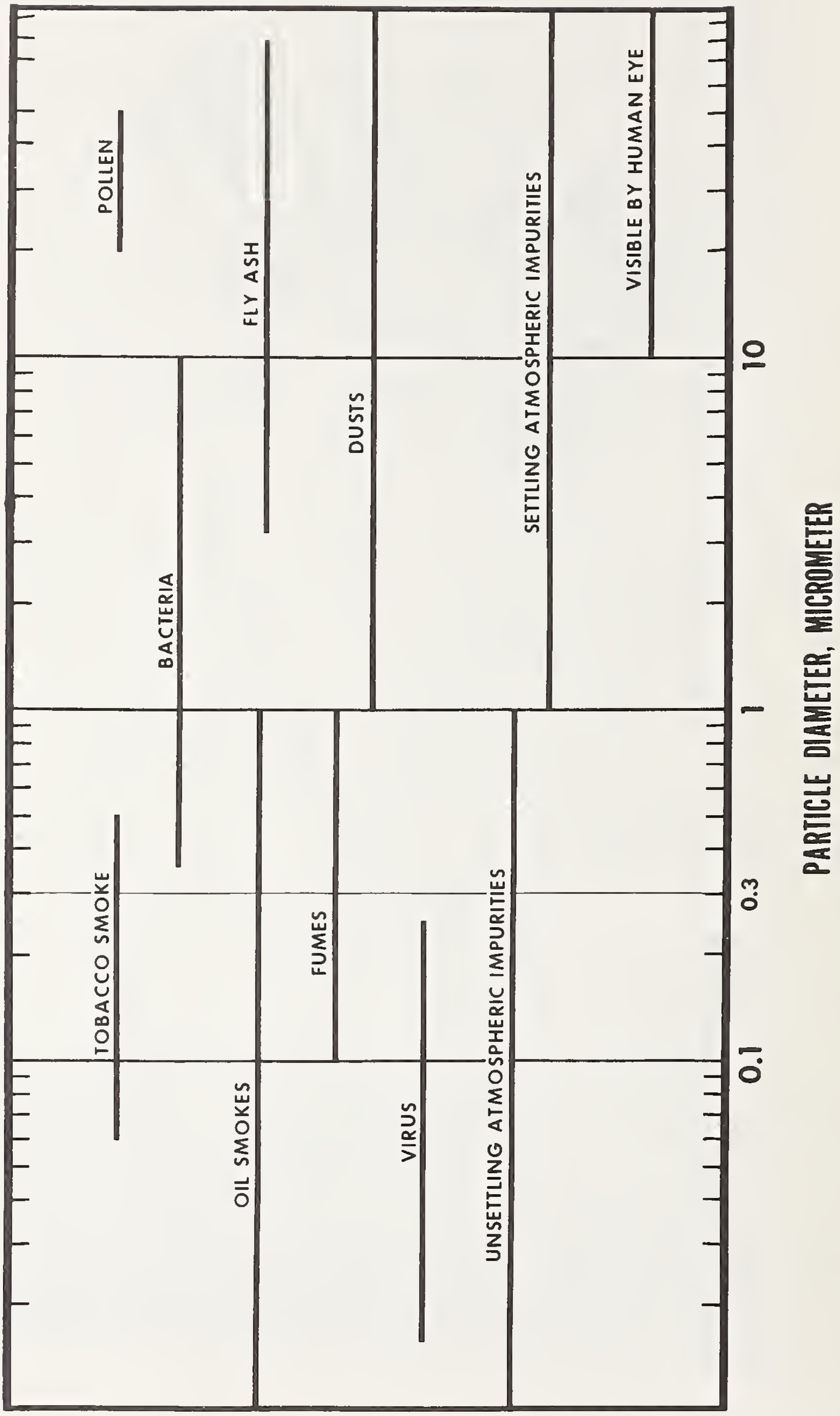

Figure 8. Relative size of common air contaminants.

B. REAGENTS

The chemical reagents used during the course of an analysis are an important source of the analytical blank. The first order of priority for a trace laboratory in regard to reagents is a readily available supply of extremely high-purity water. There are several commercial systems on the market for producing "conductivity water"; that is, water whose conductivity approaches the theoretical conductivity of 0.055 micromho/cm at 25 °C [15,16]. These systems are based on the use of mixed-bed or monobed ion exchangers, in which cation and anion exchange resins are mixed in a single unit, and sub-micron filtration. Measured conductivity of deionized water has been reported as low as 0.05 micromho/cm (temperature not specified) [16]. However, only ionized compounds are detected by conductivity measurements and soluble unionized compounds or particulates are not detected. Both soluble organic materials and particulates are generated by ion-exchange columns. Studies at the Philips' Laboratories [17] have shown that deionized water with a conductivity of 0.06 micromho/cm contained up to 100 ppb of cation contamination. They postulated that the detected impurities were present in particulate or colloidal form and were not appreciably ionized. Another possibility is that the cations form unionized complexes with dissolved resin material. In fact there is some literature evidence [18-20] to show that small amounts of heavy metals can be masked in deionized water and lost to polarographic analysis due to chelation by soluble resin. Whatever the reason, there is ample evidence in the literature [17] to prove that conductivity is not a reliable measure of trace element concentration in water.

Dr. Ralph Thiers [8] of Harvard wrote in 1957, "Since non-ionic materials are not held by ion-exchange resins, and since traces of nitrogeneous compounds are leached off the resin by water, probably the best treatment for obtaining purest water in all ways is ion-exchange followed by distillation from fused quartz." Nothing has happened in the last two decades to change the validity of that statement and this position has been supported by other investigators [21-23].

The system used by our group at NBS consists of taking the "building distilled" water as it is supplied to the laboratory and redistilling it in a conventional still equipped with a quartz condensing system. The distillate from this still is fed to a quartz "sub-boiling" still (Quartz Products Corp., Plainfield, N.J.) where the water is again distilled, but by a non-boiling technique which will be described later. The "building distilled" water consists of ordinary city water that has been passed thru a mixed-bed deionizer, distilled in a tin-lined still, stored in a tin-lined tank and distributed thru tin pipes to the laboratory.

Table 4 shows the results of the analysis of the "sub-boiling" distilled water and the "building distilled" water by spark source isotope dilution mass spectrometry (SS-IDMS). There was better than a tenfold reduction in impurities from "building distilled" water which is really good quality water for a high-volume operation. Copper at 3 ppb is the principal impurity in this water. The analysis of the "sub-boiling" distilled water, which totaled 0.5 ppb for the elements determined, really represents an upper limit for most impurities since no attempt was made to correct for a blank during the evaporation of the water. This water compares favorably with the best water reported in the literature. While it is one problem to produce high quality distilled water, it is quite another to keep it pure before use. We have been using quartz for storage and this analysis is for water stored in quartz for 2 weeks. We are currently studying the storage of water in Teflon.

Studies in the literature have shown that the trace element content of water stored in Teflon or polyethylene increased by a factor of 5 to 10 for some elements after 30 days storage [22]. As a general rule, distilled water should be used as soon as possible after preparation.

TABLE 4. *Impurity concentration in distilled water*

	Sub-boiling distilled (ng/g)	Building distilled (ng/g)
Pb	0.008	0.1
Tl	.01	<.01
Ba	.01	.004
Te	.004	.02
Sn	.02	.2
Cd	.005	.03
Ag	.002	.005
Sr	.002	.002
Zn	.04	1
Cu	.01	3
Ni	.02	0.1
Fe	.05	.4
Cr	.02	—
Ca	.08	1
K	.09	0.06
Mg	.09	2
Na	.06	0.1
Total Impurity	0.5 ppb	8.0 ppb

The next most important group of reagents for the trace analyst are the mineral acids. In recent years high-purity acids have been available from commercial suppliers. While these acids may prove quite satisfactory for a number of trace applications, the concentrations of some trace elements are too high for low level trace analyses so the analyst will have to purify his own acids in these cases. High-purity hydrochloric acid, hydrobromic acid, and hydrofluoric acid have been produced by saturating pure water with the pure gaseous compound [7,8,24-30] or by isopiestic or isothermal distillation [31,32]. The two-bottle sub-boiling method of Mattinson [33] has been used to produce high-purity HCl and HF [34]. Nitric acid, perchloric acid and sulfuric acid are usually purified by repeated distillations [35].

We have been purifying these acids by "sub-boiling" distillation from quartz or Teflon stills [11,36]. Figure 9 is a schematic of a quartz "sub-boiling still which is used for the production of high-purity water and the mineral acids with the obvious exception of hydrofluoric acid. The still is fed by a 6- to 8-lb bottle of ACS Reagent Grade acid through a liquid level control. Heating of the liquid being distilled is accomplished by a pair of infrared radiators positioned on both sides of the condenser.

The surface of the liquid is heated and evaporated without causing the liquid to boil. This positioning of the heaters also serves to heat the walls above the liquid, tending to keep them dry which minimizes creep of

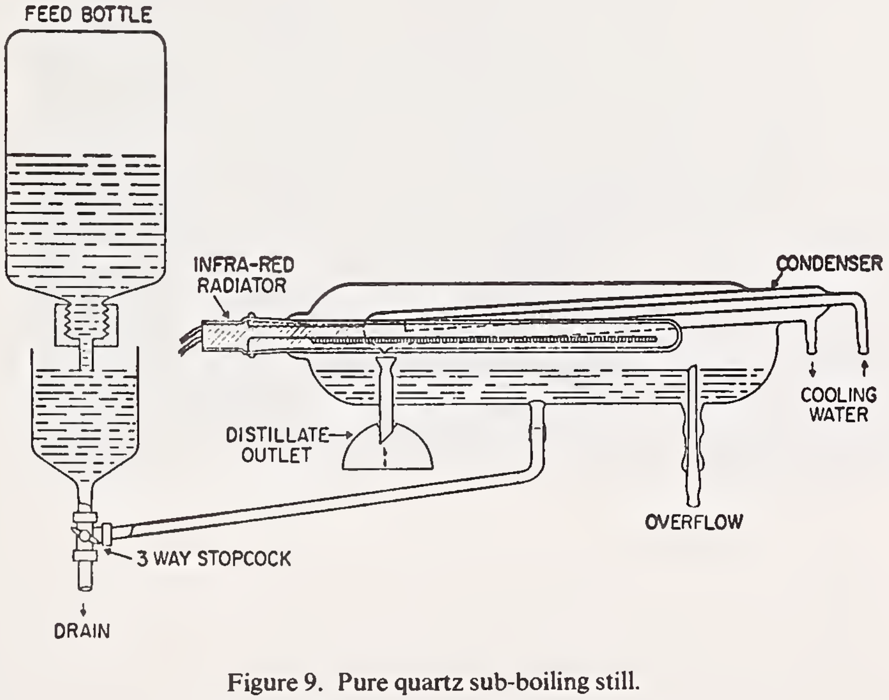

Figure 9. Pure quartz sub-boiling still.

liquid between the cold finger condenser and the liquid reservior. The cold finger condenser is tilted downward to allow the condensed liquid to flow to the tip above the outlet. The distillate is caught in Teflon FEP bottles which have been rigorously cleaned with nitric and hydrochloric acids.

Figure 10 is a schematic for the all Teflon sub-boiling still [11]. It was fabricated from a 2-liter TFE Teflon bottle and is designed on the same principal as the quartz still except that a trough of Teflon was hung from the cold finger to catch the drops of hydrofluoric acid dropping from the condenser.

Each "sub-boiling" still is housed in a clean air chamber, that is, a Class 100 hood, to protect the distillation process from external contamination. Figure 11 is a view of the laboratory for producing these high-purity acids. We produce enough high-purity acid in this facility to supply the entire Analytical Chemistry Division and some other laboratories with special needs.

Table 5 shows the results of the analysis of sub-boiling distilled hydrochloric acid, the starting ACS reagent grade acid, and a lot of commercial high-purity acid. A summation of these impurity elements shows that the sub-boiling distilled acid contained 6.2 ppb, the ACS reagent grade 820 ppb, and the commercial high purity, 70 ppb. The only element found in the sub-boiling distilled acid at a level higher than 1 ppb was iron

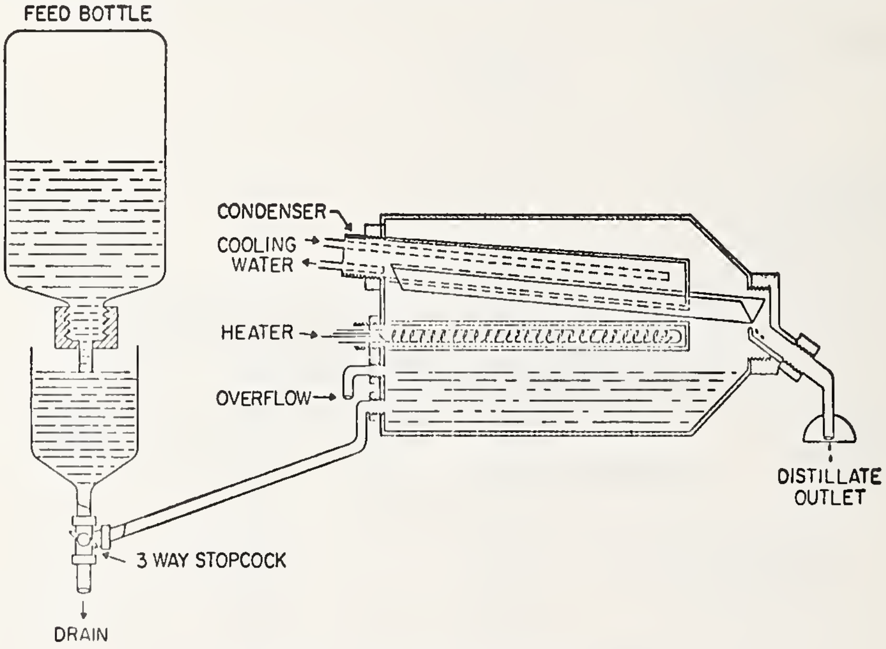

Figure 10. All-Teflon sub-boiling still.

Figure 11. Laboratory for production of high-purity acids.

TABLE 5. *Impurity concentration in hydrochloric acid*

	Sub-boiling distilled (ng/g)	ACS reagent grade acid (ng/g)	Commercial high purity (ng/g)
Pb	0.07	0.5	<1
Tl	.01	.1	—
Ba	.04	2	—
Te	.01	0.1	—
Sn	.05	.07	<6
In	.01	—	—
Cd	.02	.03	0.5
Ag	.03	.05	.2
Sr	.01	.05	—
Zn	.2	2	4
Cu	.1	4	1
Ni	.2	6	3
Fe	3	20	7
Cr	0.3	2	0.3
Ca	.06	70	24
K	.5	200	10
Mg	.6	10	20
Na	1	500	—
Total impurity	6.2 ppb	820 ppb	70 ppb

at 3 ppb. The other elements were at the sub-ppb level, generally lower than 0.1 ppb.

The results for the analyses of sub-boiling distilled nitric acid, the ACS reagent grade acid, and a lot of commercial high-purity acid are shown in table 6. The totals of the impurity elements determined were 2.3 ppb for the sub-boiling distilled acid, 220 ppb for the ACS starting acid, and 240 ppb for the commercial high-purity acid. No element was found in the sub-boiling distilled acid a concentration greater than 1 ppb and only sodium was detected at that level. Most of the elements were in the 0.05 to 0.01 ppb range.

Similar analyses for perchloric acid are shown in table 7. These analyses demonstrate the efficiency of sub-boiling distillation when the concentrations of impurity elements are compared to the starting acid. The concentration of barium which was greater than 1000 ppb was reduced to 0.1 ppb, a purification factor of greater than 10,000. Another example is calcium which was reduced to 0.2 ppb from 760 ppb in the starting acid, a factor of 3,800. It should also be noted that chromium which was present at 10 ppb in the starting acid was not significantly changed in the purified acid probably due to the formation of volatile

TABLE 6. *Impurity concentration in nitric acid*

	Sub-boiling distilled (ng/g)	ACS reagent grade acid (ng/g)	Commercial high purity (ng/g)
Pb	0.02	0.2	0.3
Tl	—	.2	—
Ba	.01	8	—
Te	.01	0.1	—
Sn	.01	.1	1
In	.01	—	—
Cd	.01	0.1	0.2
Ag	.1	.03	.1
Sr	.01	2	—
Se	.09	0.2	—
Zn	.04	4	8
Cu	.04	20	4
Ni	.05	20	3
Fe	.3	24	55
Cr	.05	6	130
Ca	.2	30	30
K	.2	10	11
Mg	.1	13	—
Na	1	80	—
Total impurity	2.3 ppb	220 ppb	240 ppb

TABLE 7. *Impurity concentration in perchloric acid*

	Sub-boiling distilled (ng/g)	ACS reagent grade acid (ng/g)	Commercial high purity (ng/g)
Pb	0.2	2	16
Tl	.1	0.1	—
Ba	.1	>1000	10
Te	.05	0.05	—
Sn	.3	.03	<1
Cd	.05	0.1	4
Ag	.1	0.1	0.5
Sr	.02	14	—
Zn	.1	7	17
Cu	.1	11	3
Ni	.5	8	0.5
Fe	2	330	10
Cr	9	10	18
Ca	0.2	760	7
K	.6	200	9
Mg	.2	500	4
Na	2	600	—
Total impurity	16 ppb	>3400 ppb	100 ppb

TABLE 8. *Impurity concentration in sulfuric acid*

	Sub-boiling distilled (ng/g)	ACS reagent grade acid (ng/g)
Pb	0.6	0.5
Tl	.1	.1
Ba	.3	.2
Te	.1	.1
Sn	.2	.6
Cd	.3	.2
Ag	.3	.6
Sr	.3	.4
Zn	.5	2
Cu	.2	6
Ni	.2	0.5
Fe	7	6
Cr	0.2	0.2
Ca	2	123
K	4	9
Mg	2	4
Na	9	50
Total impurity	27 ppb	200 ppb

chromyl chloride, CrO_2Cl_2. Chromium accounts for over half of the total impurities of 16 ppb found in the purified acid.

The analyses of sub-boiling distilled sulfuric acid, shown in table 8, showed that it contained 27 ppb of the elements determined. Sodium and iron were the principal contaminants, accounting for over half of the total impurities.

Hydrofluoric acid was purified using the all-Teflon still. Table 9 shows the results of the analyses of the starting ACS grade acid and the purified product. The total of the impurities in the sub-boiling distilled acid was 17 ppb compared to 320 ppb in the starting acid. The two principal impurities in the purified acid were calcium and chromium at 5 ppb, which accounted for over half the total impurities found.

The situation for salts and other reagents is not as favorable as for the acids. Again, there are special high-purity grades of some of these reagents available from commercial sources which are a major improvement over ACS reagent grade materials. However, there are relatively few of these reagents available and they often contain impurities at a level too high for use in low level trace analysis [22,23,37]. Hume [38] has stated in a recent article that natural sea water contains much lower concentrations of many heavy metals than artificial sea water made up from the

TABLE 9. *Impurity concentration in hydrofluoric acid*

	Sub-boiling distilled (ng/g)	ACS reagent grade acid (ng/g)
Pb	0.05	0.8
Tl	.1	.2
Ba	.1	.5
Te	.05	.1
Sn	.05	11
Cd	.03	2
Ag	.05	0.1
Sr	.1	.5
Zn	.2	4
Cu	.2	3
Ni	.3	12
Fe	.6	110
Cr	5	20
Ca	5	14
K	1	28
Mg	2	10
Na	2	100
Total impurity	17 ppb	320 ppb

purest available reagent chemicals. An example of a high-purity, commercially available reagent that has met a need is phosphorus pentoxide. The specifications for the ACS reagent grade would allow for up to 100 ppm of lead. One supplier of high purity reagents has a limit of 0.1 ppb for lead in this material and it has found wide use in the silica gel method for lead by isotope dilution mass spectrometry [39]. On the other hand, the specifications for high-purity sodium acetate allow a maximum of 0.05 ppm of lead. A total of 3 g of sodium acetate is sometimes used during the sample processing for the polarographic determination of lead, so the lead contamination could be as high as 150 ng Pb from this reagent alone. In cases like this the analyst will have to purify his reagents before use. The purification method used will depend on the nature of the reagent and the impurities to be removed. Mercury cathode electrolysis, extraction with dithizone or cupferron, ion-exchange, and crystallization have all found use in this regard [7,8,21,35].

C. APPARATUS

The third important source of contamination is that due to apparatus that comes into direct contact with the sample or sample solution, such as beakers, bottles, filters, mortars, *etc.*

Table 10 shows the results of Vasileyeskaya [23] for the analysis of high-purity hydrofluoric acid, hydrochloric acid, and nitric acid after evaporation in Teflon, platinum, and quartz containers. The results show higher trace element concentrations when the evaporations were performed in either platinum or quartz than in Teflon with the evaporation in quartz showing the highest values. Note the increase in aluminum, iron, calcium, and magnesium when the evaporations were performed in quartz compared to Teflon.

Table 11 shows the data compiled by Hetherington, Stephenson, and Witherburn [40] for the maximum recorded impurity levels in various types of fused silica or quartz. There are two main types of vitreous silica, translucent or opaque quartz, and transparent quartz. Translucent quartz has the highest trace element concentrations and should be avoided. Transparent Types I and II quartz are made from naturally occurring quartz crystals or sands. Type I is made by electric melting and Type II by flame melting. Type II quartz has a somewhat lower trace element content because some impurities are partially volatilized in the flame. Type III quartz is a synthetic quartz made by vapor phase hydrolysis of pure silicon compounds such as $SiCl_4$. It has a much lower trace element content than natural quartz with the exception of chloride which runs about 50 ppm and it contains about 0.1 percent hydroxide. There is yet another type of transparent quartz, Type IV, which is also a synthetic quartz made by the oxidation of $SiCl_4$ and electrical fusion. It has about the same trace element content as Type III, is virtually free from hydroxide but has a chloride content of several hundred ppm. Notice that the principal impurities in Types I and II quartz are aluminum, calcium, iron, and magnesium, the same elements that increased when the pure acids were evaporated in quartz. Obviously synthetic quartz should be used whenever possible. One problem is that it is usually not available in the form of laboratory ware such as beakers, dishes, or crucibles.

Table 12 shows the trace element concentrations of some container materials from the literature [7,48,53,54]. While variations of impurity content from batch to batch are to be expected, the compilation is useful for comparative purposes. Borosilicate glass can seriously contaminate solutions [8] and should be avoided unless the analyst is sure that the contamination of the element being determined is negligible such as for rhenium. In addition to these elements contamination from arsenic and lead have been reported. The quartz reported here is a Type 1 quartz made from the melting of pure domestic quartz sand which is claimed to be purer than the imported quartz crystal. Both polyethylene and Teflon are purer than natural quartz. The polyethylene reported here is produced by

TABLE 10. *Results of spectrochemical analysis of hydrogen fluoride, hydrogen chloride and nitric acid after evaporation in teflon, platinum and quartz dishes*[a]

Acid	Material	Elements determined, ng/g										
		Al	Fe	Ca	Cu	Mg	Mn	Ni	Pb	Ti	Cr	Sn
HF	Teflon	3	3	1	<0.04	<3	0.1	<0.4	<0.1	0.1	<0.4	ND[b]
	Platinum	10	10	10	.4	10	.2	.3	.5	1	0.5	ND
HCl	Teflon	<4	3	5	0.2	3	0.1	ND	<0.4	ND	ND	ND
	Platinum	2	2	10	1	6	.2	0.6	<.4	0.4	Tr[c]	<0.4
	Quartz	10	10	60	1	10	.4	2	.5	2	0.6	0.4
HNO_3	Teflon	2	8	4	<0.01	7	0.1	ND	ND	Tr	ND	ND
	Platinum	20	20	30	.4	20	.6	Tr	1	0.8	ND	ND
	Quartz	20	20	60	.1	10	.6	ND	1	0.3	ND	ND

[a] See reference [23].
[b] ND = not detected.
[c] Tr = trace, not evaluated quantitatively.

TABLE 11. *Maximum recorded impurity levels in various types of vitreous silica*[a]

Element	Translucent vitreous silica	Concentration (ppm) in transparent vitreous silica		
		Type I	Type II	Type III
Al	500	74	68	<0.25
Sb	ND[b]	0.3	0.1	.1
As	ND	ND	ND	<.02
B	9	4	.3	.1
Ca	200	16	0.4	<.1
Cr	ND	0.1	ND	.03
Co	ND	ND	ND	.0001
Cu	ND	1	.1	<1
Ga	ND	ND	ND	<0.02
Au	ND	ND	ND	<.1
Fe	77	7	1.5	<.2
Li	3	7	1	ND
Mg	150	4	ND	ND
Mn	ND	1	0.2	<0.02
Hg	ND	ND	ND	<.1
P	ND	0.01	0.005	<.001
K	37	6	<1	.1
Na	60	9	5	<.1
Ti	120	3	2	ND
U	ND	ND	0.0006	ND
Zn	ND	ND	ND	<0.1
Zr	15	3	ND	ND

[a] See reference [40].
[b] ND = not detected.

TABLE 12. *Trace element concentration of container materials*

Element	Borosilicate glass (μg/g)	Quartz (μg/g)	Polyethylene (μg/g)	Teflon (μg/g)
Al	Major	50	0.3	
B	Major	0.5	.09	
Ca	1,000	12	.2	0.002
Cr			.015	<.030
Cu			.004	.022
Fe	3,000	5	.6	.035
K	3,000	4		
Mg	600	2	.08	
Mn	1,000		.01	
Na	Major	4	.17	
Sb	2.9		.005	.0004
Ti		2		
Zn	0.73			.093
Zr		<1	.09	

the high pressure noncatalyzed process which is superior in trace element content to the low-pressure process catalyzed by organic compounds of aluminum or oxides of transition metals [3,8,41].

Table 13 lists an order of preference for container materials based on the purity of the material. Teflon FEP bottles and beakers have been used at NBS for the past several years with favorable results after thorough cleaning with nitric and hydrochloric acids to remove contaminants introduced during fabrication. The high-purity acids described earlier were all stored in Teflon FEP bottles for at least 2 weeks and no significant levels of contamination were observed.

Filter paper is another source of trace element contamination. Quantitative ashless filter paper has been shown to contain 20 trace elements at greater than 1 ppm [42]. Membrane filters, while not free from trace element impurities are significantly better than paper [41]. All plastic filtration assemblies are available commercially which have been designed to minimize contamination. Glass filtration assemblies have been shown to contaminate pure water [43]. The trace element concentration of membrane filters which are fabricated from cellulose acetate, polypropylene, fluorocarbons, or polycarbonates can be lowered by acid leaching before use [41,44]. Maienthal [44], for example, has shown, table 14, that the concentrations of Fe, Cu, and Pb can be lowered by acid washing of cellulose ester filters, but the contamination is still too high for low level work. Whenever possible, centrifugation in plastic tubes should be substituted for filtration.

The grinding and sieving of samples prior to analysis is another serious contamination problem [7,41,45]. Mortars made from single crystal alumina, tungsten carbide or pure molybdenum have been used for this purpose since these mortars introduce significant contamination of only one

TABLE 13. *Container materials in order of increasing impurities*

1. Fluorocarbons
    Teflon TFE and FEP; Tefzel; Halar; Kel-F

2. Quartz—Synthetic

3. Polyethylene
    High Pressure—Conventional

4. Quartz—Natural

5. Platinum

6. Borosilicate

TABLE 14. *Reduction of contamination of celluolus acetate filters by acid leaching*[a]

	μg/47mm sheet		
	Fe	Cu	Pb
Unwashed	0.30	0.50	0.10
Acid washed	.036	.040	.041

[a] See reference [44].

or two elements which would be neglected in the analyses. Standard sieves made of metal should not be used for sieving [46]. Instead fine silk cloths have been recommended as a substitute. Whenever possible, it is best to avoid grinding and sieving altogether by dissolving large samples and aliquoting.

Rubber stoppers and tubing are to be avoided as they are extremely dirty materials with regards to trace element concentrations [48]. Likewise, polyvinyl chloride tubing is high in trace elements. Tygon tubing, for example, has been shown to contain lead and nickel in excess of 200 ppm and five other elements in excess of 10 ppm [48]. The choice of materials for stoppers or tubing would be Teflon or polyethylene, both of which are low in trace element content. Heating by gas using metallic burners is a possible source of contamination. Ceramic electric hot plates are the least contaminating heat source since metal hot plates corrode and are attacked by acids. Ovens and muffle furnaces are also possible sources of contamination. Fused silica liners are available for muffle furnaces which help to reduce contamination [7].

D. ANALYST

This brings us to the fourth source of contamination, the analyst. Careless manipulations can cause serious contamination. The touching of surfaces that will come into contact with either the sample or a solution of the sample can cause contamination with a number of elements besides sodium and chlorine. Sweat has been shown to contain potassium, lead, ammonium, calcium, magnesium, sulfate and phosphate ions [49].

Table 15 shows the results of a test for lead from the fingers of 16 individuals. Two fingers were soaked for two minutes in 15 ml of 1N HNO_3 and the lead determined by isotope dilution mass spectrometry. The results, which showed an average 3.1 μg of lead, indicate that one must be very careful in handling solutions containing trace amounts of lead.

TABLE 15. *Lead leached from fingers of 16 individuals by dilute nitric acid*

	Lead found (μg)
High reading	13.1
Low reading	0.8
Average	3.1

The use of cosmetics by analysts can cause serious trace element contamination since they can contain high concentrations of Al, Be, Ca, Cu, Cr, K, Fe, Mn, Ti, and Zn [23,50]. Some hair dyes contain lead acetate and eye make-up may contain mercury as a preservative. Trace analysts would be well advised to avoid the use of such products. Even medications can be a problem. Calamine lotion, for example, which is used to treat skin irritations such as poison ivy, is practically pure zinc oxide when dry and has been known to cause contaminations. Watches and jewelry such as rings and bracelets should not be worn in the trace laboratory because of contamination hazards.

To keep blank levels as low as possible the analyst must exercise care in keeping the volume of reagents to a minimum, and the time or temperature of evaporations or reactions to a minimum. Excess of reagents, time, or temperature, all cause higher and more variable blanks.

Unless great care is exercised, cross-contamination from other work in the laboratory can contaminate a sample. The analyst must be aware of the history of beakers and other containers so that vessels that have been exposed to major concentrations of one element are not used for trace determinations of that element even after rigorous cleaning treatment. Great care must also be exercised in the handling of ultra-pure reagents least they become contaminated due to careless acts such as opening a container in a unclean atmosphere or pouring a liquid from the container into another solution.

And, finally, the analyst must "think blank"; that is, he must be aware as to the effect on the blank of every step of the procedure. He must ask himself "If I do this, what is the effect on the blank?" and avoid those operations which tend to increase the blank or whose effect is not known, whenever possible.

The importance of the analyst in this regard has also been noted by others. Burriel-Marti [51] has stated that the analyst must really work under "chemically aseptic" conditions. Libby [21] has stated that "low level radiochemistry (and low level trace analysis as well) is something like the discipline of surgery—cleanliness, care, seriousness, and practice." Alimarin [52], has written that "a major factor is also the experience and the skill of the analyst, which obviously cannot be described statistically." One last quote is from Ruzicka and Stary [21], "It is interesting to note that often an analytical chemist trained in trace determinations by spectrophotometry or spectrography is more successful in this field (substoichiometry) than a radiochemist who is used to working on neutron-activation analysis where the value of the reagent blank can be neglected."

III. Conclusion

In order to decrease the variability of the analytical blank and increase the accuracy of the blank correction, the analyst must reduce the contamination from each source, (1) by working in a Class 100 clean air environment, (2) by using specially purified reagents, (3) by selecting apparatus materials with the lowest possible impurities, and (4) by being constantly aware of his own effect on the blank.

The methods discussed above for the control of the analytical blank have been applied at NBS for the reduction of blank values and hence the variability of the blank correction. Table 16 shows our experience with lead in the Trace Elements in Glass (TEG) Standard Reference Materials over a period of 4 years. Since the lead blanks have been reduced to about 2 ng with an uncertainty of ± 1 ng, we have been able to analyze lunar rocks and other materials containing sub-ppm amounts of lead with less than 1 percent uncertainty. Table 17 shows our experience with silver. Again by lowering the silver blank from 970 ng to 3 ng, the variability was also reduced. These two examples illustrate the fact that control of contamination is not a hopeless task but does take special care, patience, and financial support.

TABLE 16. *Example of lead blank reduction*

	Lead found (μg)
Initial analysis of TEG[a] standard	330 ± 250
TEG analysis using selected acids	260 ± 200
TEG analysis in Class 100 hood	20 ± 8
TEG analysis using special acids in Clean Room (Lunar also)	2 ± 1

[a] TEG = Trace element in glass, SRM's 610 through 619.

TABLE 17. *Example of silver blank reduction*

	Silver found (μg)
Initial analysis of TEG[a] standard	970 ± 500
TEG analysis using Class 100 hoods	207 ± 200
TEG analysis using special acids in Clean Room	3 ± 2

TEG = Trace element in glass, SRM's 610 through 619.

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APPENDIX III

Evaluation of Lyophilization for the Preconcentration of Natural Water Samples Prior to Neutron Activation Analysis

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Neutron activation analysis (NAA) has been applied successfully to a variety of complex environmental matrices for trace element determination. Because of its excellent sensitivity for many elements and general lack of matrix effects, instrumental neutron activation analysis (INAA) has been used to determine up to 30 elements in rocks (*1*), soils (*2*), atmospheric particulates (*3*), sediments (*4*), and biological tissues (*5*).

Although NAA is presently used to analyze various aquatic samples, the applicability of the technique to the water matrix is hindered by two main factors: very low concentrations of the elements of interest, and interferences from more concentrated dissolved species.

Except for Na and Cl in sea water, most natural waters contain such low concentrations of most elements that few can be accurately determined directly on bulk water samples by completely instrumental techniques. The sensitivity of analysis can be greatly improved by concentration of the dissolved species from the water into a different medium, or removal of water to leave a residue of dissolved material that can be irradiated in a small sample container.

The latter approach was used by Mamuro et al. (*6*) who evaporated the water prior to irradiation. Since evaporation is generally a slow process carried out in the open, it is subject to possible difficulties. These difficulties include contamination by fallout particles from laboratory atmosphere, dissolution of ions from container surfaces, and loss of volatile species if performed at an elevated temperature.

Other workers have devised chemical methods for removal of specific elements from water. Selective anion exchange was used by Robertson (*7*) to determine Ag in sea water and by Becknell et al. (*8*) to measure Hg in fresh water. Nagatsuka et al. (*9*) used an initial iron hydroxide coprecipitation step for concentration of rare earths from natural waters. Fujinaga et al. (*10*) found that elements producing short to medium lived isotopes when irradiated, including V, Mo, and U, could be concentrated from water by liquid–liquid extraction followed by organic coprecipitation. In all of these treatments, there is a risk of contamination from reagent and container walls.

Some reactors are equipped with facilities for irradiation of very large volume samples. However, this is not a totally satisfactory solution to the problem of analysis of natural water for several reasons. First, there may be substantial variations of flux over large volumes requiring very careful flux mapping and monitoring. Second, the handling and containment of very large samples may cause severe blank problems. Finally, the counting of large volume samples will necessarily involve an unusual (and inefficient) geometrical configuration for which accurate calibration may be difficult.

The work presented here deals with the preconcentration of water by freeze drying using a method which virtually eliminates sample contamination and trace element losses. Freeze drying is a method commonly used for drying biological tissues in which trace elements may be bound organically. Also, it has been used for drying natural water although without associated evaluations of the technique (*11–14*). However, questions may be raised regarding the suitability of this method of concentration that point to the possibility of losses of volatile elements during the drying process and the ability to transfer quantitatively the dry residue from the freeze drying container to an irradiation container.

The first question arises because it is known that some trace elements can exist in chemical forms that have significant vapor pressures at room temperature, with respect to that of water. When a sample containing such compounds is placed in a vacuum system for an extended length of time, trace element losses from the sample will most likely occur. A major object of this work was to determine if there are significant losses of various elements in water when the water is subjected to freeze drying.

To evaluate this question, known quantities of radioactive tracers for 21 elements (including many known to be volatile) were added to water, the solutions freeze dried and the tracer residues counted. The results confirm that at least 95% of all but the most volatile elements studied (Hg and I) were retained in the residue. The second question, concerning sample transfer, was eliminated by designing a freeze drying container which also would serve as an irradiation and counting container. The material chosen was linear polyethylene film (Phillips Petroleum's Marlex). This preconcentration and containment system has been used successfully in our laboratory for the INAA of river and estuarine water samples.

EXPERIMENTAL

Apparatus. The freeze dryer used for the tracer studies consists of a high capacity two-stage pump, glass vacuum manifold, and three freeze drying units. Each freeze drying unit was made up of a glass sample chamber and cold trap. An O-ring gasket on a flat flange served to seal the sample chamber when under vacuum. All other connections were made with ground glass stopcocks, ball joints, and straight standard taper joints. An extra liquid nitrogen cold trap was used between the oil pump and the manifold to prevent back diffusion of oil vapor.

The counting equipment used to determine tracer yields were a 7.6 × 7.6-cm NaI(Tl) γ-ray detector, and a 13% efficient Ge(Li) detector which produced a peak with full width at half maximum of 3.0 keV for the ^{60}Co 1332-keV line. The NaI(Tl) detector was used to obtain good counting statistics on samples which contained only one radioactive tracer. The Ge(Li) detector was used to resolve the photopeaks from the solutions spiked with two or more radioactive tracers or from single isotope solutions that had a significant amount of radioactive daughter present.

The bags used to contain the water samples were made of 0.0025-cm (1-mil) linear polyethylene film. The film was cut and heat sealed to make approximately cubic shaped, open topped bags. Each bag was soaked in 50% HNO_3 for 24 hours to remove surface contamination. Although HNO_3 is probably not the ideal leaching agent, it was felt that HCl followed by HNO_3 could present Cl contamination difficulties. Different cleaning procedures are presently being investigated.

Linear polyethylene was chosen over conventional polyethylene because of its superior performance with respect to structural deg-

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Table I. Trace Element Content of Linear Polyethylene Film

Element	Concentrations in ng/g	
	Average	Range
Na	3400	580–6600
Cl	5300	3700–6900
Al	1000	870–1200
Br	990	790–1300
Sm	0.26	0.18–0.31
Co	14	0.90–27
Zn	410	150–820
Fe	2200	1000–4700
Sc	0.34	0.13–0.73
Sb	11	2.2–30
La	4.5	3.0–6.8
Cr	1300	1200–1500
Th	4.0	0.95–13
Sr	<180	<180
Au	5.3	2.4–7.0
Ag	4.4	<3–5.1
Ba	<250	<250
Mn	<350	140–300
Ce	35	6.0–92
Eu	<0.14	<0.14
V	210	210
Se	<3.5	<2.5–5.6
Mg	<60,000	<60,000
Ca	<100,000	<100,000

Table II. Trace Element Content of Conventional Polyethylene Film

Element	Concentration, ng/g
Na	30,000
Cl	24,000
Al	19,000
Br	120
Sm	1.4
Co	81
Zn	1,600
Fe	11,000
Sc	6.9
Sb	33
La	8.1
Cr	170
Th	3.0
Ba	28,000
Mn	110
Ce	27
Eu	4.2
V	150
Se	43
Mg	12,000
Ca	7,700

Table III. Trace Element Retention Yields for Freeze-Drying Water

Element	Isotope	n	Range, %	Average, %
Na[a]	^{24}Na	3	95.8–99.4	97.4 ± 1.8
Sc	^{46}Sc	5	91.5–103.3	97.9 ± 4.3
V	^{48}V	2	100.0–100.8	100.4 ± 0.3
Cr	^{51}Cr	4	94.3–98.5	95.9 ± 2.0
Fe	^{59}Fe	1	...	101.1
Co	^{60}Co	6	94.2–100.0	97.5 ± 2.2
Zn	^{65}Zn	1	...	102.6
As	^{74}As	6	94.8–98.5	96.3 ± 1.8
Se	^{75}Se	6	93.5–100.0	96.2 ± 1.8
Br[a]	^{82}Br	3	97.4–100.8	99.3 ± 1.7
Rb	^{86}Rb	4	99.5–103.6	101.2 ± 1.8
Sr	^{85}Sr	1	...	101
Ag	^{100m}Ag	1	...	98.1
Cd	^{109}Cd	4	94.9–113	102 ± 8
Sb	^{124}Sb	6	96.7–99.7	98.6 ± 1.1
I	^{126}I	3	46.9–88.0	68 ± 21
Cs	^{137}Cs	1	...	99.3
Ba	^{133}Ba	6	91.8–100.6	97.7 ± 3.0
Au	^{195}Au	4	92.1–95.0	94.0 ± 1.3
Hg	^{203}Hg	4	50.1–72.0	61 ± 9
Tb	^{160}Tb	1	...	98.7
Ce	^{141}Ce	2	97.5–99.1	98.3 ± 1.1

[a] Tracer solution used was not acidified.

radation during long neutron irradiation at high flux. Experience in the laboratory shows that a 4-hr irradiation at a thermal neutron flux of 5×10^{13} n cm^{-2} sec^{-1} renders a thin film of conventional polyethylene almost to a powder whereas, after the same dose linear polyethylene film is in a manageable form, somewhat more rigid and with some chance of cracking. It was anticipated that, in future work, it would be useful to be able to reopen the bags after irradiation and add chemicals to redissolve the residue; therefore, the need for a non-degrading film.

The linear polyethylene film chosen was quite clean compared to conventional polyethylene film which has been analyzed in this laboratory. Typical trace element concentrations in the acid washed bags, made exactly as for sample containment, are shown in Table I. A representative trace element profile of the conventional film is given in Table II. The results in Table I compare quite favorably to those in Table II with the exception of Cr.

If the new cleaning procedures being investigated do not substantially reduce the trace element content of the bags used, other materials must be sought.

Solutions. Inorganic radioactive tracers of one to three elements were added to 500 ml of filtered river water, tap water, or deionized water (generally filtered river water was used). Each element was added in amounts that would give concentrations less than 1 mg/liter in the resulting solution. In some cases, known volatile oxidation states of elements were used as tracers, i.e., ^{48}VOCl$_2$.

The pH of the prepared tracer solutions was adjusted to about 1.5 with HNO$_3$. The purpose of the pH adjustment was to follow the common practice of preserving water samples by acidification (*12*). In most cases, the stock tracer solutions were allowed to equilibrate for at least 24 hours in a polyethylene bottle prior to a freeze drying run.

Procedure. One-hundred-ml aliquots of tracer solution were transferred to the polyethylene bags. Each sample was then frozen in liquid nitrogen. Concentration gradients due to zoning when samples are frozen slowly probably do not occur when they are "flash" frozen in this manner. An additional 100 ml of tracer solution was transferred to a polyethylene bottle and set aside as a reference sample.

The frozen samples were placed in the freeze-drying chambers which then were evacuated. The freeze drying process is essentially a low temperature, low pressure distillation of water which sublimes from the surface of the ice and condenses in the cold trap. The heat of sublimation removed from the sample, together with the low pressure conditions and the insulation provided by the vacuum, is sufficient to keep water with salinity below 9 mg/g frozen during the drying period even when the apparatus is at room temperature. Two to three days under a vacuum of 1.3 to 6.5 pascals (10 to 50 millitorr) is needed to dry 100 g of ice to a residue, which remains on the bottom of the bag. Depending on the substances present in the water used, the residue may appear granular or as a film.

To determine the retention yields of the tracers added, the bags containing freeze-dried residue were transferred to the same size polyethylene bottle used for the reference aliquot. Concentrated acid was added to redissolve the dry residue. The volume in each bottle was brought up to 100 ml. The activity from each isotope was then measured in the reference sample and compared to that in the freeze-dried sample.

In order to verify the radiochemical purity of samples spiked with only one isotope, one sample in each such set was counted on

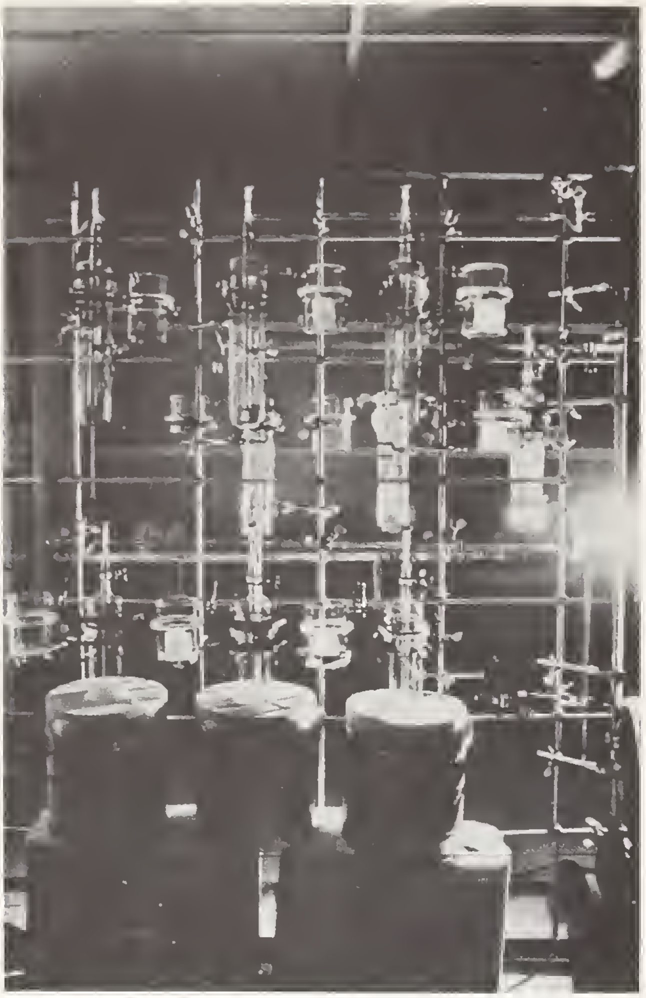

Figure 1. Nine-chamber freeze dryer made of glass and Teflon with O-rings and polyethylene gaskets, installed in Class 100 clean room

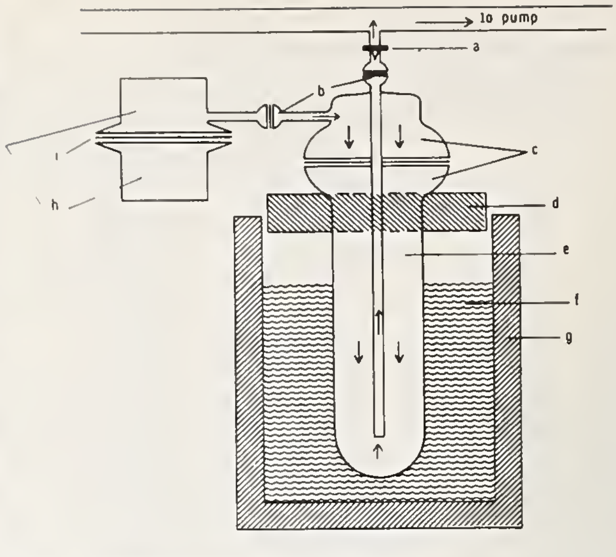

Figure 2. Diagram of single freeze-drying unit

(a) Teflon valve, (*b*) 15-mm O-ring joint, (*c*) 75-mm O-ring joint, (*d*) Styrofoam flask lid, (e) cold trap, (*f*) liquid nitrogen, (*g*) stainless steel insulating flask, (*h*) freeze drying chamber, and (*i*) gasket of polyethylene film

Table IV. Results of INAA of Freeze Dried Residue of Back River Sample

Element	Concentration in freeze dried residue, ng/g of water	ng in sample / ng in Poly bag
Eu	0.24	>20
Sc	0.31	118
Th	0.089	2.5
Cr	5.4	0.51
Fe	530	30
Co	1.2	10
Sr	440	>300
Ag	0.24	7.7
Zn	12.3	3.2
Ba	<35	
Sb	0.64	6.0
Se	0.33	10
Na[a]	0.53 mg/g	
Cl[a]	0.84 mg/g	
Mn[a]	0.23 μg/g	

[a] The results for Na, Cl, and Mn were obtained on a liquid sample and are presented for informational purposes only.

a Ge(Li) detector. If no significant radioactive impurities or daughters were present, all samples in the set were assayed with the NaI(Tl) detector. For all samples, the maximum error due to counting statistics was 1%.

To minimize geometry counting errors due to possible incomplete dissolution of residue, the samples were counted at a distance as far from the detector as practicable, generally 5 to 10 cm from the Ge(Li) detector and 20 cm from the NaI(Tl).

RESULTS AND DISCUSSION

The results of this investigation (Table III) indicate that, for all but two or three of the observed elements, freeze drying is a quantitative preconcentration technique for inorganic trace elements in water. No consistent retention value was obtained for those elements (Hg and I) which were lost substantially during freeze drying. Bromine, added as a bromide salt, was lost from acidified solutions but quantitatively retained in neutral solutions. The results obtained with the three different water types (filtered river, tap, and deionized) were indistinguishable, and therefore are not specifically identified in Table III. In general, single determinations were carried out using a filtered river water tracer solution and multiple results contain one or two runs each of river, deionized, and tap water.

A critical factor in obtaining good retention yields, particularly for volatile elements, is to keep the sample frozen solid during the lyophilization process. Loss of vacuum is the primary reason for sample melting except, as previously mentioned, in the case of saline samples. In addition to leaks in the system and malfunction of the pump, a common cause of vacuum loss was blockage of cold traps. This results because the water vapor which is frozen in the trap is not uniformly distributed on the glass surface but accumulates at a small area around the level of the liquid nitrogen. If the cryogenic flask has a tight fitting cover, the ice in the trap will accumulate at the level of the cover rather than the level of the liquid nitrogen. Since such a small portion of the total capacity of the trap is used to freeze out the water vapor, the ice condensing from a large sample may collect until it fills the available space, thus blocking the path to the sample chamber. A standard size trap (used in the system described) which has 13-mm o.d. tubing and a 38-mm diameter body has to be changed twice when freeze drying a 100-g sample. The use of a Dry Ice–acetone mixture as a coolant does not alleviate the problem.

To avoid the inconvenience of changing traps every 24 hours, an improved freeze-drying system has been developed. This system is fitted with 75-mm traps which provide adequate area to freeze dry at least two 100-g water samples consecutively before changing traps. Other improved features of this system are glass O-ring joints for all connections and Teflon valves in place of greased stop cocks. With these changes, contamination originating from construction materials of the freeze dryer itself are minimized. The entire new system, with nine chambers for samples is shown in Figure 1. An expanded diagram of one of the units is shown in Figure 2. Since this freeze drier was installed in a Class 100 clean room facility, contamination of the dry residue from laboratory air particulates is minimized (*15*). Under normal laboratory conditions, it is recommended that air which is bled through inlet valves be filtered.

It was previously stated that one of the advantages of this method of freeze drying water was the elimination of the need to transfer the dry residue. The bag containing the residue after freeze drying may be heat sealed, and then folded to make a small sample (1 cm × 2 cm × 0.5 cm) ready for irradiation and counting.

The results of a typical analysis of dissolved species in water by INAA following the described preconcentration procedure appear in Table IV. This sample was taken from the Back River, just east of Baltimore, Md. The ratio of trace element content in the sample to the average trace element content in a polyethylene bag is sufficiently high for most elements to result in reliable data, particularly considering errors due to the sampling procedure alone. Work carried out in this laboratory to determine the variations in trace element concentration attributable to sampling techniques, suggest that such errors may easily exceed ±20%.

The use of neutron activation for the analysis of trace elements in the aquatic environment is now well established. The multielement analyses of fresh to moderately saline water is greatly aided by the ability to handle relatively large samples with a minimum of pre-irradiation manipulation, as reported here. In addition, the use of freeze drying does not preclude subsequent post-irradiation chemical separations for elements that cannot be observed instrumentally.

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RECEIVED for review November 21, 1974. Accepted March 26, 1975. Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

APPENDIX IV

REPRINTED IN PART FROM

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CODEN: NBTNA

Activation Analysis Section:

Summary of Activities, July 1969 to June 1970

Philip D. LaFleur and Donald A. Becker, Editors

Activation Analysis Section
Analytical Chemistry Division
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3. ACTIVATION ANALYSIS WITH THE NUCLEAR REACTOR

A. Introduction

During this year we have continued our efforts to attain a high degree of versatility in activation analysis and have spent much of our time in developing a greater expertise in nondestructive activation analysis, particularly coupled with computer data reduction. We intend, of course, to continue our efforts in obtaining the highest possible versatility in both destructive and nondestructive activation analysis and in the investigation of parameters affecting accuracy and precision in activation analysis.

We have spent a great deal of time in characterizing the two pneumatic tube facilities which became available this year. All four of the originally installed facilities are now available and have been very carefully studied in terms of temperature effects, relative neutron fluxes and to a more limited extent on neutron energy spectra. We have maintained a very satisfactory relationship with the Reactor Operations Section and with the Health Physics Section.

A greater portion of our activities this year than in past years has been spent in service analyses for organizations outside the Bureau of Standards and for other groups within the Bureau of Standards. Particularly notable are our efforts in the analysis of lasers and silicon chips. We are presently beginning a service analysis program for the Department of Agriculture, involving the determination of mercury in wheat and peas and with the National Institutes of Health in the determination of iodine in blood serum samples. It is our hope that contacts with other governmental organizations in the Washington area, such as these, may continue and that interesting cooperative research programs may develop therefrom.

B. Facilities

1. Characterization of the NBSR for Neutron Activation Analysis

Since the last report [1] much additional information has been obtained on the irradiation characteristics of the NBSR. This information has included thermal neutron flux variations within the irradiation areas, neutron energy distribution in the various irradiation positions, temperature effects, and measurements of the gas production from several different biological materials. These different types of measurements will be treated separately here, with the techniques used presented along with the results obtained. For comparative purposes, all results obtained to date will be included here.

The current status of the NBSR irradiation facilities are given in table 1. The operational facilities include

Table 1. NBSR irradiation facilities.

Pneumatic Facilities

Ident.	Position	Attitude	Access Diameter	Status
RT-1	Core gap edge	Horiz.	1.5 in.	Operational
RT-2	In core	Horiz.	1.5 in.	Operational
RT-3	Core gap, D_2O	Horiz.	1.5 in.	Operational
RT-4	D_2O reflector	Horiz.	1.5 in.	Operational
RT-V	Vertical thimble	Vert.	0.75 in.	Under const.
RT-C	Vertical thimble	Vert.	0.75 in.	Under develop.
(RT-V-2)	(Converter) J-4	Vert.	0.75 in.	Under const.
RT-T	Thermal column	Vert.	1.5 in.	Under const.

Manual Access Facilities

Ident.	Position	Attitude	Access Diameter	Status
Vertical thimble	In core, G-2	Vert.	1.5 in.	Operational
Vertical thimble	Reflector, V-4	Vert.	1 in. (7 Positions)	Planning

the four pneumatic tubes (fig. 1) and the manually accessed Long Term Irradiation Facility (LTIF) located in the G-2 v vertical thimble. The program of characterization has included measurements on all of these operational facilities, but with particular emphasis on the pneumatic facilities which are used for the majority of the activation analysis irradiations.

a. Pneumatic Tube Irradiation Facilities

The four operational pneumatic tube facilities have diameters of 1 1/2 inches, are powered by CO_2, and terminate in significantly different neutron environments (fig. 1).

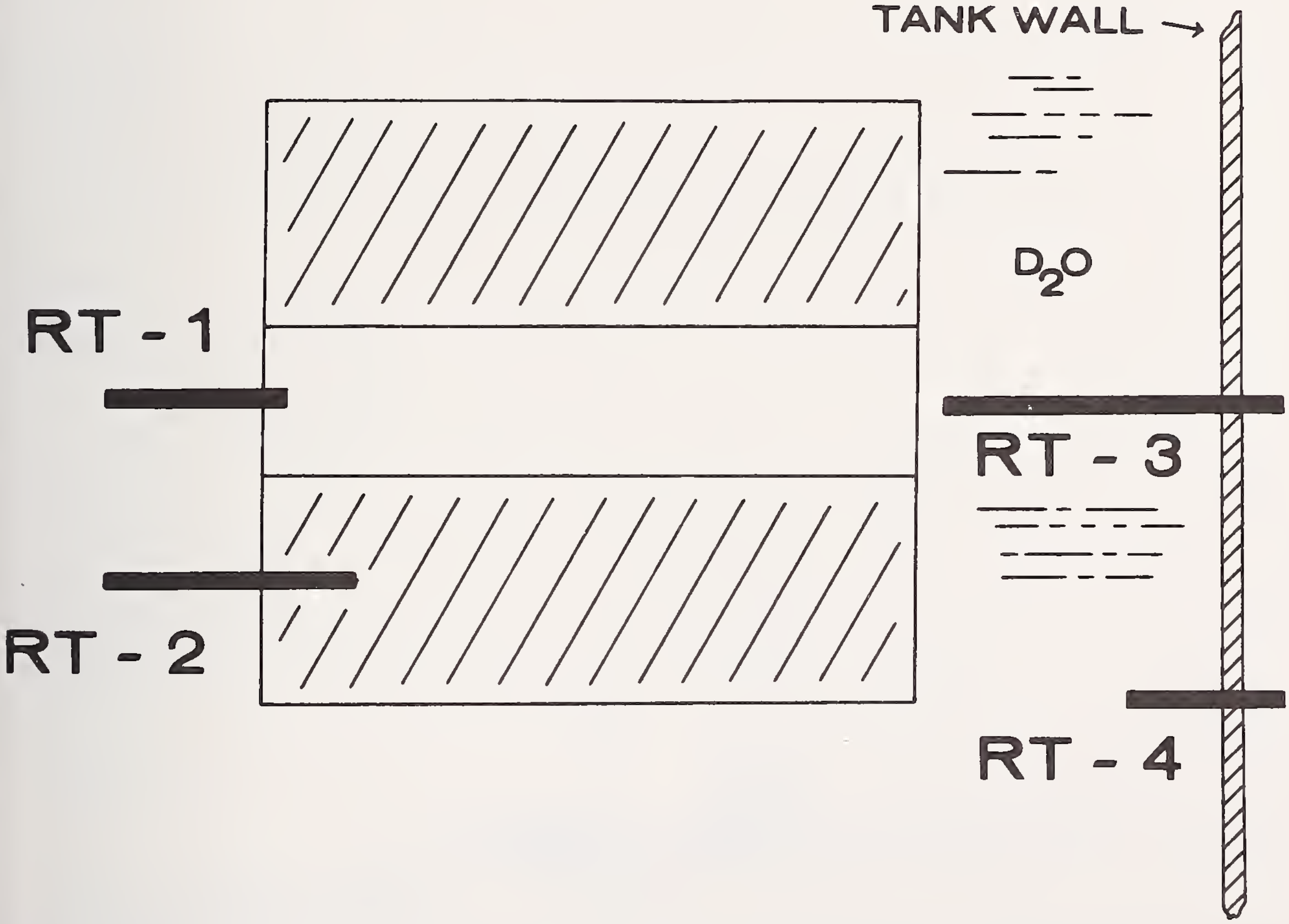

Figure 1. Positions of the pneumatic tube terminals in the NBSR. (Terminology: The proximal end of the rabbit is that end closest to the reactor core vertical centerline; the distal end is that furthest from the core centerline.)

Linear polyethylene rabbits, which have a capacity of approximately 42 cm^3 (2.6 cm dia x 8 cm long) are used in these facilities [1].

(1) Neutron Flux Measurements

Initial measurements in the pneumatic tubes were for the thermal neutron flux. Of interest was the absolute thermal neutron flux, and the variation of this neutron flux within each irradiation position. Some measurements also have been made of the neutron energy distribution characteristics within each facility.

(2) Thermal (Sub-cadmium) Neutron Flux

The thermal (sub-cadmium) neutron flux measurements were made using the thin foil technique [2]. Two different detector foils, gold and copper, were used for these measurements. Copper foils were preferred, due to the absence of significant resonance peaks in its neutron cross section (fig. 2). Some measurements were also made on gold foils,

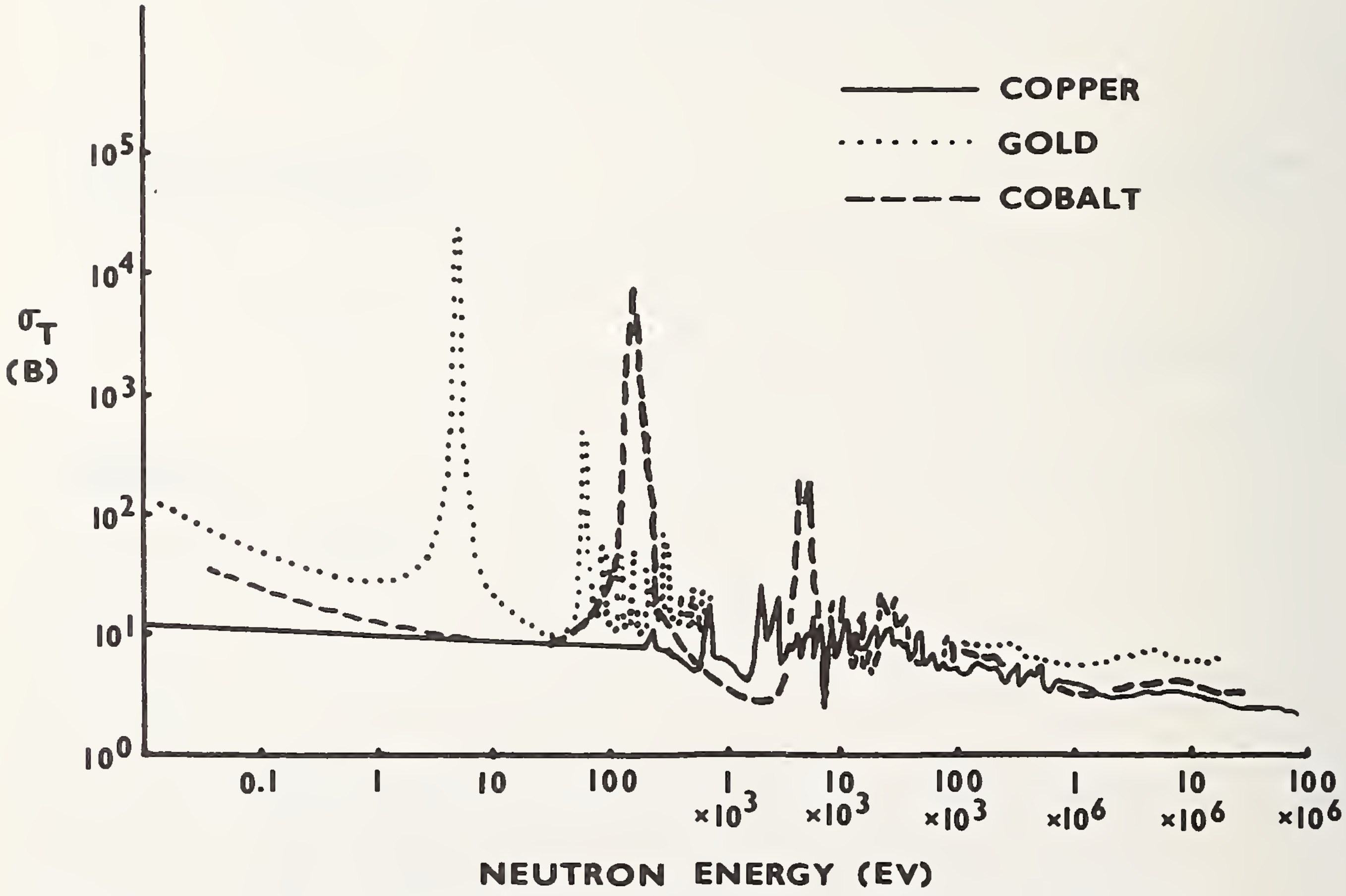

Figure 2. Neutron cross sections of copper, gold and cobalt as a function of neutron energy.

since gold is often used in other laboratories. However, since gold has significant neutron self-absorption problems, slight variations in foil thickness can lead to appreciable errors in flux determinations.

The technique used consisted in irradiating a thin foil (0.005 in Cu foil; 0.001 in Au foil) of the element of interest in the appropriate facility, then counting the radioactive species formed on a large volume Ge(Li) detector. This detector has been calibrated for absolute photopeak counting efficiency using NBS calibrated radioactive sources. Neutron fluxes were then calculated from nuclear constants. The thermal (sub-cadmium) neutron flux was obtained after correction for epicadmium contribution to the foil activity. For copper, this correction did not exceed 7%, however, for gold this correction was in excess of 25%. No neutron self-shielding corrections were made.

The results of the flux determinations are found in table 2. It is apparent that the thermal neutron flux in tubes RT-1, RT-2 and RT-3 are very similar, with a significantly lower flux in RT-4. The gold foils gave higher flux numbers (relative to those from Cu measurements) for the tubes RT-1, RT-2 and RT-3, where a larger epicadmium neutron flux exists, but a value very close to that for copper in RT-4, where the neutrons are highly thermalized. Repeated determinations of these flux measurements gave results agreeing well with the original values.

Table 2. Experimental neutron flux-NBSR pneumatic facilities.

	Sub-Cadmium Neutron Flux-Proximal End ($n.cm^{-2}sec^{-1}$)			
Detector Foil	RT-1	RT-2	RT-3	RT-4
Gold	$7.0x10^{13}$	$6.9x10^{13}$	$5.8x10^{13}$	$1.4x10^{13}$
Copper	$5.6x10^{13}$	$6.3x10^{13}$	$4.9x10^{13}$	$1.3x10^{13}$

(3) Neutron Flux Variation Measurements

In order to obtain accurate and precise results in neutron activation analysis using a nuclear reactor, the geometrical variation of the flux within each irradiation position must be accurately evaluated. Previous studies of the NRL Nuclear Reactor [3] revealed serious neutron flux variations within the sample irradiation area, and thus emphasized the need for such measurements.

The flux measurements for the NBSR were made on the inside dimensions of the polyethylene rabbits for the 1 1/2 in. pneumatic tube system (RT-1 to RT-4). Since the irradiation space available for each facility approximated a right circular cylinder 2.6 cm in diameter and 8 cm long, both the circumferential flux distributions and the axial flux distributions were measured. The procedure developed used 3/16 in. disks of copper foil or 20 mil copper wire with gross gamma counting of the copper-64 radioactivity using an automatic sample changer. The copper activity was checked for extraneous radioactivities by counting on a 47cc Ge(Li) detector and 4096 channel PHA and by following the decay characteristics of the foil on the gross gamma counter for over 8 half-lives. Both procedures revealed no detectable radioactivity in either the wire or the foil other than copper-64. All samples from a particular type of measurement were counted under identical conditions.

The results obtained for the circumferential flux distribution of the pneumatic facilities are found in table 3. In all cases copper foils were used. These results are also shown graphically in figure 3. The foil placement diagram for the circumferential flux measurements is shown in figure 4. It can be readily seen from these results that there is no significant circumferential flux variation at any plane perpendicular to the axis of the right circular cylinder comprising the rabbit irradiation area.

Table 3. Circumferential flux distribution in NBSR pneumatic tube facilities.

Pneumatic Tube Facility	Location in Rabbit	No. of Monitors	Relative Neutron Flux[a]
RT-1	Proximal	7	1.000±0.003[b]
RT-1	Middle	7	0.947±0.004
RT-1	Distal	7	0.871±0.007
RT-2	Proximal	7	1.000±0.005
RT-2	Middle	6	0.902±0.002
RT-2	Distal	7	0.874±0.003
RT-3	Proximal	7	1.000±0.004
RT-3	Middle	6	0.928±0.003
RT-3	Distal	7	0.829±0.003
RT-4	Proximal	7	1.000±0.010
RT-4	Middle	7	0.787±0.007
RT-4	Distal	6	0.603±0.014

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[a] Normalized to proximal end ≡ 1.000.
[b] Uncertainties are ts/√n at 95% confidence level.

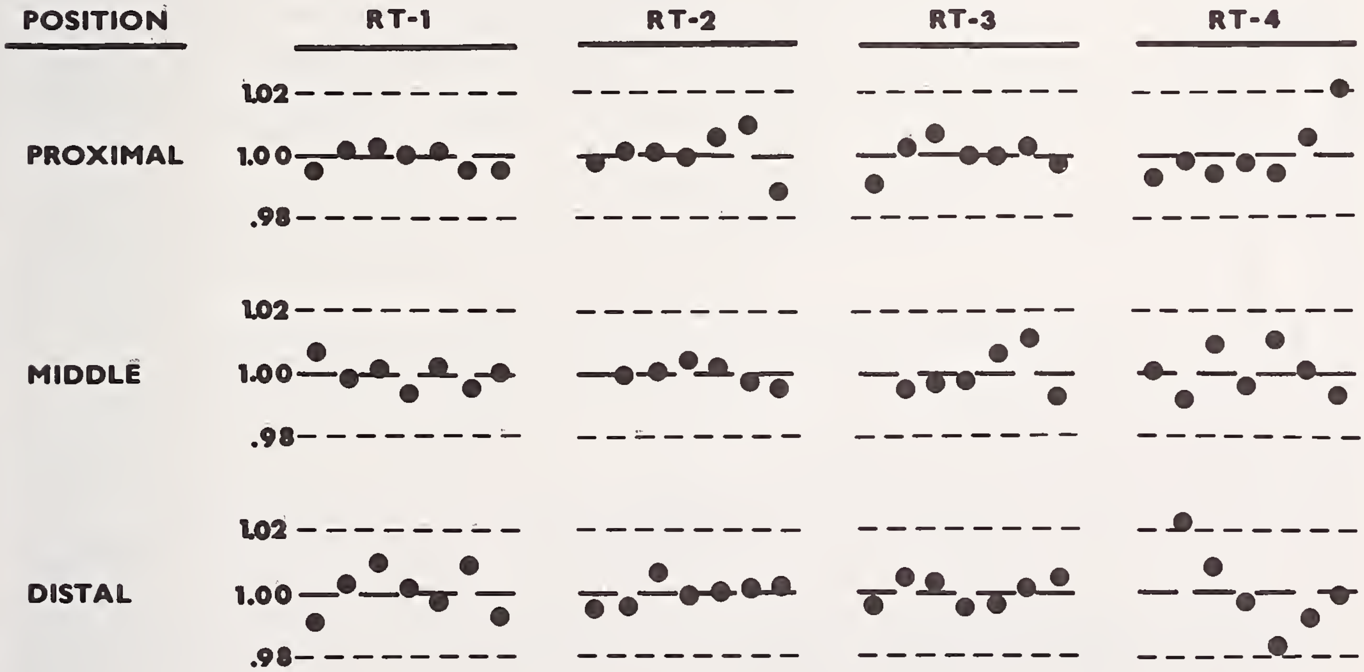

Figure 3. Diagramatic representation of the circumferential flux distribution in the NBSR pneumatic tubes at three positions inside the rabbit.

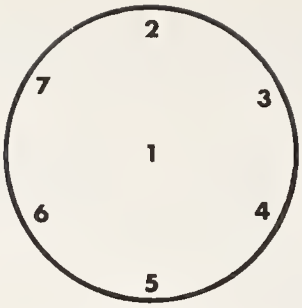

Figure 4. Copper foil placement for circumferential flux measurements in the NBSR pneumatic tubes.

The axial flux measurements were made using the copper wire. A single length of the wire was centered along the rabbit axis and held securely in position with polyethylene foam. After irradiation, the wire was cut into 1 cm sections, weighed, and counted. The results, shown in figures 5 and 6, reveal a serious neutron flux dropoff along the axis of the rabbit. The magnitude of this dropoff over the length of the rabbit ranged from approximately 11% for RT-1

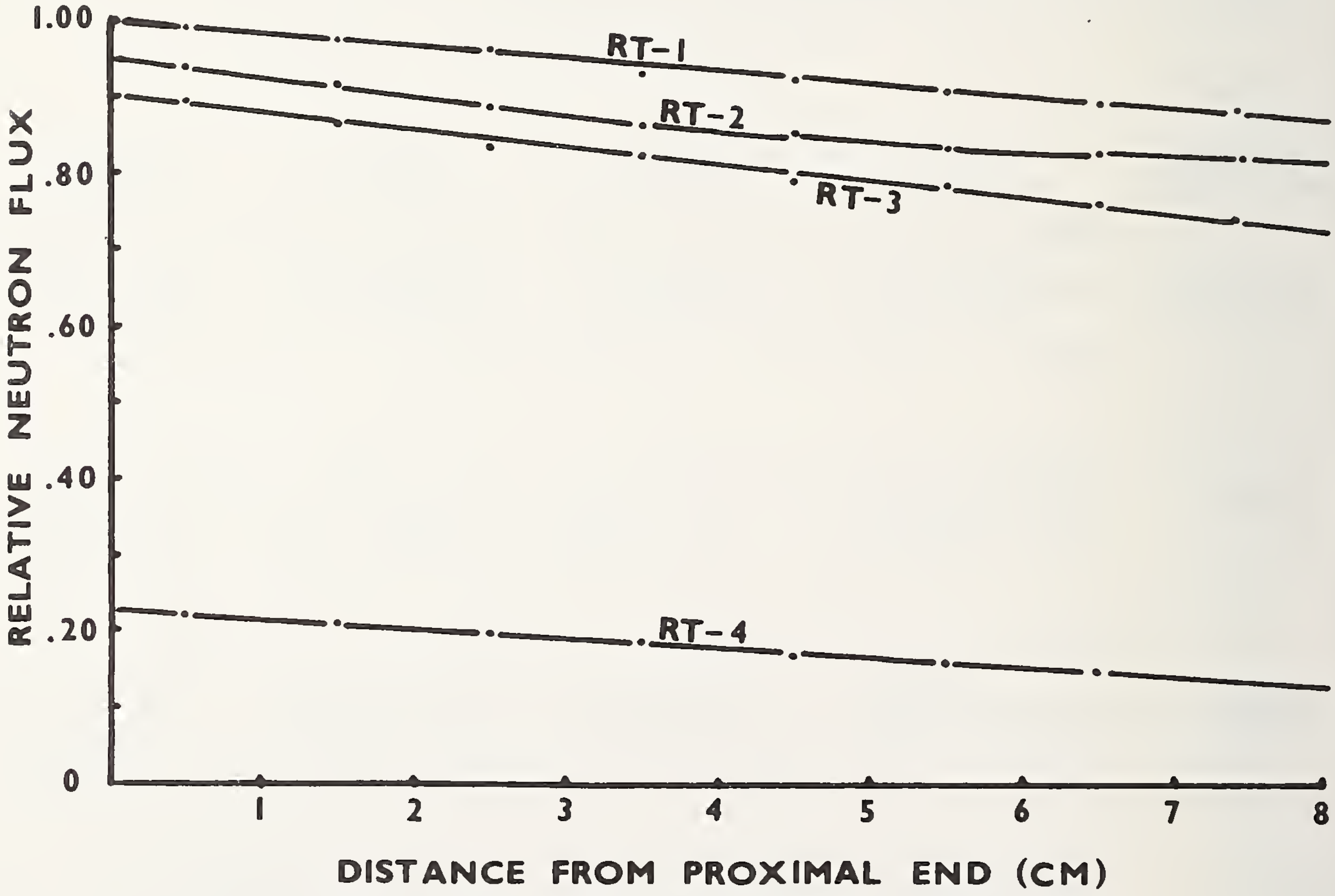

Figure 5. Axial flux distribution in the NBSR pneumatic tubes.

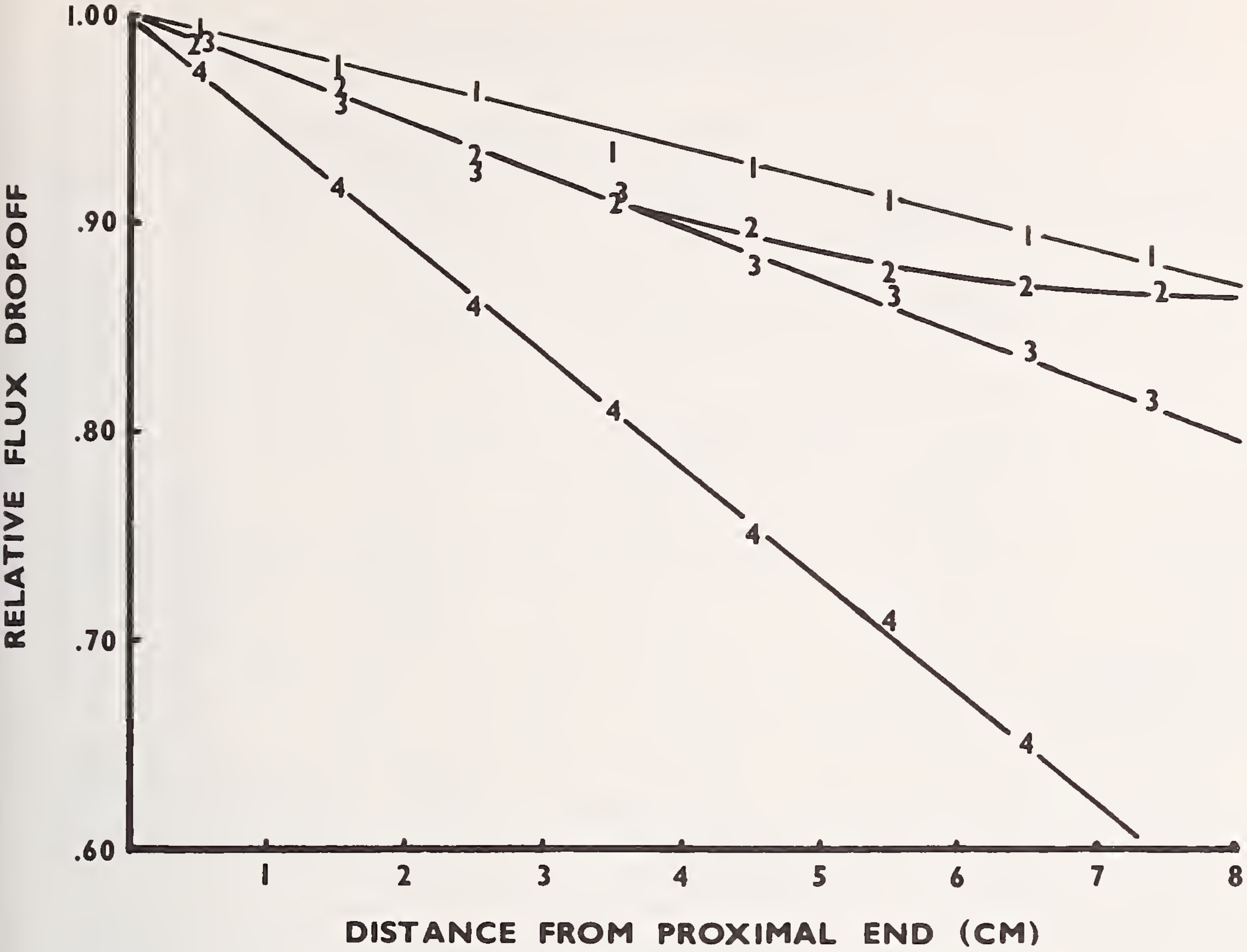

Figure 6. Axial flux dropoff inside the rabbits (normalized to proximal end ≡1.00 for each pneumatic tube).

to over 40% for RT-4. The flux dropoff was linear in all pneumatic facilities except RT-2.

(4) <u>Neutron Energy Distribution Measurements</u>

Some preliminary neutron energy distribution measurements have been made, consisting almost entirely of cadmium ratio measurements. These cadmium ratios were made at both ends of all four pneumatic facilities. Three different elemental foils were used, 1 mil thick gold foil, 5 mil copper foil, and 2 mil cobalt foil. Interlocking 20 mil cadmium covers were used for the cadmium shielded measurements.

The results of these measurements are found in table 4. The values for gold and cobalt were obtained primarily

Table 4. Cadmium ratios for the NBSR pneumatic tube facility.

Pneumatic Facility	Location In Rabbit	Experimental Cadmium Ratios[a] Au(Cd)	Cu(Cd)	Co(Cd)
RT-1	Proximal	7.3	46	29
RT-1	Distal	10	64	-
RT-2	Proximal	3.7	15.7	11
RT-2	Distal	4.0	15.8	-
RT-3	Proximal	10.3	65	42
RT-3	Distal	16.5	80.5	-
RT-4	Proximal	87	536	395
RT-4	Distal	111	582	-

[a] For elemental foils using 20 mil cadmium covers.

for intercomparisons with other laboratories, since these two elements are the ones generally used for flux and cadmium ratio measuarements. However, as mentioned previously, the large resonance neutron cross sections (fig. 2) casts some doubt on usefulness of measurements using these foils. The copper foils, which behave as true "infinitely thin" foils throughout the neutron energy range seen in a nuclear reactor, should yield results which can be compared directly to neutron fluxes above and below the cadmium cutoff.

Additional efforts will be expended in the direction of neutron energy measurements in these facilities by the use of threshold detectors. These threshold detectors yield integrated neutron fluxes above their reaction thresholds, and will be used to plot diagrams of the integral neutron flux vs. neutron energy similar to the work done by us at the NRL nuclear reactor [3].

(5) Temperature Measurements

An extensive series of measurements were made in the pneumatic facilities using stick-on type temperature sensors.

These sensors were described previously [1] as were the various techniques employed and some preliminary results. Essentially all of the measurements have been completed at this time, and the results obtained are presented in tables 5, 6, 7 and 8. The equilibrium temperatures were lower than those expected, and therefore maximum irradiation times are based on factors other than temperature, e.g. radiation

Table 5. Radiation damage and temperature measurements at 10 MW in RT-1.

Material and Configuration	Wt.(g)	Length of Irrad.[a]	Results
Empty rabbit -	-	6 h	Radiation damage not excessive[b]
Quartz ampoule, empty	3.5g	20 m	170±10°F
Lead in quartz ampoule	0.6g Pb 3.5g Quartz	20 m	225±5°F
Iron in quartz ampoule	0.6g Fe 3.5g Quartz	20 m	<180°F

---

[a] 20 minutes required to reach equilibrium temperature

[b] In this and succeeding tables, this phrase means the rabbit is not so brittle as to break upon deceleration in receiver.

Table 6. Radiation damage and temperature measurements at 10 MW in RT-2.

Materials and Configuration	Wt.(g)	Length of Irrad.	Results
Empty rabbit	-	20 m	155±5°F
Empty 2 dram poly vial	3.25g poly	10 m	205±5°F
Empty heat sealed sections of poly tubing	0.7g poly (total)	10 m	205±5°F

Table 7. Radiation damage and temperature measurements at 10 MW in RT-3.

Material and Configuration	Wt.(g)	Length of Irrad.	Results
Empty rabbit -	-	20 m	<110°F
Empty rabbit -	-	8 h	Radiation damage not excessive.
Lead pieces (6) in sealed quartz ampoule	0.6g Pb 3.7g Quartz	4 h	195±5°F
Quartz block	6.0g	15 m	170±10°F
Quartz block	7.0g	20 m	190±10°F
Lead and quartz - lead (single piece) in sealed quartz ampoule	1.0g Pb 3.2g Quartz	10 m	>220°F
Empty rabbit, containing two 2/5 dram polyvials, with polyvial packing	-	8 h	Radiation damage not excessive to rabbit or polyvials. Polyfoam crumbly.

Table 8. Radiation damage and temperature measurements at 10 MW in RT-4.

Material and Configuration	Wt.(g)	Length of Irrad.	Results
Empty rabbit -	-	16 h	Radiation damage not excessive
Empty rabbit -	-	16 m	105±5°F
Lead in sealed quartz ampoule	0.6 g Pb 3.5 g quartz	15 m	<130°F

damage to the sample carrier. Irradiations of up to 8 hours are made routinely in the polyethylene rabbits at a thermal neutron flux of 5×10^{13} n.cm^{-2}sec^{-1}.

Initially, reactor operations would permit temperatures of up to 200°F in the rabbit facilities. However, a few tests were made of the melting point of these rabbits and the effect of irradiation on the melting point. The results of these tests are given in table 9. As a result of these tests, the maximum permissable temperature in the pneumatic facilities was raised to 240°F.

Table 9. Heat resistance of polyethylene rabbits: effect of irradiation time[a].

Length of Irradiation[b]	Effect of Temperature (°F)			
	230°F	240°F	260°F	280°F
none	none	none	slight softening	completely melted
10 sec	none	none	slight softening	mostly melted
1 min	none	none	slight softening	completely deformed
10 min	none	none	slight softening	transparent and starting to deform

---

[a] Melting point of conventional polyethylene is ∿250°F; high density polyethylene ∿270°F.

[b] Rabbits irradiated in RT-1.

(6) Pressure Measurements

When the request was made for the irradiation of freeze dried biological materials in the NBSR, a number of questions were raised which could not be definitively answered. One of these questions involved the danger of explosion of a quartz ampoule due to the pressure generated by gaseous decomposition products of the material under irradiation. To effectively answer this question, and to establish criteria for the safe irradiation of a variety of aqueous solutions, organic materials, and biological materials, a series of pressure measurements was initiated. The pressure testing system used to test irradiated samples is shown in figure 7. It consists of an appropriate sized rubber balloon, a section of polyethylene tubing which will fit inside the balloon but is still large enough to hold the irradiated quartz ampoule, and a gas-tight clamp for the open end of the balloon. To make a pressure measurement, an irradiated sample (inside the quartz ampoule) is inserted into the tubing and the balloon, the end of the balloon clamped shut and the ampoule struck smartly with a hammer. The polyethylene tubing prevents the shattered quartz from puncturing the balloon, and the pressure inside the ampoule estimated from the degree of expansion of the balloon.

Tests with a hypodermic syringe (less needle) snugly fitted to the balloon opening indicated that 1/2 cm^3 of gas could be readily detected. The quartz ampoules being tested had volumes of 1 cm^3 or greater, therefore excess pressures of 1 atm could most certainly be measured. Since even poor quality glass blowing produces ampoules which can readily withstand 2 atm excess pressure, and good quality quartz glass blowing can produce ampoules which will withstand internal pressures in excess of 5 atm excess pressure, a preliminary limit for testing purposes of 1 1/2 atm excess pressure was established.

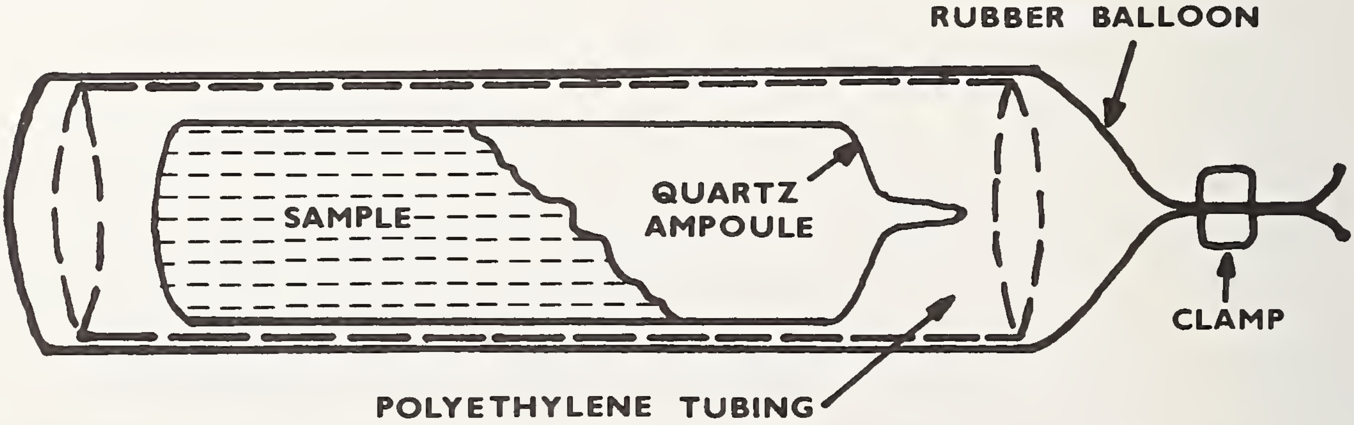

Figure 7. Device used to measure pressures generated from irradiated samples.

The results of these pressure tests are found in table 10. From these results it can be seen that freeze-dried biological materials produce only small quantities of gaseous products upon irradiation in the pneumatic facilities RT-1, RT-3 and RT-4. For example, 1/2 gram of freeze-dried orchard leaves, irradiated for 6 hours in RT-3 at a neutron flux of $5 \times 10^{13} n.cm^{-2} sec^{-1}$ produced only about 1 cm^3 of gaseous decomposition products (which produced approximately 1 atm of excess pressure in the ampoule size used). These conditions of excess pressure are well within the tentative limits set up for these tests.

Table 10. Pressure measurements on neutron irradiated samples.

Sample	Wt (g)	Length of Irrad.	Facility	Results[a]
Orchard leaves freeze dried	0.25	2 h	RT-1	Small pressure buildup
Alfalfa, freeze dried	0.25	2 h	RT-3	No significant pressure buildup
Blood, freeze dried	0.25	2 h	RT-3	No significant pressure buildup
Liver, freeze dried	0.25	2 h	RT-3	No significant buildup
Water, in heat-sealed polyethylene	2.0	5 m	RT-3	No significant pressure buildup
Orchard leaves, freeze dried	0.50	8 h	RT-4	Small pressure buildup
Orchard Leaves, freeze dried	0.50	6 h	RT-3	Small pressure buildup

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[a] Limit of detection ∿1/2 cm^3; "small pressure buildup" estimated to be 1/2 - 1 cm^3.

b. Long Term Irradiation Facility (LTIF)

The flux measurements made on the LTIF Vertical Thimble (see [4] for details of construction) included only neutron flux measurements and cadmium ratio determinations. Since this facility has its own recirculating D_2O cooling system, the temperature measurements were not immediately essential. The measurement of pressures due to sample decomposition have not yet been made on this facility, at least partly due to the probable applicability of those measurements made with the pneumatic tubes.

The flux variation measurements on this facility were made using two different techniques. For the vertical flux measurements a copper wire inside of sealed polyethylene tubing was quickly inserted the entire length of the vertical irradiation facility and irradiated for 30 m at a power level of 10 KW. At the end of the irradiation time, the copper wire was quickly removed from the reactor, the polyethylene tubing removed, and the copper wire cut into small pieces for gross γ counting of the 12.9h copper-64 radioactivity. At the lower end, where the activity level was relatively high, the wire was cut into 1/2 inch lengths. As the induced radioactivity decreased in the upper portions of the wire (above the core area), sections were increased to 1 inch, and finally to 6 inches at a point considerably above the upper core area. After this vertical flux diagram was obtained, the piece having the highest specific activity (from the core gap area) was taken for an absolute flux determination.

Circumferential flux measurements were made during irradiations for the cadmium ratios. These measurements were taken using suitably weighted polyethylene rabbits at the end of a nylon fishing line. The copper wire was wrapped around the rabbit in which the bare copper foil was irradiated. The cadmium covered copper foil had its separate irradiation. This set of two irradiations was necessary for each area measured. Four areas were measured this way, as shown in figure 8 and table 11.

The results of these measurements are shown in figure 8 and tables 11 and 12. Figure 8 shows the vertical distribution of the total neutron flux in the LTIF, and demonstrates the effectiveness of the core gap area as a region of maximum thermal neutron flux. The maximum neutron

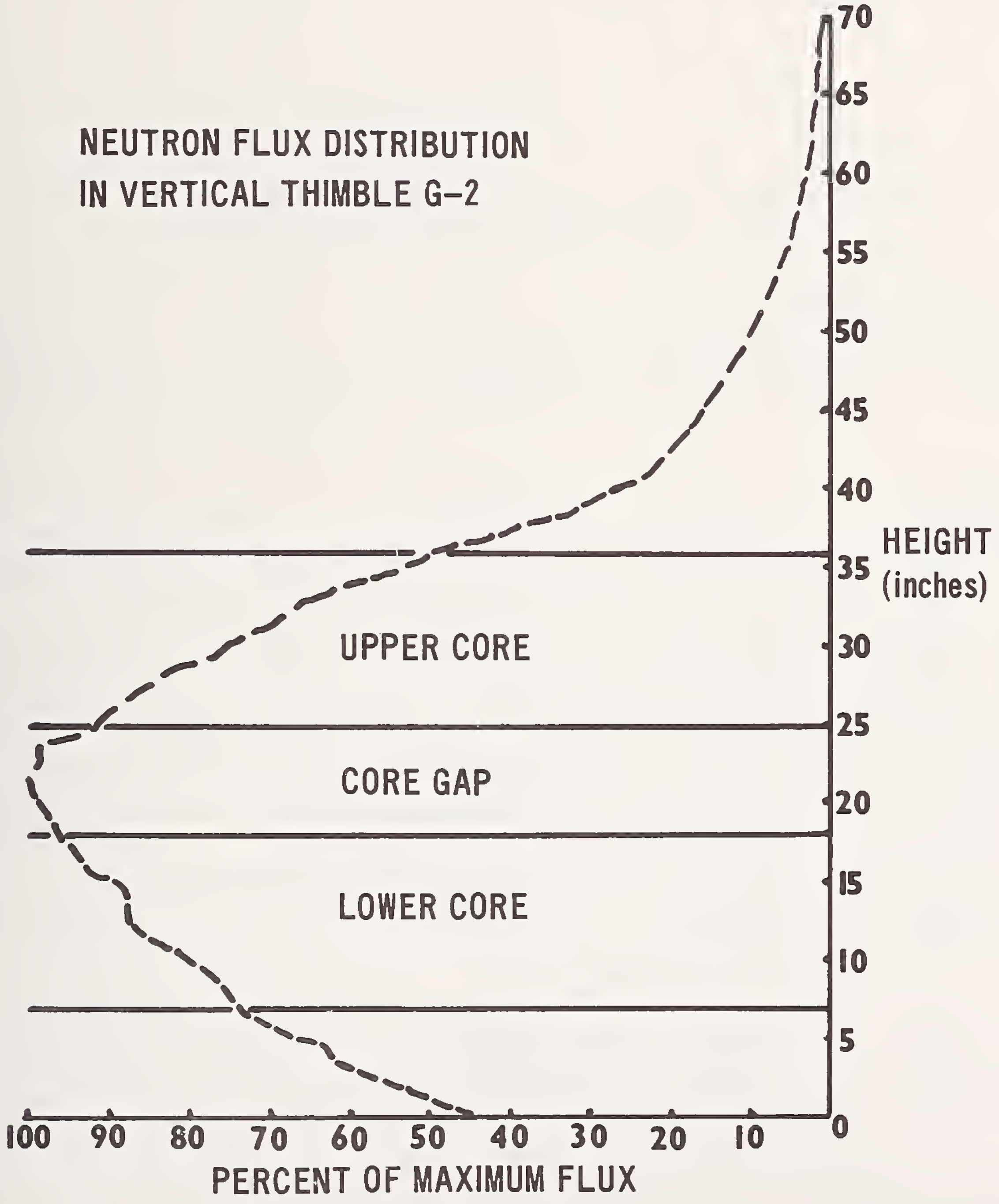

Figure 8. Vertical distribution of the total neutron flux in the NBSR LTIF.

Table 11. Cadmium ratios in the LTIF.

Area	Height (in.)	Cadmium Ratio (Copper)
Below core	0.5	84.1
Lower core	11	32.8
Core gap	19.5	54.9
Above core	56	1830

Table 12. Circumferential flux variation in the NBSR LTIF irradiation facility.

Location in LTIF				
Area	Height (in)[a]	Location in Rabbit	No. of Monitors	Relative Neutron Flux[b]
On bottom	0.5	Bottom	9	1.000±0.010[c]
On bottom	1.8	Middle	9	1.122±0.008
On bottom	3.0	Top	9	1.238±0.009
Lower core	11.5	Bottom	9	1.000±0.018
Lower core	12.8	Middle	9	1.055±0.026
Lower core	14.0	Top	9	1.088±0.015
Core gap	20.0	Bottom	9	1.000±0.021
Core gap	21.3	Middle	9	0.997±0.016
Core gap	22.5	Top	9	0.980±0.018
Upper core	28.5	Bottom	9	1.000±0.081
Upper core	29.8	Middle	9	0.837±0.170
Upper core	31.0	Top	9	0.725±0.092
Above core	56.5	Bottom	9	1.000±0.011
Above core	57.8	Middle	9	0.885±0.013
Above core	59.0	Top	9	0.774±0.011

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[a] Measured from bottom of polyethylene rabbit (see figure 8).

[b] Normalized to bottom ≡ 1.00.

[c] Uncertainties are $ts/\sqrt{n}$ at 95% confidence level.

flux for 10 MW operation was found to be approximately 1.1×10^{14} n.cm^{-2}sec^{-1}. The cadmium ratios are given in table 11. The core gap cadmium ratio of 55 is significantly higher than the core area, which has a cadmium ratio of approximately 33. All of these cadmium ratios are somewhat higher than would normally be expected, due to the highly thermalizing effect of the D_2O filled thimble. The copper cadmium ratio of 1830 at a hight of 56 inches in the thimble (with a 10 MW neutron flux of $\sim5\times10^{12}$ n.cm^{-2}sec^{-1}) suggests the potential use of this facility for obtaining a highly thermalized neutron environment. The results of the circumferential flux distributions in the LTIF reveal a small but significant variation in the neutron flux from side-to-side in the thimble. This variation is strongly dependent upon the area chosen for the irradiation, but usually is less than 10% over the outer diameter of the polyethylene rabbits used for the measurements.

c. Conclusions

The NBSR has been characterized for many of its irradiation parameters, both for the pneumatic facilities RT-1, RT-2, RT-3 and RT-4, and for the LTIF (G-2 Vertical Thimble). While some additional measurements remain to be made, the irradiation facilities available for use are revealed as a set of extremely useful and convenient facilities under which a wide variety of irradiation environments can be obtained.

(D. A. Becker and P. D. LaFleur)

APPENDIX V

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CHARACTERIZATION OF A NUCLEAR REACTOR FOR NEUTRON ACTIVATION ANALYSIS

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Ouelques caractéristiques du réacteur nucléaire NBSR utilisé pour l'analyse par activation neutronique ont été évaluées; les techniques de mesure développées sont décrites. La discussion porte sur les caractéristiques suivantes: (1) le flux de neutrons thermiques absorbés par le cadmium, (2) la distribution énergétique des neutrons mesurée grâce aux rapports cadmium et à des détecteurs à seuil. L'excès de pression dans les échantillons engendre l'irradiation.

Introduction

Optimum utilization of a nuclear reactor for neutron activation analysis requires a careful and complete characterization of all the available irradiation facilities. This information is important both for reactor and personnel safety, and for complete control of the irradiation parameters affecting the precision and accuracy of the technique. When the NBS Nuclear Reactor (NBSR) started up several years ago, an extensive program of characterization was initiated. During this reactor characterization a number of techniques and procedures were developed which were felt to be of interest to other activation analysis laboratories.

The design and operating characteristics of the NBSR have been reported previously.[1,2] These reports also contain some of the preliminary results on the characterization studies. Due to space limitations, this paper will be limited to new or improved techniques developed or results obtained during these characterization studies. The are presented in the hope that other activation analysis laboratories will find them useful in the evaluation and characterization of their own nuclear reactors.

The techniques discussed below are the thermal (sub-cadmium) neutron flux determination, neutron energy distribution measurements using cadmium ratios and threshold foil-detectors, and the determination of excess sample pressures generated during irradiation.

Thermal (sub-cadmium) neutron fluxes

In all measurements reported here, the thermal (sub-cadmium) neutron flux was determined utilizing the thin foil technique, in which the measurement is made with minimum disturbance of the surrounding neutron environment.[3] For most of these measurements, reagent grade copper foil or wire was used. The advantages of this material include easy availability at adequate purities, low cost, and lack of high resonance neutron cross section peaks. Some measurements were also made with 0.0025 cm thick gold foils, but the neutron self-shielding occurring due to the very high resonance neutron cross sections made these results subject to large corrections. The technique used consisted in irradiating a thin foil or wire of the element of interest in the appropriate facility, then counting the radioactive species formed on a large volume Ge(Li) detector at a reproducible counting geometry. This detector had been calibrated for absolute photopeak counting efficiency at this geometry using NBS calibrated radioactive point sources. Neutron fluxes were then calculated from the nuclear datas shown in Table 1. For the flux determinations using copper foils, care must be taken to insure total annihilation of the positrons in close proximity to the detector foil. In this case, covering the foil with approximately 0.1 cm of alu-

Table 1

Data for nuclear calculations[a]

Nuclear reaction	Isotopic abundance	σ_{eff} (σ_{th})	Effective threshold energy, MeV	Eγ	Gamma-ray abundance	Half-life	Detector efficiency[d]	Sample form	Sample purity,%
^{63}Cu(n,γ) ^{64}Cu	.691	(4.5b)	thermal	0.511	0.38	12.8 h	0.00161	Cu foil	99.9+
^{197}Au(n,γ)^{198}Au	1.00	(98.8b)	thermal	0.412	0.95	2.70 d	0.00200	Au foil	99.99+
^{58}Ni(n,p) ^{58}Co	0.678	420 mb^{b}	2.9^{b}	0.810	0.99	71.3 d	0.00096	Ni wire	99.98
^{54}Fe(n,p) ^{54}Mn	0.0584	610 mb^{b}	4.2^{b}	0.835	1.00	303 d	0.00093	Fe wire	-^{e}
^{46}Ti (n,p) ^{46}Sc	0.0799	230 mb^{c}	5.5^{c}	0.889	1.00	83.9 d	0.00087	Ti wire	-^{e}
				1.120	1.00		0.00068		
^{24}Mg(n,p) ^{24}Na	0.786	60 mb^{b}	6.3^{b}	1.369	1.00	15.0 h	0.00054	Mg foil	-^{e}
				1.120	1.00		0.000235		
^{56}Fe(n, p) ^{56}Mn	0.917	110 mb^{b}	7.5^{b}	0.847	0.99	2.58 h	0.000915	Fe wire	-^{e}
^{27}Al(n,α) ^{24}Na	1.00	130 mb^{b}	8.4^{b,c}	1.369	1.00	15.0 h	0.00054	Al wire	99.9+
				2.754	1.00		0.000235		

[a] Nuclear data taken from Ref.[4] unless otherwise noted.
[b] Data taken from Ref.[5]
[c] Data taken from Ref.[6]
[d] Experimentally determined using NBS calibrated radioactive sources; 47 cm^3 Ge(Li) detector at a distance of 5.0 cm.
[e] See text.

minum was sufficient. Also it must be noted that the positron decay fraction of 19% for copper-64 leads to a 0.511 MeV photon abundance of 38% for the nuclear calculation. In all cases, the thermal (sub-cadmium) neutron flux was obtained after correction both for epicadmium contribution to the foil activity and for neutron self-shielding. For copper, the epicadmium correction did hot exceed 7% in the worst case (RT-2), however, for gold this correction was much greater.

The results of these flux measurements for the pneumatic tubes are found in Table 2. This table includes values obtained using both the copper foils and the gold foils. It is apparent that the thermal neutron flux in tubes RT-1, RT-2 and RT-3 is very similar, with a significantly lower flux in RT-4. As expected, the thermal column tube RT - T had a neutron flux two orders of magnitude lower. The gold foils gave higher flux numbers (relative to those from Cu measurements) for the tubes RT-1, RT-2 and RT-3, where a larger epicadmium neutron flux exists, but a value very close to that for copper in RT-4, where the neutrons are highly thermalized. Several redeterminations of these flux measurements gave results agreeing well with the original values. A later, independent flux determination using a multiple foil activation iterative method to evaluate the reactor neutron flux spectra,[5] produced a thermal neutron flux value for RT-4 of $1.33 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot sec^{-1}$,[7] in good agreement with the $1.3 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot sec^{-1}$ reported here using the copper foil and simple calculation from nuclear constants.

Table 2

Experimental neutron flux—NBSR pneumatic facilities

Detector foil	Maximum sub-cadmium neutron flux $n \cdot cm^{-2} \cdot sec^{-1}$				
	RT-1	RT-2	RT-3	RT-4	RT-T
Copper	$5.9 \cdot 10^{13}$	$5.6 \cdot 10^{13}$	$4.9 \cdot 10^{13}$	$1.3 \cdot 10^{13}$	$1.6 \cdot 10^{11}$
Gold	$7.0 \cdot 10^{13}$	$6.9 \cdot 10^{13}$	$5.8 \cdot 10^{13}$	$1.4 \cdot 10^{13}$	—

Neutron energy distribution measurements

Preliminary neutron energy distribution measurements consisted almost entirely of cadmium ratio measurements.[2] These cadmium ratios were made in all five pneumatic facilities. A total of three different elemental foils were used. They were 0.0127 cm thick copper foil, 0.0025 cm thick gold foil, and 0.0051 cm thick cobalt foil. Interlocking 0.051 cm cadmium covers were used for the cadmium shielded measurements. The results of these

Table 3

Cadmium ratios for the NBSR pneumatic tube facilities

Pneumatic facility	Location in rabbit	Experimental cadmium ratios[a]		
		Cu(Cd)	Au(Cd)	Co(Cd)
RT-1	Proximal	46	7.3	29
RT-1	Distal	64	10	–
RT-2	Proximal	15.7	3.7	11
RT-2	Distal	15.8	4.0	–
RT-3	Proximal	65	10.3	42
RT-3	Distal	80	16.5	–
RT-4	Proximal	540	87	390
RT-4	Distal	580	111	–
RT-T	Bottom	3400	–	–

[a] For elemental foils using 20 mil cadmium covers, where

$$\text{Cd Ratio} = \frac{\text{subcadmium + epicadmium neutrons}}{\text{epicadmium neutrons}} = \frac{\text{Bare foil activity at T zero}}{\text{Cd covered foil activity at T zero}}$$

measurements are found in Table 3. The values for gold and cobalt were obtained primarily for intercomparisons with other laboratories, since these two elements are the ones generally used for flux and cadmium ratio measurements. However, as mentioned previously, the large resonance neutron cross sections casts some doubt on the usefulness of measurements using these foils. The copper foils, which behave more closely to true „infinitely thin" foils throughout the neutron energy range seen in a nuclear reactor, yield results which should be more representative of the neutron fluxes above and below the cadmium cut-off. The copper cadmium ratios for the pneumatic tube facilities (Table 3) range from less than 16 for RT - 2 to over 3000 for RT - T, the thermal column rabbit. Variations in the cadmium ratio from end-to-end of the irradiation container (rabbit) were especially large for both RT - 1 and RT - 3.

More recently, a program has been initiated to extensively characterize the fast neutron spectra present in all the NBSR irradiation facilities. Besides the useful information this would inevitably provide for NBSR users, it was felt that an evaluation of suitable threshold foils in the well characterized NBSR facilities would assist other activation analysis laboratories in their own reactor evaluation programs.

At present six different nuclear reactions have been used to determine the integrated fast neutron flux, with threshold energies of 2.9 MeV to 8.4 MeV. These threshold foils and wires were irradiated in the pneumatic tubes RT - 1 through RT - 4, for periods of 15 seconds to 30 minutes. In all cases interlocking 0.102 cm thick cadmium covers were used to reduce the thermal neutron activation.

In order to establish that no significant attenuation of fast neutrons occurred through the use of the cadmium covers, several experiments were made using elemental nickel. The nuclear reactions used were $^{64}Ni(n, \gamma)^{65}Ni$ and $^{58}Ni(n,p)^{58}Co$, for thermal and fast flux measurements respectively. The results are shown in Table 4, and indicate that above the 2.9 MeV threshold for the fast neutron reaction, no significant neutron attenuation occurred due to the cadmium covers. This result is not complicated by cobalt-58 burn-up problems, since the conditions employed here result in less than 1% burn-up for a bare nickel foil.[9]

The nuclear reactions and sample materials used for the neutron energy distributions as well as the nuclear data used for the calculations are found in Table 1. After each irradiation, the radioisotope of interest was counted using the same calibrated 47 cm^3 Ge(Li) semiconductor detector used for the thermal neutron flux determinations, and the fast flux calculated from the nuclear constants and threshold values given. Copper foil flux monitors were included with each irradiation at the opposite end of the rabbit from the cadmium to normalize the values obtained for each irradiation position. It was determined experimentally that the thermal neutron flux depression 8 cm distant from 6.5 grams of cadmium was only 2.0±0.5%.

The purties of the foils and wires used are also given in Table 1 if known. Whenever the product nuclide could be formed by an (n, γ) nuclear reaction, the radioactivity produced both with and without a cadmium cover was observed. In all cases, with a simple post-irradiation wash of the sample material, no interference was noted from the (n,γ) product. Initial work with the iron reaction forming manganese-56 did indeed re-

Table 4

Variation of neutron flux with cadmium thickness using elemental nickel

Wire No.	Cadmium thickness	Relative fast flux[a]	Relative thermal flux
1	bare	1.00	1.000
2	.020 in	0.981	.0033
2	.040 in	0.987	.0011

[a] Absolute value 1.00 ≡ $5.21 \cdot 10^9$ $n \cdot cm^{-2} \cdot sec^{-1}$; integral neutron flux above 2.9 MeV for RT-4.

sult in a significant interference from the (n,γ) product, even with a cadmium cover. However, a sample of extremely pure iron wire was obtained which did not produce an interference, and this material was used for the threshold reactions. Analysis of the iron wire later revealed a concentration of only about 2 ppb manganese.

The resulting integral neutron flux spectra for the four pneumatic tubes RT - 1 through RT - 4 are shown in Fig. 1, along with a spectrum of a pure fission neutron flux.[10] The data points obtained fall very close to a straight line, with a slope similar to that of the fission spectrum. The fast flux levels observed for each of the pneumatic facilities are close to those expected, showing increasing thermalization of the neutron flux with distance from the core area.

For comparison purposes, the only other fast neutron data available for the NBSR is that of McELROY et al., for RT - 4 from thermal up to 6 MeV.[8] His data show a very similar spectrum shape, with an absolute magnitude somewhat lower. At present, only data points for neutron energies greater than 2.9 MeV have been determined. Additional work is in progress to lower this to 1.0 MeV, using the ^{115}In(n,n')^{115m}In nuclear reaction, and even lower with other nuclear reactions. With the use of additional suitable threshold

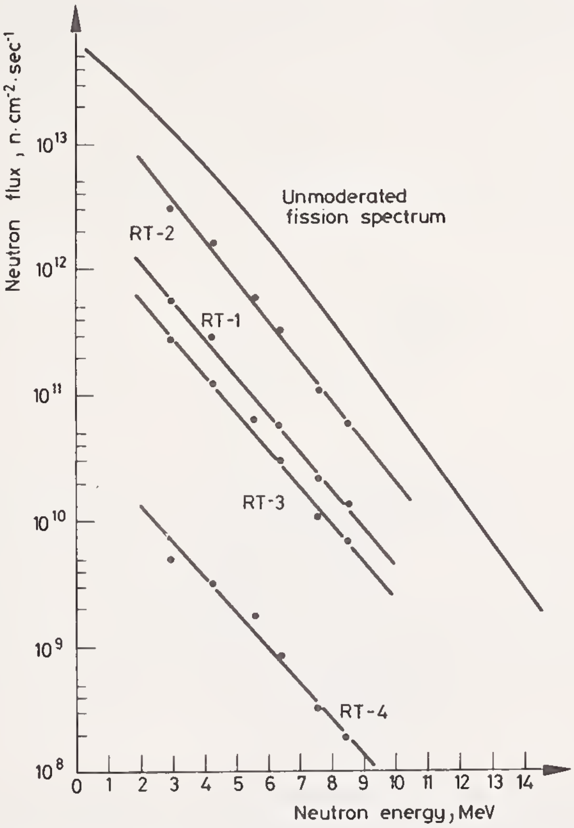

Fig. 1. Integral fast neutron flux for the NBSR pneumatic tube facilities

reactions, it should soon become quite simple to make 3 to 8 irradiations with readily obtainable materials, and obtain a reasonably good approximation of the fast neutron spectrum in any reactor facility.

Pressure measurements

With the increased emphasis on the analysis of trace elements in organic materials, aqueous solutions, and freeze dried biological materials in the NBSR, a number of questions were raised which could not be definitively answered. One of these questions involved the danger of explosion of a quartz ampoule due to the pressure generated by gaseous decomposition products of the material under irradiation. To effectively answer this question, and to establish criteria for the safe irradiation of such materials, a series of pressure measurements was initiated. The pressure testing system used to test irradiated samples shown in Fig. 2. It consists of an appropriate sized rubber balloon, a section of polyethylene or other tubing which will fit inside the balloon but is still large enough to hold the irradiated quartz ampoule, and a gas-tight clamp for the open end of the balloon. To make a pressure measurement, an irradiated sample (inside the quartz ampoule) is inserted into the tubing and the balloon, the end of the balloon clamped shut, and the

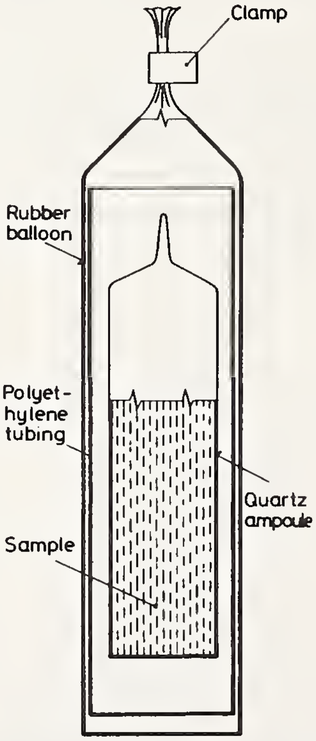

Fig. 2. Irradiated sample pressure test apparatus using rubber balloon

ampoule struck smartly with a hammer. The polyethylene tubing prevents the shattering quartz from puncturing the balloon, and the pressure inside the ampoule estimated from the degree of expansion of the balloon.

Tests with a hypodermic cyringe (less needle) snugly fitted to the balloon opening indicated that 0.5 cm^3 of gas could be readily detected. The quartz ampoules being tested had volumes of 1 cm^3 or greater, therefore excess pressures of 1 atm could most certainly be measured. Since even poor quality glass blowing produces ampoules which can readily withstand 2 atm excess pressure, and good quality quartz glass blowing can produce ampoules which will withstand internal pressures of more than 5 atm excess pressure, a preliminary limit for testing purposes of 1.5 atm excess pressure was established.

From the results of these pressure tests it can be seen that freeze-dried biological materials produce only small quantities of gaseous products upon irradiation in the pneumatic facilities RT - 1, RT - 3 and RT - 4. For example, 1/2 gram of freeze-dried orchard leaves, irradiated for 6 hours in RT - 3 at a neutron flux of $5 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot sec^{-1}$, produced only about 1 cm^3 of gaseous decomposition products (which produced approximately 1 atm of excess pressure in the ampoule size used). These conditions of excess pressure are well within the tentative limits set up for these tests, and in many cases permit irradiations of these materials in heat sealed polyethylene instead of quartz.[2]

A modification of the balloon technique was recently developed, which permits a more quantitative measurement of the excess pressure in irradiated samples. This modification uses heavy walled rubber tubing as the fracture chamber, with the volume change determined using a calibrated water manometer. Using this modified system, a large number of various materials are in the process of being checked for pressure generation during irradiation. These results, when completed, will be reported in the literature.

Conclusion

In conclusion, the NBSR has been characterized for many of its irradiation parameters, some of which are reported here. While additional measurements remain to be made, especially in the area of threshold foil measurements of neutron flux energies, the irradiation facilities available for use are revealed as a set of extremely useful and convenient facilities under which a wide variety of irradiation environments can be obtained. In addition, it is hoped that the procedures and techniques developed will be found to be useful in the characterization of other irradiation facilities.

*

The authors wish to acknowledge very substantial assistance of the NBS Reactor Operations staff in the performance of this work. They also wish to acknowledge the very helpful and able assistance of a summer intern, Mr. R. SPERBURG, for much of the threshold foil work reported here.

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APPENDIX VI

Method for Determination of Mercury in Biological Materials by Neutron Activation Analysis

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A method is described for the determination of mercury in a variety of matrices. Three significant improvements over currently used procedures have been achieved: The procedure has a minimum of chemical manipulations, thereby minimizing technique related errors; the radiomercury separation is quantitative, thus eliminating unnecessary errors involved in the determination of chemical yields; the procedure is based on a simple combustion separation of radiomercury allowing the same technique to be used on a wide variety of matrices. The method was tested using radiotracer experiments and by analyzing samples of flour and coal which had been independently analyzed. The procedure has been subsequently used to determine the mercury concentration of two new Standard Reference Materials being offered by the National Bureau of Standards.

In recent years, mercury contamination of the environment has been recognized as a significant health problem. Because of the severe toxicity of some organic mercury compounds, notably methyl mercury, levels of less than 1 part per million (ppm) must be routinely determined to ensure the safety of human and animal life. Because of high sensitivity, neutron activation is an ideal technique for this analytical problem. Nondestructive neutron activation analysis has been reported for the determination of mercury above the 0.1 ppm level (*1–4*). However, both useful isotopes of mercury have low energy gamma emissions, usually necessitating a chemical separation of mercury from the activated matrix.

Most separation methods reported in the literature involve acid dissolution followed by a chemical separation specific for mercury, coupled with NaI(Tl) counting (*5–22*). These methods were usually developed for a specific matrix type and are not easily adapted to changed composition. This type of activation analysis is often time-consuming, requires yield corrections, and gives results which are often technique-dependent.

Recent separation methods reported use combustion techniques with mercury absorbed either on selenium paper (*23*) or in various solutions (*24*). In each case, however, the separated mercury was again required to be radiochemically pure.

In this work, a rapid, quantitative separation of volatile elements was carried out followed by counting using a high efficiency, high resolution Ge(Li) detector and gamma ray spectrometer.

Using this method, samples of flour and coal containing from 0.015 to 5 ppm were analyzed to test the accuracy of the procedure. Samples of Standard Reference Material 1571 and 1577, Orchard Leaves and Beef Liver, were also analyzed for mercury, and concentrations of 0.155 ppm and 0.0145 ppm, respectively, were found. It is of interest to note that excellent agreement was obtained later by flameless atomic absorption spectrometry and isotope dilution spark source mass spectrometry.

EXPERIMENTAL

Apparatus and Reagents. The sample combustion train (Figure 1) was made from an outer 19–38 standard taper Vycor joint which had been extended to a total length of 30 cm. The mercury condenser was made from an inner 19/38 standard taper Vycor joint, extended to 25 cm, which was inserted through a liquid nitrogen cold trap made from a small polyurethane acid shipping container.

Standard solutions were made by dissolving a weighed quantity of triply distilled metallic mercury in 1:1 high purity nitric acid and diluting to volume. The concentration used was 1.0065 mg/ml which was dilute enough to prevent any significant neutron self absorption, but concentrated enough to negate loss due to wall absorption of mercury in the storage container.

Procedure. For analysis, 0.5-gram samples were encapsulated in cleaned, heat treated quartz tubes. Standard solutions were encapsulated in a like manner. Five sample tubes were arranged in a concentric ring with a standard in the center in a polyethylene rabbit and irradiated in the pneumatic transfer facility RT-3 of the NBS Reactor for 2 to 4 hours at a thermal neutron flux of approximately 6×10^{13}n cm^{-2} sec^{-1}. Flux monitors were not used as the radial flux variation is less

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than ±2% in RT-3. The samples were allowed to decay 3 days to minimize personnel radiation exposures.

The quartz tubes were washed in 1:1 nitric acid, cooled to liquid nitrogen temperature, and broken 5 mm from the top. The samples were weighed into a ceramic combustion boat, and 25 mg of mercuric oxide carrier added. The boat was inserted into the combustion chamber, an oxygen flow of ~30 cc/min passed over the sample and the sample ignited with an oxygen-gas torch. The sample was allowed to burn freely with the downstream quartz wool plug heated to red heat to ensure complete combustion of volatile hydrocarbons and carbon produced during the sample burn. After combustion ceased, the ash was heated to approximately 800 °C for 5 minutes and the entire combustion tube flamed down to the standard taper joint to drive all volatile components of the sample into the condenser.

The combustion tube was allowed to cool for 5 minutes, the liquid nitrogen cold trap removed, and the condenser placed joint end down into a 4-oz polyethylene bottle. The condenser was warmed to room temperature and the mercury washed into the bottle with 10 ml of concentrated nitric acid and three 10-ml portions of distilled water. The total volume of solution was adjusted to 50 ml and counted on a 60-cc Ge(Li) detector. The 77-keV gamma ray of mercury-197 was used for the determination.

Primary standards were made by sealing 1-ml aliquots of the previously mentioned standard solution in quartz vials and irradiating them in the same configuration as that of the sample. After irradiation, the standard was frozen in liquid nitrogen, broken in a beaker, allowed to melt, and decanted into a 1-liter volumetric flask. The broken quartz vial and beaker were washed with six 5-ml portions of distilled water and the final volume adjusted to 1 liter. One milliliter of the dilute solution was pipetted into a 4-oz polyethylene bottle and diluted to 50 ml. The specific activity at the end of irradiation was compared to that of the sample for quantitative results.

A method of additions analysis also was carried out to determine if mercury was lost during analysis. This procedure is described in a following section.

Bromine Separation. The only isotope to interfere after the combustion separation is bromine-82 and then only when its concentration is at least a factor of 100 times that of mercury. To eliminate this interference, either of two courses of action may be employed. Bromine-82 has a half-life of 35.3 hours while mercury-197 has a half-life of 65 hours. Thus, allowing the sample to decay 10 to 15 days optimizes the reduction of bromine activity while maintaining usually adequate mercury sensitivity. If decay does not give the necessary improvement of the mercury signal relative to bromine, a silver bromide separation can be carried out with quantitative recovery of mercury-197 due to the relatively high solubility of mercury bromide in warm water. The procedure is as follows:

The mercury-197 plus carrier was washed from the condenser into a 40-ml centrifuge tube with 10 ml of concentrated HNO_3 followed by four 5-ml portions of distilled water. The solution was warmed to 40 °C in a hot sand bath, 2 mg of bromide carrier were added, and bromide was precipitated with $AgNO_3$. The solution and precipitate are stirred at 40 °C to ensure complete dissolution of $HgBr_2$ and precipitation of AgBr. The solution was centrifuged, decanted into a 4-oz polyethylene bottle, and the walls of the tube were washed down with 3 ml of $2N$ HNO_3. The precipitate was washed twice with 2-ml portions of warm $2N$ HNO_3 followed by centrifugation. The wash solutions were added to the original solution. The final solution was adjusted to 50-ml total volume and counted as before. A reduction to less than 5% of the initial bromine activity was obtained with quantitative retention of mercury-197 in the solution.

Method Evaluation. The method was first tested for complete recovery of mercury by burning non-irradiated samples of orchard leaves with mercury-203 tracer added. The recovered mercury-203 was brought to 50-ml volume and compared to the activity of a like quantity of tracer diluted directly to 50-ml volume and counted in a standard configuration. The results of these tests indicated complete recovery of the mercury-203 tracer. A total of eight separations was carried out with a mean recovery of 99.52% and a relative standard deviation of ±1.68%.

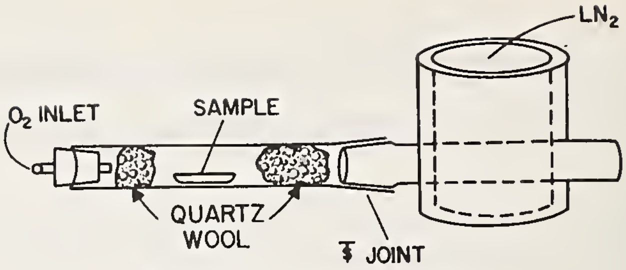

Figure 1. Combustion apparatus

Table I. Determination of Mercury in Characterized Materials

Sample	Hg found, ppm	Comparative value
IAEA flour		
Nondestructive	4.82	
	4.90	
Destructive	4.88	
Average	4.87 ± 0.04	4.9 ± 0.3 (*25*)
FDD flour		
Destructive	0.0105	
	0.0107	0.013 ± 0.003 (*26*)[a]
Average	0.011	0.011 ± 0.003 (*27*)[b]

[a] Results obtained by flameless atomic absorption.
[b] Results obtained by neutron activation.

The procedure described above did not, however, test the recovery of mercury incorporated into an organism. To ascertain that the mercury could, in fact, be recovered in this case, mercury-203 nitrate was added to the water in a tank containing goldfish. The fish survived for varying periods from one day to three weeks. The dead fish were removed from the tank, frozen, and lyophilized. The fish were then counted whole, followed by analysis for ^{203}Hg using the combustion technique. After burning, the solution from the cold trap was placed in a vial that approximated the length and diameter of the fish, and the solution was counted. In all cases, counting was done using a 7.6 cm × 7.6 cm NaI(Tl) detector about 25 cm from the detector surface. As a further check, one fish was counted, dissolved in nitric acid, and diluted to the standard 50-ml geometry. The combustion effluent from a second fish was also diluted to this volume. The comparative results still showed quantitative recovery.

The experimental results showed a mean recovery of 98.9% with a relative standard deviation of ±1.0%. Although one of the fish had lived for three weeks, speciation of the mercury present in the fish was not determined. It is not anticipated, however, under the conditions of the analysis, that organomercury compounds would behave differently than inorganic mercury.

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Table II. Mercury Content of SRM-1571 Orchard Leaves

Sample	Hg, ppm
OL-01	0.158
OL-02	0.149
OL-11	0.156
OL-12	0.154
OL-13	0.152
OL-14	0.154
OL-15	0.155
OL-17	0.157
OL-10	0.155
OL-20	0.155
OL-21	0.159

Mean = 0.155.
2 s = 0.0056.
$ts/\sqrt{n}$ = 0.0019.

Table IV. Mercury in Beef Liver

Hg, ppm
0.0140
0.0141
0.0118
0.0140
0.0173
0.0137
0.0152
0.0138
0.0169

Mean = 0.0145.
2 s = 0.0034.
$ts/\sqrt{n}$ = 0.0013.

RESULTS AND DISCUSSION

The work undertaken in this laboratory was to develop a single analytical method, preferably with quantitative recovery of mercury, which could be applied without change to a large number of sample types. Since all mercury compounds are volatile above 400 °C, sample combustion or heating in an oxygen stream seemed the best approach. The collection of mercury was carried out with a simple liquid nitrogen condenser which quantitatively trapped mercury and was easily washed clean after combustion. With this system, complete collection of mercury was accomplished on such diverse matrices as orchard leaves, wheat flour, coal, fuel oil, freeze dried fish, and river sediment.

After the previously mentioned preliminary tests, the method was checked by analyzing samples of flour and coal having mercury concentrations ranging from 0.01 to 5 ppm. Where mercury levels were high enough (>1 ppm), samples were analyzed nondestructively by irradiation followed by direct counting of the mercury-197. These samples were then analyzed by the described combustion technique and the results compared. The analyses were carried out on the following samples: a flour sample prepared by the International Atomic Energy Agency which had been doped with approximately 5 ppm of mercury; a sample of flour containing approximately 0.01 ppm of mercury analyzed by the U.S. Food and Drug Administration by both atomic absorption and activation analysis and by the Food and Drug Directorate of Canada using atomic absorption. The results of these analyses are given in Table I.

With the procedure giving satisfactory results, an intensive analytical program was carried out on a new Standard Reference Material—SRM 1571, Orchard Leaves. The intent was to determine the mercury content using two or more non-related analytical techniques with an accuracy in the final results of better than ±10% at a 95% confidence level. A total of 11 samples from three different bottles was analyzed by the procedure described. The samples were found to contain 0.155 ± 0.006 ppm of mercury (Table II).

The absolute value of the mercury concentration was checked by carrying out a method of additions analysis on the orchard leaves. Four 40-gram samples of the base leaves were spiked with standard mercury solutions to give samples containing approximately 0.0, 0.5, 0.5, and 1.0 μg added mercury per gram of leaf, respectively. The samples were freeze dried, tumbled for four hours, and mixed in a ball mill for a minimum of 6 hours. Two extra samples were prepared in the same manner and spiked with mercury-203 tracer to ascertain that no losses occurred during freeze drying and that the mixing was uniform. The tracer experiments indicated complete mixing with an inhomogeneity of less than ±1%.

Aliquots of each group were analyzed by the described procedure and the base concentration of mercury in the orchard leaves was determined by fitting a least squares regression to the individual results. The least squares fit gave a base concentration of 0.161 ± 0.010 ppm of mercury. The individual results are given in Table III.

Table III. Method of Addition of Hg in Orchard Leaves

Sample	Hg added, ppm	Hg found, ppm	Hg calculated by least squares, ppm	$\left[\begin{matrix}\text{PPM Hg}\\ \text{Found}\end{matrix}\right]-\left[\begin{matrix}\text{PPM Hg}\\ \text{Calculated}\end{matrix}\right]$
5-1	0	0.151	0.161	−0.0096
5-2	0	0.156	0.161	−0.0046
5-3	0	0.169	0.161	+0.0084
5-4	0	0.154	0.161	−0.0066
5-5	0	0.154	0.161	−0.0066
1-1	0.495	0.699	0.667	+0.0316
1-2	0.495	0.665	0.667	−0.0023
4-1	0.485	0.621	0.657	−0.0361
4-2	0.485	0.702	0.657	+0.0439
2-1	1.012	1.168	1.196	−0.285
2-2	1.012	1.207	1.196	+0.0104

$Y = A + Bx$.
A = 0.1606 ± 0.910.
B = 1.024 ± 0.0201.
Base mercury content = 0.161 ± 0.010.

The mercury concentration in the SRM Orchard Leaves also was determined using flameless atomic absorption spectrometry and isotope dilution spark source mass spectrometry. The results obtained by these techniques were 0.160 ± 0.012 and 0.145 ± 0.022 ppm of mercury, respectively.

A second new Standard Reference Material, Beef Liver, with a considerably lower mercury content was also analyzed by this technique. Nine samples were analyzed using the bromine separation. The samples contained 0.0145 ± 0.0034 ppm of mercury. The individual results are given in Table IV. The mercury concentration in the SRM Beef Liver was determined using flameless atomic absorption spectrometry. The results obtained by this technique were 0.0160 ± 0.0012 ppm of mercury.

ACKNOWLEDGMENT

The cooperation of T. C. Rains, P. J. Paulsen, and Robert Alvarez is gratefully acknowledged. Their investigations and analyses gave special credence to this work. The Authors would also like to thank H. P. Yule for his help in the data reduction.

RECEIVED for review October 26, 1971. Accepted February 7, 1972. In order to specify procedures adequately, it has been necessary to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

APPENDIX VII

Simultaneous Determination of Trace Elements in Platinum by Isotope Dilution and Spark Source Mass Spectrometry

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An isotope dilution technique using the spark source mass spectrograph was investigated for applicability to simultaneous multi-element trace determinations. Isotopically altered Ag, Cu, Ni, Pb, and Pd were separated from a 250-mg sample of platinum by cation exchange, and electrodeposited onto gold electrodes for sparking in the spectrograph. Electrodeposition provided the spiked analytes in an adherent form, relatively free of anions and organic residue from the ion exchange resins, both of which could complicate the spectrum. Contamination, the principal limitation of the method, was minimized by isothermally distilling the reagent acids and by isolating the operations from the laboratory environment. After determining the isotope ratios, the concentrations were computed, ranging from 0.5 ppm (μg/gram) for Ni to 14 ppm for Pb. Improved precision and accuracy was obtained compared to conventional spark source analysis. The results were compared with those of other methods and the platinum material was issued by NBS as Standard Reference Material 681.

Stable isotope dilution analyses are usually performed using mass spectrometers with thermal ionization sources. These methods depend on the chemical form of the element for optimum results and are generally not suitable for simultaneous multi-element trace determinations. This is particularly true if elements having high ionization potentials are to be included in the analysis. Webster (*1*) presents an excellent description of the general method including applications. The spark source mass spectrograph has been employed by Leipziger (*2*) to determine copper in Nickel Oxide NBS Standard Reference Material (SRM) 673 and antimony in Tin SRM 835 using isotope dilution techniques. The average values obtained, 21 and 121 ppm, respectively, agreed with the NBS certificate values.

Because the high voltage spark source ionizes all elements with approximately the same efficiency, isotope dilution spark source mass spectrometry (ID-SSMS) should enable the simultaneous determination of many trace elements in a sample. The object of this investigation was to apply this method to determine five trace elements in a sample of platinum. Isotopically altered Ag, Cu, Ni, Pb, and Pd were separated from the platinum matrix by cation exchange and eluted with HCl into an electrolysis cell. After neutralizing the acid, the spiked analytes were electrodeposited onto gold wires and sparked in the spectrograph. The mass spectra were photographically recorded, isotopic ratios determined, and the results calculated. After comparing these results with those of other analytical methods, this platinum material, previously examined for homogeneity, was subsequently issued by the National Bureau of Standards as SRM 681.

The authors have also developed an ID-SSMS method for determining trace elements in each of two NBS zinc standard reference materials (*3*). Compared to this zinc method, the platinum procedure required a greater number of analytical operations using special techniques and apparatus to reduce contamination to an acceptable level.

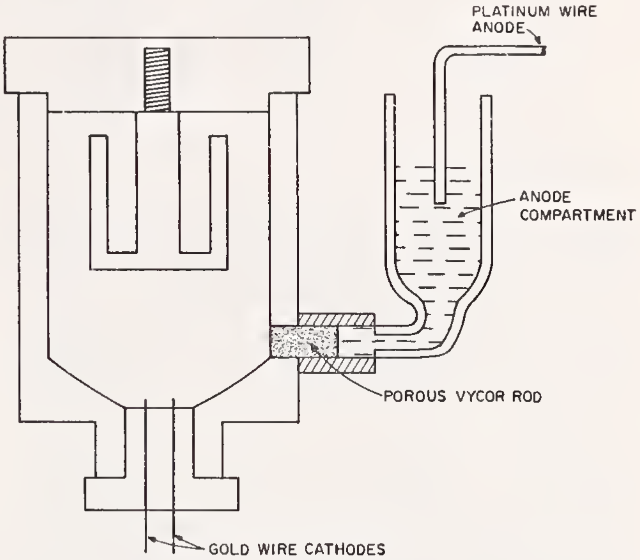

Figure 1. Cell for acid neutralization and electrodeposition

EXPERIMENTAL

Reagents. Deionized water is made immediately before use by passing distilled water from the laboratory distribution system through a mixed bed resin column. HCl and HNO_3 are prepared by isothermal distillation. Aqueous ammonia is prepared by bubbling NH_3 into deionized H_2O, after passing the gas into a gas washing bottle.

Evaporator for Sample Solutions. A borosilicate glass chamber, similar to the one described by Thiers (*4*), provides a clean environment for evaporating solutions. The apparatus is fabricated from a crystallizing dish 150 mm in diameter by 75 mm high, and a culture dish of the same diameter. A lateral displacement of the coincident edges of the two units is prevented by three lengths of glass rod that are fused to the outside of the culture dish (lower unit) and project upward. Filtered nitrogen is introduced through a tube sealed at the center of the crystallizing dish, and escapes from between the edges of the modified dishes to prevent entry of particulate contaminants. The gas is filtered by a cellulose filter which has a mean pore size of 0.1 μm and is supported by porous polypropylene disks in a Nylon filter holder.

Glove Box. A fiber glass glove box is employed to reduce airborne contamination during ion exchange and miscellaneous operations.

Ion Exchange Column. The column consists of an 8-mm i.d. borosilicate glass tubing drawn to a fine tip, containing a resin bed 4 cm in height. The resin has a 100 to 200 mesh size and is of an analytical-grade, sulfonic acid type with an 8% divinylbenzene crosslinkage. Before use, the column is

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Table I. Natural and Spike Isotopic Abundance of Isotopes

Isotope	Natural abundance, atomic per cent	Isotopic abundance in spike, atomic per cent
^{107}Ag	51.83	0.9
^{109}Ag	48.17	99.1
^{63}Cu	69.17	0.30
^{65}Cu	30.83	99.7
^{58}Ni	67.88	0.38
^{62}Ni	3.66	99.02
^{108}Pd	26.71	10.6
^{110}Pd	11.81	87.5
^{206}Pb[a]	—	92.15
^{208}Pb[a]	—	1.255

[a] Lead exhibits isotopic variability in nature and is therefore not listed.

Table II. Trace Element Concentrations in Platinum Standard Reference Material 681 Determined by Isotope Dilution Analysis

Element	Concentration in ppm (μg/gram)	No. of samples	95% Confidence limits in ppm for the concentration[a]
Ag	2.09	7	±0.15
Cu	5.04	6	±0.54
Pd	5.92	4	±0.32
Pb	13.6	6	±0.9
Ni	0.46	4	±0.06

[a] These confidence limits are based upon $tS_{\bar{x}}$ where $S_{\bar{x}}$ is an estimate of the uncertainty in the average concentration and is based upon the observed variation between the k samples. The t is Student's t factor for 95% confidence and $k - 1$ degrees of freedom.

pretreated with 50 ml of 6*M* HCl and washed with 5 ml of water.

Neutralization and Electrolysis Cell. The cell shown in Figure 1 was designed for neutralization of the acid eluate and subsequent electrodeposition of the isotopically-altered trace elements. The components are fabricated of polytetrafluoroethylene (PTFE) except as otherwise indicated. The cell body has a 25-mm i.d. and a volume of 13 ml. For the neutralization step, the cylindrical compartment, shown suspended by a reentrant centerpost threaded into the lid, is filled with 1 ml of aqueous NH_3. This assembly is removed prior to electrodeposition. Two high-purity gold wires, inserted into a removable PTFE plug, serve as the cathode during electrodeposition. When this plug is fitted tightly into the body of the cell, the 0.7-mm diameter cathode wires project 2 mm into the cell body. An isolated anode compartment is formed by inserting a 3.5-mm diameter by 6-mm long porous Vycor (*5*) rod into an undersize hole at the side of the cell and connecting this rod to a glass reservoir with plastic tubing. A platinum wire makes an electrical contact with diluted HNO_3 added to this compartment as an electrolyte. During electrodeposition, the cells are housed in a plastic enclosure under a slight positive pressure of nitrogen to minimize airborne contamination.

Enriched Isotope ("Spike") Solutions. With the exception of ^{206}Pb, the enriched isotope materials in amounts equivalent to 10 mg of the element were obtained from the Oak Ridge National Laboratory. Solutions containing one mg per ml of ^{109}Ag, ^{65}Cu, ^{62}Ni, and ^{110}Pd were prepared by weighing each material to ±0.02 mg, dissolving it in the appropriate acid, and diluting the solution to volume in a 10-ml volumetric flask. The possible presence of impurities in these materials and the small sample weights used made it advisable to verify the solution concentrations. However, because these solutions were diluted to add the required submicrogram additions of the spikes to the sample solution, the concentrations of the diluted spike solutions were determined by isotope dilution as follows: Measured volumes containing 5 μg of each spike were mixed with solutions containing known amounts of the normal elements. The pure element additions were computed from Equation 1 to yield isotope ratios approximating one for all elements except Ag (see Calculations and Results). The solution was electrolyzed for one hour at a current of 2 mA in the previously described cell. The gold wire electrodes were then sparked, the isotope ratios were determined, and the spike weights were computed from Equation 1. A reliable ^{206}Pb solution could be prepared by weighing 100.0 mg of the NBS radiogenic lead isotopic standard, SRM 983 (*6*), dissolving it in HNO_3, and diluting to volume with water in a 100-ml volumetric flask.

Mass Spectrograph. A double-focusing Mattauch-Herzog design, spark source instrument (Consolidated Electrodynamics Model 21-110) that had been modified to give 22 exposures per plate is operated at an ion accelerator voltage of 24 kV.

Microphotometer–Analog Computer. A microphotometer having a precision screw (Jarrell-Ash Model 23-500) and equipped with an analog computer to measure peak areas (*7*) is used. A function generator, which is the basic component of the analog computer, provides an output proportional to relative ion intensities when the input is a voltage proportional to per cent absorption. An integrator follows the function generator to give signals proportional to peak intensity areas as the line is scanned.

Procedure. A 250-mg sample of platinum was treated with warm aqua regia for several minutes and rinsed in water to remove possible surface contamination. The sample was weighed into a 25-ml quartz erlenmeyer flask and heated with 3 ml of HCl and 1 ml of HNO_3 until dissolved. After adding measured volumes of the spike solutions, the platinum solution was transferred to a 20-ml low form, quartz crucible and evaporated almost to dryness in the chamber described. The resulting salts were dissolved in 5 ml of H_2O and the solution was passed through the cation exchange column using the full flow rate of the column. During this step, the isotopically altered trace elements were adsorbed on the resin and the chloroplatinate solution was the effluent. The column was washed with 4 ml of H_2O, and eluted with 5 ml of 3*M* HCl into the electrolysis cell after the washings had been discarded. To neutralize the acid eluate with a minimum of contamination, aqueous ammonia was pipetted into the cylindrical compartment and the cell was closed with its tightly fitted lid. This distillation step yielded a small solution volume that was favorable for the electrodeposition of the analytes. After removal of the cylindrical compartment, the acidity of the solution was adjusted to read approximately 6 with indicating pH paper. The acidity is not critical. The solution was then electrolyzed for 5 hours at a current of 2 mA, while stirring at approximately 200 rpm. After withdrawing the solution, the gold electrodes were rinsed in water and transferred to the mass spectrograph.

A graded series of exposures was made with the pair of electrodes at integrated beam currents of 0.3×10^{-10} to 1×10^{-7} coulomb to obtain optimum intensities for the isotope lines of the various amounts of electrodeposited elements. By moving one electrode so as to expose a fresh surface, the electrodeposit was consumed more effectively and a greater signal was obtained. The ion-sensitive photographic plates (Ilford Q-2), were developed in a high contrast

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(5) R. A. Durst, *J. Chem. Educ.*, **43**, 437 (1966).

(6) E. J. Catanzaro, T. J. Murphy, W. R. Shields, and E. L. Garner, *J. Res. Natl. Bur. Stand.*, **72A**, 261 (1968).

(7) P. J. Paulsen and P. E. Branch, NBS Technical Note 401, Washington, D. C., Sept. 1966.

Table III. Comparison of Results by Isotope Dilution with Other Analytical Methods for Platinum Standard Reference Material 681

Concentration in ppm (μg/gram)

Element	Isotope dilution	Activation analysis[a]	Polarography[b]	Optical emission spectrochemical[c] Lab A	Lab B	Lab C	Lab D
Ag	2.1	1.8		1.4	2.0	2	...
Cu	5.0	5.0	5.2	6.3	3.0	2	...
Pd	5.9	5.6		5.0	6.1	4.0	...
Pb	13.6		10.3	8.5	15.0	10	12.3
Ni	0.46			<1	N.D.[d]	0.8	0.44

[a] Activation analyses by Michel Crambes and Gilbert W. Smith, NBS Analytical Chemistry Division.

[b] Polarographic analyses by E. June Maienthal, NBS Analytical Chemistry Division.

[c] Spectrochemical analyses by outside laboratories cooperating with NBS.

[d] N.D. Not Detected.

developer (Kodak D-19) for 2½ min, placed in a short stop solution for 10 sec, fixed for 1 min, washed 15 min in tap water, and rinsed in distilled water. The intensity areas of the lines for the isotopes listed in Table I were measured and their ratios were calculated. From 6 to 20 ratio measurements were made for each element depending on the availability of lines having suitable intensity.

To correct the determination for contamination, the entire analytical procedure was performed using the same sample size of high-purity platinum, SRM 680. A direct mass spectrographic comparison of SRM 680 with SRM 681 had indicated that the elements of interest except for Ni were substantially lower in SRM 680 than in the material being analyzed. Consequently, to obtain favorable intensity ratios, the SRM 680 solution was spiked with one tenth of the amount added to SRM 681 and both materials were analyzed concurrently. Use of the higher-purity matrix to evaluate contamination, which did not exceed 10% of the reported values, yielded more reproducible results than were obtained by spiking the reagents alone. For Ni however, this latter procedure had to be used.

CALCULATIONS AND RESULTS

The concentrations were computed from Equation 1.

$$C = \frac{WK(A_{sp} - B_{sp}R)}{M\,(BR - A)} \tag{1}$$

where C is the concentration in ppm (μg/gram), W is the weight of isotopically enriched material ("spike") added in μg, M is the weight of sample in grams, A and B are the natural abundances of the analyte isotopes a and b, A_{sp} and B_{sp} are the abundances of isotopes a and b in the spike, R is the measured altered ratio of isotope a to isotope b, and K is the ratio of the natural atomic weight to the atomic weight of the spike.

In the method, it is desirable to alter the isotopic compositions of the analytes to obtain isotope ratios, R, approximating one whenever possible. This minimizes the effect of photographic emulsion calibration errors, and could be done for all analytes except Ag. For that element, ^{109}Ag spike was added to change the ^{109}Ag/^{107}Ag ratio from its natural value of 0.93 to 2. To obtain the desired R values, the spike additions were computed from Equation 1 using the elemental concentrations estimated from a direct sparking of the platinum sample. This photographically recorded spectrum was also used to determine the ^{206}Pb and ^{208}Pb natural abundances in the platinum material. These determinations were necessary because of the isotopic variability of Pb in nature (*6*). For the other analytes, an experimental determination of the natural abundances of the isotopes was not required; and the values listed in Table I, supplied by the NBS Analytical Mass Spectrometry Section, were used. The isotopic analyses provided by the Oak Ridge National Laboratory for its isotopically enriched materials and by Catanzaro *et al.*, (*6*) for the radiogenic lead isotopic standard, SRM 983, are also listed in this table. These isotope analyses are of sufficient accuracy that errors from this source do not significantly affect our results.

In all, seven samples were run, the first three using experimental conditions that did not satisfactorily preconcentrate all of the elements. However, using the experimental conditions described under Procedure, the last four samples yielded all of the analytes for simultaneous determination. The elemental concentrations obtained for the first three samples are also included in the results. The determination of Ag was satisfactory for all of the samples. Table II lists the average concentrations obtained, the number of samples, and the 95% confidence limits. A comparison of the isotope dilution results with the results obtained by other analytical methods is given in Table III. Except for Pb, the agreement among methods having high precision was satisfactory.

DISCUSSION AND CONCLUSIONS

Unlike most trace analytical methods, isotope dilution analysis does not require analyzed or synthesized standards of the same matrix material for reliable determinations. As applied to spark source mass spectrometry, the simplest procedure consists of evaporating a portion of an isotopically spiked solution of the sample on a suitable substrate for sparking in the spectrometer. Compared to direct sparking of the sample, poorer limits of detection will be obtained. Moreover, a trace element may be undeterminable if the only isotope lines suitable for measurement are interfered with by isotope lines of the matrix elements or complex ionized species of the matrix and anion fragments. For example, copper could not be determined in platinum by this direct-evaporation technique because one of its two stable isotopes, ^{65}Cu^{+}, is interfered by ^{195}Pt^{3+}.

To obtain improved limits of detection and remove these interferences, the isotopically spiked analytes can be separated from the matrix before sparking. A preconcentration procedure should be selected that minimizes contamination which is the principal limitation of these methods. These procedures can be relatively simple or incompletely characterized because determinations by isotope dilution methods are unaffected by analyte losses once equilibrium has been established with the added spikes. However, to obtain isotope lines of sufficient intensity for precise ratio measurement, a high recovery of the spiked analytes is desirable.

Concentration limits of detection comparable and even superior to those obtained by the direct sparking technique are possible if contamination can be reduced to an acceptable value. Although the experimental procedure should be designed to achieve a low method blank, its variability is an important factor affecting the precision of the results. Therefore, the least number of manipulations is desirable and should be performed in a clean environment to reduce spurious contamination. In the platinum method, contamination can occur during sample dissolution, evaporation, ion exchange, and transfer of the spiked analytes to the substrate for sparking. Gold is a suitable substrate for it does not react with the solution being electrolyzed; it is mononuclidic thus producing a simple spectrum; and it is obtainable in high purity. The gold wire that was used has the composition of NBS Standard Reference Material 685-W listed in the Certificate of Analysis.

For the dissolution step, minimal quantities of isothermally distilled acids are used. The contribution to the total blank from the reagents is relatively constant and can be corrected for. The spiked platinum sample solution is evaporated in a quartz vessel surrounded by filtered nitrogen. The ion exchange step is performed in a glove box using methylmethacrylate rods and holders to support the ion exchange columns. The last stage, during which the submicrogram amounts of the analytes are being transferred to the wire substrate for sparking, is particularly sensitive to spurious contamination. Although the eluate solution can be evaporated to a small volume and pipetted onto the gold wires, it is preferable to electrodeposit the analytes. This procedure yielded an adherent form for sparking, relatively free of anions and organic residue from the resin, both of which would complicate the spectrum. Moreover, electrodeposition required less handling and, therefore, was less subject to contamination. The electrolysis cell design incorporated a replaceable porous Vycor plug to prevent cross-contamination from the eluate solutions.

To determine elements that are not ordinarily electrodeposited, evaporation of the eluate would have been required. In this case, the electrodeposition step could be followed by evaporation and possible ignition of the residue on fresh electrodes. Ignition would remove the organic residue, one of the disadvantages of this evaporation procedure.

In conclusion, isotope dilution techniques provide spark source mass spectrometry with methods for independently analyzing homogeneous materials that can serve as standards for the direct sparking comparison procedures. In general, these standards of the matrix either are not available or often have values that are not as precise as required. Although ID-SSMS is not a rapid method (for the procedure developed, four samples required approximately 8 days to run), its capability of simultaneous multi-element determinations and applicability to most of the elements having two or more stable isotopes, makes it very attractive for reliable trace element determinations.

RECEIVED for review March 3, 1969. Accepted April 4, 1969. Presented in part before the Division of Analytical Chemistry, 155th National Meeting, ACS, San Francisco, Calif., April 1, 1968. Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

APPENDIX VIII

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Determination of trace elements in zinc by isotope dilution spark source mass spectrometry*

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Abstract—The applicability of the isotope dilution technique in spark source mass spectrometry has been investigated for the determination of Pb, Cu, Cd, Ag, Tl, and Sn in zinc metal. In the procedure developed, a solution of the zinc is spiked with known amounts of stable isotopes of the elements to be determined, and the elements are electrodeposited onto gold wires that subsequently serve as electrodes for the mass spectrographic isotopic analysis. Chemical operations, including isothermal distillation of reagents, dissolution of the zinc, and the electrodeposition step are conducted in a closed system to minimize contamination. The results of the analysis of two NBS zinc standard reference materials include determinations ranging from 11 ppm (11 μg/g) for Pb to as low as 0.02 ppm (20 ng/g) for Sn. It is concluded that this method is of general utility for simultaneous multi-element trace analysis and is especially applicable in providing much needed standardization in spark source mass spectrometry.

INTRODUCTION

SPARK source mass spectrometry (SSMS) is potentially capable of determining all elements in a sample at ppb† concentrations. In practice this capability is limited by specific interferences and background generated by the matrix being analyzed, instrument memory, and instrument background for gases in the source (C, N, O, CO, hydrocarbons, etc.). The accuracy of analysis depends on the availability of suitable reference standards for each material to be analyzed. If standards are not available, the analysis is based on estimated relative sensitivity factors for the elements; this type of analysis will have an uncertainty of a factor of three or more. If a standard is available [1] or if the sample is amenable to the preparation of synthetic standards [2], accuracies to within 5–10% can be obtained under favorable conditions. For many materials, however, standards of the same matrix are not readily available and, for high-purity metals, synthetic standards are not practical. This situation points up the need both for standards at the ppm level suitable for SSMS and for additional techniques that can give accurate analyses without comparison to a reference standard.

Stable isotope dilution analysis using SSMS to measure isotopic ratios offers the possibility of meeting these needs. With this technique the sample to be analyzed is mixed with a known amount of a separated stable isotope (spike) of the element to be determined. The spike must have a known isotopic composition significantly different from that of the element in the sample. Measurement of the

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* Contribution of the National Bureau of Standards, not subject to copyright.

† In this paper the abbreviations ppm and ppb represent respectively, parts per million by weight (μg/g) and parts per billion by weight (ng/g).

[1] R. K. Skogerboe, A. T. Kashuba and G. H. Morrison, *Anal. Chem.* **40,** 1096 (1968).

[2] G. D. Nicholls, A. L. Graham, E. Williams and M. Wood, *Anal. Chem.* **39,** 584 (1967).

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resulting ratio of isotopes in the mixture by mass spectrometry, enables the calculation of the amount of the element present in the original sample. Analysis by stable isotope dilution requires no reference standards, and is specific and sensitive. It can be applied to most elements having two or more stable isotopes. Thermal ion source mass spectrometry has been applied to stable isotopic dilution analysis for many years and is a widely accepted means of analysis [3]. In applying the method to SSMS the procedure is basically the same. However, the generation of ions by a high voltage r.f. spark combined with photographic plate detection of ions gives the SSMS considerably different capabilities in terms of sensitivity and element coverage than the thermal ion instruments in which ions are detected electronically. Stable isotope dilution analysis with SSMS has been applied by LEIPZIGER [4] to the determination of Cu in NBS 673 nickel oxide and Sb in NBS 835 tin standard reference materials.

The object of this work has been to develop a procedure to apply the techniques of preconcentration, combined with stable isotope dilution and SSMS, to the determination of ppm and lower level trace elements. Of particular interest is its application to the analysis of Standard Reference Materials (SRM) which could serve as composition standards for SSMS. Analysis of zinc samples proposed as NBS standard reference materials, SRM 728 and SRM 683, offered an opportunity for comparison of results of SSMS isotope dilution with those of other trace analytical techniques.

EXPERIMENTAL

Reagents

Distilled water from the building distribution system was passed through a mixed bed ion exchanger prior to use.

Hydrochloric acid was isothermally distilled just before it was used to dissolve the zinc samples. Open beakers of A.C.S. reagent grade HCl were placed in a sealed container overnight with a quartz dish containing deionized water. This procedure yielded approximately $9M$ HCl in the quartz container when 3 vol. of HCl were used for 1 vol. of water.

The separated stable isotopic spikes used in these experiments were obtained from Oak Ridge National Laboratory. The material selected for spiking an element is always an enriched sample of the isotope that has a low natural abundance. When an element has more than two isotopes, the selection of the spiking isotope is based on freedom from interferences from isotopes of other elements, its abundance with respect to the major isotope of the element, the available isotopic purity of the enriched isotope, and its cost. Enriched ^{206}Pb, ^{203}Tl, ^{117}Sn, ^{111}Cd, ^{109}Ag, and ^{65}Cu were obtained in 10 mg quantities and stock spike solutions were prepared at concentrations of approximately 1 mg/ml using accurately weighed samples. A.C.S. reagent grade HCl and HNO_3 were used to prepare the spike solutions. Subsequent dilutions of these spike stock solutions with distilled water were so large that impurities from these reagents could not contribute significantly to the analysis blanks.

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[3] R. K. WEBSTER, *Advances in Mass Spectrometry* (Edited by J. D. WALDRON), pp. 103–119. Pergamon Press (1959).

[4] F. D. LEIPZIGER, *Anal. Chem.* **37**, 171 (1965).

The diluted stock solutions employed for analysis were assayed by reverse spiking to determine the concentration of the element. In this operation, solutions containing known amounts of the pure natural elements were mixed with precisely measured volumes of the spike solutions, and the altered isotopic ratios were measured. The procedures and calculations were similar to those for the zinc analysis described under Procedure. Analysis of the diluted solutions avoids errors that might occur during the dilution step.

Electrodeposition cell

Figure 1 shows the electrodeposition cell used to preconcentrate the trace elements in zinc. The tetrafluoroethylene polymer (Teflon) cell had been employed previously [5] to electrodeposit silver onto the surface of a spectroscopic graphite electrode. For the present work the graphite electrode was replaced with a plug of the same diameter through which two high purity (6–9's grade) gold wires, 0.63 mm dia., were inserted to serve as cathodes. The anode compartment consists of a 15 mm length of porous Vycor sealed to Vycor tubing. The compartment contains dilute HNO_3 and a high purity platinum wire as anode. The electrodeposition cell is protected from external contamination by placing it inside a small plastic box having a flow of filtered nitrogen gas, and mounting this box and its external stirring motor inside a portable clean box through which filtered air is passed. Clean environments for all stages of sample handling are provided by either clean boxes or covered containers flushed with filtered nitrogen.

Spark source mass spectrograph

A double-focussing Mattauch–Herzog design, spark source instrument (modified Consolidated Electrodynamics Model 21-110 [6]) was operated at an ion accelerator voltage of 24 kV. The ion source pumping system is a combination of an ion pump and a titanium sublimation pump. The instrument has been modified to give 22 exposures per plate.

Microphotometer

A microphotometer (Jarrell–Ash Model 23-500) having a precision screw had been equipped in our laboratories with an analog computer to measure peak areas [7]. The analog computer is basically a function generator the output of which can be adjusted to conform to the plate response curve to ions. Thus when its input is a voltage proportional to percent absorption profile of a line image from the photographic plate, its output is a voltage proportional to the intensity profile of the ions that generated the image on the plate. The function generator is followed by an

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[5] R. Alvarez, Electrodeposition of trace constituents as a preconcentration technique for optical emission spectroscopy—deposition of silver from zinc solution. *Symp. Trace Characterization*, National Bureau of Standards, October 3–7 (1966).

[6] P. J. Paulsen and P. E. Branch, Instrument modifications. *NBS Tech. Note* 286, pp. 2–6 (1966); *NBS Tech. Note* 401, pp. 70–73 (1966); *NBS Tech. Note* 422, pp. 50–55 (1968); P. J. Paulsen and D. E. Kelleher, *NBS Tech. Note* 452, pp. 45–47 (1968).

[7] P. J. Paulsen and P. E. Branch, Electronic analog computer for measuring intensity areas of peaks. *NBS Tech. Notc* 401, pp. 62–70 (1966).

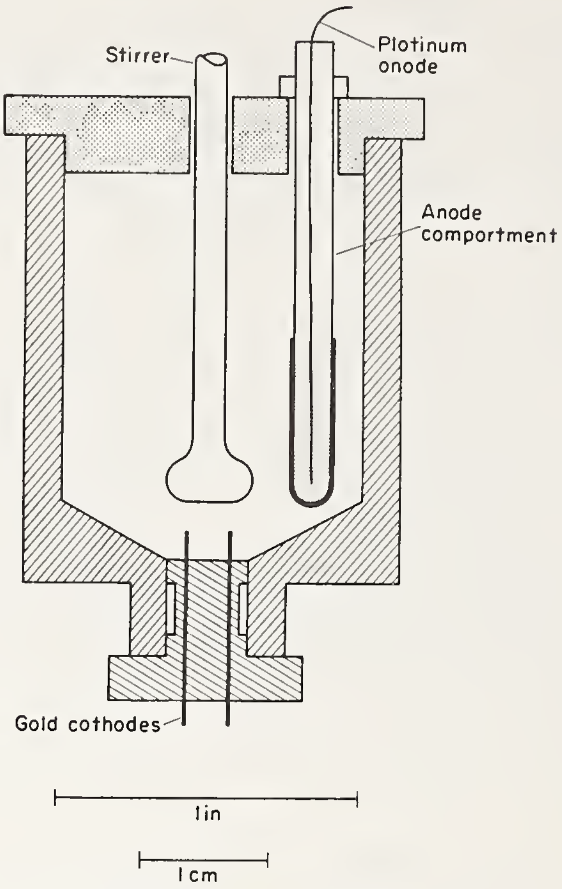

Fig. 1. Electrodeposition cell.

integrator which measures the peak area under the intensity profile. The area thus recorded is proportional to the total number of ions generating the line image.

Preliminary experiments

Since most of the trace elements of interest in the zinc samples are more noble than zinc, electrodeposition was selected as a means of preconcentration. Electrodeposition of a neutralized zinc solution obtained by dissolution of the zinc in HNO_3 yielded a deposit which, when analyzed by SSMS, proved to be mostly zinc containing increased concentrations of the trace elements Ag and Cu. Electrodeposition of a sample obtained by dissolution of the zinc in HCl yielded a zinc deposit with Pb, Tl, Sn, Cd, Ag, and Cu highly enriched over their concentrations in the original zinc sample. For this reason HCl was selected as the solvent.

Procedure

One gram samples of zinc were etched lightly ($<1\%$ removal) in dilute HCl to remove surface impurities, rinsed in distilled water, dried, and weighed. The samples were then dissolved in a minimum volume of HCl (about 4 ml HCl to 1 g of zinc) that had been purified by isothermal distillation. Measured quantities of the separated stable isotopes were added to the zinc samples while they were in the early stages of dissolution. The solution was placed in the electrodeposition cell where the more noble impurities were electrodeposited onto two high purity gold cathodes by passage of a 2 mA current for 2–4 hr. At the end of the electrodeposition period the sample solution was removed and the gold cathodes were washed with distilled water with the cell potential still applied. The gold cathodes were then loaded into the spark source mass spectrograph.

Two plates (Ilford Q-2) were exposed by sparking half the available plated surface area of the gold cathodes for each plate, using a graded series of exposures starting with an integrated beam current of 0.3×10^{-10} coulombs and increasing to 1×10^{-7} coulombs. The electrode surfaces were moved during the exposures to spark as much of the deposit as possible. The combination of electrode movement and increasing exposure levels insured isotope ratio measurements over a wide range of impurity concentration levels as well as optimum usage of all the available sample for elements present in low amounts. The plates were developed in high contrast developer (Kodak D-19) for $2\frac{1}{2}$ min, placed in short stop solution for 10 sec, fixed for 1 min, washed 15 min in tap water and rinsed in distilled water. One plate was selected for isotope ratio measurements based on the level of line intensities and the relative freedom from fog and scratches on the plate. The isotope ratios measured were Pb 208/206*, Tl 205/203*, Sn 120/117*, Cd 112/111*, Ag 109*/107, and Cu 65*/63 (*indicates the stable isotopic spike). In general the ratios of the singly charged ions were measured; however, ratios of multiply charged ions also were measured when appropriate to obtain additional data.

The formula for calculating concentrations is shown in equation (1).

$$\text{ppm (by weight)} = \frac{W\,K\,(A_{\text{sp}} - B_{\text{sp}}\,R)}{M\,(BR - A)} \tag{1}$$

In this equation W is the weight of the stable isotopic spike in μg, M is the weight of the sample in grams, R is the measured "altered" isotope ratio (isotope a/isotope b), K is the ratio of natural atomic weight/atomic weight of the spike, A and B are the natural abundances (atomic fraction) of isotopes a and b, and A_{sp}, B_{sp} are the abundances (atomic fraction) of isotopes a, b in the spike. This is a general equation which applies to elements with two and more isotopes.

Calculation of concentration from the measured isotopic ratios normally requires two additional measured quantities: (a) the weight of the sample and (b) the weight of the separated stable isotope added. The Oak Ridge values for the isotope abundances in the enriched spike, which accompany each spike purchased, and table values of natural abundances were used in calculation. The one exception was for lead, the abundance of which varies in nature [8]. The natural isotopic abundance of the lead in the zinc was measured from SSMS spectra of the original zinc sample.

When the natural ratio of the major isotope to the minor isotope (the spiking isotope) is approximately two or larger the amount of spike isotope added was adjusted to give a final ratio in the spiked sample of close to one. This procedure minimizes the errors in the determination of isotope ratios that may arise from errors in the photographic plate calibration. If the natural ratio is close to one, as is the

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[8] R. D. Russell and R. M. Farquhar, *Lead Isotopes in Geology*. Interscience (1960).

case for silver, the element was spiked to give a ratio of approximately two. An initial spike of the sample was made based on the results of a normal SSMS analysis of the sample. The concentrations found from this spiking were used to calculate the exact amount of spikes to add in order to obtain the optimum isotope ratios for measurement.

Reagent and system blanks were evaluated by adding stable isotopic spikes to a zinc sample of much higher purity and following the same analysis procedure. All elements except tin gave blanks too small to affect the results. An evaluation of the tin blank by this technique was not possible since a direct analysis of the higher purity zinc by the spark source showed it to have almost the same tin content as the samples being analyzed. Blank determinations using the same procedures and volumes of reagents as in a normal determination but without the dissolution of a zinc sample gave inconclusive results.

The time required for carrying out this procedure in practice has been estimated. We assume that reagents, spike solutions, and apparatus have been readied for the analysis and a group of 4–6 samples is to be run. The time required is 2–3 days per sample for the six listed elements, or less than one-half day per element for each sample.

RESULTS

Table 1 gives the results of analysis of the two ends of two zinc bars for silver and tin. The two sets of values listed are from completely independent runs starting with new spiking solutions. After the first set of results for tin was obtained (run 1) there was some concern that sorption losses could have occurred from the solution used to make the tin 117 spike addition. This solution contained 0.04 μg/ml of tin 117 and 1 ml of this solution was added to provide only 4×10^{-8} g of tin 117 to the zinc sample. In the second set of samples (run 2) two modifications were made in order to minimize any possible sorption losses. First, high purity zinc was added to the tin 117 spike to serve as a carrier with 100 parts zinc to 1 part tin. This ratio was selected so that the impurities from this zinc sample would be too low to cause interferences with any of the elements being determined. Second, the tin spike additions were made from a 10-fold higher concentration of tin, 0.4 μg /ml, using only 0.1 ml. All spikes were added to the samples immediately after being diluted from the 0.1 mg/ml working solutions. The agreement between the two sets of tin results indicated that sorption losses were not a problem for either spike concentration. This was further confirmed when the 0.4 μg/ml solution was analyzed by reverse spiking with pure tin and found to be 93% of its original concentration 11 days after it was used to spike the samples.

Three lots of zinc in the form of shot (SRM 728) and both ends of two zinc bars (SRM 683) were analyzed for Pb, Tl, Sn, Cd, Ag, and Cu. Both the shot and the bars were found to be homogeneous for all elements tested within the precision limits of the method. Therefore, the data for each standard were pooled to give an average value.

The analyses of both the zinc bar and the zinc shot by isotope dilution SSMS are given in Table 2. Determinations of Pb, Cd, Cu, and Ag by other techniques are also listed for comparison. The close agreement between the isotope dilution results

Table 1. Independent duplicate determinations of Ag and Sn in zinc SRM 683 (bar form)

	Bar 1		Bar 2	
	End A	End B	End A	End B
	(ppm by wt.)			
Silver				
Run 1	1.18	1.06	1.13	1.02
Run 2	1.14	1.18	1.33	1.25
Average	1.16	1.12	1.23	1.14
Tin				
Run 1	0.019	0.018	0.013	0.016
Run 2	0.023	0.019	0.014	0.016
Average	0.021	0.019	0.014	0.016

Table 2. Comparison of results by isotopic dilution and other analytical techniques for zinc standard reference materials 683 and 728

	SRM 683		SRM 728	
	Isotope dilution SSMS	Other techniques	Isotope dilution SSMS	Other techniques
	(ppm by wt.)			
Lead	11.2 ± 0.5*	10.8†	11.3 ± 0.4	10.8†
Copper	5.6 ± 0.3	6.4†	5.5 ± 0.5	5.8†
Cadmium	1.17 ± 0.09	1.12†	1.13 ± 0.07	1.13†
Silver	1.16 ± 0.12	1.46‡	1.16 ± 0.05	1.09‡
Thallium	$0.17_2 \pm 0.015$		$0.16_3 \pm 0.01_2$	
Tin	0.017 ± 0.001		0.021 ± 0.009	

* The ± values are the 95% confidence limits for the limiting mean expressed in ppm. This is equal to $t_{0.95}S\sqrt{n}$, where S is the standard deviation of the mean and n is the number of independent determinations, ranging from 6 to 8, and t is student's t for 95% confidence.

† Polarography, E. J. Maienthal (NBS).

‡ Neutron activation analysis, B. A. Thompson and D. A. Becker (NBS).

for the two standards for all six elements arises from the fact that both were produced from a common lot of zinc. This agreement is also a measure of the precision of the isotope dilution technique. Good agreement was found with the other methods of analysis for all determinations except the Cu and Ag in SRM 683. These differences on Cu and Ag are not excessive considering the low concentrations involved. It should be noted that isotope dilution SSMS provided values for six of the seven elements that were certified for these two standards.

DISCUSSION

Preconcentration

Measurement of the isotopic ratios for the impurities in the zinc without the electrodeposition–preconcentration step is a possibility. Direct evaporation of the zinc chloride solution onto high purity gold wires might serve this purpose; however, the amount of sample on the surface of the gold wires would be relatively small compared to that available when zinc metal is sparked directly. Larger samples could be loaded but this would probably involve pelletizing large amounts of zinc chloride with a high purity conducting powder (Ag, Au, graphite, etc.); this binder would in effect dilute the zinc chloride sample. Either system of loading the sample for SSMS measurement of isotopic ratios would result in poorer sensitivity for the isotope dilution analysis than would exist in a direct analysis of the metal by SSMS. It is estimated that sample evaporation onto gold wires would give detection limits of about 1–10 ppm for isotope dilution as compared to 1–10 ppb found for a direct SSMS analysis.

The chloride ions introduced in the dissolution step act to dilute the zinc sample as well as to introduce additional lines into the mass spectrum. An example of the complications that these additional lines could cause was observed when the electrodeposition procedures were being investigated. Zinc plated electrodes which were not washed with distilled water retained sufficient zinc chloride on their surfaces to contribute significantly to the spectrum. The mass spectra of these samples contained lines for $ZnCl^+$, $ZnOCl^+$, and $ZnClOH^+$, as well as Cl^+. The $ZnOCl^+$ lines were intense enough to interfere with the tin lines which have the same nominal mass. Washing the electrodeposit with distilled water removed this interference. Electrodeposition thus served two functions: it removed the chloride interferences and it increased the sensitivity of the method. Preconcentration in part compensates for the sensitivity lost because of the sample dissolution which is necessary to perform the spiking step.

Preconcentration of a 10 ppb impurity from a 1 g sample into a consumable sample size of about 10 mg or less would provide 1×10^{-8} g of the impurity. This is 1000 times the 1×10^{-11} g that gives a just detectable line and should give sufficient signal for measuring isotopic ratios on several exposures with reasonable precision. These figures would predict quantitative determinations down to 10 ppb for most elements with preconcentration, provided of course that reagent and system blanks did not set a higher limit. In our experiments a comparison of the line intensities obtained from direct SSMS analysis of the zinc metal to those from the samples preconcentrated onto the gold electrodes indicates that electrodeposition results in a 1000 fold increase in the trace element concentrations in the zinc deposit. From the intensities of the lines obtained for the different elements reported it has been concluded that all six elements could have been determined at the 20 ppb level that was found for tin, and with comparable precision.

The electrodeposition technique applied to the preconcentration of the impurities in the zinc represents one of the simplest possible separation methods. No chemical other than the easily purified HCl required to dissolve the zinc sample was used. Little physical handling was involved in the process. These conditions plus the fact that all the impurity elements determined were separated from a single sample simultaneously should keep the sample contamination (blank level) to a minimum. Modifications of this method should be applicable to preconcentration from most active metals. More complex preconcentration procedures have also been used successfully for isotope dilutions SSMS analysis. In a separate investigation [9] five elements were preconcentrated from a platinum matrix using a cation exchange column to separate these impurities from the platinum complexed as a chloride anion. All five elements were determined simultaneously with the concentration ranging from 0.5 to 14 ppm by weight.

The six trace elements determined in zinc represent a range of more than 500 (Sn to Pb) in concentration for elements that could be simultaneously determined from a single sample. There is of course no upper limit on the concentrations that could be covered by isotope dilution, and it should therefore be possible to simultaneously determine elements from a single sample over a concentration range from the ppb level to the per cent level. The ppb to ppm range, however, will encompass the levels where this technique should prove most useful.

Comparison to other mass spectrometric methods

SSMS analysis by direct comparison to a standard reference material must be carefully controlled in order for the precision of the measurements to approach the photographic plate limiting value of 3–5% relative standard deviation. The precision is normally affected by the variations in the amount of the impurity elements reaching the plate from one exposure to the next. These variations can arise from inhomogeneities in the sample on a micro scale, changes in the point of sparking with respect to the "optical" axis of the instrument, distance between sample electrodes, rf and dc voltages of the instrument, etc. None of the factors however, have any detectable effect on the measured isotopic ratio for an element; but only affect the absolute amount of the impurity measured. The precision of the analysis by stable isotope dilution SSMS is therefore independent of the forementioned instrumental factors and is controlled only by the limitations of the photographic plate. Isotope dilution analysis could therefore be expected to give better precision than that of direct analysis by SSMS.

The comparison of spark source to thermal ion source mass spectrometry for analysis by stable isotope dilution is of interest. Thermal ion instruments can measure isotopic ratios of many elements with precisions of 0.01% relative standard deviation while the photographic plates used by SSMS limits its precision to about 3% at best. In an actual analysis the difference in precision will be less than indicated by the ability to measure isotope ratios since the precision of a determination will also be affected by other factors such as sample homogeneity relative to the amount of sample dissolved for spiking, the accuracy of spike additions, reproducibility of blanks, etc. The sensitivity of SSMS is relatively independent of the ionization potential of an element. Sensitivity varies markedly with ionization potential for a thermal ion source; its sensitivity is substantially better than the SSMS for low ionization potential elements, but is much poorer for the elements with high ionization potentials.

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[9] R. Alvarez, P. J. Paulsen and D. E. Kelleher, *Anal. Chem.*, **41**, 955 (1969).

Thus, the spark source can extend the range of elements determined by stable isotope dilution to elements not attainable with the thermal ion source instrument, but would not be competitive for the other elements if precisions of better than 3–5% are needed. If the analysis requirements or blank problems make this precision acceptable, the ability to analyze for many elements simultaneously, over wide ranges in concentration, gives the spark source a definite advantage.

SUMMARY

Isotope dilution spark source mass spectrographic analysis when combined with preconcentration techniques has yielded reliable determinations, down to the 20 ppb level. A comparison of isotope dilution determinations to those of polarography and neutron activation has shown good agreement for the trace elements. This technique gives absolute values without the use of a reference standard and therefore should be particularly applicable to the analysis of standard reference materials that are needed for direct trace analysis by SSMS. The recording of the entire mass range by SSMS on each exposure makes it possible to determine a large number of elements simultaneously from a single sample. This not only represents a saving of time for the analysis but also allows for simple methods of preconcentration which should minimize reagent blanks. The nearly constant detection sensitivity of SSMS for all elements would predict that most elements should be measureable at the 20 ppb level found for tin, providing, of course, that preconcentration can be accomplished and blanks do not set higher limits of detection. This should be particularly important for elements with high ionization potentials where, in general, isotope dilution analysis using thermal ion sources is not possible. The preconcentration procedure adopted here for the determination of trace elements in zinc should be applicable to most other active metal matrices.

APPENDIX IX

Spark Source Mass Spectrographic Analysis of Ingot Iron for Silver, Copper, Molybdenum, and Nickel by Isotope Dilution and for Cobalt by an Internal Standard Technique

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A NUMBER of trace elements are known to significantly affect the properties of ferrous materials. As compositions are being changed to meet the need of new applications, additional trace elements are becoming important. The increased interest in these trace elements makes it desirable to provide more reliable methods for their determination by using new analytical instrumentation and techniques. Analysis by isotope dilution spark source mass spectrometry (ID-SSMS) enables many trace elements in a matrix to be determined simultaneously with high sensitivity and precision (*1*, *2*). Moreover, the methods do not require a quantitative recovery or even a determination of the recovery. Because of the inherent high sensitivity of the spark source mass spectrograph, simplified separation procedures that have low recoveries but are relatively contamination-free can be used. Contamination is often the limiting factor in reliable trace determinations.

The object of this investigation was to develop an ID-SSMS method for simultaneously determining trace amounts of silver and other elements in ingot iron, a matrix having a greater number of elements at higher concentrations than the high-purity platinum (*1*) and zinc (*2*) analyzed previously. In this method, silver, copper, molybdenum, nickel, and cobalt were satisfactorily electrodeposited onto gold wire electrodes after extracting the iron from a solution of ingot iron, NBS-SRM 1165. The aqueous layer had been neutralized before electrolysis. By spiking the sample solution with known amounts of enriched isotope solutions, the elements Ag, Cu, Mo, and Ni could be determined. Co, a mononuclidic element, was also determinable because of its chemical and electrochemical similarity to Ni.

EXPERIMENTAL

Reagents. Deionized water was prepared by passing distilled water from the laboratory distribution system through a mixed bed resin column. Hydrochloric and nitric acids, previously prepared by isothermal distillation and stored in quartz flasks, were used for sample dissolution. Ammonia gas was bubbled into a gas washing bottle and then into deionized water to produce aqueous ammonia. Reagent grade isopropyl ether, with a reported boiling range of 67.8 to 69.0 °C and a nonvolatile matter content of 0.003%, was shaken before use with an equal volume of 7*M* HCl in a separatory funnel. Enriched isotope materials, in amounts equivalent to 10 mg of the element, were obtained from the Oak Ridge National Laboratory. Spike solutions containing one mg per ml of ^{109}Ag, ^{65}Cu, ^{62}Ni, and ^{97}Mo were prepared by weighing each material to ±0.02 mg, dissolving it in nitric acid, adding aqueous NH_3 to the Mo solution, and diluting each solution to volume in a 10-ml volumetric flask. Standard solutions of natural Ag, Cu, Ni, Mo, and Co were similarly prepared by weighing 100 mg of each high-purity metal to ±0.05 mg, dissolving in ACS reagent grade nitric acid, adding aqueous NH_3 to the Mo solution, and diluting the solutions to volume in 100-ml volumetric flasks.

Evaporator for Sample Solutions. The borosilicate glass chamber, which uses filtered nitrogen to prevent entry of particulate contaminants and provides a clean environment, has been described previously (*1*). It is similar to that described by Thiers (*3*).

Electrolysis Cell. The polytetrafluoroethylene cell, which has two 0.7-mm diameter high-purity gold wire cathodes and an isolated anode compartment, has been described in detail previously (*1*).

Mass Spectrograph. The double-focusing Mattauch-Herzog design, Spark Source Mass Spectrograph and the microphotometer with its analog computer have been described previously (*1*).

Procedure. Approximately 100-mg samples of ingot iron, NBS-SRM 1165, were weighed to 0.1 mg and introduced into 30-ml borosilicate beakers. The ^{109}Ag, ^{65}Cu, and ^{62}Ni solutions were diluted and combined to make a multiple-spike solution having elemental concentrations ranging from 7 μg/ml for Cu, to 0.3 μg/ml for Ag. The ^{97}Mo solution was diluted to 3 μg/ml. Immediately after preparing these solutions, 2 ml of 7*M* HCl were added to each of the beakers. While the samples were dissolving, 1 ml of the multiple-spike solution and 100 μl of the diluted ^{97}Mo solution were pipetted into the beakers. In addition, for future verification of the elemental concentrations in the multiple and diluted ^{97}Mo spike solutions, aliquots of these solutions were combined with solutions containing known amounts of the natural elements. The Co solution was diluted to 50 μg/ml and 250 μl of this solution were pipetted into half of the sample beakers. The covered beakers were heated to dissolve the samples and several drops of HNO_3 were added. The solutions were then evaporated to dryness in the clean-environment chamber and the resulting residues were dissolved by adding 9 ml of 7*M* HCl to each beaker and warming.

The solutions were cooled in an ice bath and introduced into 60-ml separatory funnels. Each beaker was rinsed twice with 0.5 ml of 7*M* HCl and the washings were added to the appropriate separatory funnel. Ten milliliters of cold isopropyl ether was added to each separatory funnel and the iron was extracted into the ether layer by shaking for one minute. The aqueous layer containing the isotopically altered analytes was withdrawn into the original beaker used for sample dissolution. The extraction step was repeated using the same ether which had been back-extracted with two 10-ml portions of water to remove the iron and shaken with 7*M* HCl. The aqueous layer was then transferred to the original beaker, and evaporated to 2–3 ml in the clean-environment chamber. Aqueous NH_3 was added until a precipitate formed from the residual iron remaining in solution. The solution was then heated to remove excess NH_3, transferred to the electrolysis cell, and electrolyzed for 3 hrs

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(1) R. Alvarez, P. J. Paulsen, and D. E. Kelleher, ANAL. CHEM., **41**, 955 (1969).

(2) P. J. Paulsen, R. Alvarez, and D. E. Kelleher, *Spectrochim. Acta*, **24B**, 535 (1969).

(3) R. E. Thiers in "Trace Analysis," John H. Yoe and H. J. Koch, Eds., John Wiley and Sons, Inc., New York, N. Y., 1957, Chap. 24.

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Table I. Average Concentrations in Ingot Iron NBS-SRM 1165 Determined by Spark Source Mass Spectrometry Compared to NBS Certified Values

		Concentration (% by weight)	
Element	Method	This work[a]	NBS certified values[b]
Ag	Isotope dilution	0.00050 ± 0.00003	...[c]
Cu	Isotope dilution	0.0172 ± 0.0008	0.019
Ni	Isotope dilution	0.0247 ± 0.0009	0.026
Mo	Isotope dilution	0.0042 ± 0.0003	0.005
Co	Standard addition	0.0092 ± 0.0013	0.008

[a] Uncertainty is expressed as 95% confidence limits on the limiting mean $t_{0.95}S/\sqrt{n}$. For Ag, Cu, Ni, and Mo, the value includes uncertainties associated with the variations among the individual samples and the analysis of the spike solution. For Co, it includes the variations in the concentrations computed from Equation 2 and the variations in determining R_1.

[b] These values are considered reliable to ±1 in the last digit.

[c] Not certified.

at 4 mA while stirring at 200 rpm. After withdrawing the solution, the gold electrodes were rinsed by introducing approximately 7 ml of water into the cell and stirring.

The pair of electrodes was sparked in the mass spectrograph and a graded series of exposures was made from 3×10^{-13} to 1×10^{-8} coulomb. The ion-sensitive photographic plates (Ilford Q-2) were processed using the bleach and internal image developer MK-7 described by Cavard (*4*). They were placed in the dichromate bleach for 4 minutes, rinsed in water for $^1/_2$ min, developed for 7 min, fixed for 1 min, and washed for 15 min. The intensity areas of the lines on the photographic plate for the elements were measured and the ^{109}Ag/^{107}Ag, ^{66}Cu/^{68}Cu, ^{62}Ni/^{60}Ni, and ^{97}Mo/^{96}Mo ratios were determined for all samples. The ^{59}Co/^{58}Ni ratios were also determined for samples with added Co, and the ^{59}Co/^{60}Ni ratios determined for samples without the Co addition. From 6 to 14 ratio measurements were made for each element depending on the availability of lines having suitable intensity.

To correct the determinations for contamination, the entire analytical procedure was performed under the same experimental conditions using the same quantities of reagents and 5 mg of high-purity iron. To obtain more favorable isotope ratios, the iron was spiked with one-tenth of the amounts added to the ingot iron samples and both materials were analyzed concurrently. The blanks were found not to exceed 2% of the reported values.

To verify the elemental concentrations in the multiple-spike and diluted ^{97}Mo solution, aliquots of the solutions that had been reserved for this purpose were pipetted into the polytetrafluoroethylene electrolysis cell. After electrolyzing the stirred solutions for 3 hours at a current of 4 mA, the gold wire electrodes were sparked in the mass spectrograph. Except for Mo, the altered isotope ratios were measured and the spike weights computed from Equation 1. The isotope lines of Mo were too weak to be measured and therefore an evaporation procedure was used. Approximately 0.5 ml of the combined diluted ^{97}Mo and natural Mo solution was evaporated to one tenth of the volume in a quartz crucible. The evaporated solution was pipetted onto gold wires and dried. After sparking the wires in the mass spectrograph, the ^{97}Mo spike weight was computed from the measured isotope ratios.

CALCULATIONS AND RESULTS

The concentrations of Ag, Cu, Mo, and Ni were computed from Equation 1

$$C = \frac{WK(A_{sp} - B_{sp}R)}{M\,(BR - A)} \tag{1}$$

were C is the concentration in μg/g, W is the weight of isotopically enriched material (spike) added in μg, M is the weight of sample in grams, A and B are the natural abundances of the analyte isotopes a and b, A_{sp} and B_{sp} are the abundances of isotopes a and b in the spike, R is the measured altered ratio of isotope a to isotope b, and K is the ratio of the natural atomic weight to the atomic weight of the spike.

The spike isotopes provided by Oak Ridge National Laboratory were all highly enriched; the abundances of the isotopes ^{109}Ag, ^{66}Cu, ^{97}Mo, and ^{62}Ni being 99.1, 99.7, 92.8, and 99.0 atomic per cent, respectively. The quoted accuracy of the abundances was such that errors from this source do not significantly affect our results.

To minimize the effect of photographic emulsion calibration errors, it is desirable in determining R to measure isotope lines that have approximately the same intensity. This was done for all elements except silver. Silver has only two naturally occurring isotopes, ^{109}Ag and ^{107}Ag, which have almost the same abundance. Therefore, an amount of ^{109}Ag spike was added to change the value of the ^{109}Ag/^{107}Ag ratio to 2.

Table I lists the average concentrations for Ag, Cu, Mo, and Ni obtained by isotope dilution, the 95% confidence limits, and a comparison of the results with the NBS certified values. The results were derived by running ten samples, in two groups of five. Separate spike solutions were prepared and added to each group. The individual results from each group did not vary significantly and therefore the data could be pooled for statistical evaluation.

In addition to the elements being determined by isotope dilution, cobalt, a mononuclidic element, was also found to be electrodeposited on the gold electrodes. Because of the similar chemical and electrochemical behavior of cobalt and nickel, it was postulated that both elements would be preconcentrated on the electrodes with a constant relative recovery. To test this hypothesis, the ratios of the ^{69}Co to ^{60}Ni line intensities were measured on each exposure together with the altered isotope ratios used for the isotope dilution determinations of Ag, Cu, Mo, and Ni. The ratios were found to be constant among the samples. We concluded that under these experimental conditions, Ni would serve as an internal standard to monitor the recovery of Co which could vary from sample to sample. Co would then be determinable by a standard addition of Co. The ratio of the ^{59}Co to ^{58}Ni line intensities were determined for each sample having a known and constant amount of Co added. By using the more abundant ^{68}Ni instead of the ^{60}Ni, a ^{59}Co/^{58}Ni ratio approximating unity could be obtained by adding the appropriate amount of Co.

An average ^{59}Co/^{60}Ni ratio, R_1, of 1.04 ± 0.05 was obtained for seven samples without added cobalt. The cobalt content, Co(s), of a sample was computed from the following equation:

$$\mathrm{Co}(s) = \frac{\mathrm{Co}(a)\, R_1\,{}^{60}\mathrm{Ni}}{R_2\,{}^{58}\mathrm{Ni} - R_1\,{}^{60}\mathrm{Ni}} \tag{2}$$

where R_2 is the measured ^{69}Co/^{68}Ni ratio for a sample with added cobalt, Co (*a*) is the added cobalt, and ^{60}Ni, ^{68}Ni are the nickel contents including the small amounts added with the ^{62}Ni spike. All concentrations are in μg-atom/gram of ingot iron. The average of six determinations of Co, the 95%

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(4) A. Cavard in "Advances in Mass Spectrometry," E. Kendrick, Ed., The Institute of Petroleum, London, 1968, pp 419–429.

confidence limits, and the NBS certified value are given in Table I.

Recovery Experiments. One of the advantages of the isotopic dilution technique of analysis is that only enough spiked sample required for an accurate isotope ratio determination need be recovered from the original sample. A knowledge of the recovery efficiencies is not required for computation of results of analysis. The efficiency of recovery of a preconcentration technique however, is of interest because the amount of recovery will effect the detection limits for the method. Experiments were performed in order to determine the recovery for the procedures up to and including the electrodeposition step.

A set of samples was run using the previously described experimental procedure but omitting the spike additions. For comparison, electrodeposition periods of one hour were also used in addition to the 3-hour periods used in the procedure. The material recovered on the high-purity gold cathodes was redissolved in 0.2 ml of warm HNO_3, spiked with the stable isotopes, and neutralized with aqueous ammonia. The recovered trace elements were then electrodeposited onto the same gold electrodes. The electrodes were sparked in the SSMS and the amounts of material recovered on the electrodes were computed from Equation 1. This procedure gave results for Ag, Cu, and Ni; however, Mo could not be detected in this second plating.

Increasing the plating time from one to three hours increased the total recovery for Ag, Cu, and Ni from 20 to 40%. The high sensitivity of the spark source mass spectrograph method is illustrated by realizing that only 0.2 μg of silver on the gold electrodes was more than adequate for the determination of silver.

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APPENDIX X

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Trace Element Determinations in a Low-Alloy Steel Standard Reference Material by Isotope Dilution, Spark Source Mass Spectrometry*

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A stable isotope dilution procedure using the spark source mass spectrograph was developed for the simultaneous determination of cerium, copper, neodymium, selenium, silver, tellurium, and zirconium in a low-alloy steel material. Except for copper, the elements were present at trace concentrations that are difficult to determine by most analytical methods. In the procedure, known amounts of the isotopically enriched elements were added to 100-mg samples, which were dissolved in perchloric and hydrofluoric acids. After evaporation of the solutions almost to dryness, dissolution of the residues, and addition of hydrofluoric acid

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* Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

to complex the iron, the resulting solutions were electrolyzed in polytetrafluoroethylene cells. The electrodeposit on high purity, gold cathode wires was sparked in the mass spectrograph and the isotope ratios of the isotopically equilibrated elements were measured. The concentrations, ranging from 0.041% for copper to 3.1 μg/g (ppm) for neodymium, were calculated from the general isotope dilution equation. The low-alloy steel is available from NBS as Standard Reference Material 1261.

Index Headings: Analysis, for trace elements; Mass spectroscopy, spark source; Methods, analytical.

INTRODUCTION

A set of low-alloy steel Standard Reference Materials (SRMs) was issued by the National Bureau of Standards in 1957 primarily for use in optical emission and x-ray spectrometric methods of analysis. At that time, several trace elements present in this set were not certified either because they were at extremely low concentrations or because they were generally regarded as having an innocuous effect on the physical properties of steel. Consequently, the anticipated benefits of providing certified values for these elements would not have justified the cost of developing analytical methods having the requisite reliability.

Since this set of SRMs was issued, new applications of ferrous products, mainly for the nuclear and aerospace industries, have necessitated more stringent specification limits and quality control determinations of additional trace elements. Coinciding with an increased interest in the effects of trace elements on the properties of ferrous materials has been the increased use of spark source mass spectrometry as a powerful tool for estimating the concentration of nearly every element in a sample down to a few nanograms per gram (parts per billion). However for reliable quantitative determinations, SRMs were needed having certified values for the trace elements of interest and having concentrations of the major constituents, similar to those of the samples being analyzed.

A new set of iron and low-alloy steel SRMs was made in the late 1960's to replace the earlier set. The SRMs were fabricated in the form of rods, 3.2 mm in diameter by 51 mm long, for spark source mass spectrometry and microchemical techniques as well as in the form of 32-mm diameter discs for x-ray and optical emission spectrometry. This replacement set was intended to provide concentration ranges for approximately 40 elements.

Certification of the trace elements in these materials required sensitive and reliable methods. Moreover, for the efficient characterization of these materials with respect to trace elements, analytical methods that would yield results for a number of elements simultaneously were desirable. Isotope dilution procedures using the spark source mass spectrograph (ID-SSMS) has been found to meet these requirements.[1-3]

The object of this investigation was to develop an ID-SSMS method for determining a number of analytically difficult trace elements such as selenium, tellurium, and neodymium in a low-alloy steel material SRM. In a previous application of an ID-SSMS method to a ferrous material, copper, molybdenum, nickel, and silver had been determined in an ingot iron, SRM 1165.[3] Although the low-alloy steel material was a more complex matrix than the ingot iron, a relatively simple ID-SSMS procedure was developed which enabled a number of chemically diverse elements to be determined simultaneously.

I. EXPERIMENTAL

A. Reagents and Special Solutions. Deionized water was prepared by passing distilled water from the laboratory distribution system through a mixed-bed, resin column. Commercially produced, high purity, perchloric and hydrofluoric acids were used for sample dissolution; similar high purity sulfuric, nitric, and hydrochloric acids were used for preparing solutions of the enriched isotope materials (spikes) and natural elements. The purity of the perchloric, nitric, and hydrochloric acids had been evaluated previously by an ID-SSMS procedure developed by the authors.[4] Materials, isotopically enriched with respect to ^{145}Nd, ^{142}Ce, ^{125}Te, ^{109}Ag, ^{91}Zr, ^{82}Se, and ^{65}Cu, were obtained from the Oak Ridge National Laboratory. The isotopic abundance, which was the highest available at the time of purchase, was at least 89 atomic percent. Each spike solution was prepared to contain 1 mg/ml of the element by weighing the spike material to ±0.02 mg, dissolving it in the appropriate acid, and diluting the solution to volume in a 10-ml volumetric flask. A standard solution of each natural element under investigation was prepared by weighing 100 mg of the high purity metal to ±0.05 mg, dissolving it in the appropriate acid, and diluting the solution to volume in a 100-ml volumetric flask. For cerium and neodymium, the equivalent weight of oxide was used.

B. Evaporator for the Sample Solution. The evaporator is similar in function and design to the borosilicate glass unit previously described[1,5] except that the principal components are constructed of polytetrafluoroethylene (TFE) and translucent fluorinated copolymer (TFE-FEP). The 14.5-cm diameter TFE base is 13 mm thick and has four cylindrical cavities into which 30-ml TFE-FEP beakers fit snugly. The 10-mm deep cavities are 90° apart with centers on a 3.5-cm diameter radius. A 12.5-cm diameter by 9.0-cm high cover of TFE-FEP fits tightly into a cylindrical groove in the base. Near the top of the cover are two 8-mm diameter TFE tubes, which are press-fit into holes approximately 180° apart. Filtered air enters the apparatus through one of the tubes to remove the acid vapors and prevent entry of particulate contaminants.

C. Electrolysis Cell. The TFE electrolysis cell consists of two parts: a cylindrical body and a base. The cell body has a 33-mm height, a 17-mm inside diameter, and a 3-mm wall thickness. The base makes a liquid-tight fit into the cell body and has four holes, 90° apart, on a 12-mm diameter circle. The holes are drilled undersize for inserting 0.9-mm diameter high purity gold wire electrodes. The gold wire had been examined by direct sparking in the mass spectrograph for the presence of impurities that could affect the measurements. None were found. The overall purity was determined to be comparable to that of the high purity gold, SRM 685.[6] The ends of the four wires are dipped in aqua regia, rinsed in water, and adjusted to project approximately 2 mm into the cavity of the assembled cell. Two opposite wires serve as the cathode; the other two as the anode. During electrodeposition, the solutions in the cells are stirred with TFE stirrers at approximately 200 rpm. The cells are housed in a plastic enclosure under a slight positive pressure of nitrogen to minimize airborne contamination.

D. Mass Spectrograph. A double-focusing, Mattauch-Herzog design, spark source instrument (Consolidated Electrodynamics model 21-110) that had been modified to give 22 exposures per plate is operated at an ion accelerator voltage of 24 kV. The ion-source sample chamber is evacuated with a high-speed, high-conductance ion pump having added titanium sublimation. A pressure of 7×10^{-5} Pa (5×10^{-7} Torr) can be obtained in approximately 20 min after loading a sample into the chamber. Less than 60 min is required to attain a pressure in the range of 10^{-6} Pa (10^{-8} Torr). The pressure is measured using an ion gauge mounted directly in the ion source chamber. The chamber containing a sample from the isotope dilution procedure is evacuated to a pressure of less than 1×10^{-5} Pa (1×10^{-7} Torr) before sparking. The high conductance and speed of the pumping system maintains pressures in the 10^{-5} Pa (10^{-7} Torr) range during sparking even when relatively large amounts of gas are being released.

E. Microphotometer-Analog Computer. A microphotometer having a precision screw (Jarrell Ash model 23-500) and equipped with an analog computer to measure peak areas[7] is used. A function generator, which is the basic component of the analog computer, provides an output proportional to relative intensities when the input is a voltage proportional to percent absorption. An integrator follows the function generator to give signals proportional to peak intensity areas as the line is scanned.

F. Procedure. A preliminary analysis of the steel sample was performed during the initial development of the isotope dilution procedure. The elemental concentrations determined were used to calculate the amount of spike isotope necessary to obtain an optimum altered isotopic ratio, which for the elements of interest except silver is 1. An altered isotopic ratio of approximately unity is desirable because it will minimize the effects of any errors in the calibration curve for the photographic plate and will usually yield the maximum number of measurable isotopic ratios. Silver, which has a natural isotopic ratio of approximately one, was spiked to yield an altered isotopic ratio of 2.

In the final procedure, a 100-mg sample was weighed to ±0.1 mg and transferred to a 30-ml TFE-FEP beaker. The beaker was covered with a TFE lid. Aliquots of spike solutions having compatible ions were combined and diluted in volumetric flasks. Immediately after preparing these solutions, 2 ml of 6 *M* $HClO_4$ and 0.5 ml of 26 *M* HF were added to the sample. While the sample was dissolving, known volumes of the spike solutions were added using calibrated plastic pipets. At the same time, aliquots of the spike solutions were mixed with solutions containing known amounts of the natural elements for future verification of the spike concentrations.

The beaker was then heated to completely dissolve the sample, transferred to the evaporator, and heated further until $HClO_4$ fumes were observed. After adding 0.5 ml of 26 *M* HF, the contents of the beaker were heated almost to dryness. The residue was dissolved and the iron was complexed by adding 2 ml of H_2O and 0.5 ml of 26 *M* HF, and heating the beaker. The solution was then electrolyzed for 4 h at a constant current of 6 mA while being stirred at 200 rpm. The solution was withdrawn and the electrodes were rinsed in water.

The electrodeposit on the ends of the gold wire electrodes was sparked in the mass spectrograph and a graded series of exposures was made from 3×10^{-13} to 1×10^{-8} C. The ion-sensitive photographic plates (Ilford Q-2) were processed using the bleach and internal image developer MK-7 described by Cavard.[8] They were placed in the dichromate bleach for 4 min, rinsed in water for ½ min, developed for 7 min, fixed for 1 min, and washed for 15 min. For all elements except zirconium, intensity areas of both measured isotopes of an element were determined on each suitable exposure using the microphotometer-analog computer. Maximum peak intensities, corrected for background, were measured for zirconium. The isotopic masses measured for each element are: Ag 107, 109; Ce 140, 142; Cu 63, 65; Nd 144, 145; Se 80, 82; Te 126, 125; and Zr 90, 91. The second mass listed for each element is the spike isotope; the first mass is usually the isotope of highest abundance in the naturally occurring element.

In general, the ratios of the singly charged ions were measured, but ratios of the multiply charged ions were also measured when appropriate to obtain additional data or to avoid interferences existing at the singly charged lines.

The individual elemental concentrations were calculated from the measured altered isotopic ratios (R) using Eq. (1).

$$C = \frac{WK(A_{sp} - B_{sp}R)}{M(BR - A)} \qquad (1)$$

where *C* is the concentration in micrograms per gram, *W* is the weight of isotopically enriched material (spike) added in micrograms, *M* is the weight of sample in grams, *A* and *B* are the natural abundances of the analyte isotopes a and b, A_{sp} and B_{sp} are the abundances of isotopes a and b in the spike, *R* is the measured altered ratio of isotope a to isotope b, and *K* is the ratio of the natural atomic weight to the atomic weight of the spike.

The spike concentrations in the solutions that had been added to the samples were verified by preconcentrating the isotopically equilibrated elements from the solution that had been reserved for this purpose, determining the isotopic ratios, and calculating *W* in Eq. (1). Two preconcentration procedures were used: electrolysis using the experimental procedure described for the sample, and evaporation of separate aliquots of the solution onto high purity gold wires after which the wires were ignited at 450°C for 30 min. The evaporation procedure enabled us to obtain data for elements that had not been electrodeposited satisfactorily.

The method blank was determined by performing all of the steps in the procedure using the same quantities of acids but smaller quantities of the spikes.

II. DISCUSSION AND RESULTS

The graded series of exposures used in the analysis was selected to obtain the optimum sensitivity for elements at concentration levels down to 1 $\mu g/g$ (ppm). Among other considerations, the selection of isotope lines and charge states was based on the required sensitivity and potential interferences. Some of the specific considerations for the determined elements are listed below.

1. *Copper.* Because of the high copper concentration, 0.041%, in the sample, the exposures produced Cu^+ lines, most of which were too dark to be measured reliably. Therefore, the Cu^{2+} and Cu^{4+} isotopic ratios were also measured to obtain an adequate number of ratios. For these charge states, both ^{63}Cu and ^{65}Cu isotopes occurred at fractional mass/charge positions, and therefore were free of interferences from +1 ions occupying unit mass positions in these m/e regions.

2. *Selenium.* Copper-containing samples normally yield lines at mass positions 79 and 81 corresponding to $[CuO]^+$, and less intense lines at 80 and 82 corresponding to $[CuOH]^+$. If $[CuOH]^+$ lines exist, they can interfere with the determination of the isotopic ratio, $^{82}Se/^{80}Se$, when the singly charged ions are used. This potential interference was indicated by faint lines of $[CuO]^+$ being present at mass positions 79 and 81. Because molecular species, such as $[CuOH]^+$ will not form stable multiply charged ions, the +3 charge states of the selenium isotopes were measured to obtain the isotopic ratio. Consequently, these measurements, at fractional m/e positions, were also free of interferences by any molecular species. Concentrations calculated from the Se^+ and Se^{3+} isotopic ratios were in agreement, indicating that $[CuOH]^+$ did not in fact significantly interfere with the Se^+ measurements.

3. *Zirconium.* Each of the zirconium isotope lines had a faint line on the high mass side, which was attributed to hydrocarbons and could not be resolved when measuring the customary intensity areas. Because the contribution of the hydrocarbon line to the center of each Zr isotope line was essentially zero, the maximum peak intensity, corrected for background, was measured for each isotope line. Measurements of maximum peak intensity are not as sensitive as those of intensity area. However, the electrodeposited Zr yielded a signal of sufficient intensity for satisfactory precision with either mode of measurement.

4. *Silver.* Both the +1 and +2 ions were measured for the ^{107}Ag and ^{109}Ag isotopes to obtain an adequate number of isotopic ratios.

TABLE I. Selenium concentration in sample 1, NBS-SRM 1261, low-alloy steel calculated from replicate exposures.

Exposure No.	^{82}Se intensity area	^{80}Se intensity area	Concentration in % by wt
6	713	825	0.003598
7	603	710	0.003682
8	387	470	0.003838
9	336	377	0.003455
10	378	479	0.004064
11	367	440	0.003772
12	333	402	0.003822
Average			0.00375
Relative standard deviation			5.2%
95% confidence limits of the mean			0.00018

TABLE II. Average selenium concentrations determined in test samples of NBS-SRM 1261, low-alloy steel.

Sample	Concentration in % by wt
1	0.00375
2	0.00350
3	0.00360
4	0.00373
5	0.00370
6	0.00352
7	0.00366
Average	0.0036
95% confidence limits of a single determination	0.0002

TABLE III. Results obtained by ID-SSMS for seven elements determined simultaneously in NBS-SRM 1261, low-alloy steel.

Element	Average concentration in % by wt	95 % confidence limits of a single determination	No. of samples
Copper	0.041	±0.0020	7
Zirconium	0.0071	±0.0011	5
Selenium	0.0036	±0.0002	7
Cerium	0.0015	±0.0001	7
Tellurium	0.0007	±0.0002	5
Silver	0.00036	±0.00004	5
Neodymium	0.00031	±0.00002	6

5. *Tellurium.* The singly charged ions were used to determine the isotopic ratios from which the concentration was calculated.

6. *Cerium.* The ^{142}Ce isotope line used in determining the isotopic ratio also has a contribution from ^{142}Nd present in the sample. This contribution was calculated for each exposure from a measured ^{144}Nd intensity and the natural isotopic ratio, $^{142}Nd/^{144}Nd$. This correction of the intensity area at mass position 142 was always less than 10% of the total area because of the low concentration of Nd compared to Ce in the sample and the relatively low abundance of the ^{142}Nd isotope.

7. *Neodymium.* Singly charged ions were used to determine the altered isotopic ratio.

A computer program was developed, incorporating Eq. (1), that provides a print-out of concentration values for each pair of intensity area measurements without printing the values of R used in the calculations. The program also gives an average concentration and a statistical analysis of the data.

As an example of the data, Table I shows the ^{82}Se and ^{80}Se intensity areas that were measured for a series of exposures, and the selenium concentrations calculated for each pair of intensity areas. The average concentration of selenium in samples 1, the relative standard deviation, and the 95% confidence limits of the mean are also shown. Table II shows the average selenium concentration in each test sample, and the 95% confidence limits of a single determination.

Table III shows the results obtained by ID-SSMS, for

TABLE IV. Comparision of results by ID-SSMS with other methods of analysis for NBS-SRM 1261, low-alloy steel.

Element	Average concentration in % by wt	Analytical method
Copper	0.041	ID-SSMS
	0.043	Neutron activation
	0.042	Isotope dilution, thermal ion-source mass spectrometry
	0.041	Spectrophotometry
Zirconium	0.0071	ID-SSMS
	0.009	Gravimetry
	0.008	Spectrophotometry
Selenium	0.0036	ID-SSMS
	0.003	Neutron activation
Cerium	0.0015	ID-SSMS
	0.001	Spectrophotometry
	0.0014	Isotope dilution, thermal ion-source mass spectrometry
Tellurium	0.0007	ID-SSMS
	0.0005	Polarography
Silver	0.00036	ID-SSMS
	0.00040	Atomic absorption
Neodymium	0.00031	ID-SSMS
	0.00028	Isotope dilution, thermal ion-source mass spectrometry

seven elements in NBS-SRM 1261, low-alloy steel. The table lists the average concentrations of the elements in percentage by weight, the 95% confidence limits of a single determination, and the number of samples for which results were obtained. The experimental conditions used for the first two samples did not preconcentrate all of the elements satisfactorily, but the final conditions described under "Procedure" yielded all of the analytes for simultaneous determination of the seven elements.

Table IV shows a comparison of the results obtained by ID-SSMS with other methods of analysis. Considering the difficulties in determining most of these trace elements, the agreement of results is considered satisfactory. Most other methods are specific for a single element and often involve complicated chemical separations and manipulations.

III. CONCLUSIONS

The major sources of error in trace element determinations are usually losses of the elements and adventitious contamination, the blank. The use of isotope dilution in the procedure that was developed minimizes errors due to trace element losses. The trace elements are brought to equilibrium with the spikes at an early stage of the procedure, after which the concentrations obtained are independent of losses. Although the blank is not considered a problem in the determination of these elements, small quantities of reagents and few handling operations ensure that the blank does not contribute significantly to the method error.

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APPENDIX XI

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1969

T. C. Rains[1]

Chemical Aspects of Atomic Absorption

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ABSTRACT: The phenomenal growth of atomic absorption spectrometry in the past twelve years can be attributed to many factors such as the high sensitivity of the method for a large number of elements, advances in overcoming interferences, saving of time required for analysis, and the rapid improvement of instrumentation. The major interferences in atomic absorption are of a chemical nature; however, physical interferences which are associated with the chemical matrix often are present. To overcome chemical interferences and to eliminate or minimize their influences from phosphate, aluminum, titanium, and any other elements producing nonvolatile compounds, releasing agents, or high-temperature flames are used. Also, the use of a separation and preconcentration technique often becomes necessary when determining elements at the subtrace level. A list of organic ligands and solvents used in solvent extraction for absorption is presented as a means of preconcentration and removal of chemical interferences.

KEY WORDS: atomic absorption, detection limits, electrodeless discharge, nebulizer burner, interferences, releasing agents, organic ligands, solvents, analyzing, tests

Atomic absorption spectrometry (AAS) has made phenomenal growth since its introduction by Walsh in 1955 [*1*].[2] This growth can be attributed to many factors such as the high sensitivity of the method for a large number of elements, advances in overcoming interferences, speed of analysis, and the rapid improvement in instrumentation. Today the analytical chemist has a variety of atomic absorption instruments and components from which to choose. These include different light sources, nebulizer burners, oxidant-fuel systems, optical arrangements, and associated electronics. All of these parameters must be considered in any discussion of the chemical aspects of AAS, and for that reason a brief discussion of these components also is presented.

The sensitivity and precision obtained by AAS are of concern to the analyst; however, the requirements for sample preparation prior to making an

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

absorption measurement can be of equal importance. Where the sample is a solution, the analysis, often times, can be performed on the sample as received.

The major interferences in absorption are of a chemical nature. However, physical interferences often are present and are associated with the chemical matrix. Scattered light which appears as molecular absorption may be due to high solids or large droplets produced by the nebulizer. This type of interference is very pronounced in the far ultraviolet region of the spectrum as exemplified by arsenic and selenium. Also, molecular fragments such as CH, C_2, and CN do exist and can contribute to the background as well as to scattered light. Molecular absorption also is observed from the OH bands over the wavelength region of 2800 to 3500 Å.

Sensitivity and Detection Limit

The terms "sensitivity" and "detection limits" have led to some confusion in the field of atomic absorption. Sensitivity is defined as the concentration of an analyte in solution that produces an absorption of 1 percent. Detection limits is not defined so readily. A number of papers have appeared which discuss this issue [*2-4*]. Winefordner and co-workers [*5-6*] have derived theoretical equations for the calculation of the detection limit based on instrumental and spectral constants. In general the term is defined as the concentration, micrograms per milliliter, that produces an absorption equal to twice the magnitude of the fluctuations of the blank or background noise. The major problem is the selection of a blank. Usually, the blank is distilled water which really cannot be considered a true blank in reporting a detection limit in a sample. Table 1 presents the detection limits obtained with a variety of instruments and under various conditions [*7-9*].

Instrumental Components

The instrumental components are best illustrated by a schematic diagram, as shown in Fig. 1. The basic components are the light source, nebulizer burner, monochromator, photodetector, and readout system.

Light Source

To attain maximum absorption the light source should emit radiation of the desired wavelength that is sharp, intense, and stable. There are many types of line sources used in absorption work; however, the most commonly used source is a hollow-cathode lamp. Another source which fulfills the first two requirements is the electrodeless discharge lamp. The lamp developed by Meggers and Westfall [*10*] is an excellent source for use in absorption. In conjunction with the lamp various types of power sources and cavities are used [*11-13*]. The purpose of the cavity is to transfer the power from the microwave generator, such as a medical diathermy unit, to the inert gas within the lamp. The charged inert gas ions then bombard the metal present producing an excited metallic atom which emits its characteristic radiation.

TABLE 1–*Detection limits reported by atomic absorption spectrometry.*

Element	Wave-length, Å	Detection Limit, μg/ml	Element	Wave-length, Å	Detection Limit, μg/ml
Ag	3281	0.005[a]	Mo	3133	0.1
Al	3093	0.1[b]	Na	5890	0.005
As	1937	0.2[c]	Nd	4634	2[b]
Au	2676	0.01[a]	Ni	2320	0.01[e]
B	2497	6	Pb	2170	0.01[e]
Ba	5536	0.1[b]		2833	0.02
Be	2349	0.003[b]	Pd	2476	0.5
Bi	2231	0.02	Pr	4951	10[b]
Ca	4227	0.003[a]	Pt	2659	0.5
Cb	4059	20[b]	Rb	7800	0.005[f]
Cd	2288	0.001[d]	Re	3460	1.5[b]
Co	2364	0.007[e]	Rh	3435	0.03
Cr	3579	0.005	Ru	3499	0.3
Cs	8521	0.05[b]	Sb	2176	0.2
Cu	3248	0.005	Sc	3912	0.2[b]
Dy	4211	0.2[b]	Se	1961	0.5
Er	4008	0.2[b]	Si	2516	0.1[b]
Eu	4594	0.2[b]	Sm	4297	5[b]
Fe	2483	0.01	Sn	2246	0.1[h]
Ga	2874	0.07	Sr	4607	0.01
Gd	3684	4[b]	Ta	2715	6[b]
Ge	2651	2[b]	Tb	4326	2[b]
Hf	3072	15[b]	Te	2143	0.3
Hg	2537	0.2[g]	Ti	3643	0.1[b]
Ho	4163	0.3[b]	Tl	2768	0.2
In	3039	0.05	Tm	4094	0.1[b]
Ir	2850	4[b]	U	3585	30[b]
K	7665	0.005[b]	V	3184	0.02[b]
La	3928	8[b]	W	4008	3[b]
Li	6708	0.005	Y	4077	0.3[b]
Lu	3312	50[b]	Yb	3988	0.04
Mg	2852	0.0005	Zn	2139	0.002
Mn	2795	0.005	Zr	3601	5[b]

[a] Laminar flow burner with preheater.
[b] Nitrous oxide-acetylene.
[c] Argon (entrained air)-hydrogen.
[d] Quartz tube.
[e] High-brightness lamp.
[f] Osram lamp.
[g] Mercury germicidal lamp.

One of the more effective cavities which meets the requirement for absorption is the Evenson cavity [*14*] shown in Fig. 2. To match the resonance frequency and impedance of the source, the cavity is provided with a coupling slide and tuning screw. To facilitate tuning a RF power meter is placed between the source and cavity. When the resonance frequency of the cavity is tuned to the frequency of the diathermy unit and the impedance is then matched, the power reflected from the cavity is at a minimum.

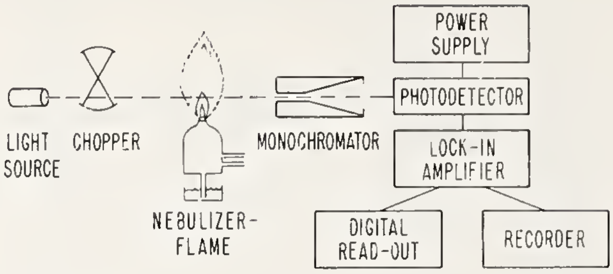

FIG.1–*Schematic diagram of atomic absorption instrument.*

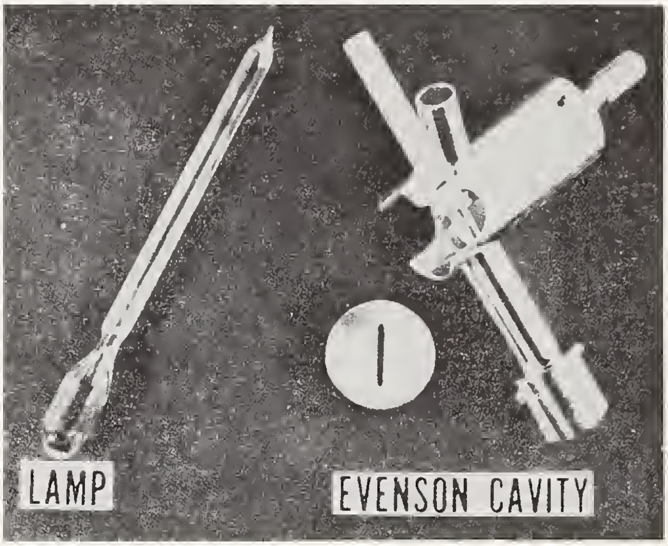

FIG. 2–*Evenson cavity and lamp.*

The major objection to the electrodeless discharge lamp as a source for absorption measurements is the instability or drift of the source. The effect of intensity and stability of lead lamps have been studied as a function of argon pressure as shown in Table 2. Lamps prepared for arsenic, bismuth, copper, lithium, sodium, and zinc have exhibited similar characteristics.

TABLE 2–*Effect of argon pressure in lead electrodeless discharge lamps.*

Argon Pressure, torr	Intensity, arbitrary units	Drift, %/min
<0.1	0	...
0.2	250	<1
0.4	1100	1
1.0	200	<1
2.0	1	5
3.0	1	5

A comparison of the intensity of electrodeless discharge lamps and hollow-cathode lamps is given in Table 3. In nearly every case, the electrodeless lamp was more intense than the hollow-cathode lamp, but in no case was the absorption greater (see Fig. 3). The lower sensitivity for the electrodeless lamp was attributed to self reversal. Measurement of the line width of the sodium lamp with an interferometer showed that self reversal occurred, as shown in Table 4, for the sodium resonance line at 5890 Å when the power of the RF generator exceeded 15 W. To eliminate the line reversal of sodium, the RF generator is operated at a power of 10 W, and the air to the lamp is preheated 180 to 200 C. This approach is found to increase the intensity of the lamps without any loss of absorption.

TABLE 3–*Comparison of intensity of electrodeless discharge and hollow-cathode lamps.*

Element	Wavelength, Å	Hollow Cathode		Electrodeless Discharge	
		Current, mA	I	Power, W	I
Ag	3280	12	1100	30	1000
Bi	3068	10	400	30	200
Cu	3247	12	2300	30	8400
Fe	2483	30	200	30	200
Hg	2537	...	...	30	5400
Na	5890	15	640	20	900
Pb	2833	12	96	30	1100
Zn	2138	12	14	30	530

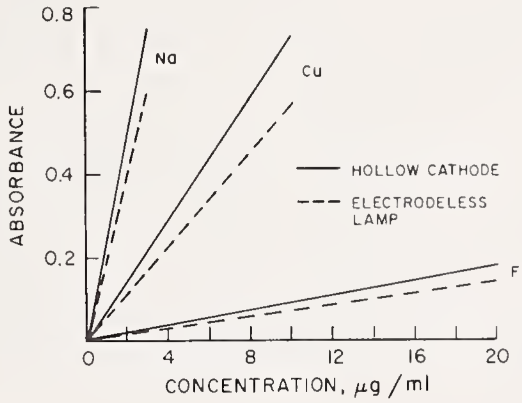

FIG. 3–*Comparison of sensitivities of hollow-cathode and electrodeless discharge lamps.*

Nebulizer-Burner System

The nebulizer-burner system is probably the most important component in any absorption measurement. It is the function of this system to convert the analyte in the sample solution to atomic vapor. This process includes the

TABLE 4–*Absorbance for sodium with electrodeless discharge lamp.*

Burner, triflame-air/C_2H_2
Wavelength, Å: 5890
Na, μg/ml: 1.0

RF Generator, W	Line Width, Å[a]	Absorbance
5	...	0.170
6	0.035	0.165
10	0.04	0.160
15	0.06	0.130
20	0.08	0.100
40	...	0.020

[a] Interferometer measurement, resolution: 0.012 Å.

following steps: (1) dispersion of solution in the form of small droplets, (2) evaporation to dryness, (3) decomposition of salt or oxide, and (4) formation of atomic vapor. The extent to which these occur will depend upon the matrix, type of nebulizer burner, oxidant, and fuel gases.

The most commonly used system for the production of atomic vapor is the premixed gas or laminar flow burner. The solution is sprayed into a spray chamber where the coarse and fine droplets are separated. The fine droplets are mixed with the flame gases; they then pass into the flame where they are vaporized.

The major advantages of the laminar flow burner over the diffusion or total consumption burner in absorption are increased sensitivity and a minimum of interference. Since only atoms in the ground state will absorb energy at the resonance wavelength, the flame should be of sufficient temperature to dissociate the molecules, but not so high as to produce ions. Many elements in relatively cool flames such as argon (entrained air)-hydrogen or air-propane are fully dissociated, others, such as the alkaline earth metals, require air-acetylene flame. Aluminum, silicon, and titanium require a fuel-rich nitrous oxide-acetylene flame. Also, the length of time that the atoms remain in the observed area of the flame will depend upon the gas velocity. The flame front propagation rate for an oxygen-acetylene flame in a diffusion burner is very high (approximately 1200 cm/s); therefore, the residence time of the atoms is very short. However, the flame velocity for the air-acetylene or nitrous oxide-acetylene flame is 160 or 180 cm/s, respectively. The decrease in flame velocity will permit a longer residence time for the atoms in the observed area and give an increase in sensitivity with a minimum number of interferences. The temperature and burning velocities for various gas mixtures are given in Table 5 [*15-17*].

Another method for producing atomic vapor is by use of a high-temperature furnace. Woodriff and Ramelow [*18*] report the use of a high-temperature graphite-tube resistance furnace capable of attaining a temperature of 3000 C. The solution is aspirated with argon into the furnace

TABLE 5—*Temperature and burning velocities of oxidant-fuel gases used in absorption.*

Oxidant Fuel	Temperature Measured, deg C	Burning Velocity, cm/s
Air-natural gas	1700 to 1900	55
Air-C_2H_2	2125 to 2400	160
Air-H_2	2000 to 2050	320 to 440
O_2-natural gas	2740	...
O_2-C_2H_2	3060 to 3135	1100
O_2-H_2	2550 to 2700	2000
N_2O-C_2H_2	2867	180
N_2O-H_2	2607	380

where the free atoms are produced. This system was reported to be useful for eliminating those interferences due to refractory elements. The coupling of an ultrasonic nebulizer with a high-temperature furnace undoubtedly would provide optimum conditions for the determination of trace elements in the presence of refractory oxides.

Optical Arrangement and Associated Electronics

Of equal importance in atomic absorption are the optical arrangement, detection system, and the overall electronic components. These components are essential and must be evaluated in any discussion of atomic absorption. The monochromator should have sufficient resolution to separate the spectral line under investigation from other spectral lines. Any emitted line not resolved by the monochromator, whether from the filler gas or from any impurity in the metal in the hollow-cathode lamp, can produce a severe loss of sensitivity. Therefore, a spectrum of the desired region should be prepared for each source of radiation. There are some special instances where a narrow slit width is required to avoid this type of interference.

To detect the radiation a multiplier phototube with its associated power supply and measuring system is essential for high sensitivity and precision. Because the detection limit is affected directly by the stability of the measuring circuit, the multiplier phototube, power supply, amplifier, and readout system must be sensitive and stable. The most commonly used phototubes for absorption as well as emission are given in Table 6.

Interferences

Chemical interferences occur in varying degrees for all elements in atomic absorption spectrometry. A chemical interference is defined as any reaction which affects the analyte or the element to be determined. This may occur in the liquid, solid, or gaseous phase of the flame. Any cation or anion present in the sample which will form compounds with the analyte and are not dissociated easily will reduce the absorption. An example of this type of interference which usually is cited is the effect of aluminum, phosphate,

TABLE 6–*Multiplier phototubes commonly used in absorption measurements.*

Multiplier Phototube	Spectral Response	Range, Å
R-106	S-19	1600 to 6500
RCA-1P21	S-4	3000 to 6000
RCA-1P28	S-5	2000 to 6500
RCA-6217	S-10	3300 to 8000
RCA-7102	S-1	4000 to 10000
EMI-6256.	S-13	1650 to 6700
EMI-9558 Q	S-20	1650 to 8500
FW-118	S-1	3200 to 10000
Dumont 6291	S-11	3200 to 6000

NOTE–R: Hamamatsu TV Co., Ltd., Hamamatsu-City, Japan.
RCA: Radio Corporation of America, Harrison, N. J.
EMI: E.M.I. Electronics Ltd., Middlesex, England.
FW: International Telephone and Telegraph Corporation, Fort Wayne, Ind.
Dumont: Allen B. Dumont Laboratories, Inc., Clifton, N. J.

titanium, or silica on the determination of alkaline-earth metals. The effects of aluminum and phosphate on magnesium for the total consumption and laminar flow burners are given in Figs. 4 and 5.

The mechanism of this interference is discussed in great detail by many investigators [*19-21*]. In general, most of the workers agree that the suppression is caused by an interferent which affects the vaporization rate of the alkaline-earth element such as magnesium from the solid to the gaseous state.

To eliminate or control chemical interferences in atomic absorption, it is essential that various parameters be optimized. These include the type of burner (laminar flow or total consumption), oxidant fuel, flame temperature, flame region, and sample medium. The premixed gas or laminar flow burner is used primarily in absorption. This system suffers less from chemical interferences than the diffusion or total consumption burner because smaller droplets are introduced into the flame and the burning velocity of the oxidant-fuel mixture is low.

The flame temperature and the flame region play a major role in the extent of the interference. With a fuel-rich nitrous oxide-acetylene flame the chemical interference of aluminum, titanium, or silicon on the alkaline-earth metals is removed. However, this high-temperature flame usually introduces another type of interference which is due to ionization of the analyte. The alkali and alkaline-earth metals are especially susceptible to ionization, but this is controlled by the addition of a cation having a similar or lower ionization potential than that of the analyte.

Another way to eliminate the suppression of the analyte due to formation of involatile compounds is by the addition of releasing or protective chelating agents. Releasing or protective chelating agents are defined as substances

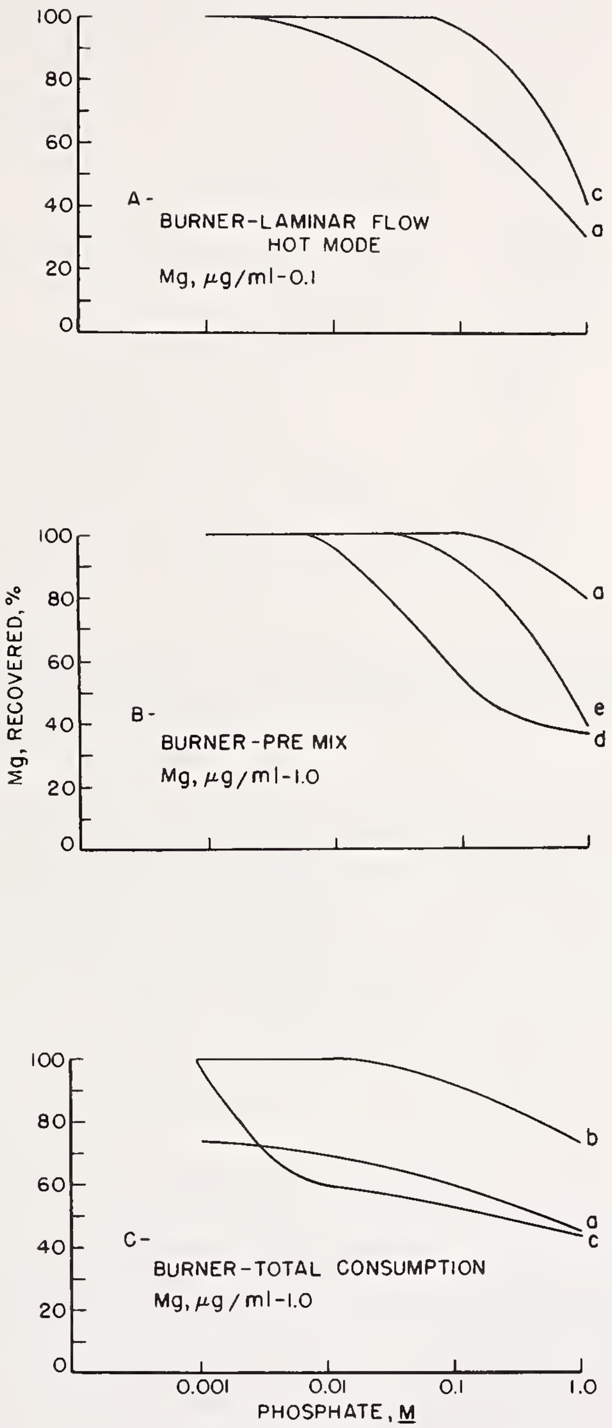

FIG. 4—*Effect of phosphate on magnesium in absorption for three different burners:* A *and* B—*air-acetylene flame;* C—*oxygen-hydrogen.* (a) H_3PO_4 (b) *glycerol, 10 (v/v)% plus* $HClO_4$ *0.1* M (c) *lanthanum, 1 mg/ml* (d) $(NH_4)_2HPO_4$ (3) $(NH_4)_2HPO_4$ *plus glycerol, 10 (v/v)% and* $HClO_4$, 0.1 M.

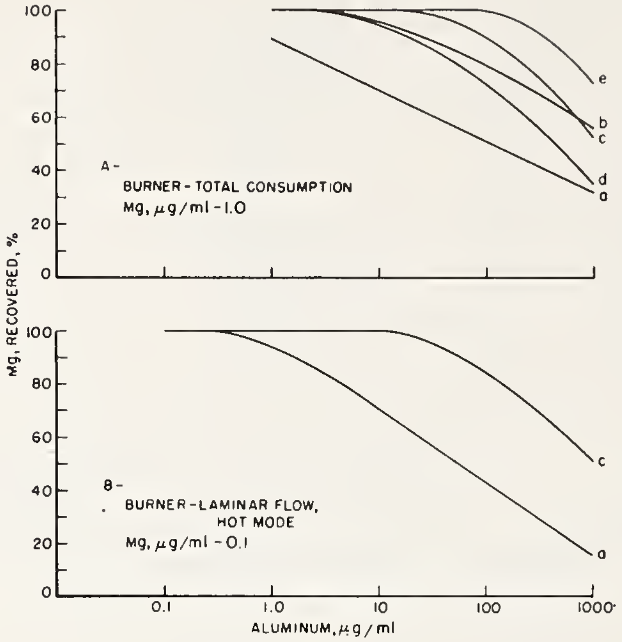

FIG. 5–*Effect of aluminum on magnesium in absorption with and without releasing agents:* (a) *aluminum* (b) *glycerol, 10 (v/v)% plus* $HClO_4$*, 0.1* M (c) *lanthanum, 1 mg/ml* (d) *EDTA, 0.05* M (e) *lanthanum, 1 mg/ml; glycerol, 10 (v/v)% and* $HClO_4$*, 0.1* M.

which, when added in sufficient quantity in the presence of an interferent, will restore the absorption of the analyte to its original value. The manner in which these chelates and releasing agents prevent condensed phase type of interference or an interference that occurs in the solid state is not understood clearly. Compounds such as ethylenediaminetetraacetic acid (EDTA) are known to form strong complexes with the alkaline-earth metals, and will preferentially complex the alkaline-earth metals even in the presence of phosphate or aluminum. However, the similar action of the simple sugars and glycerol has not been explained. A list of releasing and protective chelating agents is given in Table 7.

The effects of phosphate in the analysis for magnesium by atomic absorption with and without releasing and protective chelating agents for three different burner systems are given in Fig. 4. The suppression of magnesium is far greater with the total consumption burner (Fig. 4*C*) than with the laminar flow burner. This is due to the high-burning velocity of the oxygen-hydrogen flame and the larger droplet size produced by this type of burner. Also, a solution 10 percent in glycerol and 0.1-*M* perchloric acid ($HClO_4$) was more effective than lanthanum in releasing magnesium. With the laminar flow burner, phosphate as orthophosphate (H_3PO_4) is not a major interferent; however, ammonium orthophosphate ($(NH_4)_2HPO_4$) or H_3PO_4 adjusted to a pH of 4 to 5 interferes strongly. In a solution containing glycerol [10 volume/volume (v/v) percent] and 0.1 *M* in perchloric acid,

TABLE 7–*Releasing and protective chelating agents used in absorption.*

Reagent	Type	Interferent	Analyte	Ref
La	releaser	Al, Si, PO_4^{3-}, SO_4^{2-}	Mg, Ca	*22, 23*
Sr	releaser	Al, B, Te, Se, NO_3^{1-} PO_4^{3-}, SO_4^{2-}	Mg, Ca Ba	*24, 23, 25* *26*
Mg	releaser	Al, Si, PO_4^{3-}, SO_4^{2-}	Ca	*27*
Ca	releaser	Al, PO_4^{3-}	Mg, Sr	*27*
Glycerol, HClO4	protector	[Al, Fe, Th, rare earths, Si, B, Cr, Ti, PO_4^{3-} SO_4^{2-}]	[Mg, Ca, Sr, Ba]	*28, 29*
NH4Cl	protector	Al	Na, Cr	*30*
NH_4Cl	protector	Sr, Ca, Ba, PO_4^{3-}, SO_4^{2-}	Mo	*31*
Ethylene glycol	protector	PO_4^{3-}	Ca	*29*
Mannitol	protector	PO_4^{3-}	Ca	*29*
Dextrose, sucrose	protector	PO_4^{3-}	Ca, Sr	*29*
EDTA	chelate	[Se, Te, B, Al, Si, NO_3^{1-}, PO_4^{3-}, SO_4^{2-}	Mg, Ca	*26*
8-hydroxyquinoline	chelate	Al	Mg, Ca	*32*

recovery of 1 μg/ml of magnesium was complete in the presence of 0.05-*M* phosphate. By increasing the acidity to a pH of 0.5, complete recovery was obtained up to 0.5-*M* phosphate.

Lanthanum is used frequently as a releasing agent for the alkaline-earth metals in the presence of aluminum or phosphate. The releasing action of lanthanum has been postulated to be due to the high heat of formation of lanthanum phosphate [*22*]. Dinnin [*33*] suggested that the releasing action is a mass action effect,

$$Ax + By \rightleftarrows Ay + Bx$$

where:

A = analyte,
B = releasing agent,
x = anion which forms a refractory compound, and
y = anion which forms an easily dissociated compound.

As the concentration of B is increased, the reaction will be forced toward Bx, thus leaving Ay free to dissociate at a lower temperature. This reaction alone will not explain why some cations will act as releasing agents and others will not. Since the process which occurs within the flame gases is rate controlled, as indicated by studies with low-velocity flames and variable heights within the flame, the correct explanation is most probably a combination of the two mechanisms.

Lanthanum was found to be more effective than glycerol or EDTA for the determination of magnesium or calcium in the presence of aluminum, as shown in Fig. 5. However, a weight ratio of 10:1 for lanthanum-to-aluminum was required to provide complete recoveries of magnesium or calcium. The high concentration of lanthanum required to release the alkaline-earth metals in the presence of aluminum will often produce burner clogging. If, however, glycerol is used in conjunction with the lanthanum, a lanthanum-to-aluminum ratio of only 2:1 is necessary for complete release of alkaline-earth metals. Also, the addition of a 10 percent solution of glycerol to the standards, as well as to the unknown, has the advantage of improving the burning characteristics and controlling the viscosity, thus increasing the accuracy and precision of the method. Rubeska and Moldan [*21*] have observed that the releasing effect of lanthanum is facilitated by the addition of 8-hydroxyquinoline. Instead of requiring a 1 percent solution of lanthanum to overcome the suppression of aluminum, a 0.2 percent solution of lanthanum in 1 percent 8-hydroxyquinoline suffices. This corresponds to a lanthanum/aluminum molar ratio of 2. Similar results have been reported using a combination of EDTA and lanthanum [*34*].

Role of Organic Solvent

The sensitivity and detection limit can be improved with organic solvents. The increase in sensitivity is not as great in absorption as reported for flame emission; however, the possibility of concentrating the analyte by solvent extraction techniques permits the determination of many trace elements. Also, chemical, as well as physical interferences, often can be removed and higher accuracy obtained. In absorption the addition of miscible organic solvents such as alcohols, ketones, and organic acids to an aqueous solution is of limited value. Usually the increase in sensitivity is less than fivefold, and the analyte is diluted inevitably by the addition of the solvent.

By the judicious selection of an organic ligand and solvent, many trace elements are removed from the sample matrix and then determined by atomic absorption spectrometry. Table 8 lists many of the organic ligands and solvents used in emission and absorption spectrometry.

Ammonium pyrrolidine dithiocarbamate (APDC), diethylammonium diethyldithiocarbamate (DDDC), thenoyltrifluoroacetone (TTA), and dithizone are used extensively in chelate extractions for absorption as well as flame emission. Many of these organic ligands are made selective by controlling the acidity and the use of masking agents. The chelates formed can be extracted readily with a variety of solvents.

The most frequently used organic solvent is methyl isobutyl ketone (MIBK). Benzene and kerosene are inferior to MIBK because they produce a large luminous and smoky flame. Carbon tetrachloride or chloroform can be used; however, the enhancement is considerably less than with MIBK. Apart from the fact that the solvent should extract the chelate, it should burn and provide a stable flame. In addition, the physical properties of the solvent such as viscosity, surface tension, boiling point, and mutual solubility in an aqueous medium must be taken into account. It should not produce toxic products during combustion or give a high background in the flame.

TABLE 8—*Organic ligands and solvents used in solvent extraction for atomic absorption and flame emission spectrometry.*

Organic Ligand	Solvent	Element	Material	Ref
HAA	MIBK	Be	air sample	*35*
APDC	MIBK	Co, Cu, Fe, Ni, Pb, Zn	sea water	*36*
		Cu, Zn	plants, soils	*37*
		Pb, Bi, Hg, Ni, Sb	urine	*38*
		Co, Cu, Pb, Cd, Fe, Mn, Ni	KCl	*39*
		Cd, Tl, Hg	blood, urine	*40*
Cupferron	MIBK	Al	Mg alloys,limestone	*41*
		V	. . .	*42*
DDC	MIBK	Te	. . .	*43*
	$CHCl_3$	Cu, Ni, Mn	Al alloys	*44*
DDDC	$CHCl_3$	Cu, Mn	. . .	*45*
		As	cast iron, Se	*46*
Dithizone	$CHCl_3$	Hg	. . .	*47*
Oxine	MIBK	Mg	natural water,brine	*48*
	Butanol	Mo	Cb and Ta	*49*
	3-methyl-1-butanol	Ca	H_3PO_4	*50*
	MIBK	Ca, Mg, Fe, Ni	Al	*51*
Naphthenic Acid	MIBK	Ca	. . .	*52*
Salicylic acid, di-n-butylamine	MIBK	Ag	. . .	*53*
TTA	MIBK	Cu	zinc	*8*
		Al	minerals,bronzes, Zn-base alloys	*41*
		Fe, Cu, Pb, Bi	. . .	*8*
		rare earths	. . .	*54*
		Sb, Fe, Mo, Se, Sn, Au, In, Pb, Cb		*55*

NOTE—HAA = acetylacetone
APDC = ammonium pyrrolidine dithiocarbamate
Cupferron = N-nitrosophenylhydroxylamine
DDC = sodium diethyldithiocarbamate
DDDC = diethylammonium diethyldithiocarbamate
Dithizone = diphenylthiocarbazone
Oxine = 8-hydroxyquinoline
TTA = 2-thenoyltrifluoroacetone

The major objection to MIBK is the increased solubility in a highly acid medium. By using a 3:1 mixture of MIBK-cyclohexane the solubility in the aqueous phase is decreased without any significant change in the extraction of the various chelates or burning characteristics of the ketone.

Preparation of Standards, Samples, and Evaluation of Data

The standard stock solutions are prepared best in hydrochloric or nitric acids from high-purity metals or nonhygroscopic reagent grade chemicals. If possible, sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared generally at concentrations of 1.000, 5.000, or 10.000 mg/ml. The standards are prepared by an appropriate dilution from the stock solution as needed. The final anion concentrations of the standards and samples should be approximately the same. The final accuracy of the analysis may depend upon the care in the preparation of the standard solutions.

In atomic absorption a curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorption of 0 to 80 percent. The correct method for plotting data derived from an atomic absorption instrument equipped with a linear readout system is to convert percent absorption to absorbance and plot the absorbance on linear coordinates against concentration. The following relationship is used to convert absorption values to absorbance:

$$\text{absorbance} = \log(100/\%T) = 2 - \log \%T$$

where $\%T = 100 - \%$ absorption.

Frequently, the curve is nonlinear especially at high absorption values. These curves can be used; however, the number of standards should be increased especially in the nonlinear portion of the curve. If the nonlinear portion of the curve is used it is essential that the concentration and the absorbance be very carefully read.

The sample should be prepared by a standard laboratory procedure. Many of the high refractory oxides and silicates are dissolved with hydrofluoric acid in a Teflon lined bomb [*56*]. By this technique the silicates and aluminates are dissolved within 4 h at a temperature of 120 to 140 C. The excess fluoride is removed by fuming the sample with $HClO_4$. This procedure eliminates the need for a basic fusion to dissolve the refractory oxides and silicates which contribute to high concentration of undesirable salts. The final choice and concentration of acid, such as $HClO_4$, hydrochloric acid (HCl) or nitric acid (HNO_3) are important since the acid concentration may affect the rate of atomization and the production of atomic vapor.

Frequently, a separation or preconcentration step is required before making the final measurement. Ion-exchange resins are helpful in separating trace elements from the matrix; however, ion-exchange procedures have a tendency to be time consuming. Preconcentration by coprecipitation is usually fast and very effective. An excellent example is the coprecipitation of barium with lead chromate. Usually, a solvent extraction procedure is the best method for separation and preconcentration.

To check interferences and to determine the need for separations or the use of releasing agents, the method of standard additions can be utilized.

While there are only two basic methods (single and multiple) for standard addition, the method has a variety of names such as the standard addition method, mixture, incremental addition, autostandarization, and method of additions. The multiple addition method generally is preferred to the single addition; however, if improperly used the multiple method can lead to a serious error. The curve must be linear, and corrections must be made for any absorption which results from scattered light or reagents. This method requires the transfer of three to five test portions of the sample to volumetric flasks. One flask is diluted to volume, and incremental amounts of the standard solution containing 1 to 4 times the concentration of the analyte are added to the remaining flasks and then diluted to volume. The absorbance is measured and plotted against the concentration on linear graph paper. The concentration is determined graphically by extrapolating the linear curve through the Y axis until the line intersects the X or concentration axis. The concentration of the unknown is determined from the point of intersection [*57*].

In the single addition method duplicate aliquots of the sample are transferred to flasks, A and B. An aliquot of a standard from a stock solution is added to B and both solutions are then diluted to volume. The concentrations of the standard and the analyte should be approximately equal. If there is a suppression or enhancement due to the matrix, the standard addition will be affected in a similar manner. The absorptions of Samples A and B are determined, and their concentrations are determined from a calibration curve. If the recovery was either high or low, the true concentration is determined by the following equation [*58*].

$$X \cdot \frac{S}{Y-X} = C$$

where:

X = μg per ml of analyte in unknown (A) as determined by the calibration curve,

S = standard added, μg per ml,

Y = μg per ml of analyte found in unknown (B) containing the standard addition as determined by the calibration curve, and

C = corrected concentration of analyte, μg per ml.

Advantages of the single addition over the multiple addition include: (1) only two test portions are required, (2) the method may serve as a duplicate determination when there is no interference, and (3) it is not essential to prepare the standards for the calibration curve in the same matrix as in the unknown sample.

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APPENDIX XII

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Atomic Absorption Spectrometry—General Considerations for the Application of Experimental Techniques

REFERENCE: Rains, T. C., "**Atomic Absorption Spectrometry—General Considerations for the Application of Experimental Techniques,**" *Some Fundamentals of Analytical Chemistry, ASTM STP 564,* American Society for Testing and Materials, 1974, pp. 50–67.

ABSTRACT: In applying atomic absorption spectrometry to an analytical problem, the analyst must have an understanding of the basic instrumental components. The essential components of an atomic absorption instrument consist of a primary source of radiation, a means of producing atomic vapor from the analyte, wavelength selection, signal detection, and readout. While several types of radiation sources are available, hollow cathode lamps are the primary choice for most workers in the field.

The production of atomic vapor of the analyte is probably the most important parameter in atomic absorption spectrometry. The selection of the oxidant-fuel or nonflame method of producing neutral atoms will depend upon the concentration of analyte and the matrices. While the analyst has a wide choice of methods at his disposal, an understanding of the problems related to the production of atomic vapor is essential to obtain the maximum precision and accuracy. Also, interferences, sample preparation, and methods for evaluation of data are discussed.

KEY WORDS: chemical analysis, accuracy, atomic spectroscopy, evaluation, interferences, light sources, precision, atomic vapor

Atomic absorption spectrometry (AAS) is a unique anaytical technique for the determination of metallic elements. To take advantage of the method, it is essential that the analyst become familiar with the basic components of his instrument and have a working knowledge of the chemical processes ocurring in the production of atomic vapor. The results obtained by AAS, for the most part, are dependent upon the ability of the analyst to apply many of the experimental techniques which have been

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developed over the years. The principles and practices discussed here are not the only techniques that can be applied but are intended only to act as guidelines.

Essential Features of Atomic Absorption Spectrometry

Sources of Radiation

The basic components of all atomic absorption spectrometers are depicted in Fig. 1. The function of the primary source of radiation in AAS is to generate radiation at the wavelength at which absorption is to be measured. This source should radiate the wavelength of the resonance lines of the analyte without interference from other spectral lines. The resonance lines should be sharp with very low background. At the present state of the art, a number of light sources are commercially available which fulfill these requirements in AAS, for example, hollow cathode, vapor discharge, and electrodeless discharge lamps. Hollow cathode lamps (HCL) are available for some 60 elements and, in general, are satisfactory for most AAS work. Although the operation of hollow cathode lamps is extremely simple, one may sometimes obtain better results by deviating from the recommended conditions. The choice of operating conditions depends to a great extent on whether the operator is searching for a maximum precision at concentrations near the detection limit or over a wide analytical range. To determine the optimum conditions, it is necessary to examine the effect of absorbance of an analyte by varying the lamp current and the spectral bandpass of the monochromator. The principal effect of increasing lamp current is to increase the light intensity; however, this may lead to an increase in line width as a result of self-absorption or Doppler broadening. These effects are discussed in great detail by Butler and Brink [*1*].[2] In general, the best sensitivity is obtained with a low current; however, a poor signal-to-noise ratio may be experienced because of the resultant low intensity. As a result one should balance the benefits of maximum signal-to-noise against sensitivity. Also, the spectrum produced by the lamp should be scanned over the area of analytical importance and all lines identified. This serves as a warning of possible spectral interference due to the carrier gas or impurities in

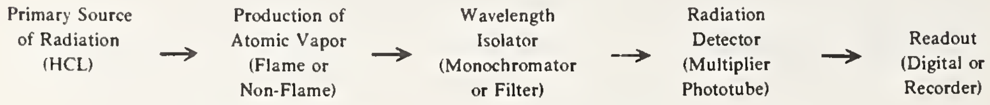

FIG. 1—*Essential features of an atomic absorption spectrometer.*

[2] The italic numbers in brackets refer to the list of references appended to this paper.

cathode material and as a means of correcting light scatter with a nonabsorbing line.

Batchelor [*2*] has reviewed the present state of development of the HCL. The major emphasis by manufacturers has been on improvement in stability and greater light intensity by electrode design and control of the carrier gas pressure.

Other radiation sources used include vapor discharge lamps and electrodeless discharge lamps. Vapor discharge lamps are known for their high intensity; however, self-absorption is inherently present in these lamps which limits their sensitivity.

Electrodeless discharge lamps (EDL) were originally described by Jackson [*3*]. Meggers and Westfall [*4*] reported the construction of an EDL using ^{198}Hg as a spectroscopic source. With the single element isotope, the lamp gave very sharp spectral lines which were measured to eight significant figures. The subsequent development of lamps using metallic halides [*5-9*] has made available light sources for wavelength calibration, atomic absorption, and fluorescence spectrometry. While EDL's are known for their high spectral intensity, they lack reproducibility and ease of operation. The difficulty encountered with lamp drift has been overcome by controlled heating of the lamp [*10,11*]. More recently two commercial manufacturers have made available EDL's having power supplies which operated at radio-frequencies of 29 and 951 mHz. These lamps for a few elements, for example, arsenic and selenium, produce relatively high emission signals with excellent stability. However, the limiting factor for these sources is the number of elements which can be excited at these frequencies.

Sources of Atomic Vapor Production

Historically a flame was the original means of producing atomic vapor for AAS. The flame is still the basic source for the vast majority of AAS measurements, and it will probably remain so for the foreseeable future. While a lot of development work is in progress with nonflame techniques (graphite furnace, carbon rod, and tantalum strip) they are not expected to replace the flame except where additional sensitivity is needed.

There are two basic type of nebulizer burners. When the liquid is sprayed into a mixing chamber and the droplets are mixed with the combustion gas, the process is called indirect nebulization and is referred to as a premixed chamber or laminar flow burner system. In the second type the aerosol passes directly into the flame where the fuel and support gas are mixed. This is the so-called turbulent (sprayer) burner. Of the two types of nebulizer-burners, the premixed system is used generally in all commercial systems. Schematics of each type are given by Herrmann [*12*].

The aerosol produced by an indirect nebulizer is mixed in the spray chamber with the combustible gas before entering the burner. This spray chamber also performs another function by removing the large droplets before they reach the flame. To achieve optimum sensitivity in AAS the spray chamber should produce uniform fine aerosol particles (less than 10 μm in diameter) which are mixed with the support gas. Normally, the efficiency of this system is less than 10 percent. The typical spray chamber used in AAS has varied very little from the original design used by Walsh [*13*]. This can be attributed to one of two causes, either the original design left nothing to be desired or there has been a surprising lack of initiative by investigators.

Various ways to improve the efficiency of atomization in a flame have been proposed. One is the so-called "sample boat" system. In this system, a few microliters of the sample are placed in a small tantalum boat. The boat is mounted on a sliding device that allows it to be pushed into the flame in a reproducible manner. The sample is first dried in the boat near the flame. After drying, the boat is inserted into the flame, and the metal content is rapidly atomized to form a transient atomic vapor cloud above the boat. The radiation source is focused just above the top of the boat. A sharp peak of absorbance versus time is recorded, and the height is proportional to the concentration of metal vaporized. This technique is most successful for the more volatile elements. The major disadvantage of the system is the inability to reproducibly dry the sample before introduction it into the flame. Delves [*14*] modified the sampling boat technique for the determination of blood lead by vaporizing samples from nickel crucibles into a quartz absorption tube. Blood lead results were superior with this system. Also, there were fewer interferences with increased sensitivity.

An entirely different concept of introducing the analyte into the flame is that of hydride generation. In this method, the sample in solution is reacted in a flask with stannous chloride and potassium iodide solutions and finally with zinc metal [*15*] or sodium borohydride [*16*] to produce hydrides such as AsH_3, H_2Se, and SbH_3. The gas is swept from the solution with argon carrier gas into an argon (entrained air)-hydrogen flame in which the hydride is readily decomposed to give the metal (atomic vapor). The sensitivity from this technique is much greater than for direct aspiration of the solution into a flame. For arsenic the sensitivity is 1 ng/ml/1 percent absorption.

In summary, the major advantages of the flame as a means of production of atomic vapor are: (*a*) simplicity of the technique, (*b*) speed with which a determination can be made, and (*c*) relative little maintenance of system. The major disadvantages are: (*a*) a relative large quantity of sample is required for a determination, (*b*) a hostile environment is created for the production of ground state atoms, (*c*) large quantities of oxidant and fuel gases are required, and (*d*) sensitivity is limited for many elements.

Nonflame Absorption Devices

A relatively new technique of producing atomic vapor is with nonflame devices. These methods differ from flames in that an environment is provided which is more conducive to production of atoms in their ground state. Also, a relatively small quantity of the sample (1 to 50 μl) is necessary for an analysis which gives these methods improved sensitivity over flame methods. However, high precision is more difficult to attain.

Nonflame methods can be grouped into categories such as: (*a*) cathodic sputtering, (*b*) graphite furnace or carbon rod devices, (*c*) tantalum ribbon, and (*d*) cold vapor. Cathodic sputtering was first described by Gatehouse and Walsh [*17*]. It consists of making the sample the cathode in a demountable hollow cathode lamp. Atomization of the material of the cathode is achieved by the process of cathodic sputtering. A major disadvantage of the technique is the need to prepare a cathode from the sample which tends to restrict it to metallic samples. Dogan et al [*18*] has demonstrated the feasibility of mixing a nonmetallic sample with a metallic powder and pressing the mixture into pellets. These pellets are buffed and used as the cathode in a demountable lamp. This technique has a potential advantage over other nonflame devices, since it can be used in conjunction with a vacuum monochromator to determine those elements such as carbon, sulphur, phosphorus, and the halides which emit in the far ultraviolet region of the spectrum. As of this date, only limited work has been reported on this technique, but it does possess some interesting analytical possibilities.

The first furnace device proposed for AAS was that described by L'vov [*19*]. In his early work, a solution was placed on the end of the carbon electrode and evaporated to dryness. The sample was then vaporized by a d-c arc into the carbon furnace containing a tantalum liner heated with an a-c current. With this device very impressive absolute detection limits were reported. Typical detection limits ranged from 10^{-12} to 10^{-14} g of the analyte. However, the analytical capabilities of this device were limited because of the power requirements and poor precision.

Massmann [*20*] constructed a somewhat simpler graphite furnace. In his design, the sample was placed in the graphite tube through the hole in the top, and then the tube was thermally heated to vaporize the sample. Comparison of sensitivities reported by L'vov and Massmann devices are summarized in Table 1. L'vov has shown that the sensitivity is inversely proportional to the square of the diameter of the graphite tube if small amounts of the sample are analyzed. The sensitivity and detection limits in these methods are expressed in absolute mass rather than concentration since the solvent is evaporated before atomization.

Modifications to the graphite furnace have been made by Woodriff and Ramelow [*21*]. West [*22*] described a slightly different approach at the

TABLE 1—*Sensitivities obtained by atomic absorption with graphite cells.*

		Sensivity, weight/1% absorption	
Element	Wavelength, Å	L'vov Furnace	Massmann Furnace
Ag	3281		0.8 pg
Al	3093	7.7 pg	
As	1890		0.2 ng
Ba	5535	41.0 pg	
Bi	3068	26.0 pg[a]	0.2 ng
Cd	2288	0.5 pg	2.0 pg
Co	3527	200.0 pg[a]	
Cr	4254	41.0 pg	
Cs	4555	3.3 ng[a]	
Cu	3248	1.8 pg	9.0 pg
Fe	2967/2483	17.0 pg	20.0 pg
Hg	2537	170.0 pg[a]	200.0 pg
In	3039	3.0 pg	200.0 pg
K	4044	960.0 pg	
Li	6708	20.0 pg	
Mg	2852		0.5 pg
Mn	2795	0.5 pg[a]	0.8 pg
Mo	3133	11.0 pg[a]	
Na	5890		6.0 pg
Ni	3525	180.0 pg[a]	70.0 pg
Pb	2833	15.0 pg[a]	10.0 pg
Rb	4202	1.5 ng[a]	
Sb	2311	16.0 pg[a]	0.1 ng
Se	1961		1.5 ng
Sr	4607	8.2 pg	10.0 pg
Te	2259	290.0 pg[a]	
Tl	2768		40.0 pg
Ti	4982	2.0 ng	
Zn	2139	0.2 pg[a]	0.8 pg

[a] Analyses were made at a pressure between 3 and 6 atm.

NOTE:
pg = picogram (10^{-12} g).
ng = nanogram (10^{-9}g).

International Conference on Atomic Absorption Spectroscopy in Sheffield, England. He used an electrically heated carbon filament or graphite rod as the atomizer. In this device, 1 to 5 μl of the sample was placed on the carbon filament mounted horizontally between two metal supports. To prevent oxidation of the carbon filament, it was placed in a glass cell through which argon flowed. The carbon filament was heated slowly to vaporize the solvent, and a current of 100 A at 7 V was then passed through the filament to vaporize the analyte and produce a cloud of atomic vapor. Absorption was measured by passing the radiation from a hollow cathode lamp just above the filament.

At the present, two types of graphite rod or furnace devices are commercially available. These instruments have been redesigned from the original designs of Massmann and West for compactness and ease of operation. Both of these devices produce excellent sensitivity for a number of elements. Regardless of the devices selected by the analyst, it is important that he observe certain precautions. The sample (5 to 100 μl depending upon device) must be transferred to the graphite cell in a reproducible manner. Then the sample is dried with very gentle heating. If the heating is too rapid, vigorous boiling and spattering will result. The drying time will vary with different sample types, but it should be long enough to dry the sample completely. If volatile organic and inorganic compounds are present, the sample must be heated at a higher temperature to remove these compounds. This step is frequently referred to as the ashing stage. The selection of temperature and time parameters for the ashing stage is vital for good precision. If the temperature is too low or the time too short, some of the matrix will not be removed and will cause light scattering during the atomization step. On the other hand, if the ashing temperature is too high, some of the more volatile metals will be lost. Usually a setting can be selected so that the matrix is removed but the analyte remains. For some samples the ashing step may have to be repeated several times to completely remove the volatile matrix. The final stage is atomization. The temperature of furnace and time required for complete vaporization will depend upon the analyte and matrix. As a rule, the lowest possible temperature is advisable to increase the life of the graphite rod or tube. To increase the life of these rods or tubes, 3 to 5 percent methane is introduced to the inert gas sweep during the atomization state.

Interferences encountered with graphite rods or tubes can be classified as physical, chemical, and interelement in nature. Physical interferences are more pronounced with graphite rods or tubes than in most flame systems. Light scatter due to incomplete volatization of organic or inorganic compounds is of major importance. To minimize this type of interference, the time of ashing should be increased. However, if it persists, background measurements should be made with a continuum light source or at a nearby nonabsorbing line and then substracted from the absorbance value obtained for the analyte.

Three possible mechanisms account for chemical interferences. The analyte may be lost by the formation of a volatile compound, by occlusion in a nonvolatile matrix, and by the formation of carbides. As an example, lead chloride which boils at 950°C has a considerable vapor pressure at lower temperatures and can be lost in the ashing step. Therefore, it is frequently necessary to add a reagent which will react with the analyte to produce a less volatile species. Hydrogen peroxide has been observed to minimize the losses of lead in the presence of chloride. Atomic arsenic is volatilized readily from aqueous residues, but arsenic in a metal matrix is volatilized slowly. This is an example of an element forming an occlusion to produce a less volatile compound. The net result is that the rate of volatilization will vary, and this can lead to erroneous results, especially if peak heights are being measured. Another major interference is from the reaction of the furnace material to form nonvolatile metal carbides. Although carbide formation does occur, it can be controlled with the use of a pyrolytic coating on the inner surface of the rod or tube. Also the continued use of methane during the atomization stage should greatly help to maintain the pyrolytic coating for many hours of operation.

The interelement effect is more pronounced in the flameless techniques than in flame systems. It occurs when the analyte reacts with another element which may produce a suppression at certain atomic ratios and an enhancement under certain other conditions. This type of interference can sometimes be corrected by the standard addition method; however, the best technique is to prepare the standards in a similar matrix as the unknowns [*23*].

Feldman [*24*] described a slightly different system in which the carbon filament is replaced by a tantalum strip or ribbon. The major advantage of the tantalum strip over the graphite furnace or rod is the power requirements; however, temperatures high enough to excite the more refractory elements are not obtained with the tantalum strip. A comparison of absolute detection limits for the three systems is given in Table 2.

Cold Vapor Method

The earliest application of AAS extends many years before the first paper by Walsh [*13*]. Mercury has an appreciable vapor pressure at room temperature, and the volatile mercury vapor is capable of absorbing at the resonance lines of mercury. This technique has been employed for years by geologists and industrial hygienists for monitoring mercury levels in the atmosphere. The first use of the technique was described by Poluektov et al in 1964 [*25*]. In 1968, Hatch and Ott [*26*] described a similar method. It is well known that mercury and many of its compounds are highly toxic, but the wide distribution of mercury in our environment was not fully realized until our analytical capability was developed to detect mercury at trace and subtrace levels. Since the early publication by Hatch and Ott, there have been numerous publications. A review of the techniques has been made by Manning [*27*]. Rains and Menis [*28*] modified the Hatch and Ott method by wrapping the absorption cell with a heating tape and by heating the absorption cell to 200°C. This modification eliminated the need for a drying tube prior to the absorption cell and improved the precision of analysis. Since losses of mercury at the nanogram level may occur due to absorption on the wall of the vessel or to its high vapor pressure, it is essential that an oxidant such as $K_2Cr_2O_7$ be added to standards and unknowns when these solutions are prepared. Feldman [*29*]

TABLE 2—*Detection limits for flameless atomic absorption spectrometry.*

	Detection Limit, g		
Element	Graphite Furnace[a]	Carbon Rod[b]	Tantalum Ribbon[c]
Ag	2×10^{-13}	2×10^{-13}	4×10^{-12}
Al	3×10^{-12}	3×10^{-11}	3×10^{-11}
As	...	1×10^{-10}	2×10^{-9}
Au	8×10^{-12}	1×10^{-11}	1×10^{-11}
Be	...	9×10^{-13}	3×10^{-13}
Bi	1×10^{-11}	7×10^{-12}	...
Ca	...	3×10^{-13}	...
Cd	1×10^{-13}	1×10^{-13}	2×10^{-12}
Co	4×10^{-12}	6×10^{-12}	4×10^{-11}
Cr	5×10^{-12}	5×10^{-12}	8×10^{-12}
Cs	...	2×10^{-11}	...
Cu	1×10^{-12}	7×10^{-12}	1×10^{-12}
Eu	...	1×10^{-10}	...
Fe	3×10^{-12}	3×10^{-12}	...
Ga	...	2×10^{-11}	...
Hg	...	1×10^{-10}	5×10^{-10}
K	...	9×10^{-13}	...
Li	...	5×10^{-12}	...
Mg	...	6×10^{-14}	1×10^{-12}
Mn	1×10^{-12}	5×10^{-13}	5×10^{-12}
Mo	...	4×10^{-11}	...
Na	...	1×10^{-13}	...
Ni	1×10^{-11}	1×10^{-11}	2×10^{-12}
Pb	6×10^{-12}	5×10^{-12}	7×10^{-11}
Pd	...	2×10^{-10}	...
Pt	...	2×10^{-10}	...
Rb	...	6×10^{-12}	...
Sb	2×10^{-11}	3×10^{-11}	9×10^{-10}
Se	...	1×10^{-10}	...
Si	8×10^{-12}	...	...
Sn	...	6×10^{-11}	2×10^{-10}
Sr	...	5×10^{-12}	...
Tl	1×10^{-11}	3×10^{-12}	...
V	...	1×10^{-10}	4×10^{-10}
Zn	6×10^{-14}	8×10^{-14}	5×10^{-11}

[a] Perkin-Elmer Corporation brochure RE 67210, 1972, "High-Sensitivity Sampling Systems for Atomic Absorption."

[b] Varian Techtron Carbon Rod Atomizer, Model 63 brochure, April 1972.

[c] Instrumentation Laboratory, Inc., "Sensitivities and Detection Limits in I. L. Model 355 Flameless Sampler," June 1971.

studied the effect of 5 percent (volume per volume) HNO_3 plus 0.01 percent $Cr_2O_7^{2-}$ on 0.1 to 10 ng Hg/ml in glass and found the solutions to remain stable for as long as five months.

Optical Design

Commercial instruments for AAS are of two basic designs — single beam and double beam. In a single-beam system the source (HCL) is focused by means of two lenses through the flame and onto the entrance slit of the monochromator. In a double-beam system the light from the source is interrupted periodically, and diverted around the flame, and recombined before being focused on the entrance slit by a series of mirrors, lenses, and rotating mirrors. The chief advantage of a double-beam system is that the intensity of the resonance line is periodically monitored even while a sample is in the flame. Thus, any source noise, drift, or instability may be easily corrected electronically. However HCL's have been improved to the extent that the flame is the limiting factor in precision in AAS. In AAS, the monochromator is an essential part of the system. The monochromator must isolate the analytical line from the various other lines emitted by the source. Failure to resolve the analytical line from all spectral irradiation will result in a loss of sensitivity and nonlinear calibration curve.

Another important component of an optical system is the slits to the monochromator. It is desirable that the slit widths be variable as they control the resolution of the monochromator. Normally, we operate at a slit width which gives the desired resolution from any adjacent lines. For some elements the minimum slit width fails to give the desired resolution of the analytical line, and, in that case, a tradeoff is made usually between spectral resolution and sensitivity of the analyte. The effect of slit width on resolution (spectral bandwidth) of the nickel HCL is shown in Fig. 2. The most sensitive AAS ground state resonant line of nickel is located at 2320 Å. However, it is very close to a nonresonant line at 2321.4 Å, and only by means of a high resolving monochromator can these two lines be completely resolved. The effect of spectral bandwidth on the absorbance of nickel is shown in Fig. 3.

Electronic and Readout

The basic electronics most often used in AAS consist of a power supply for the HCL, a photosensitive detector and its necessary power supply, an a-c amplifier, and readout device. The choice of a HCL/power supply will depend upon the limit and accuracy of the desired detectability. It will also depend upon the type of instrument that is being used. For precise single-beam measurement, a well-regulated current supply providing 0.1 percent or better current regulation is desirable. With a double-beam system the requirements are less stringent, and a regulated power supply of 1 percent is adequate for most purposes.

The multiplier phototube is by far the most widely used detector in AAS. A list of the most commonly used multiplier phototubes is given by Rains [*30*]. These devices require voltages ranging from under −500 to −2000 V, most being between −500 and −1500 V. The voltages are

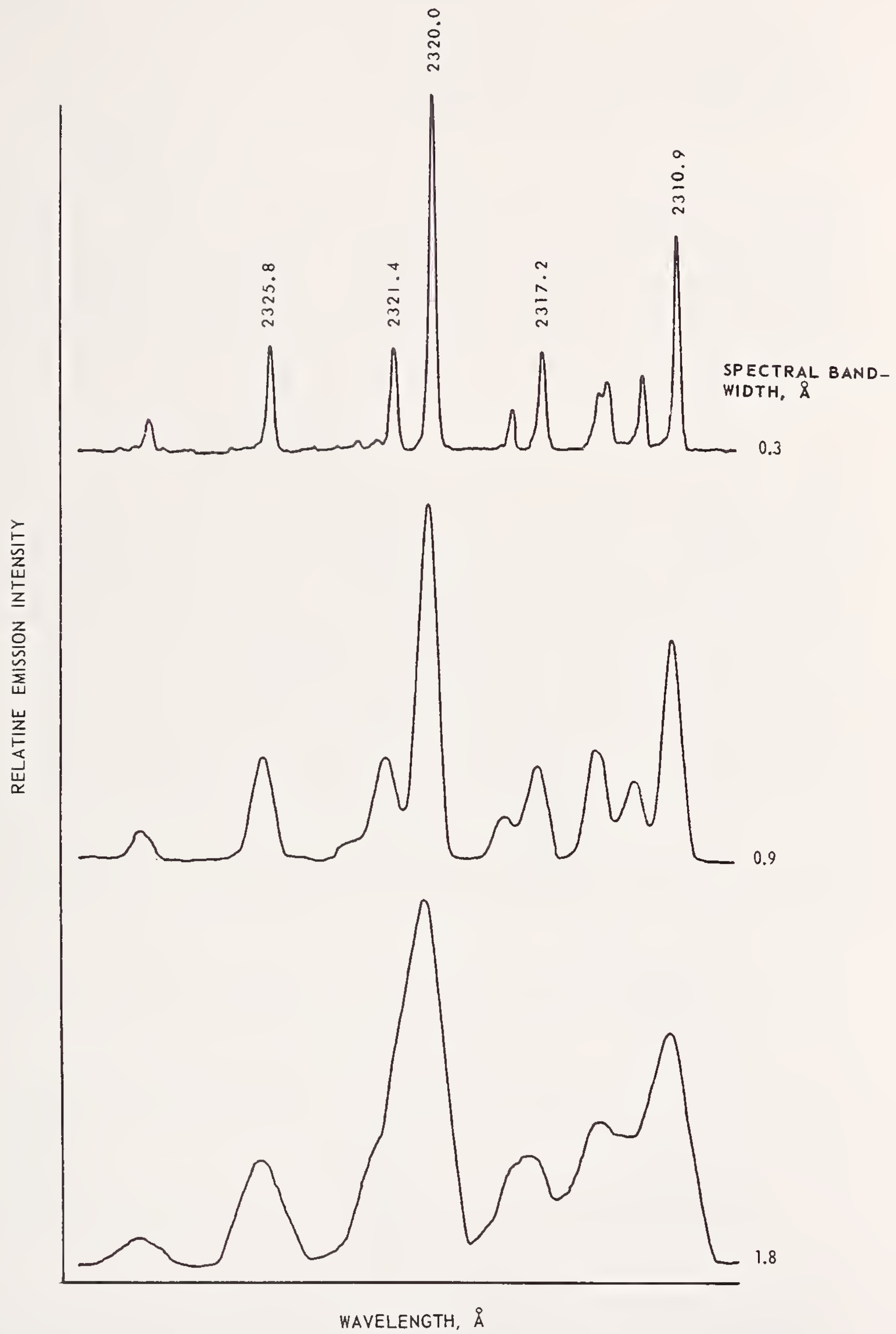

FIG. 2—*Spectra of nickel hollow cathode lamp for different spectral bandwidths of monochromator.*

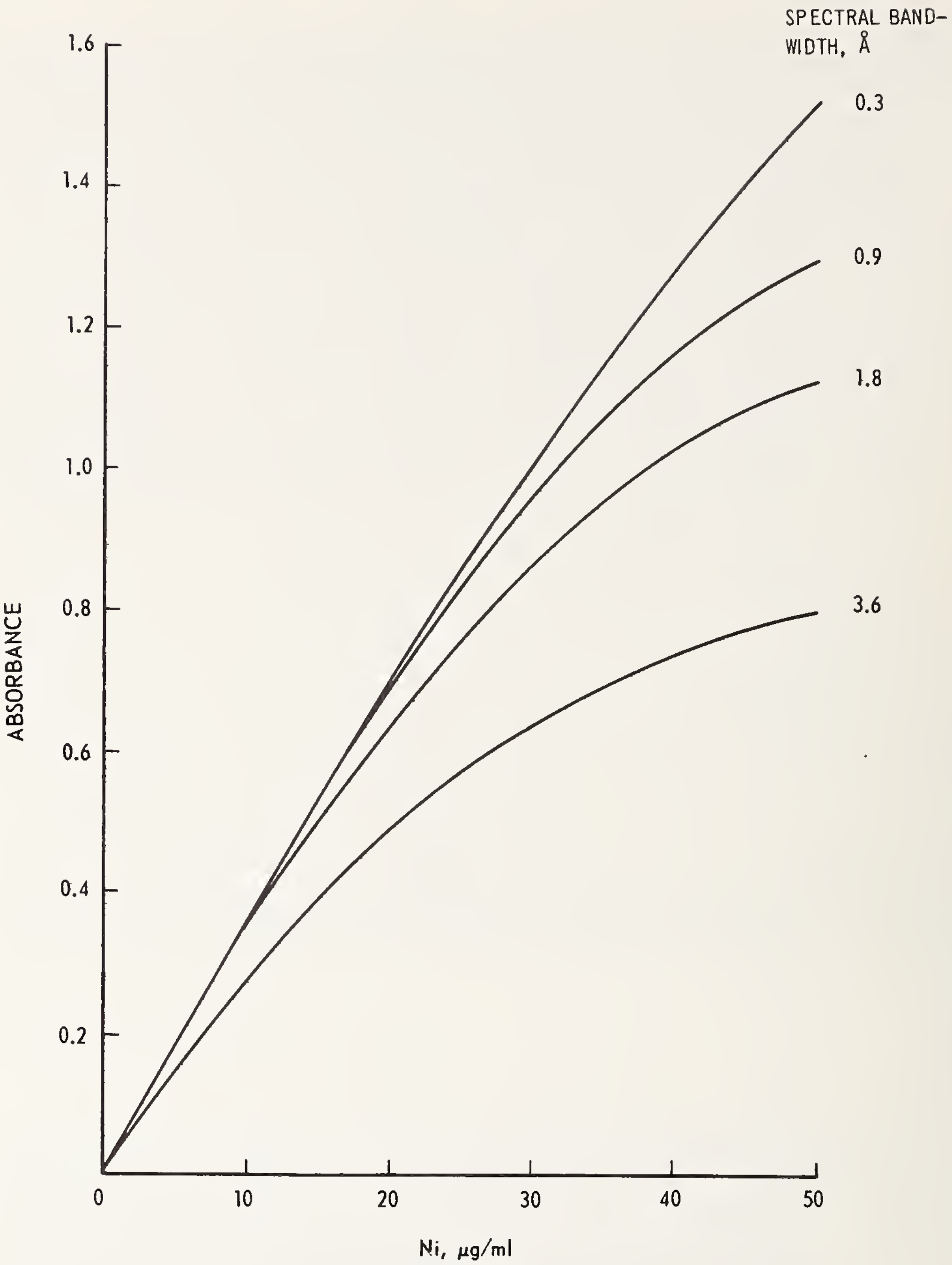

FIG. 3—*Effect of spectral bandwidth on absorbance of nickel at 2320Å.*

negative with respect to ground, and the positive terminal is usually at ground potential. The power supply for these tubes should provide outputs of up to −2000 V at several milliamperes of current regulated to within 0.001 percent against line voltage and load current changes. Also, it should provide a stability of better than 0.01 percent over periods of hours with a-c ripple components of less than 1 mV.

The signal produced by the multiplier phototube is usually too weak to drive indicators and requires amplification. It is essential for the optimum signal-to-noise ratio (S/N) that the amplifier have high gain stability and low noise. The principles, type, and operation of amplifiers are discussed in detail by Veillon [*31*].

For readout devices, meters and recorders have been popular. Digital readout devices are gaining in popularity and may be considered essential for highly precise work. Advantages are that operator bias in making readings is eliminated, and since the digital device employs a decimal-to-binary or BCD converter on the output, the signal can be fed to a printer or tape punch for subsequent computation on a computer.

Preliminary Instrumental Operations

After the analyst has a basic understanding of the components of his instrument, he is ready to perform the analysis. Prior to the actual determination, there are several basic operations. The primary light source must be "turned on" with optimum operating current and allowed to "warm up." The time required for the HCL to stabilize will vary with different lamps, but, as a general rule, the operator should allow 15 min. Next, a resonance line of the analyte is selected. Usually the manufacturer of the instrument will provide a listing of the most sensitive analytical lines. Then the wavelength dial of the monochromator is set to that wavelength and adjusted until maximum intensity is obtained on the readout device. For this operation the prior discussion on slit widths should be considered for optimum operating conditions.

The selection of oxidant-fuel and burner is made if a flame system is being used. There are several gas combinations available (see Table 3), but greater than 90 percent of all AAS measurements are made using an air-acetylene or nitrous oxide-acetylene flame. Selecting the optimum conditions for a given analysis is somewhat difficult, and usually one must

TABLE 3—*Temperatures and burning velocities of common premixed flames.*

Gas Mixture	Burning Velocity, cm/s	Temperature, °C
Air-methane	70	1875 to 1950
Air-propane	82	1925
Air-acetylene	160	2125 to 2400
Air-hydrogen	320	2050 to 2115
Nitrous oxide-acetylene	160 to 680	2600 to 2955

resort to experimentation with various gases and flow ratios or consult the literature for data on a specific problem.

Sample Preparation

The samples suitable for analysis by AAS cover a wide range of materials and concentrations. The analyte may be present as a trace or as a major constituent. The amount and nature of sample preparation required will depend on a number of variables, such as the type of sample, the elements to be determined, and the precision and accuracy desired. Therefore, no general method can be described for the preparation of all samples. Solution samples are nebulized directly into the flame and the measurement taken. Solid samples are dissolved in hydrochloric, nitric, or perchloric acids. Sulfuric acid may be substituted for perchloric acid with certain samples; however, sulfates are undesirable and should be avoided, if possible. For the more refractory materials, a fusion with lithium metaborate [*32*] or with a high pressure "bomb" vessel [*33*] may be required. Fluxes for fusions must be completely free of trace inorganic ions. They may also add high concentrations of solids to the solution which may result in clogging of the burner. The advantage of a high pressure vessel is that the sample is dissolved in mineral acids which later can be removed by fuming. However, these devices have a tendency to leak, especially after long periods of use, and some of the volatile elements may be lost.

After the sample has been dissolved, a separation or preconcentration may be required. As a rule, interferences can be corrected without a separation, but preconcentration steps may be required when the sensitivity of the analyte is insufficient for the sample concentration. Preconcentration is accomplished by liquid-liquid extraction, evaporation, ion-exchange, or coprecipitation. These methods are discussed in detail by Ellis [*34*].

Calibration and Data Evaluation

Before discussing methods used for preparing a standard curve for a particular element, we should consider some factors which may offset the accuracy of the results. Impurities in the reagents can decrease the practical detection limit or if contamination or impurities occur at random concentrations, correction is difficult and accuracy may falter. Therefore, high-purity reagents and a clean environment are essential for the highest precision and accuracy in AAS. Also, cleanliness of glassware is of the utmost importance in trace analysis. Cleaning of glassware with dichromate-sulfuric acid cleaning solution is a common means of obtaining grease-free walls; however, this glassware should not be used for chromium analyses. The boiling of glassware in aqua regia followed by several rinses with ultra pure distilled water will result in essentially a metal-free surface. In spite of precautions taken to prevent contamination, it is very difficult to completely eliminate all traces of impurities. Therefore, it is essential that sample and reagent blanks be processed along with the sample.

Preparation of Standard Solution

Standard stock solutions should be prepared from high-purity metals or salts of known stoichiometry. Michaelis [*35*] has compiled a comprehensive listing of suppliers of high purity materials for virtually every element. A standard stock solution should contain at least 1.000 mg/ml of the analyte in an appropriate acid to prevent hydrolysis. Working solutions should be prepared daily from this stock solution. Procedures for the preparation and storage of standard solutions are given by Dean and Rains [*36*].

Preparation of Calibration Curve

There are several ways to prepare a standard calibration curve. The simplest method is to prepare a series of standard aqueous solutions of the analyte to cover the desired concentration range and to measure their absorbance at an appropriate wavelength. Failure to select the appropriate concentration range could lead to a nonlinear calibration curve. Solutions of the unknown sample are then measured, and their concentrations are determined from a calibration graph. This is often the least reliable way because of matrix or inter-element effects. Therefore, possible interferences must be considered in the preparation of a calibration curve.

Interferences

Interference effects which occur in flames and nonflame systems can be classified as physical, chemical, inter-element, and ionization.

Physical interferences occur when components of the sample alter their physical properties such as viscosity, surface tension, and density. To minimize these effects it is essential that the physical properties of standards and samples be similar. The standards should contain about the same acid concentration as the samples. As a general rule, the acid concentration should not exceed 5 percent, but the preferred acid concentration for most elements is 0.1 to 1 percent. High salt concentrations would change the viscosity and density of the sample. To compensate for these effects, it is advisable, whenever possible, to add an equal concentration of the major ions of the sample to the standards.

Chemical interferences originate during the desolvation of the analyte in the flame or nonflame cell forming a compound which volatilizes at a different rate than the standard solutions. This type of interferent may be overcome with a releasing agent or protective chelate added to sample and standards. Lanthanum or strontium are the most frequently used. although calcium, magnesium, and rare earth elements have been used. It is essential that the releasing agent be free of the analyte or high blanks will result.

Inter-element interferences are not well understood. For example, the absorption of nickel can be suppressed or enhanced by iron depending upon the iron concentration and instrumental conditions. Also, titanium has been observed to enhance the absorption of aluminum and vanadium, and aluminum will enhance the absorption of vanadium. To prevent this inter-element effect, the interfering element should be added to standard solutions in approximately the same concentration as the sample.

Ionization interference occurs when the analyte is ionized in the flame. In the cooler flames, ionization is not a serious problem. With high temperature flames such as nitrous oxide-acetylene, it is a serious problem, especially for those elements which have a low ionization potential. If ionization cannot be avoided by the choice of flame, an easily ionizable element is added to standard and samples to suppress ionization. As a rule, 500 to 1000 μg/ml of potassium or cesium is sufficient to suppress the ionization of most analytes. Other elements have been used but a higher concentration may be required.

Accuracy of Method

After optimization of all instrumental parameters and consideration of possible interferences, the analyst must evaluate the reliability of the data or accuracy of the method. Grant [*37*] has defined accuracy as "a quantitative measure of the variability associated with the relation of analytical results with what is assumed to be the true value." The obvious way of checking the accuracy of an AAS method is to compare the analytical results with those obtained by an "accepted method." This must be done with discretion as an "accepted method" may have a bias. Another approach is to evaluate the method using Standard Reference Materials which have been certified by two or more independent analytical techniques.

If similar material of known composition is not available, a check of the accuracy of the method can be made by the following techniques. (1) The dilution method is useful for revealing interferences. In this method the aliquots or dilution should cover as wide a range of concentrations as practical. (2) The accuracy can be checked by recovery experiments. It is advisable to add approximately the same concentration of analyte as was originally found in the test sample. A complete recovery of the added test portion, however, does not always assure an accurate value. (3) The method of standard addition can be used to check for possible chemical interferences. (4) The presence of light scatter or molecular absorption should be checked using a nonabsorbing line or a continuum source. (5)

And, finally, if in doubt, the analyte can be separated from the matrix by liquid-liquid extraction, coprecipitation or ion-exchange techniques. While this final approach will add considerable time to the analysis, it may be essential to prove the accuracy of the method.

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Flame Emission Spectrometry with Repetitive Optical Scanning in the Derivative Mode

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A flame emission spectrometer using a rapid repetitive scan of a narrow wavelength region has been developed. By this method of wavelength scanning the second derivative of the output intensity is measured. The use of this approach to minimizing spectral interference in matrices and the use of microsamples greatly enhance the potentialities for flame emission spectrometry, and minimize the need for a monochromator of high resolving power. A quartz plate, made to vibrate at 145 Hz, is mounted behind the entrance slit of the monochromator. The ac amplifier is synchronized with the oscillations of the quartz plate. When the amplifier is tuned to twice the frequency of vibration, the second derivative of the spectrum is obtained. This permits the measurement of weak line spectra nested in or on a broad band or continuum. It is demonstrated that spectral interference due to CaOH bands and/or a continuum are minimized in the measurement of barium. The elimination of interferences from bands and flame structure led to an improvement in detection limits of alkali and alkaline earth elements in the presence of many matrix ions. An analysis can be performed with 50 μl of solution which makes it applicable to biochemical and air pollution studies.

THE MEASUREMENT of the radiant intensity of an atomic line which is located on a bandhead arising from the concomitant or flame gases is of concern to the flame emission spectroscopist. Frequently, an atomic line cannot be used because of interferences from some overlapping band structure. Two typical examples are the CaOH bands (5430–6220 Å), which interfere with the Na 5890 Å and Ba 5536 Å lines, and the MgOH bands (3600–4000 Å) which contribute to high background for the Fe 3720 Å and Ru 3727 Å lines. Also, the OH band system, covering the region of 2800 to 4000 Å, limits the measurement of the radiant intensity of many atomic lines in flame emission spectrometry. These interferences have discouraged many workers in the field of flame emission. However, Buell (*1*) in using a high resolution monochromator has shown that many atomic lines in this region can be used.

A technique which permits the measurement of weak line spectra nested in or on a broad band or a continuum resulted in an improvement in detection limits. In addition, microliter samples can conveniently be taken for analyses. The newly designed optical system permits a rapid repetitive scan of a narrow wavelength region. This scan is synchronized with the ac amplifier. With the ac amplifier tuned to the same frequency as the vibrating quartz plate, the signal produced is the first derivative of the emission intensity with respect to wavelength. At twice the frequency, the second derivative is obtained. This mode of operation permits the measurement of weak line spectra without the interference from background radiation or broad band spectra. When operating at high frequencies (145 Hz), the apparent signal-to-noise ratio is improved by eliminating the low frequency flicker noise of the flame. This technique was applied to the determination of lithium in 50 μl of solution containing high concentrations of sodium, and to the determination of barium in a calcium matrix.

Derivative spectroscopy has been described by several authors (*2–4*). Giese and French (*5*) used it to detect low intensity bands by measuring the first derivative of the transmission curve with respect to wavelength. Under certain conditions, a recording of the first or second derivative of an absorption spectrum can give increased resolution over a normal spectrum. In magnetic resonance spectroscopy the first derivative and occasionally the second derivative are recorded to increase resolution of the spectrum (*6*).

There are various ways for obtaining the derivative of absorption lines or bands with respect to wavelength. Balslev (*7*) vibrated the exit slit of his spectrometer and synchronously detected the signal at the vibrating frequency while Gilgore *et al.* used optical wobblers (*8*). Snelleman (*9*) was able to in-

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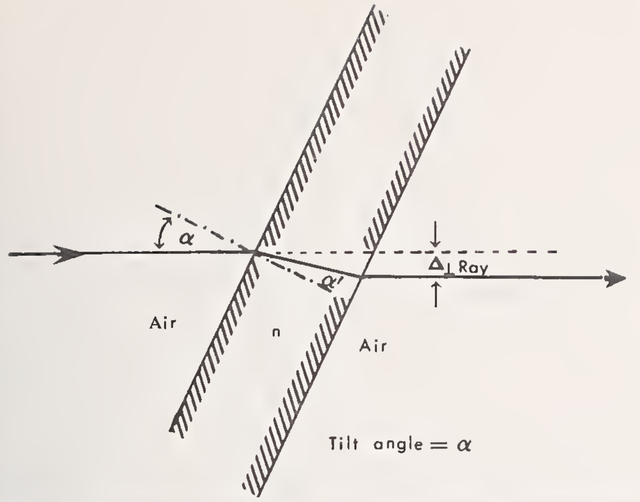

Figure 1. Displacement of an oblique ray laterally and parallel to its initial direction

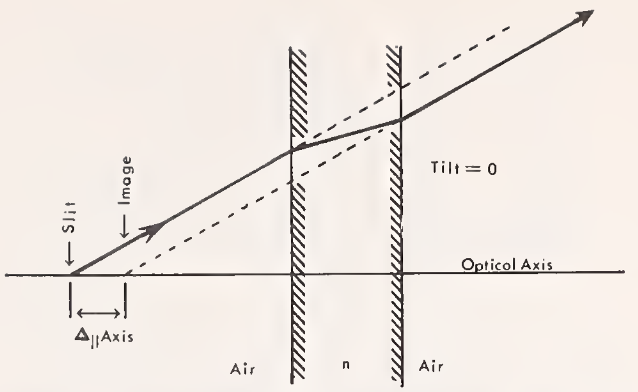

Figure 2. Displacement of an image along the optical axis

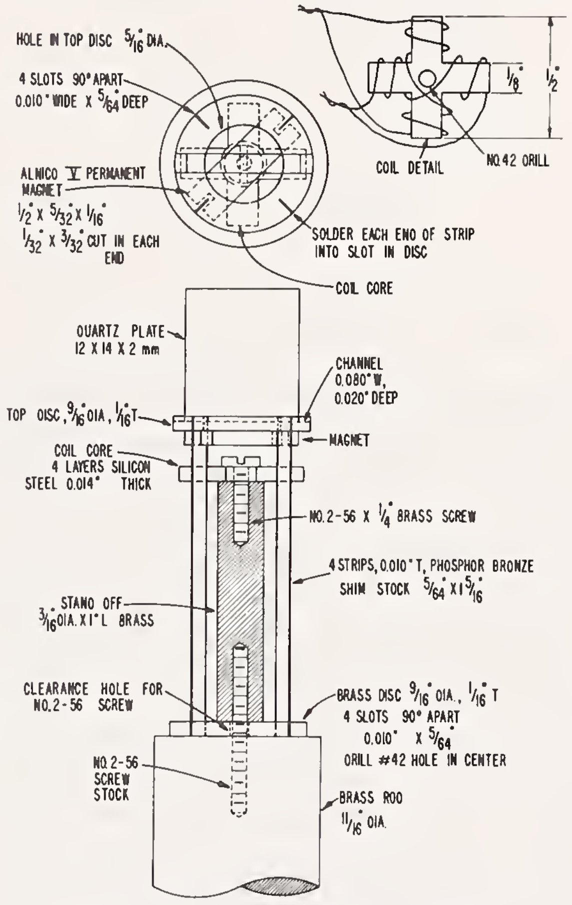

Figure 3. Mechanical oscillator for optical scan

crease the sensitivity of the measurement of copper by atomic absorption using a continuum source and optically scanning part of the continuum. It was accomplished by placing in the optical path a vibrating mirror which was mounted on the movement of a milliammeter. While this arrangement clearly demonstrated the feasibility of optical scanning in atomic absorption, it had certain limitations because of alignment difficulties. The current investigation led to the development of a system utilizing an oscillating quartz plate which provided a stable and easy to operate apparatus. Also, it was demonstrated that this technique had special applications in flame emission spectrometry.

EXPERIMENTAL

Apparatus. GENERAL INSTRUMENTATION. The instrumental system used in this study consists of a 0.75m Czerny-Turner mount monochromator, f/6.5 aperture, curved slits, exchangeable gratings blazed for 3000 and 7500 Å with 1180 grooves/mm; an oxygen–hydrogen flame with a total consumption burner and an air–acetylene flame with a premixed nebulizer burner; gas flow meters and pressure regulators; an end-on multiplier phototube, EMI 9558AQ, with 44-mm diameter photocathode and S-20 spectral response; a 0 to 2100 V multiplier phototube power supply, 0–30 mA, 0.001% regulation (line and load), ±0.25% accuracy; a phase sensitive lock-in amplifier with full-scale sensitivity ranges of 100 nV to 500 mV, and a 10-mV strip-chart recorder, 0.2 sec full-scale response time.

QUARTZ PLATE. A quartz plate 12 × 14 × 2 mm serving as the displacement element was mounted on a rotating mechanical oscillator with a variable amplitude of up to 6° peak to peak. The light beam, in passing through the plate (as shown in Figure 1), will be displaced laterally (perpendicular to the axis) and parallel to its initial direction when measured normal to the ray, and is given by the following relationship:

$$
{}^{\Delta}\perp_{\text{ray}} = t \cdot \cos\alpha\,(\tan\alpha - \tan\alpha')
$$

$$
\sim [t\alpha(n-1)/n]
$$

where t = the thickness of the plate, α = radians in air, α' = radians in the plate, and n = index of refraction of the material. The image shift is approximately proportional to the thickness of the quartz plate and the angle of rotation. In this experiment with a peak to peak amplitude of 5°, the perpendicular shift was 132 μ using $\alpha_{\text{mean}} = 0°$ which corresponded to about 1.5 Å of the spectrum. A larger displacement can be obtained by using a thicker quartz plate and by increasing the angle of rotation. However, to avoid an off-set of the wavelength calibration of the monochromator and light losses due to increased reflection at large tilt angles, an angle of $\alpha = 0°$ was selected.

The ray in addition to being displaced laterally and parallel to its initial direction will be shifted longitudinally. The displacement of the image from the exit slit by the quartz plate, as shown in Figure 2, is given by the following relationship (*10*):

$$
{}^{\Delta}\|_{\text{axis}} = t\,(n-1)/n
$$

$$
\sim (t/3 \text{ for common crown glass quartz})
$$

Because the image was defocused at the exit slit due to the change in optical path length, the quartz plate was ground to a slight convex curvature corresponding to a focal length of 12 m.

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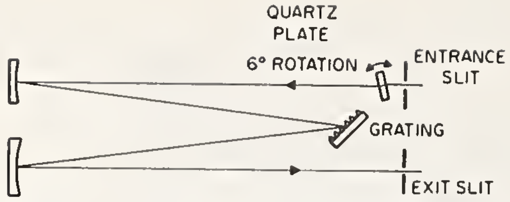

Figure 4. Location of quartz plate within the optical system

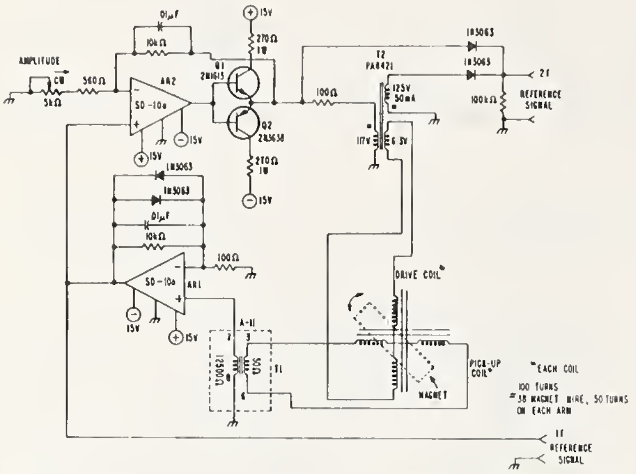

Figure 5. Electrical circuit for mechanical oscillator

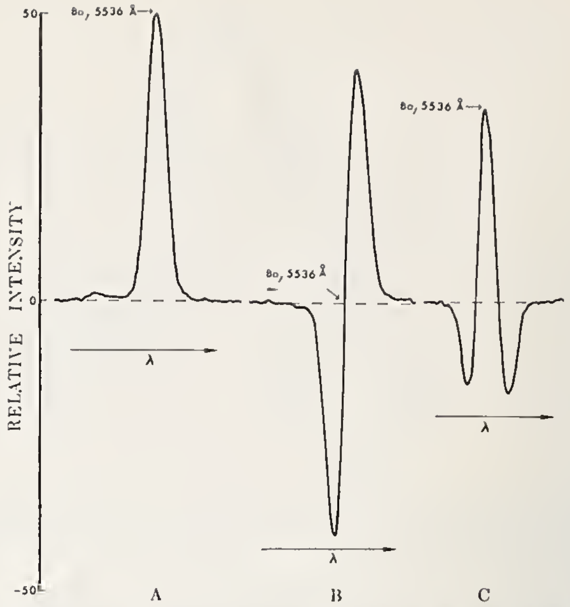

Figure 6. Flame emission spectrum of 10 μg/ml of barium

(*A*) Mechanical disk chopper, (*B*) Optical scan-first derivative, (*C*) Optical scan-second derivative

Design of High Frequency Wavelength Oscillator. The mechanical oscillator shown in Figure 3 consists of two brass disks connected by four narrow phosphor bronze strips cut from 0.010″ thick shim stock. The strips are soldered at each end into slots cut radially 90° apart at the edges of the disks. One disk is rigidly attached to the end of a rod which provides a large mass for an inertial reference. The other disk will oscillate in a rotational mode about the axis. The spring structure allows a large angular amplitude while retaining a high stiffness for other vibrational modes. The quartz plate is mounted on edge in a channel cut in this disk. The frequency of oscillation is determined by the stiffness of the spring strips and the moment of inertia of the top disk, including any attachments. The *Q* of the device is approximately 300. The torque required to overcome the losses is produced by the force between current carrying coils and the ends of a permanent-magnet bar cemented to the underside of the moving disk. The angle between the magnet and the drive core is 45°. The actual core is in the shape of a cross. The two halves of the drive coil are wound on opposite arms of the cross, and an identical pick-up coil is wound on the remaining two arms. The signal induced in the pick-up coil is amplified and fed back to the drive coil. The system oscillates at a frequency determined by the mechanical resonance. Operation at the mechanical resonance is necessary to obtain sufficient angular displacement with a reasonable driving power, and to ensure a constant phase relation between the oscillator motion and its driving voltage.

The lower disk holds the bottom ends of the spring strips rigidly. This construction simplified the assembly of the delicate parts. To assemble the springs without strain, a jig was used to position the disks the desired distance apart and perpendicular to the axis. The strips were soldered into the slots using a minimum amount of heat and solder. The core was mounted on a standoff which also served as a nut for attaching the bottom disk to the rod. The magnet was cut to size with a thin abrasive-filled cutting disk. The slots in each end provide clearance for the spring strips. The magnet and quartz plate must be assembled after the coil assembly has been installed. The quartz plate is placed within the optical path as shown in Figure 4.

Associated Electronic Controls. The electrical circuit for the oscillator, shown in Figure 5, consists of the magnet, pick-up coil, impedance step-up transformer *T1*, limiting amplifier circuit of *AR1*, variable gain amplifier circuit of *AR2*, impedance stepdown transformer *T2*, and the drive coil. The drive and pick-up coils are oriented to eliminate any direct magnetic coupling. The varying magnetic field of the moving permanent magnet induces a voltage in the pick-up coil. This voltage is applied to the input of amplifier *AR1* through transformer *T1*. Amplifier *AR1* is connected as a gain of 101 amplifier with output voltage limiting. For all useful oscillation amplitudes, the peak output voltage is approximately ±0.5 V. The limited voltage is amplified by the adjustable gain circuit of AR2. Transistors *Q1* and *Q2* form a complementary-emitter-follower output stage to increase the available output current. At maximum gain, the output voltage is nearly ±10 V peak. Reducing the gain lowers the output voltage and the oscillation amplitude. The output voltage is applied to the drive coil through transformer *T2*. The 100 Ω resistor in series with the primary increases the dc resistance seen by the amplifier. The offset voltages of *AR1* and *AR2* should be adjusted for less than ±100 mV at the emitter of *Q1*. An auxiliary winding of *T2* provides an output equal in amplitude and 180° out of phase with the voltage from *Q1* and *Q2*. These two voltages are half-wave rectified and are added to provide sufficient signal at twice the oscillation frequency to drive the ac-coupled tuned amplifier in the reference channel of the lock-in amplifier used. A reference output at the frequency of oscillation is obtained from the output of *AR1*. The capacitors across the feedback resistors of *AR1* and *AR2* are selected for zero phase shift around the loop at the mechanical resonant frequency. The loop may be opened between the two amplifiers and *AR2* driven by a frequency-stable audio oscillator at the resonant frequency. The feedback capacitors should then be adjusted for zero phase shift between the input voltage and the output voltage from *AR1*. Alternatively, with the system oscillating, the feedback capacitors may be adjusted for maximum voltage at the secondary of *T1*.

Reagents. All solutions used were prepared from high purity metals or salts.

Operating Characteristics. The spectrum of the resonance line of barium, obtained in an oxygen–hydrogen flame with a total consumption burner, is shown in Figure 6*A*. The wavelength region of the barium line at 5536 Å was scanned in the normal mode of a rate of 5 Å/min with a monochromator having a spectral band width of 0.6 Å. The light signal was chopped at 87 Hz using a mechanical disk chopper.

The mechanical disk chopper was then removed from the optical system and the quartz plate was placed behind the entrance slit within the optical path (Figure 4). By means of the drive coil, the quartz plate was oscillated at 145 Hz. The synchronous lock-in amplifier was tuned to this frequency. As shown in Figure 6*B*, a wavelength scan of the 5536 Å barium resonance line was repeated. The resulting spectrum was the first derivative with the peak corresponding to the zero crossing of the *X* axis. While the first derivative has been used in spectroscopy (*5*) for identifying overlapping band structures, a scan of the wavelength region is required and offers no advantage in flame emission over the mechanical disk chopper. The experiment was repeated, with the lock-in amplifier turned to twice the frequency of the vibrating quartz plate. The signal (Figure 6*C*) which is the second derivative with respect to wavelength is proportional to the concentration of the analyte. The effect of calcium on barium was investigated to evaluate the use of the optical scan in the second derivative mode for the measurement of the intensity of a line nested on a broad continuum. Operating in the normal mode with a mechanical disk chopper the wavelength region of 5500 to 5560 Å was scanned at a rate of 25 Å/min with 4 µg/ml of barium in the presence of 20 µg/ml of calcium in an oxygen–hydrogen flame. The spectrum is shown in Figure 7*A*. The spectrum produced with the vibrating quartz plate within the optical path is shown in Figure 7*B*. The recorded data shown in Figure 8 were obtained by setting on the peak intensity of the barium line and repetitively scanning a narrow wavelength region. By measuring the emission intensity in the second derivative mode, the signal is proportional to the analyte concentration. However, to obtain the maximum signal, the amplitude of the optical scan is adjusted with 5K Ω variable resistor, shown in Figure 5.

RESULTS AND DISCUSSION

In flame emission spectrometry, the barium resonance line at 5536 Å suffers serious spectral interferences from calcium, magnesium, and sodium (*11*, *12*). Also in atomic absorption, the CaOH band system with its peak at 5540 Å will interfere in the determination of barium in an air–acetylene flame (*13*, *14*). As shown in Figure 7*A*, barium can be determined in the presence of calcium by flame emission spectrometry provided the calcium to barium ratio does not exceed 10:1. For this purpose the wavelength region of 5530 to 5540 Å must be scanned and the proper background correction applied. By operating with a smaller spectral band width, the calcium band structure is reduced; however, to obtain the desired sensitivity for barium, a spectral band width of 1.0 to 1.5 Å is usually necessary. Under these conditions the high background emission from CaOH band structure becomes a limiting factor and zero offset is required to shift the spectrum on the recorder scale. Also, in making a wavelength scan of this region, two to five milliliters of solution are required.

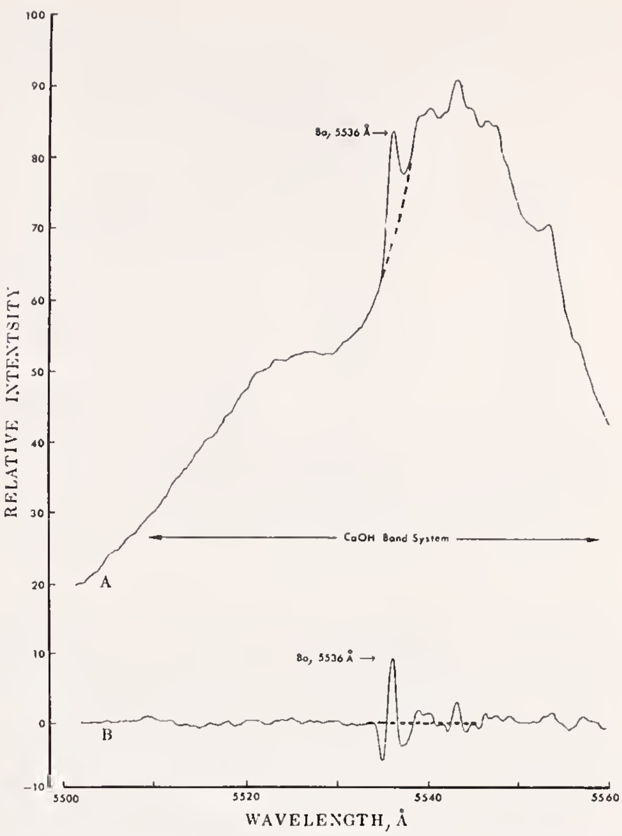

Figure 7. Flame emission spectrum of 4 µg/ml of barium in the presence of 20 µg/ml of calcium in an oxygen-hydrogen flame with (*A*) a mechanical disk chopper and (*B*) optical scan and derivative mode

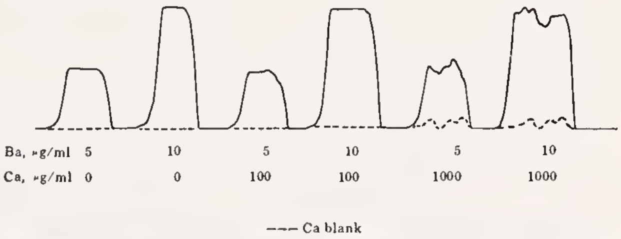

Figure 8. Effect of calcium on barium in flame emission spectrometry using optical scanning and derivative mode

With the optical scan and taking the second derivative, the high background emission due to the CaOH band structure is eliminated as shown in Figure 7*B*. The intensity of the barium line is measured from the dotted base line to the peak height, and is approximately two-thirds the height obtained with the disk chopper.

The continuum of unresolved band structure with a nominally zero curvature which lies under the analytical line is not detected. The amount of band structure or continuum which can be tolerated with the optical scanning technique will depend upon the optical system and the photodetector. The major limiting factors are the cathode loading and fatigue of photodetector. Under the optical conditions used the radiant intensity of analytical lines that were 0.1% of the relative intensity of broad band structure have been measured without interference. However, narrow band peaks still appear as a slight deviation from the background.

The unique advantage of this technique is shown in the study of the effect of various concentrations of calcium on the

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Table I. Detection Limits by Flame Emission Spectrometry with Optical Scanning in the Presence of Matrix Ions

Burner-diffusion
Oxidant-fuel-oxygen-hydrogen
Sample size-0.25 ml

Matrix, element 1 mg/ml	Detection limit,[a] ng/ml		
	Li	K	Ca
Li	...	0.2	3.0
Na	0.02	0.08	0.5
K	0.02	...	3.0
Rb	0.02	1.0[b]	3.0
Mg	0.02	0.1	[c]
Ca	0.02	0.03	...
Fe	0.02	0.2	3.0

ng = 10^{-9} grams

[a] Detection limit is defined as 2σ of background.
[b] Rubidium free of potassium not available.
[c] Magnesium free of calcium not available.

measurement of the barium emission line. As shown in Figure 8, by setting on the resonance line of barium and measuring the peak height of the second derivative with respect to wavelength, barium was determined in the presence of a 100-fold concentration of calcium with an air-acetylene flame. By scanning a narrow wavelength region of one Å an appropriate background correction is made. While in this case the peak height measurement was obtained with 2 ml of solution and a time constant of 1 sec, the analysis can be performed with a fraction of this sample. With a higher temperature flame, such as oxygen-hydrogen or nitrous oxide-acetylene with an appropriate burner, the calcium to barium ratio can be extended to 1000:1. A higher weight ratio can be tolerated in the presence of magnesium or sodium. The correction for background even in the presence of 1000 µg of calcium is easily applied, and the need for extensive zero offset in the electrical circuit is eliminated.

The detection limits determined for lithium, potassium, and calcium in the presence of 1000 µg/ml of various matrix elements are given in Table I. The continuum or unresolved band structure produced by the matrix element did not show a shift in the base line. The detection limit of potassium in rubidium could not be extended below 1 ng because potassium-free rubidium was not available.

The detection limits which are generally reported in the literature are usually based on pure water solution. These values can be very misleading when applied to samples containing other cations. Generally, for a complex matrix the optical scan led to an improvement in the detection limits of an analyte of 1 to 2 orders of magnitude over the normal wavelength scan with a mechanical chopper. However, in a pure water solution and with an oxygen-hydrogen flame, the detection limits of the two methods were identical and corresponded to the values reported in the literature (*15*, *16*).

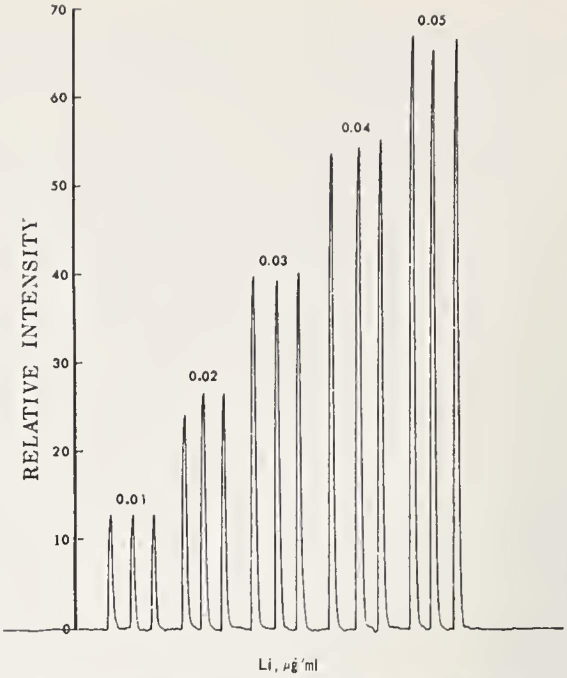

Figure 9. Lithium calibration results of flame emission spectrometry using optical scanning and derivative mode

Another unique feature of the technique is the amount of sample required for analysis. Normally with the mechanical disk chopper, three to five milliliters of solution are required for a scan of the wavelength region of interest and for the base line recording for measuring the peak height. By setting on the peak of a line with the optical scan and measuring the second derivative of the output signal, a fraction of a milliliter of solution is only required. In this manner, with a total consumption burner and a small bore capillary, lithium was determined in a sodium matrix. The data in Figure 9 show replicate determinations of lithium in 50 µl of solution. The precision in this method was 2% of the full scale. In this case the response of the electronics was the limiting factor in determining the volume of the solution needed. With a faster electronic detection system or an integrating system, this could be reduced further.

In flame emission spectrometry this technique, in many cases, will eliminate the need for a high resolution spectrometer to minimize spectral interferences. Because the optical scan is applicable to microliter samples, it should be of great assistance in the analysis of biochemical materials and air pollution particulates. Also, it is being extended to atomic absorption spectrometry with a continuum light source.

RECEIVED for review September 15, 1969. Accepted January 9, 1970.

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APPENDIX XIV

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13 Standard Solutions for Flame Spectrometry

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I. Introduction

In all evaluation methods one must have available standard samples and high-purity materials for each element being determined, often in the same matrix as the sample. Quite often several standards must be prepared for a given element, one for each matrix or system that contains the test element. To assist the individual chemist who must prepare these standard solutions, this chapter will outline the preparation of various individual stock solutions and suggest sources where high-purity materials may be obtained or from whom standard samples may be purchased. An excellent report on available standard reference materials and high-purity materials has been compiled by Michaelis (*1*).

A. Sources of Standard Reference Materials

The National Bureau of Standards (U.S.) offers a wide selection of standard alloys, steels, ores, glasses, and miscellaneous types of materials in the form of chips, turnings, powders, or granules. Full information concerning the values that are certified, the weights, and prices is contained in Ref. (*2*).

The Bureau of Analysed Samples, Ltd. (Newham Hall, Middlesborough, Yorkshire, England) also offers a wide selection of standard samples. Many of these standards may be obtained through the Jarrell-Ash Division of Fisher Scientific Company (590 Lincoln Street, Waltham, Mass. 02154) or from Spex Industries, Inc. (3880 Park Avenue, Metuchen, N.J. 08841).

A series of 20 ceramic powders are supplied by Applied Research Laboratories (9545 Wentworth Street, Sunland, Calif. 91040) for the analysis of barium, calcium, magnesium, and strontium titanates, and titanium dioxide. The standards have a variation of composition to cover the range of impurity constituents normally found in ceramic materials.

In addition to the various standard samples, reference samples are also available. Generally compositions are less accurately known. Smith and Underwood (1023 Troy Court, Troy, Mich. 48084) supply over 1000 different analyzed materials, primarily for student use in universities and colleges.

B. Types of Standard Reference Materials Available

Three aluminum-base alloys prepared in the form of turnings are available from the National Bureau of Standards (NBS), and seven chip samples are issued by the Bureau of Analysed Samples (BAS). These samples possess certificates of analysis for Cu, Fe, Mg, Mn, Pb, Si, Ti, and Zn in all cases; individual samples may contain also Cr, Ga, Ni, Sb, Sn, and V.

Two cobalt-base alloys are issued by NBS and contain Ni, Mn, Si, Fe, Cr, Mo, W, Nb, and Cu.

Nine copper-base alloys are available from NBS and five from BAS, all in chip form. In addition to Cu, Zn, Sn, Pb, Ni, and Fe, certain standards also contain Al, As, Ag, Co, Mn, Sb, Si, S, P, and Mg. Six standards in the form of turnings from high-purity copper are available from Bundensanstalt für Materialprüfung (Berlin-Dahlem, Unter den

Eichen 87, Berlin, Germany). These standards contain less than 0.07% of Pb, Sn, Bi, As, Sb, Fe, and Ni.

Over 120 standards for iron-base alloys are available from NBS and BAS in the form of chips. These include cast iron, ingot iron, B.O.H. and A.O.H. steels, plain-carbon steels, mild steels, and alloy steels. The mild steels and alloy steels contain accurately determined traces of a number of residual elements (W, Co, Ti, As, Sn, Al, Zr, Pb, Nb, Ta, B, and Ag) in addition to the usual constituents: Mn, P, S, Si, Cu, Ni, Cr, V, and Mo.

Two lead-base standards are issued by NBS and one by BAS; these contain Sn, Sb, Bi, Cu, As, and traces of Ag and Ni.

One magnesium-base alloy is available from NBS and one from BAS. The former contains Al, Zn, Mn, Si, Cu, Pb, Fe, and Ni; the latter contains total rare earths, Zn, Zr, Cu plus traces of Mn, Ni, and Fe.

The NBS issues three primary standards of nickel oxide (powder form) and four nickel-base alloys (Monel, nickel-base casting alloy, Ni-Cr alloy, Waspaloy). The BAS supplies one standard (Nimonec 90).

One tin-base alloy is available from NBS and from BAS. The standard contains Sb, Cu, As, Pb and traces of Bi, Ag, Ni, and Fe.

Only one zinc-base alloy is available from NBS. It contains Al, Cu, Mg, and traces of Fe, Mn, Pb, Ni, Sn, and Cd.

One zirconium-base alloy, Zircaloy 2, is issued by NBS. It contains Sn, Fe, Cr, and traces of Ni, Mn, and Cu.

Steel-making alloy standards from NBS and BAS include refined silicon, ferrovanadium, ferrochromium, spiegeleisen, ferrophosphorus, ferroboron, and calcium molybdate.

A set of six cement standards is available from the NBS with these constituents certified: SiO_2, Al_2O_3, Fe_2O_3, TiO_2, P_2O_5, CaO, SrO, MgO, SO_3, Mn_2O_3, Na_2O and K_2O.

Miscellaneous standard samples issued by the NBS include: three alumina refractories, two silica refractories, one chrome refractory, a bauxite, a plastic clay, a glass sand, four glasses, and argillaceous limestone, a silica brick, a burned magnesite, titanium dioxide, and silicon carbide. These are supplemented by three basic slags, a silica brick, a firebrick, and a sillimanite from the BAS.

Among ore samples available are six iron ores from the BAS. A phosphate rock, a Mesabi iron ore, three lithium ores (Spodumene, Petalite, and Lepidolite), one manganese ore, two tin ores, and one zinc ore are available from the NBS. Except for the phosphate rock and Mesabi iron ore, the NBS ores are certified only for the component of interest.

A syenite rock sample and a sulfide ore are also available (Department of Geological Sciences, McGill University, Montreal, P. Q., Canada).

Four horticultural standards of apple, cherry, citrus, and peach leaves have been prepared (Horticultural Department, Michigan State University, East Lansing, Mich.).

II. Aqueous Stock Solutions

High-purity materials (99.9% or greater) can be obtained from several sources: Alpha Metals, Inc. (60 Water Street, Jersey City, N.J.), Johnson Matthey & Co., Ltd. (Hatton Garden, London, E.C.1, England), Spex Industries, Inc. (Section I.A.), and various chemical supply houses, for example, Baker & Adamson, J. T. Baker & Co., Fisher Scientific Co., Mallinckrodt Chemical Works, and Merck and Co. A comprehensive listing of suppliers of high-purity materials for virtually every element is available (*1*).

In selecting a suitable compound or material for use as a standard, several criteria must be met: (1) It must be available commercially in a high degree of purity and meet A.C.S. specifications or a similar "official" certification. Established methods should be available for confirming its purity (*3*). (2) The compound should not be hygroscopic, nor should it be efflorescent. It should be stable under the conditions specified for drying. (3) The composition of the selected material must be known; if not, the final stock solution will have to be standardized. (4) Metallic and other contaminants present in these standard materials must not be in amounts greater than that of the trace element to be determined in any particular sample, otherwise mixed standards could not be prepared.

Procedures which provide standard stock solutions containing 1000 μg/ml of the element of interest are listed in Appendix 1. Precautions outlined in Chapters 10 and 11 (Section II.E) should be reviewed. Molarity of the reagents used is as follows:

Reagent	Molarity	Reagent	Molarity
Acetic acid	17.4	HNO_3 (69%)	15.4
HCl (38%)	12.0	H_3PO_4 (85%)	14.7
$HClO_4$ (70%)	11.6	H_2SO_4 (94%)	17.6
HF (45%)	25.7	Ammonia (27%)	14.3

Many stock solutions should be slightly acidic to prevent hydrolysis. Unless stated otherwise, final dilution should be made to 1000 ml with deionized water—ordinary distilled water which has been passed through a mixed-bed ion-exchange resin such as Amberlite MB-3, then freshly boiled and cooled to room temperature. Solutions are stored in polyethylene containers unless a special containment material is specified. A crystal of thymol in each stock solution will inhibit bacterial growth.

A. RELATION OF CONCENTRATION UNITS

The interrelationship between various expressions for concentrations is:

1 μg/ml $\equiv$ 1 mg/liter $\equiv$ 1 ppm (w/v)
1 meq/liter = (weight in grams per equivalent/1000) in 1 liter
1 mg atom per liter = (atomic weight in grams/1000) in 1 liter
1 μg/ml = (1 meq/liter)(1000/weight in grams per equivalent)

III. Specialized Stock Solutions

Solutions for clinical, agronomic, and certain other special situations are listed in Appendix 2. These solutions are prepared in the same manner as described in Section II.

IV. Standards for Trace Elements in Petroleum Products

Stable, oil-soluble compounds are available from the National Bureau of Standards (U.S.) as certified standards for 24 elements in petroleum products. Appendix 3 lists the compounds; all are solids. Directions for the preparation of individual compounds have been published (*5*) for those who may wish to prepare their own materials. Some of the compounds are fairly hygroscopic. As a precautionary measure, bottles containing the standard material should be stored, tightly closed, in desiccators containing P_2O_5, and that, before use, the required amount of a compound (plus a slight excess) should be dried over P_2O_5 in an open container for the length of time recommended in Appendix 3, column 4.

To prepare an oil solution containing one or several elements of interest, a solubilizing agent is prepared by placing 5 ml of 2-ethylhexanoic acid, 4 ml of 6-methyl-2,4-heptanedione, and 2 ml of xylene in a weighed 200-ml flask. The calculated weight of standard sample (Appendix 3, column 5) is carefully transferred to the flask. The suspension is gently heated on a hot plate, with swirling, until the salt has dissolved to a clear solution.

The salts are added, one at a time, and completely dissolved before the next compound is added. After each addition, the mixture is gently heated, tilted, and rotated in order to wash down any particles adhering to the inside of the flask. After the last compound has been added and dissolved, 2 ml of bis(2-ethylhexyl)amine is added. The beaker is now washed with six 15-ml portions of lubricating oil, and these rinsings are all transferred to the flask. This last step is omitted if the sample is transferred directly to the flask from the sample container, and not weighed into an intermediate beaker.

The oil solution is now allowed to cool to room temperature, and cool lubicating oil is added to the flask until the weight of the solution is 100 ± 0.5 g. The solution is reheated to 85°C, allowed to cool to room temperature, transferred to a storage bottle, and tightly stoppered.

Compounds of silver and mercury are sensitive to prolonged heating and so, they should be added last to any mixture. For the other compounds, the order of addition is immaterial.

Appendix 1: Standard Stock Solutions*

Element	Procedure
Aluminum	Dissolve 1.000 g Al wire in minimum amount of 2 *M* HCl; dilute to volume.
Antimony	Dissolve 1.000 g Sb in (1) 10 ml HNO_3 plus 5 ml HCl, and dilute to volume when dissolution is complete; or (2) 18 ml HBr plus 2 ml liquid Br_2, when dissolution is complete add 10 ml $HClO_4$, heat in a well-ventilated hood while swirling until white fumes appear and continue for several minutes to expel all HBr, then cool and dilute to volume.
Arsenic	Dissolve 1.3203 g of As_2O_3 in 3 ml 8 *M* HCl and dilute to volume; or treat the oxide with 2 g NaOH and 20 ml water, after dissolution dilute to 200 ml, neutralize with HCl (pH meter), and dilute to volume.
Barium	(1) Dissolve 1.7787 g $BaCl_2 \cdot 2H_2O$ (fresh crystals) in water and dilute to volume. (2) Dissolve 1.516 g $BaCl_2$ (dried at 250°C for 2 hr) in water and dilute to volume. (3) Treat 1.4367 g $BaCO_3$ with 300 ml water, slowly add 10 ml of HCl and, after the CO_2 is released by swirling, dilute to volume.

* 1000 μg/ml as the element in a final volume of 1 liter unless stated otherwise.

Appendix 1: (Cont.)

Element	Procedure
Beryllium	(1) Dissolve 19.655 g $BeSO_4 \cdot 4H_2O$ in water, add 5 ml HCl (or HNO_3), and dilute to volume. (2) Dissolve 1.000 g Be in 25 ml 2 *M* HCl, then dilute to volume.
Bismuth	Dissolve 1.000 g Bi in 8 ml of 10 *M* HNO_3, boil gently to expel brown fumes, and dilute to volume.
Boron	Dissolve 5.720 g fresh crystals of H_3BO_3 and dilute to volume.
Bromine	Dissolve 1.489 g KBr (or 1.288 g NaBr) in water and dilute to volume.
Cadmium	(1) Dissolve 1.000 g Cd in 10 ml of 2 *M* HCl; dilute to volume. (2) Dissolve 2.282 g $3CdSO_4 \cdot 8H_2O$ in water; dilute to volume.
Calcium	Place 2.4973 g $CaCO_3$ in volumetric flask with 300 ml water, carefully add 10 ml HCl, after CO_2 is released by swirling, dilute to volume.
Cerium	(1) Dissolve 4.515 g $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ in 500 ml water to which 30 ml H_2SO_4 had been added, cool, and dilute to volume. Advisable to standardize against As_2O_3. (2) Dissolve 3.913 g $(NH_4)_2Ce(NO_3)_6$ in 10 ml H_2SO_4, stir 2 min, cautiously introduce 15 ml water and again stir 2 min. Repeat addition of water and stirring until all the salt has dissolved, then dilute to volume.
Cesium	Dissolve 1.267 g CsCl and dilute to volume. Standardize: Pipette 25 ml of final solution to Pt dish, add 1 drop H_2SO_4, evaporate to dryness, and heat to constant weight at $\ngtr 800$°C. Cs (in μg/ml) = (40)(0.734)(wt of residue)
Chlorine	Dissolve 1.648 g NaCl and dilute to volume.
Chromium	(1) Dissolve 2.829 g $K_2Cr_2O_7$ in water and dilute to volume. (2) Dissolve 1.000 g Cr in 10 ml HCl, and dilute to volume.
Cobalt	Dissolve 1.000 g Co in 10 ml of 2 *M* HCl, and dilute to volume.
Copper	(1) Dissolve 3.929 g fresh crystals of $CuSO_4 \cdot 5H_2O$, and dilute to volume. (2) Dissolve 1.000 g Cu in 10 ml HCl plus 5 ml water to which HNO_3 (or 30% H_2O_2) is added dropwise until dissolution is complete. Boil to expel oxides of nitrogen and chlorine, then dilute to volume.
Dysprosium	Dissolve 1.1477 g Dy_2O_3 in 50 ml of 2 *M* HCl; dilute to volume.
Erbium	Dissolve 1.1436 g Er_2O_3 in 50 ml of 2 *M* HCl; dilute to volume.
Europium	Dissolve 1.1579 g Eu_2O_3 in 50 ml of 2 *M* HCl; dilute to volume.
Fluorine	Dissolve 2.210 g NaF in water and dilute to volume.
Gadolinium	Dissolve 1.152 g Gd_2O_3 in 50 ml of 2 *M* HCl; dilute to volume.
Gallium	Dissolve 1.000 g Ga in 50 ml of 2 *M* HCl; dilute to volume.
Germanium	Dissolve 1.4408 g GeO_2 with 50 g oxalic acid in 100 ml of water; dilute to volume.

Appendix 1: (Cont.)

Element	Procedure
Gold	Dissolve 1.000 g Au in 10 ml of hot HNO_3 by dropwise addition of HCl, boil to expel oxides of nitrogen and chlorine, and dilute to volume. Store in amber container away from light.
Hafnium	Transfer 1.000 g Hf to Pt dish, add 10 ml of 9 *M* H_2SO_4, and then slowly add HF dropwise until dissolution is complete. Dilute to volume with 10% H_2SO_4.
Holmium	Dissolve 1.1455 g Ho_2O_3 in 50 ml of 2 *M* HCl; dilute to volume.
Indium	Dissolve 1.000 g In in 50 ml of 2 *M* HCl; dilute to volume.
Iodine	Dissolve 1.308 g KI in water and dilute to volume.
Iridium	(1) Dissolve 2.465 g Na_3IrCl_6 in water and dilute to volume. (2) Transfer 1.000 g Ir sponge to a glass tube, add 20 ml of HCl and 1 ml of $HClO_4$. Seal the tube and place in an oven at 300°C for 24 hr. Cool, break open the tube, transfer the solution to a volumetric flask, and dilute to volume. Consult (*4*) and observe all safety precautions in opening the glass tube.
Iron	Dissolve 1.000 g Fe wire in 20 ml of 5 *M* HCl; dilute to volume.
Lanthanum	Dissolve 1.1717 g La_2O_3 (dried at 110°C) in 50 ml of 5 *M* HCl, and dilute to volume.
Lead	(1) Dissolve 1.5985 g $Pb(NO_3)_2$ in water plus 10 ml HNO_3, and dilute to volume. (2) Dissolve 1.000 g Pb in 10 ml HNO_3, and dilute to volume.
Lithium	Dissolve a slurry of 5.3228 g Li_2CO_3 in 300 ml of water by addition of 15 ml HCl, after release of CO_2 by swirling, dilute to volume.
Lutetium	Dissolve 1.6079 g $LuCl_3$ in water and dilute to volume.
Magnesium	Dissolve 1.000 g Mg in 50 ml of 1 *M* HCl and dilute to volume.
Manganese	(1) Dissolve 1.000 g Mn in 10 ml HCl plus 1 ml HNO_3, and dilute to volume. (2) Dissolve 3.0764 g $MnSO_4 \cdot H_2O$ (dried at 105°C for 4 hr) in water and dilute to volume. (3) Dissolve 1.5824 g MnO_2 in 10 HCl in a good hood, evaporate to gentle dryness. dissolve residue in water and dilute to volume.
Mercury	Dissolve 1.000 g Hg in 10 ml of 5 *M* HNO_3 and dilute to volume.
Molybdenum	(1) Dissolve 2.0425 g $(NH_4)_2MoO_4$ in water and dilute to volume. (2) Dissolve 1.5003 g MoO_3 in 100 ml of 2 *M* ammonia, and dilute to volume.
Neodymium	Dissolve 1.7373 g $NdCl_3$ in 100 ml 1 *M* HCl and dilute to volume.
Nickel	Dissolve 1.000 g Ni in 10 ml hot HNO_3, cool, and dilute to volume.
Niobium	Transfer 1.000 g Nb (or 1.4305 g Nb_2O_5) to Pt dish, add 20 ml HF, and heat gently to complete dissolution. Cool, add 40 ml H_2SO_4, and evaporate to fumes of SO_3. Cool and dilute to volume with 8 *M* H_2SO_4.

Appendix 1: (Cont.)

Element	Procedure
Osmium	Dissolve 1.3360 g OsO_4 in water and dilute to 100 ml. Prepare only as needed as solution loses strength on standing unless Os is reduced by SO_2 and water is replaced by 100 ml 0.1 *M* HCl.
Palladium	Dissolve 1.000 g Pd in 10 ml of HNO_3 by dropwise addition of HCl to hot solution; dilute to volume.
Phosphorus	Dissolve 4.260 g $(NH_4)_2HPO_4$ in water and dilute to volume.
Platinum	Dissolve 1.000 g Pt in 40 ml of hot aqua regia, evaporate to incipient dryness, add 10 ml HCl and again evaporate to moist residue. Add 10 ml HCl and dilute to volume.
Potassium	Dissolve 1.9067 g KCl (or 2.8415 g KNO_3) in water and dilute to volume.
Praseodymium	Dissolve 1.1703 g Pr_2O_3 in 50 ml of 2 *M* HCl; dilute to volume.
Rhenium	Dissolve 1.000 g Re in 10 ml of 8 *M* HNO_3 in an ice bath until initial reaction subsides, then dilute to volume.
Rhodium	Dissolve 1.000 g Rh by the sealed-tube method described under iridium (*4*).
Rubidium	Dissolve 1.4148 g RbCl in water. Standardize as described under cesium. Rb (in μg/ml) = (40)(0.320)(wt of residue).
Ruthenium	Dissolve 1.317 g RuO_2 in 15 ml of HCl; dilute to volume.
Samarium	Dissolve 1.1596 g Sm_2O_3 in 50 ml of 2 *M* HCl; dilute to volume.
Scandium	Dissolve 1.5338 g Sc_2O_3 in 50 ml of 2 *M* HCl; dilute to volume.
Selenium	Dissolve 1.4050 g SeO_2 in water and dilute to volume or dissolve 1.000 g Se in 5 ml of HNO_3, then dilute to volume.
Silicon	Fuse 2.1393 g SiO_2 with 4.60 g Na_2CO_3, maintaining melt for 15 min in Pt crucible. Cool, dissolve in warm water, and dilute to volume. Solution contains also 2000 μg/ml sodium.
Silver	(1) Dissolve 1.5748 g $AgNO_3$ in water and dilute to volume. (2) Dissolve 1.000 g Ag in 10 ml of HNO_3; dilute to volume. Store in amber glass container away from light.
Sodium	Dissolve 2.5421 g NaCl in water and dilute to volume.
Strontium	Dissolve a slurry of 1.6849 g $SrCO_3$ in 300 ml of water by careful addition of 10 ml of HCl, after release of CO_2 by swirling, dilute to volume.
Sulfur	Dissolve 4.122 g $(NH_4)_2SO_4$ in water and dilute to volume.
Tantalum	Transfer 1.000 g Ta (or 1.2210 g Ta_2O_5) to Pt dish, add 20 ml of HF, and heat gently to complete the dissolution. Cool, add 40 ml of H_2SO_4 and evaporate to heavy fumes of SO_3. Cool and dilute to volume with 50% H_2SO_4.
Tellurium	(1) Dissolve 1.2508 g TeO_2 in 10 ml of HCl; dilute to volume. (2) Dissolve 1.000 g Te in 10 ml of warm HCl with dropwise addition of HNO_3, then dilute to volume.

Appendix 1: (Cont.)

Element	Procedure
Terbium	Dissolve 1.6692 g of $TbCl_3$ in water, add 1 ml of HCl, and dilute to volume.
Thallium	Dissolve 1.3034 g $TlNO_3$ in water and dilute to volume.
Thorium	Dissolve 2.3794 g $Th(NO_3)_4 \cdot 4H_2O$ in water, add 5 ml HNO_3, and dilute to volume.
Thulium	Dissolve 1.142 g Tm_2O_3 in 50 ml of 2 *M* HCl; dilute to volume.
Tin	Dissolve 1.000 g Sn in 15 ml of warm HCl; dilute to volume.
Titanium	Dissolve 1.000 g Ti in 10 ml of H_2SO_4 with dropwise addition of HNO_3; dilute to volume with 5% H_2SO_4.
Tungsten	Dissolve 1.7941 g of $Na_2WO_4 \cdot 2H_2O$ in water and dilute to volume.
Uranium	Dissolve 2.1095 g $UO_2(NO_3)_2 \cdot 6H_2O$ (or 1.7734 g uranyl acetate dihydrate) in water and dilute to volume.
Vanadium	Dissolve 2.2963 g NH_4VO_3 in 100 ml of water plus 10 ml of HNO_3; dilute to volume.
Ytterbium	Dissolve 1.6147 g $YbCl_3$ in water and dilute to volume.
Yttrium	Dissolve 1.2692 g Y_2O_3 in 50 ml of 2 *M* HCl and dilute to volume.
Zinc	Dissolve 1.000 g Zn in 10 ml of HCl; dilute to volume.
Zirconium	Dissolve 3.533 g $ZrOCl_2 \cdot 8H_2O$ in 50 ml of 2 *M* HCl, and dilute to volume. Solution should be standardized.

Appendix 2: Special Aqueous Stock Solutions

	Concentration	Procedure
Element		
Barium	0.0625 *N*	Dissolve 6.506 g $BaCl_2$ (dried at 250°C for 2 hr), dilute to volume. One ml is equivalent to 1.00 mg of sulfate sulfur.
Calcium	100 meq per liter	Dissolve a slurry of 5.006 g $CaCO_3$ (dried at 105°C) in 300 ml of water by careful addition of 10 ml HCl; after CO_2 is released, dilute to volume.
Lithium	200 meq per liter (as Li)	Dissolve a slurry of 7.392 g Li_2CO_3 in 300 ml of water by addition of 15 ml HCl; after release of CO_2, dilute to volume.
	2000 μg/ml (as Li_2O)	Dissolve 4.945 g Li_2CO_3 as above.

Appendix 2: (Cont.)

	Concentration	Procedure
Magnesium	100 meq per liter (as Mg)	Dissolve 1.2156 g Mg in 50 ml of 1 *M* HCl; dilute to volume.
Manganese	1000 μg/ml (as Mn_2O_3)	Dissolve 2.1412 g $MnSO_4 \cdot H_2O$ (dried at 105°C for 4 hr) and dilute to volume.
Potassium	100 meq per liter (as K)	Dissolve 7.456 g KCl and dilute to volume.
	1000 μg/ml (as K_2O)	Dissolve 1.5830 g KCl and dilute to volume.
Sodium	100 meq per liter (as Na)	Dissolve 5.846 g NaCl and dilute to volume.
	1000 μg/ml (as Na_2O)	Dissolve 1.886 g NaCl and dilute to volume.
Strontium	1000 μg/ml (as SrO)	Dissolve a slurry of 1.6848 g $SrCO_3$ as described for calcium.
Mixture		
Alkali-manganese solution	1000 μg/ml each Na_2O, K_2O, Mn_2O_3	Dissolve in water 1.886 g NaCl, 1.583 g KCl, and 2.1412 g $MnSO_4 \cdot H_2O$ (dried at 105°C for 4 hr) and dilute to volume.
Lime-acid solution	6300 μg/ml CaO in 1:9 HCl	Add 100 ml HCl to 11.244 g $CaCO_3$ suspended in 300 ml of water; after CO_2 is released, dilute to volume.
Sea water	Chlorinity 38%	Dissolve 47.0 g NaCl, 21.3 g $MgCl_2 \cdot 6H_2O$, 17.8 g $Na_2SO_4 \cdot 10H_2O$, 2.20 g $CaCl_2$, 1.46 g KCl, 0.38 g $NaHCO_3$, and 0.015 g $SrCl_2$; and dilute to volume.

Appendix 3: Standard Reference Materials in Lubricating Oil (Element of Interest, 500 μg/g)

NBS No.[a]	Element of interest	Compound	Drying time, hr[b]	Weight used, g[c]
1075a	Al	2-Ethylhexanoate	48	0.620
1051b	Ba	Cyclohexanebutyrate	24	0.174
1063a	B	Menthyl borate	2	2.08
1053	Cd	Cyclohexanebutyrate	48	0.202
1074a	Ca	2-Ethylhexanoate	48	0.373

Appendix 3: (Cont.)

NBS No.[a]	Element of interest	Compound	Drying time, hr[b]	Weight used, *g*[c]
1078	Cr	Tris(1-phenyl-1,3-butanediono)-chromium(III)	1	0.515
1055b	Co	Cyclohexanebutyrate	24	0.337
1080	Cu	Bis(1-phenyl-1,3-butanediono)-copper(II)	0.5	0.303
1079b	Fe	Tris(1-phenyl-1,3-butanediono)-iron(III)	1	0.485[d]
1059b	Pb	Cyclohexanebutyrate	48	0.136
1060a	Li	Cyclohexanebutyrate	24	1.22
1061b	Mg	Cyclohexanebutyrate	48	0.765
1062a	Mn	Manganese(II) cyclohexanebutyrate	48	0.362
1064	Hg	Mercury(II) cyclohexanebutyrate	2	0.138
1065b	Ni	Cyclohexanebutyrate	48	0.360
1071a	P	Triphenyl phosphate	2	0.526
1076	K	Erucate	2	0.495
1066	Si	Octaphenylcyclotetrasiloxane	0	0.141[e]
1077a	Ag	2-Ethylhexanoate	24	0.117
1069b	Na	Cyclohexanebutyrate	48	0.417
1070a	Sr	Cyclohexanebutyrate	24	0.242
1057b	Sn	Dibutyltin bis(2-ethylhexanoate)	2	0.218
1052b	V	Bis(1-phenyl-1,3-butanediono)-oxovanadium(IV)	2	0.348
1073b	Zn	Cyclohexanebutyrate	48	0.299

[a] National Bureau of Standards (U.S.) standard reference material.

[b] Dried over P_2O_5 in desiccator.

[c] Weight of dried material which contains 50 mg of element of interest.

[d] Dried in oven at 110°C.

[e] Weight of element, 20 mg, and gives a final concentration of 200 μg/g.

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APPENDIX XV

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Determination of Submicrogram Amounts of Mercury in Standard Reference Materials by Flameless Atomic Absorption Spectrometry

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In a study of the flameless atomic absorption method for the determination of nanogram amounts of mercury in organic materials, the technique was improved to provide greater precision and accuracy. The loss of mercury during the digestion of organic materials with nitric, sulfuric, and perchloric acids is prevented by controlled heating and a packed refluxing column. The reduction and absorption system was simplified by using a heated absorption cell which alleviates the interference of volatile vapors. This method has been applied to the determination of mercury in NBS Standard Reference Materials of orchard leaves, liver, and coal, and the results were compared with results obtained with 2 other analytical methods.

As part of the program for characterizing botanical and related materials for trace elements, flameless atomic absorption was evaluated for the determination of mercury in orchard leaves, liver, and coal. Flameless atomic absorption yielded results comparable in accuracy and precision to results obtained by all other methods compared for the determination of nanogram quantities of mercury.

As early as 1930 Müller (1) took advantage of the high vapor pressure of mercury for its determination in air and in 1939 Woodson (2) described an instrument used for the same purpose. Since this early work, many workers have used the same general approach. A review of flameless methods for the determination of mercury by atomic absorption spectrometry has been presented by Manning (3).

Hatch and Ott (4) used the cold vapor technique for determining mercury in nickel and cobalt metals and in rock samples. The cloud system was used in which the mercury vapor was continuously recirculated until a maximum signal was attained. The procedure included a cumbersome technique for the removal of water vapor prior to final measurement and frequent changing of the drying agent was essential to obtain reproducible values. In addition, the precision and accuracy necessary for the analysis of standard reference materials were not attainable with the method of Hatch and Ott. Further studies in our laboratory led to modifications of the general procedure. These included selection of the dissolution step, elimination of the drying agents, and provision for the heating of the absorption cell. Other parameters, such as techniques to minimize the contamination of the environment, selection of a reductant, control of reaction volume, choice of purge gas, and the role of interfering substances, were studied. Also, the use of a double beam (ratio method) was investigated.

METHOD

Reagents

(a) *Mercury standard solutions.*—(*1*) *Stock solution.*—1.000 mg/ml. Dissolve 1.000 g ultra high purity mercury (99.99%) in $0.1N$ HNO_3 and dilute to 1 L in same solvent. (*2*) *Working solution.*—Prepare fresh daily by transferring 10.0 ml stock solution to 1 L volumetric flask and dilute to volume with $0.1N$ HNO_3. Mix and transfer 1.0 ml of this solution to 1 L volumetric flask and dilute to volume with $0.1N$ HNO_3.

(b) *Reducing solution.*—To 500 ml volumetric flask, add 300 ml water and 50 ml H_2SO_4. Cool to ambient temperature, add 15 g NaCl, and shake to dissolve. After NaCl is completely dissolved, add 25 g $SnCl_2$, shake until solution occurs, and dilute to volume.

(c) *Diluting solution.*—Aqueous acid solution $1N$ in HNO_3 and $2.4N$ in H_2SO_4. Use ultra high purity acids and check for mercury content before use. (Use only acids which contain <0.5 ng Hg/ml.) Use distilled water passed through mixed ion exchange column resin bed prior to use.

Apparatus

(a) *Atomic absorption spectrometer.*—Double beam (ratio method) instrument, consisting of 0.5 and

0.25 m Ebert mount monochromators (Jarrell-Ash) with gratings blazed for 3000 Å, beam splitter, mechanical chopper, electronic circuitry comprised of 4 units (0–2100 v multiplier phototube power supply, selective amplifier and synchronous detector, ratio converter, and DCR-2 digital readout), and chart recorder. Schematic diagram of system is shown in Fig. 1.

In ratio mode, use 2 identical channels, one for signal A (Hg line at 2537 Å) and the other for signal B (Al line at 2652 Å). Use signal B as reference for obtaining A/B ratio. Input of each channel is derived from multiplier phototube powered by single dc power source. Output of photodetector is amplified and fed into digital readout. In absorption mode, outputs of 2 filter-amplifier stages provide 2 potentials for ratio measurement.

(b) *Mercury hollow cathode lamp.*—Powered by stable power supply and operated at 8 ma. Aluminum signal is obtained from aluminum-mercury amalgam on aluminum sleeve in lamp. Any commercially available hollow cathode lamp capable of providing both mercury and aluminum signals is acceptable.

(c) *Absorption cell.*—Construct from 30 cm × 0.8 cm id Vycor tubing with gas inlet and outlet ports and quartz windows. Secure quartz windows to Vycor tubing with epoxy cement. Wrap cell with heating tape to maintain surface temperature at 200°C with aid of variable autotransformer.

(d) *Reduction cell.*—125 ml gas-washing bottle with coarse fritted bubbler. Introduce purge gas into reduction cell through flowmeter (0.3 L/min) and $\frac{1}{16}$″ Teflon tube connecting reduction cell to absorption cell (length of connecting tube is not critical).

(e) *Digestion flask.*—250 ml flat-bottom boiling flask with ₮ 24/40 joint, 300 mm Allihn condenser filled to 50 mm with Raschig rings and glass beads, and heating mantle.

Calibration

(*Note:* Use ratio mode for all samples in which an interferent is suspected. If no interferent is present, use single beam system.)

In the ratio mode, adjust 0.5 and 0.25 m monochromators to read 100% transmission at Hg 2537 and Al 2652 lines, respectively. For the single beam system, adjust only 0.5 m monochromator to read 100% transmission at Hg 2537 Å. Heat absorption cell to 200°C and adjust argon flow through reduction cell and absorption cell to 0.25 L/min. Transfer aliquots of standard mercury working solution containing 0.01–0.2 μg Hg to reduction cell and dilute to 25 ml with diluting solution. Add 20 ml reducing solution and immediately close system. Record maximum absorbance and minimum ratio value of Hg/

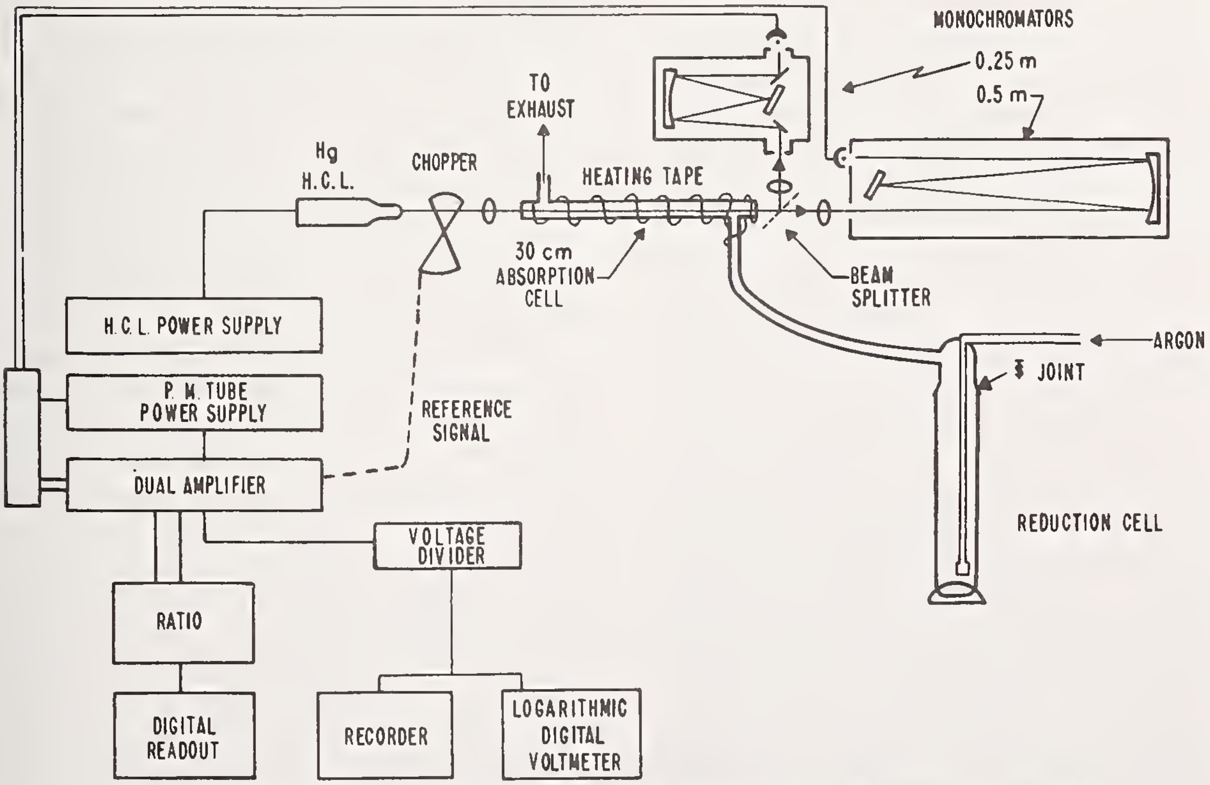

FIG. 1—Schematic diagram of instrumentation for flameless atomic absorption spectrometry.

Al line from digital readouts. Plot absorbance and/or ratio values obtained independently against μg Hg to give linear calibration curve.

Absorbance signal appears immediately, reaches maximum within 20–30 sec, remains constant ca 5 sec, and then slowly decreases to zero. Time required for signal to return to background under these conditions is ca 2 min. To speed up return of signal to baseline, remove aeration tube from sample solution in reduction cell after peak absorbance has been recorded and insert tube into clean flask containing dilute HNO_3. Analysis is completed within 1 min if this technique is used.

Determination

Transfer 2–3 g sample to digestion flask. Add 25 ml 18*N* H_2SO_4 and 20 ml 7*N* HNO_3 and connect Allihn condenser with cooling water. Using heating mantle, gently heat flask 1 hr at 150°C. (See *Note* for digestion of coal samples.) Cool flask and add 20 ml HNO_3-$HClO_4$ (1+1) through condenser. Drain water from condenser and heat flask until dense fumes of perchlorate appear. Cool and rinse condenser with two 5 ml portions of water. Reheat flask to dense fumes of perchlorate. Cool and transfer solution to volumetric flask and dilute to volume.

Note: For coal samples, digestion time will vary with particle size. Carry out $HClO_4$ digestion of coal behind safety shield.

Results and Discussion

Digestion.—The digestion step is critical, since mercury is easily reduced and subsequently lost in the vapor phase during the destruction of organic material. Therefore, several methods for digestion were screened. Combustion by the Schöninger method was examined; however, this technique is governed by flask size. For a 1 L flask, the amount of organic material was limited to 0.2 g. The sealed tube method (5) employing nitric and sulfuric acids was also investigated for digesting organic material (orchard leaves); however, 2 difficulties arose. The maximum sample size was again limited to 0.2 g and the oxides of nitrogen which were liberated during the digestion caused excessive frothing in the subsequent reduction step. To overcome this difficulty, the solution was removed from the sealed tube and gently heated. Under these conditions, and even though the mercury is present as Hg^{2+}, there is danger of loss of trace quantities of mercury (6).

The most successful digestion procedure was a modification of the one described by Munns and Holland (7). Initially, frothing and physical losses were difficult to control when refluxing was done by flame. By carefully controlling the heating rate with a heating mantle, foaming was prevented and antifoaming agents were unnecessary. Organic materials such as orchard leaves, liver, and coal were successfully digested without loss of mercury, using a mixture of nitric, sulfuric, and perchloric acids.

The recovery of mercury was verified in a study using orchard leaves and ^{203}Hg tracer. The tracer was counted with a single channel scintillation gamma counter. As shown in Table 1, loss of free mercury will occur unless the water condenser contains Raschig rings. A 20–30% loss of activity was observed when a sample of orchard leaves with ^{203}Hg added was digested under reflux conditions to oxidize the mercury and then transferred to a beaker to reduce the volume of acid with heat. Only if mercury carrier with ^{203}Hg was added to the sample solution which was subsequently evaporated did the loss of ^{203}Hg become negligible.

It was observed that carrier-free mercury had a tendency to escape. Experiments with 0.1 ml carrier-free ^{203}Hg in a 10 × 100 cm counting tube led to a reduction of 20%/day in the counting rate. Upon investigation, it was found that the ^{203}Hg activity collected on the cork stopper. This occurred regardless of the acidity (nitric or sulfuric acid) of the tracer. However, in the presence of 100 μg mercury carrier no loss of ^{203}Hg to the cork stopper of the counting tube was noted.

Interferences of Vapors.—Several methods are reported for trapping vapors which enter the absorption cell and lead to light scattering or molecular absorption. Either a cold trap with a mixture of salt and ice (−10°C) or drying agents such as magnesium perchlorate or anhydrous calcium sulfate are used (3). Each method was tested and was found satisfactory for only a short operating period. Even a vapor trap containing glass beads or glass wool was found to be unsatisfactory. The most successful method was to pass the mercury vapor from the reduction cell directly into the absorption cell by means of a Teflon tube. Since moisture condenses on the window of the absorption cell, the cell was heated with heating tape to 200°C. At this temperature, as shown in Table 2, there was no shift in the baseline over a 2 hr period while the baseline was constantly changing at the other absorption cell

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Table 1. Loss of ^{203}Hg in orchard leaves during digestion[a]

Detn No.	Conditions of Digestion	Loss of ^{203}Hg, %
1	digestion flask, water condenser, and Raschig rings	0.2
2	digestion flask, water condenser	4.1
3	250 ml Erlenmeyer flask, cover lid	12.3
4	250 ml beaker, cover lid	61.7
5	50 ml solution from No. 1 evaporated in beaker to 2 ml	23.3

[a] Digestion flask contained 1 g orchard leaves, 25 ml 18N H_2SO_4, 20 ml 7N HNO_3, and 10 ml $HClO_4$. ^{203}Hg present as tracer gave 1 × 10^6 counts/min before digestion was started.

temperatures. With this arrangement (Fig. 1) the flow rate of sweep gas was maintained at 0.2–0.3 L/min. Flow rates above 0.5 L/min introduced excessive amounts of moisture into the absorption cell and caused a continuous baseline drift.

Reduction of Mercury.—Stannous chloride, stannous chloride with hydroxylamine hydrochloride, and hypophosphorous acid were investigated as reducing agents for mercury. Hydroxylamine hydrochloride is normally added with the stannous chloride as an aid in reducing excess oxidants; however, the hydroxylamine hydrochloride was a constant source of mercury contamination, resulting in a high reagent blank. To overcome this difficulty, the hydroxylamine hydrochloride was eliminated from the procedure with no adverse effects.

Hypophosphorous acid was about as effective as stannous chloride as a reductant for solutions of mercury in dilute nitric acid. However, in solutions from samples of orchard leaves and coal, the recoveries ranged from 0 to 90%. Also, excessive foaming was observed in the reduction cell in the presence of hypophosphorous acid.

In some tests, foaming also occurred with stannous chloride as the reductant. To minimize this problem in the reduction cell, all traces of organic material must be removed. To aid in the removal of organic material during the digestion step, the sample is taken to strong fumes of perchlorate. After the sample has cooled 5 min, the reflux condenser is rinsed with water and the sample is reheated to strong fumes of perchlorate.

Effect of Volume in the Reduction Cell.—When the reduction is carried out in a 125 ml vessel, the absorbance reading is constant for sample volumes of 5–30 ml. Sample volumes greater than 30 ml give a slightly lower absorbance reading. For a sample volume of 75 ml, a 30% loss in absorbance is observed.

Table 2. Effect of temperature of absorption cell on absorption of mercury and shift in baseline from zero absorbance over a 2 hr period

Temp. of Absorption Cell, °C	Shift in Baseline	Absorbance of 0.3 μg Hg
200	0.000	1.113
170	0.010	1.100
155	0.150	1.045
145	0.224	1.085
135	0.260	1.140
125	0.306	1.197
105	0.432	1.027

Effect of Sweep Gas.—In the described flow-through system for mercury, argon and air were investigated as sweep gases. In all tests, argon was found to be superior with a 25% increase in absorbance for mercury.

Since foaming in the reduction reaction vessel is a problem associated with some types of materials, the effect of a purge with argon or air, prior to the reduction of mercury, was studied. With a prior purge of the sample solution, a 25–75% loss of mercury was observed. The loss of mercury without a reducing agent has been attributed to the reduction of Hg^{2+} to Hg^{+}, which subsequently disproportionates to Hg^{2+} and Hg^0 (6). Trace quantities of organic material which are known to be present in water-pumped air or argon gas are sufficient to reduce nanogram quantities of mercury. If a prior purge of the sample is needed, an excess of oxidant such as potassium permanganate must be present to prevent mercury loss.

Interferences.—The role of acidity and anion interference was studied. The effect of a number of anions on the release of atomic mercury is shown in Table 3. In these studies, solutions containing 0.1 μg mercury in the presence of various anions as the acid, except for the iodide and bromide, were carried through the procedure. The reference solution contained 0.1 μg mercury in 0.001N HNO_3. It is evident from this study that the anions of all acids do affect the release of mercury in varying degrees, especially iodide, bromide, sulfate, and phosphate.

In the presence of minor quantities of cations,

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Table 3. Effect of extraneous anions on recovery of mercury[a] (reduction step)

Anion	Concn, *N*	Rec., %
NO_3^{-1}	0.06	95
	0.6	88
	3.0	88
	6.0	81
	9.0	86
Cl^{-1}	0.4	95
	1.6	97
	3.6	94
	5.4	82
	7.2	73
ClO_4^{-1}	0.5	97
	1.0	88
	2.4	82
	4.8	66
Br^{-1}[b]	0.01	96
	0.02	75
I^{-1}[b]	0.002	97
	0.02	3
SO_4^{-2}	0.4	99
	0.8	95
	3.6	78
	7.2	50
$C_2O_4^{-2}$	0.2	92
	0.4	90
	0.6	77
PO_4^{-3}	0.18	98
	1.8	82
	9.0	65

[a] Total mercury present = 0.1 μg.
[b] Added as the sodium salt.

no adverse effect was observed. However, when an excess of reducible ion was present, e.g., $Cr_2O_7^{-2}$, the mercury was not released, owing to an insufficient quantity of reducing agent.

Contamination Problems.—Contamination from reagents, glassware, and the environment were encountered with mercury. To minimize this contamination, all glassware was rinsed with 10% nitric acid. Samples stored in glass for over one week showed that values for mercury increased by 50–100%. Therefore, polypropylene flasks were used for storage. To illustrate the degree of contamination of reagents by mercury, 3 bottles of the same lot of hydroxylamine hydrochloride were analyzed and were found to contain 0.008, 0.027, and 0.031 μg Hg/g, respectively. In another lot, the mercury content was 0.001 μg Hg/g. Ultra high purity acids were also tested. Some lots of ACS reagent grade nitric acid contained as much as 30 ng Hg/ml and had to be redistilled by sub-boiling distillation from an all-quartz still.

Table 4. Comparison of results obtained with different methods for the determination of mercury in NBS Standard Reference Materials[a]

Method	No. of Determinations	Hg, μg/g	Std Dev.[b]	Rel. Std Dev., %
Orchard Leaves (NBS-SRM-1571)				
AAS[c] (single beam)	7	0.160	0.006	4.0
AAS (ratio)	6	0.160	0.006	4.0
Neutron activation	11	0.155	0.003	1.8
Isotopic dilution mass spectrometry	7	0.14	0.02	16
Liver (NBS-SRM-1577)				
AAS (single beam)	6	0.0165	0.0008	5
Neutron activation	9	0.0145	0.0017	12
Coal (NBS-SRM-1630)				
AAS (single beam)	7	0.139	0.007	4.7
Neutron activation	55	0.127	0.006	4.8

[a] NBS Standard Reference Materials are available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.
[b] For a single determination.
[c] AAS = atomic absorption spectrometry.

Another possible source of contamination is the vacuum oven and/or desiccant. Samples of orchard leaves, which were dried at different intervals over a period of 3 months in 2 different vacuum ovens at 90°C for 24 hr and then cooled in a desiccator over anhydrous calcium sulfate, produced mercury values which were 25–50% higher than the undried samples. The anhydrous calcium sulfate was tested and was found to contain traces of mercury. These studies reinforce the conclusion for the need of careful checks on all sources of possible contamination.

Comparison of Single Beam and Double Beam (Ratio) Systems.—This study was designed to evaluate the accuracy of the flameless atomic absorption method for determining mercury. By comparing data in the literature by the flameless method with other analytical techniques, we observed that the flameless method produced higher values. The higher values may have resulted from improper background correction due to molecular absorption or from scattering of light. To correct these 2 sources of error, mercury was determined in orchard leaves by both the single beam and double beam (ratio) system. As shown in Table 4, the 2 methods gave the same values when the proposed method was used. However, when the temperature of the absorption cell was less than 145°C, the absorption values for mercury were erratic and higher in the single beam system. In this case, by taking a ratio of the Hg line at 2537 Å to the Al line at 2652 Å in the double beam system, a correction for light scattering and/or molecular absorption, due to water and other vapors, was made.

Application of the Method.—The method was tested on 3 types of NBS Standard Reference Materials as shown in Table 4. This technique has also been used for the determination of nanogram quantities of mercury in samples of aluminum alloys, reactor cooling water, and water effluents.

In summary, this study reveals that flameless atomic absorption analysis of mercury can be made to be precise and accurate in comparison with 2 independent techniques.

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APPENDIX XVI

DISCUSSION OF SOME EXPERIMENTAL AND FUNDAMENTAL CONDITIONS IN ANALYTICAL FLAME SPECTROSCOPY

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> « Do not all fix'd Bodies, when heated beyond a certain degree, emit Light and shine; and is not this Emission perform'd by the vibrating motions of their parts? » Sir Isaac Newton. *Opticks*, 1730.

The first part of this paper will be devoted to a more detailed discription of this measuring tool which was designed and built at NBS and is now used for analytical work and for studies of various flame parameters.

In the second part the reader will find a general discussion of nonthermal excitation phenomena occurring in combustion flames. The particular case of chilled hydrogen flames will be examined and illustrated with two examples involving the excitation of sulfur and phosphorus contained in air as inorganic and organic molecules.

Discussion de quelques conditions expérimentales et fondamentales en spectroscopie analytique de flamme.

La première partie de ce travail est consacrée à une description détaillée des procédés de mesure qui ont été conçus et réalisés au National Bureau of Standards, et maintenant utilisés dans les travaux analytiques et pour l'étude des divers paramètres de flamme.

Dans la seconde partie, le lecteur trouvera une discussion générale des phénomènes d'excitation non thermique se produisant dans les flammes de combustion. Le cas particulier de la flamme hydrogène refroidie, est examiné et illustré de deux exemples sur l'excitation du soufre et du phosphore contenus dans l'air, sous forme de molécules minérales et organiques.

Diskussion über einige experimentelle und grundlegende Bedingungen in der analytischen Flamm-Spektroskopie.

Der erste Teil dieser Arbeiten wird einer ins Einzelne gehenden Beschreibung der Messverfahren gewidmet, welche im National Bureau of Standards ausgearbeitet und durchgeführt wurden, und jetzt für die Analysen und die Studie der diversen Flammparameter zur Anwendung kommen.

Im zweiten Teil findet der Leser eine allgemeine Beschreibung über nicht thermische Erregungsvorgänge, die in der Verbrennungsflamme auftreten. Der Sonderfall der gekühlten Wasserstofflamme wird geprüft und an zwei Beispielen über die Erregung des in der Luft enthaltenen Schwefels und L-Phosphors erläutert, in Form von mineralischen und organischen Molekülen.

1. — Introduction.

This discussion will cover certain aspects of the experimental and fundamental nature of flame spectroscopy when used as a measuring tool in analytical chemistry. The underlying principles of this measuring tool have been known for a long time, and are based on the phenomenon that matter, when properly energized, may emit or absorb the exciting energy as electromagnetic radiations having frequencies characteristic of the excited species and whose energy is proportional to the number of particles involved in the process. Thus the frequencies radiated or absorbed serve to identify the excited species, whereas the amount of radiation gives a measure of the quantity of matter involved in the phenomenon. These properties constitute the basis of qualitative and quantitative analytical flame spectroscopy.

Instruments for making measurements in the emission mode have been known for a long time and include an exciting flame with its analytical sample supplying system, a radiation-dispersing instrument, and a photosensitive detector. These basic components are common to all emission spectrophotometers and can be found in the earliest instruments. Figure 1 describes the arrangement used in 1860 by Kirchhoff and Bunsen for their spectroscopic investigations (¹). The same basic elements were applied 13 years later by Champion, Pellet and Grenier who produced in 1873 the first quantitative emission spectrophotometer (²). The instrument, named by its developers the « spectronatromètre », was based on the principle enunciated by Janssen

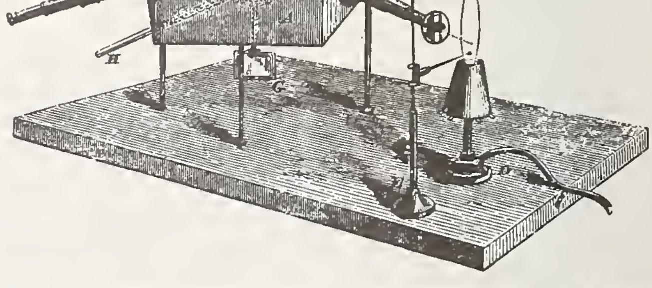


Fig. 1. — Components used by Bunsen and Kirchhoff in their spectroscopic investigations. At the right, the flame excitation source with its sample supplying system; in the middle, the spectroscope; the photosensitive device used to observe the radiations was, in this case, the human eye.

in 1870 (³). The same principle and instrumental elements have been used by Lundegardh in 1929 and 1934 in his pioneering work on analytical flame spectroscopy, and are found today in every emission flame spectrophotometer (⁴).

The instrumental means for performing measurements in the atomic absorption mode include, in addition to those mentioned for the emission mode of operation, a source emitting those radiations which originate from the chemical species to be determined. Again, as was true for the flame emission mode, the principle and the instrumental elements of flame atomic absorption have been known for a long time.

The optical arrangement described in 1872 and 1873 by John Tyndall and shown in figure 2 (⁵) can be used to illustrate the point. One can see the emission source is an electric arc, followed by the absorbing flame with its sample-supplying system, and finally a means to observe the absorption phenomenon. The same arrangement was used in 1953 by Alan Walsh and described in his pioneering works on the application of the atomic absorption principle to chemical analysis (⁶). These same components are found today in all analytical instruments using the atomic absorption principle.

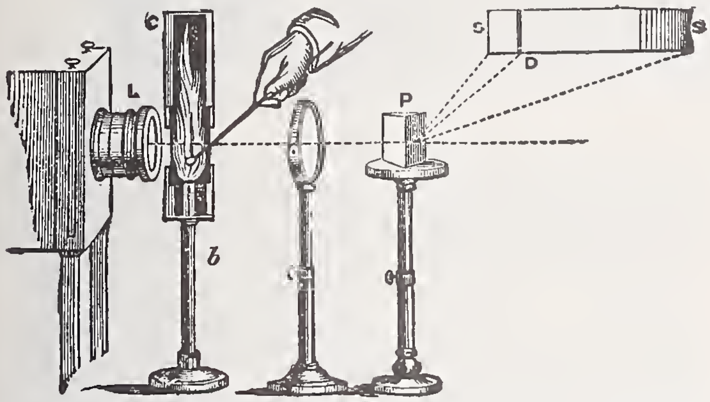


Fig. 2. — Optical arrangement used by Tyndall to demonstrate the principle of atomic absorption. From left to right, emission source followed by the absorbing flame with its sample supplying system and the means to produce and observe the spectrum.

The instrumentation which will be described now, contains the basic components described above. It was designed to utilize the fundamental property of spectral sources to emit or absorb simultaneously at all transitions originating from all species which are excited in the particular source considered. As a consequence of this property, the measuring system was designed and built to detect and measure simultaneously a number of individual radiations emitted or absorbed in the wavelength region of about 2 000 Å to 10.000 Å. The radiations are detected and their intensities are measured in a conventional manner using appropriate photomultiplier tubes and integration of the optical signal over a predetermined time interval. The current developed in the photomultipliers, which is related to the radiation intensity originating from the excitation source and to the concentration of the excited species, is displayed both in analog and digital form. The digital information is printed and punched simultaneously on appropriate tapes. The punched tape is compatible for direct use with a computer programmed to produce meaningful data to the analytical chemist. While this instrumentation does not include any original or new element, it is believed, nevertheless, that the combination of principles and instrumental elements will provide a final measuring tool showing improvements and advantages over the more conventional flame spectrometers of the past.

The first part of this paper will be devoted to a more detailed description of this measuring tool which was designed and built at NBS and is now used for analytical work and for studies of various flame parameters.

In the second part the reader will find a general discussion of nonthermal excitation phenomena occuring in combustion flames. The particular case of chilled hydrogen flames will be examined and illustrated with two examples involving the excitation of sulfur and phosphorus contained in air as inorganic and organic molecules.

2. — Instrumentation.

2.1. *The Spectrometer.*

The spectrometer used to detect the radiations originating from the exciting flame is a conventional 1 m grating instrument using the Czerny-Turner optical arrangement illustrated in figure 3 (⁷). The bilateral variable entrance slit is seen at the left of the instrument. It is followed by a collimating concave mirror which projects a parallel radiation beam on an interchangeable flat grating (100 mm by 100 mm carrying 600 lines/mm or 1 200 lines/mm).

The diffracted radiations are focused as monochromatic images of the entrance slit at the focal plane, contained in the rectangular light-tight enclosure at the right of the spectrometer. A vertical frame is located at the focal plane where it can be moved up and down through a mechanism operated from the outside. It is provided with a counter to indicate its position. The frame can accept interchangeably a bilateral variable exit slit or a cassette capable of holding a photographic plate or film 20 cm by 5 cm. An adapter for Polaroid

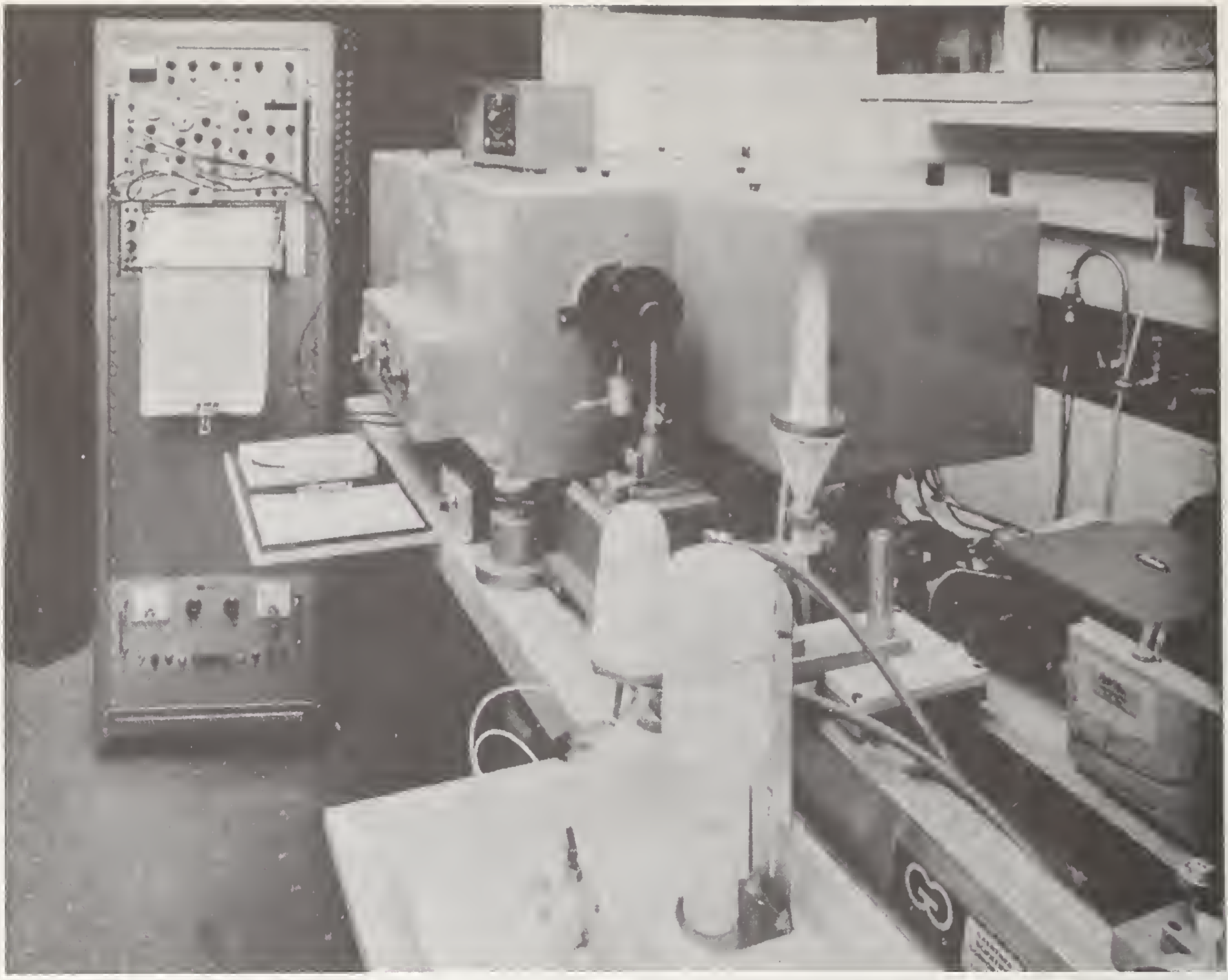


Fig. 3. — NBS flame spectrometer for simultaneous multielement emission and atomic absorption measurements. At the left, console with the electronics used in the scanning mode with digital and analog data presentation. In the center, 1 m Czerny-Turner type scanning monochromator-spectrograph-multielement instrument. At the right, lathe-bed type optical bench carrying the all-alumina sprayer and burner unit and the dual sample solution supplying system. The exponential water column manometer used to monitor the pressure inside the sprayer and burner unit is seen at the extreme right (7).

film is also available. The vertical frame is provided at its lower end with a longitudinal opening 20 cm by 2.5 cm which can accept a number of fixed exit slits or a metal plate into which can be cut a number of slits.

When the variable exit slit is placed in the proper position in the vertical frame, the spectrometer operates as a scanning monochromator. The scanning is performed by rotating the grating through a synchronous electric motor provided with 12 scanning speeds (0.5 to 2 000 Å/mn). A wavelength counter indicates the wavelength directly in 0.1 Å units. When the exit slit is exchanged for the cassette, the instrument can be used as a spectrograph. Finally, when the vertical frame is lifted in its upper position, the multislit arrangement is placed at the focal plane and permits the isolation of a number of individual monochromatic radiations. These radiations are received by individual photomultiplier tubes located on a horizontal support. In this case, the spectrometer operates as a multichannel instrument; this latter arrangement is illustrated in figure 4. In this case, six individual slits are cut in the multislit plate at wavelengths selected to isolate the radiations from Na (λ 5 893 Å); K (λ 7 667 Å); Li (λ 6 707 Å); Ca (λ 4 227 Å); CaOH (λ 6 230 Å); and Mg (λ 2 852 Å). Behind every slit is a side-on photomultiplier provided with the corresponding connections, and a seventh tube is used for the scanning mode.

As can be seen in figure 3, a precision lathe-bed type optical bench 160 cm long is placed along the optical axis in front of the entrance slit of the spectrometer. The following equipment is placed on this bench using appropriate carriers: a quartz lens which produces a demagnified image of the analytical flame on the entrance slit, and the burner and sprayer unit with its dual analytical sample solution supplying system. A second quartz lens, a mirror chopper and a dual hollow cathode arrangement

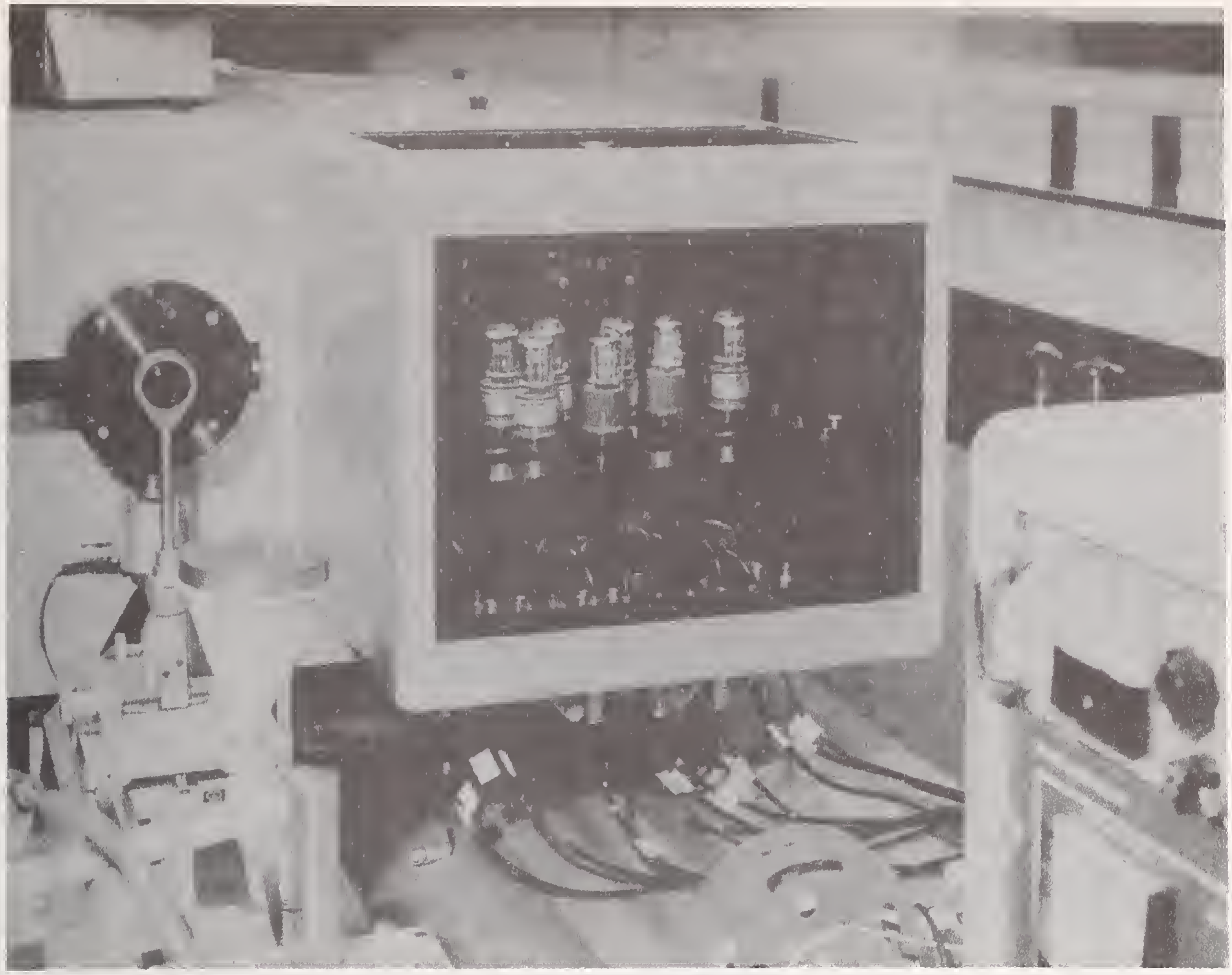


Fig. 4. — Light-tight enclosure located at the focal plane of the spectrometer. It contains seven photomultiplier tubes placed behind the exit slits carrying plate (7).

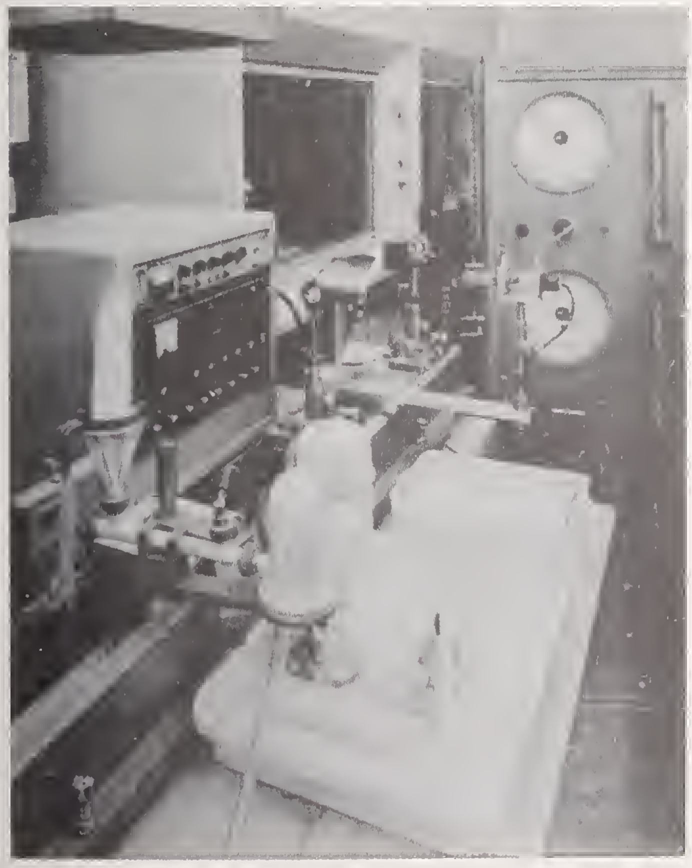


Fig. 5. — The opposite extremity of the optical bench from figure 3 is seen here with the sprayer and burner unit together with the dual sample supplying system, and with the additional equipment. This consists of a quartz lens, the mirror chopper, and the dual hollow cathode arrangement. At upper left, console containing the electronics used in conjunction with the multichannel mode of operation. At the right, console carrying the equipment used to regulate and monitor the flow of oxidant and fuel gases supplied to the sprayer and burner unit (7).

follows and is illustrated in figure 5. The mirror chopper directs successive radiations from the two hollow cathodes through the optical axis of the instrument, and at the same time generates an ac signal. Such a dual hollow cathode system was proposed previously by other workers.

The lenses, burner and sprayer unit, chopper, and hollow cathodes can be positioned along the optical axis in the x-y-z directions and can be tightly secured in the correct position.

2.2. — *Electronic Circuitry.*

The electronic equipment used with the scanning mode is shown in figure 3. It consists of conventional solid state elements, such as a wide band pre-amplifier, providing a gain of 100, a selective amplifier providing a gain of 10, and a lock-in amplifier providing a gain of 10. The output from the lock-in amplifier is supplied to a 4 digit digital voltmeter and to an analog recorder. The power supply for the scanning photomultiplier is seen at the top of the console and it has a *dc* output of 2 100 volts and 30 milliamperes with a line and load regulation of 0.001 percent and a stability of 0.005 percent per hour. At the bottom of the same console, one can see the power supply for the hollow cathode tubes which has the following general characteristics : current output range 2.2 μA to 220 mA; voltage 730 V; current regulation 0.1 percent; stability : 0.2 percent. The operation of the spectrometer in the scanning mode is conventional and does not require further discussion (since the electronic system uses a lock-in amplifier the lock-in chopper seen in figure 5 is moved between the flame source and the entrance slit of the spectrometer).

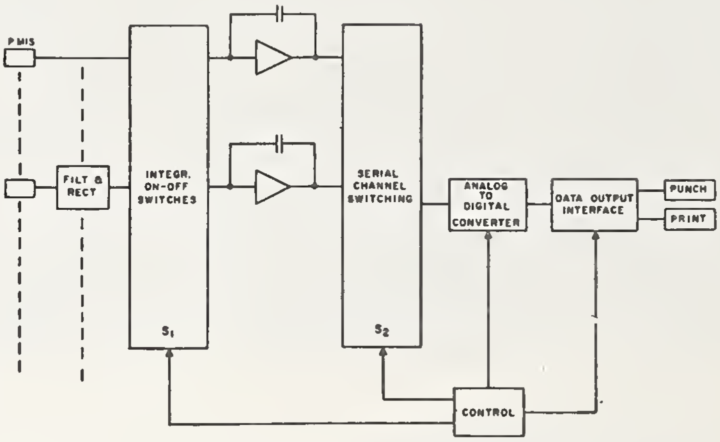


Fig. 6. — Block diagram of the electronic system used for the multichannel mode of operation (8).

The multichannel mode of operation for simultaneous flame emission and atomic absorption measurements uses a less conventional electronic arrangement which will be discussed briefly. This arrangement was designed and built in 1965 by P. Cath and G. Ziedens. Its principle is described in the block diagram shown in figure 6 (8). It consists of four major steps :

1) conversion of light intensity to electrical current;

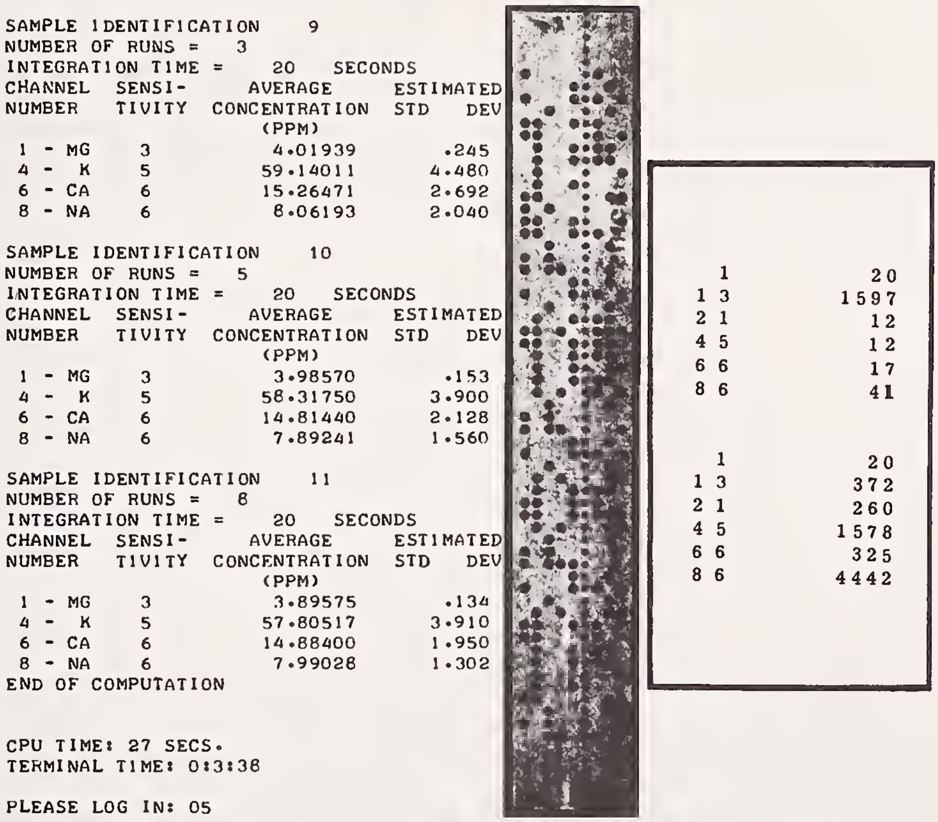
2) measurement of this current;

3) conversion of the measurement from analog to digital form;

and 4) print-out and simultaneous punch-out of the data.

The first step is achieved by a photomultiplier tube, and the system can accept up to eight such tubes. Only two tubes are described in figure 6 since the remaining six are of similar design. The measurement of the current generated by the photomultiplier is performed by individual integrating capacitors where it is stored and then sequentially converted to measurement in digital form. This information is then printed and punched simultaneously for all channels on appropriate tapes, and the punched tape is compatible for direct input to a computer. The eight channels can accept either *ac* or *dc* inputs in any combination. The *ac* (290 H_z) mode is used in conjunction with the atomic absorption measurements while the *dc* input is used for flame emission measurements. Each channel can be switched on or off and has a sensitivity adjustment and a dark current compensation capability. The integration time can be selected step-wise, as needed, for 10, 20, 40, 100, 200, 400 and 1 000 seconds. The measurements can be made with 1 to 4 repli-

Fig. 7. — Front panel of the console containing the electronic circuitry used in the multichannel mode of operation (8).



```
SAMPLE IDENTIFICATION    9
NUMBER OF RUNS =   3
INTEGRATION TIME =    20   SECONDS
CHANNEL  SENSI-     AVERAGE        ESTIMATED
NUMBER   TIVITY  CONCENTRATION   STD    DEV
                     (PPM)
 1 - MG    3         4.01939         .245
 4 -  K    5        59.14011        4.480
 6 - CA    6        15.26471        2.692
 8 - NA    6         8.06193        2.040

SAMPLE IDENTIFICATION    10
NUMBER OF RUNS =   5
INTEGRATION TIME =    20   SECONDS
CHANNEL  SENSI-     AVERAGE        ESTIMATED
NUMBER   TIVITY  CONCENTRATION   STD    DEV
                     (PPM)
 1 - MG    3         3.98570         .153
 4 -  K    5        58.31750        3.900
 6 - CA    6        14.81440        2.128
 8 - NA    6         7.89241        1.560

SAMPLE IDENTIFICATION    11
NUMBER OF RUNS =   8
INTEGRATION TIME =    20   SECONDS
CHANNEL  SENSI-     AVERAGE        ESTIMATED
NUMBER   TIVITY  CONCENTRATION   STD    DEV
                     (PPM)
 1 - MG    3         3.89575         .134
 4 -  K    5        57.80517        3.910
 6 - CA    6        14.88400        1.950
 8 - NA    6         7.99028        1.302
END OF COMPUTATION


CPU TIME: 27 SECS.
TERMINAL TIME: 0:3:38

PLEASE LOG IN: 05
```

```
  1        20
1 3      1597
2 1        12
4 5        12
6 6        17
8 6        41

  1        20
1 3       372
2 1       260
4 5      1578
6 6       325
8 6      4442
```

Fig. 8. — Digital and computer data presentation obtained from the unit from figure 6 and 7. At the right, printed tape; center, punched tape; at the left, computer data presentation.

cations or continuously, the sequence in this case being interrupted manually. The console which contains the electronic circuitry is seen in figure 5, while the panel which carries the corresponding command switches is illustrated in figure 7. The simultaneous digital print-out and punch-out display contains the following information : channel number, sensitivity setting, integration time, and the arbitrary counts corresponding to the charge of the individual capacitors. The arbitrary counts are converted to meaningful information through calibration with analytical reference solutions containing known amounts of elements. An actual example of data presentation is illustrated in figure 8 which shows a portion of the printed tape at right, followed by the corresponding punched-out tape and the computer information. The printed tape contains, from left to right, in the first column the channel number, the sensitivity setting, and the arbitrary counts corresponding to the charge of the capacitors. The first row lists an identifying number permitting the computer to identify the reference solution (0) and the unknown samples (1), followed by the integration time which, in this case, is 20 s. The computer program which handles the analytical data obtained with the multichannel spectrometer was written by Dr. J. Wing.

In the present work, the electronic system was set to accept four signals in the *dc* mode for the flame emission determination of sodium, potassium, calcium, with lithium as an internal standard and one signal in the *ac* mode for the determination of magnesium by flame atomic absorption. Since only one magnesium hollow cathode tube was needed, the chopper was placed on the optical axis in a perpendicular position and a conventional blade was substituted for the mirror blade illustrated in figure 5.

Since the amplifier system used in conjunction with the scanning mode is the lock-in type, it was necessary to select a suitable chopping frequency which would be different from that of the *ac* line current. A major source of interference in the operation of the lock-in amplifier could be the analytical flame itself and its supply system. A series of measurements was designed and performed to determine whether any periodicity originated in the flame.

These measurements were performed by setting the monochromator on the sodium emission and then connecting the output from the scanning photomultiplier to an oscilloscope. The time scan obtained with the flame alone (A), the flame supplied with distilled water (B), and the flame supplied with a sodium salt (C) is illustrated in figure 9. As can be seen, the unsupplied flame in A and B exhibits a random noise of low amplitude. When sodium was supplied to the flame through the pneumatic sprayer, the resulting signal indicated a strong periodicity with a frequency of 25 H_z as illustrated in C. This periodicity is probably due to pulsations generated in the pneumatic sprayer and their frequency should depend on the geometry and on the operating conditions of the particular unit used. As a result of these measurements, the chopping frequency in the *ac* mode was selected to avoid interferences with the fundamental frequency of the flame or any of its harmonics.

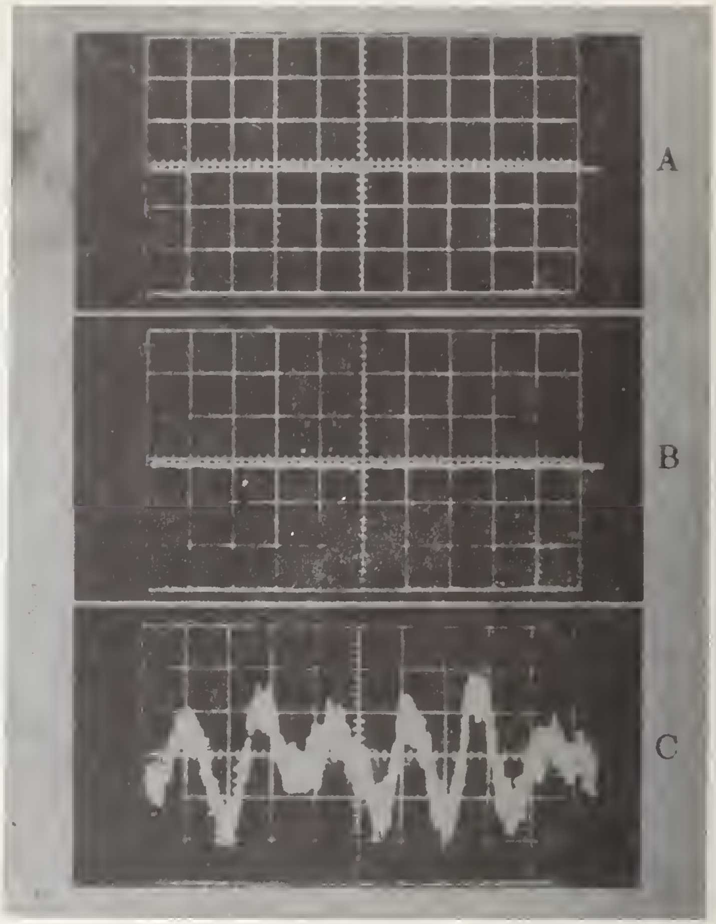


Fig. 9. — Illustration of premixed acetylene-air flame periodicity. A, oscilloscope tracing of the signal from the unsupplied flame, B, same tracing from the flame supplied with distilled water. C, same tracing with the flame supplied with a sodium salt. In all three cases, the monochromator was set on the sodium emission at λ 5 890 (⁷). The abscissa represents the time; the ordinate represents relative intensities.

The stability of the electronic circuitry, including the photomultiplier tubes, was measured by radiations provided by a fluorescent screen activated with 2 Ci of tritium (12.5 years half-life) (⁹). This source, having an output of 56 μlm, was placed at the focal plane preceding the photomultiplier tubes. An integration time of 10 s was selected for each channel, and a series of measurements was obtained for each photomultiplier tube. The standard deviation in response to this constant illumination was 0.1 to 0.3 percent.

2.3. — *Burner and Sprayer Systems.*

The burner and sprayer system used with the spectrometer is illustrated in figure 10 (¹⁰). It consists of an indirect external pneumatic sprayer, a spraying vessel, and a burner body, all made of pure and impervious alumina (99 % Al_2O_3); the interchangeable burner plate, made of tantalum, is water cooled. This unit is corrosion and erosion proof and non-combustible. The gas mixtures which can be used to produce a premixed flame are air-acetylene or nitrous oxide-propane with the same burner plate and nitrous oxide-acetylene with an appropriate burner plate. Details of the unit are given in the isometric drawing from figure 11, and various parameters are given in table I and II (¹⁰). The spraying vessel is connected to a polyethylene drain bottle through a glass hydraulic trap as illustrated in figure 12. The side tube at the top of the trap is connected to an exponential water manometer which indicates the pressure inside the burner and sprayer unit. When the air-acetylene or nitrous oxide-propane mixture is used, this pressure is of about 1 cm of water; with the nitrous oxide-acetylene the pressure should be 7 cm. Since this burner and sprayer unit has been described in previous work, no further details will be given here (¹⁰). The system for regulating and monitoring the flow of oxidant and fuel gases is illustrated in figure 5 (⁷). The oxidant gas is supplied to the panel first after passing through a two-stage pressure regulator provided with a stainless steel check valve and a flash-back safety consisting of a porous metal plate. A second pressure regulator controls the oxidant flow and its pressure is measured with a two-turn 8 1/2 in-(21.59 cm) diameter precision gauge which is capable of measuring 0.1 (0.0068 atm) *psi* per division. The flow is controlled with a 250 mm long glass flowmeter; copper tubing and appropriate fittings are used with air, oxygen, and nitrous oxide. The fuel is supplied to the panel from a corresponding container through a two-stage pressure regulator provided with a stain-

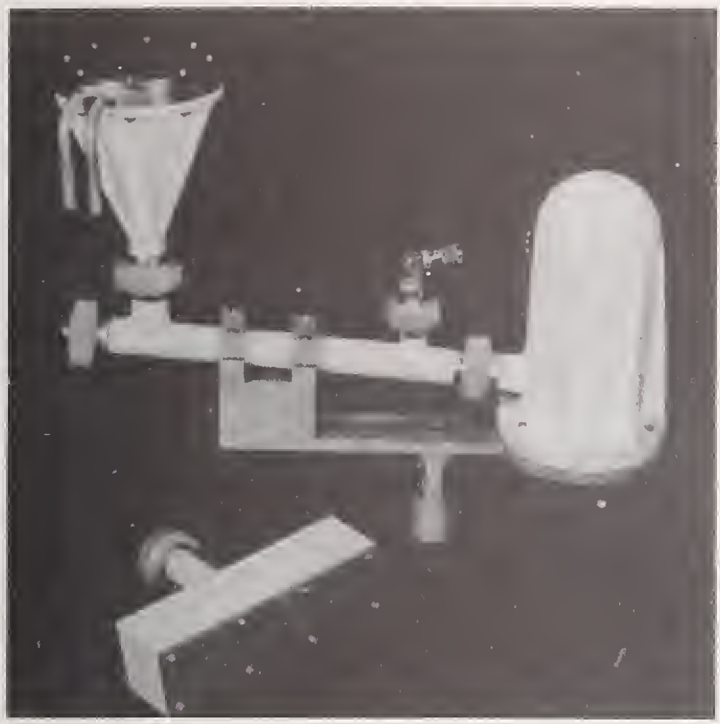


Fig. 10. — Pure alumina (99 % Al_2O_3) pneumatic sprayer and premixed burner system. At the right, spraying vessel with the external pneumatic sprayer at the bottom (only the sample supplying tube is visible). In the middle, burner body with the fuel nozzle made of tantalum. At the left, burner head with water cooled tantalum flame plate. The thin Teflon flash back safety membrane is seen at extremity of the horizontal tube (¹⁰). At the bottom, interchangeable burner head. Courtesy Plenum Press.

TABLE I

Functioning Parameters of the Sprayer.

Air to sprayer		Vacuum at sprayer inlet, cm Hg	Capillary, × 1/1 000 in.	Analytical solution			Sprayer efficiency, %	$\frac{Q_{v,\,air}}{Q_{v,\,sol}}$
Pressure psi	Flow, liter/mn			Consumed by the sprayer g/mn	Supplied to the burner g/mn	Supplied to the burner g/liter		
20	9.8	30.0	9	5.0	0.25	0.026	5.0	2 000
			6	1.7	0.21	0.017	12.4	7 353
30	12.5	42.0	9	5.7	0.32	0.026	5.6	2 200
			12	11.0	0.36	0.029	3.3	1 140
			14	14.0	0.37	0.030	2.6	890
40	15.0	38.0	9	5.5	0.33	0.022	6.0	2 730

TABLE II

Particle Size Distribution at 30 psi.

Capillary, × 1/1 000 in.	Particle diameter, μ							
	0.5 ⩽ 1	> 1 ⩽ 2	> 2 ⩽ 4	> 4 ⩽ 6	> 6 ⩽ 8	> 8 ⩽ 10	> 10 ⩽ 12	> 12 ⩽ 14
6	61.4	23.7	11.8	2.7	0.2	0.05	0.05	—
9	62.6	22.9	11.2	2.6	0.5	0.2	—	—
14	62.3	21.8	11.4	3.2	0.7	0.3	0.2	0.2
	Total weight, %							
6	2.8	8.5	33.8	30.6	8.5	3.7	6.7	—
9	2.5	7.4	29.4	31.2	17.9	11.6	—	—
14	1.5	4.3	17.7	22.9	13.6	10.5	11.4	18.1

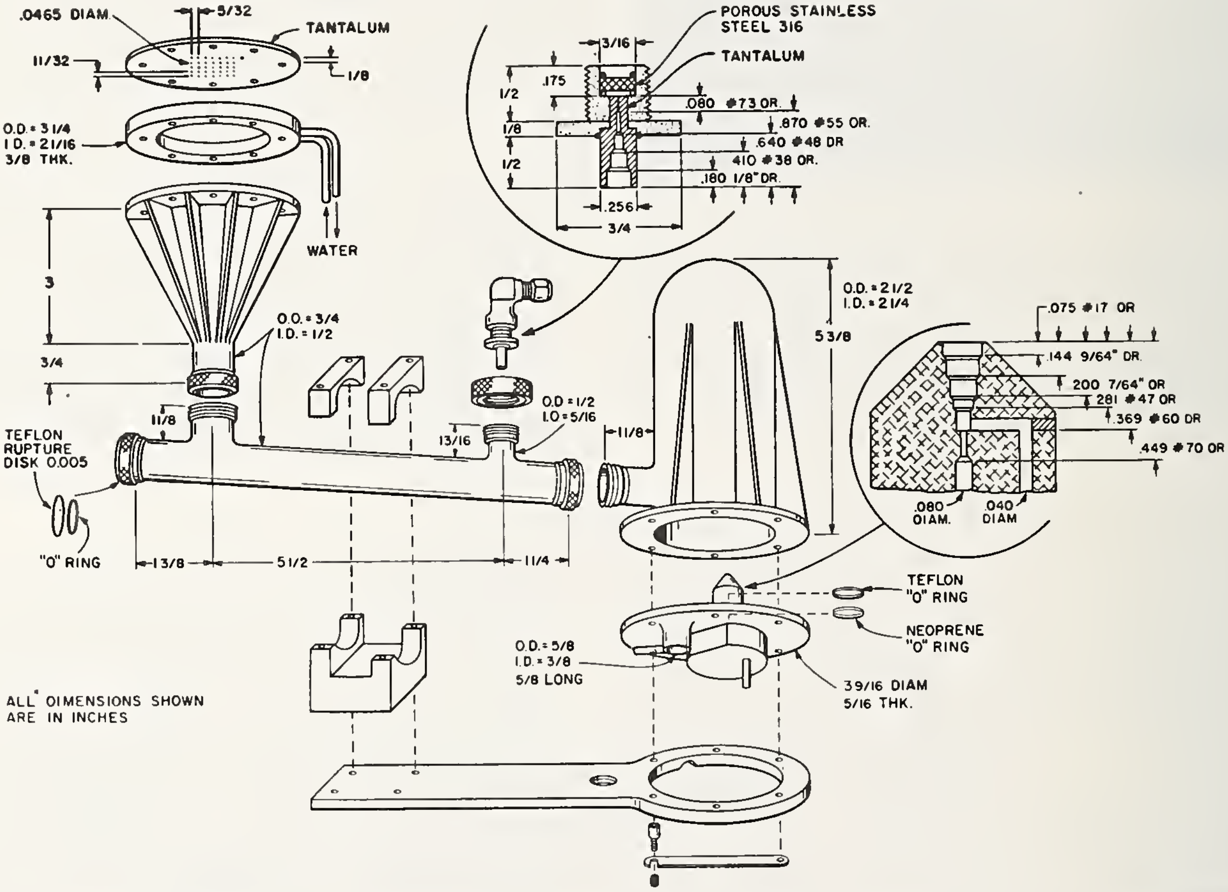


Fig. 11. — Isometric drawing of the sprayer and burner unit shown in figure 10 ([10]). Courtesy Plenum Press.

less steel check valve and flash-back safety consisting of a porous metal plate; the acetylene purifying cylinder is placed after this plate (see paragraph 2.4.1). The flow of fuel is further regulated at the panel and its pressure is monitored by a 8 1/2 in (21.59 cm) diameter two-turn precision gauge capable of measuring 0.01 psi (0.000 68 atm) per division. The flow is controlled by a 250 mm long glass flow-meter. Stainless steel tubing and appropriate fittings are used with acetylene.

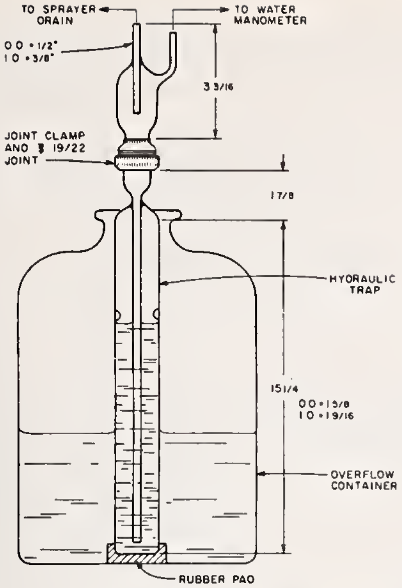


Fig. 12. — Hydraulic trap made of glass (¹⁰). Courtesy Plenum Press.

2.3.1. *Operation of the Burner and Sprayer Unit.*

We have mentioned that the sprayer can be supplied through a two-way Teflon (*) stopcock in succession with the analytical solution or with the distilled water blank solution. This dual supplying system is illustrated in figure 5 (⁷). One can see the stopcock, the constant level polyethylene flask, and the polyethylene capillary tubing which connects the sprayer with the stopcock and the constant level flask on one side, and the analytical sample container on the other side. This dual arrangement simulates to some extent a double-beam operation. Indeed, if one assumes that the emission source and the flame, with its supply system, are stable during the interval required to change from the sample to the blank, the system is equivalent to a double beam operation. This interval of 15 s which is required to change from sample to blank is determined by the memory of the sprayer and burner units. Since we use 20 s integrations of the sample and blank signals, the total time required to perform a sample measurement is 35 s; a similar interval of 35 s is required for the blank. Hence, one sample-blank measurement cycle requires 70 s.

TABLE III

Accuracy of Analytical Results for Mg, K, Ca, Na *Determined Simultaneously.*

Number of Runs	Element determined, µg/ml							
	Mg (Δ) = 4.00		K(*) = 60.00		Ca(*) = 15.00		Na(*) = 8.00	
	Found	% Diff	Found	% Diff	Found	% Diff	Found	% Diff
3	4.02	+ 0.50	59.14	— 1.43	15.26	+ 1.73	8.06	+ 0.75
5	3.99	— 0.25	58.32	— 2.80	14.81	— 1.27	7.89	— 1.38
8	3.90	— 2.5	57.81	— 3.65	14.88	— 0.80	7.99	— 0.13
12	3.97	— 0.75	58.66	— 2.23	15.01	+ 0.07	8.00	0.0
15	3.95	— 1.25	58.32	— 2.80	14.92	— 0.53	7.97	— 0.38
20	3.92	— 2.0	58.04	— 3.27	14.88	— 0.80	7.96	— 0.50
25	3.90	— 2.5	57.68	— 3.87	14.84	— 1.07	7.93	— 0.88

(Δ) By flame atomic absorption.
(*) By flame emission.

2.3.2. *Analytical Data.*

The technique described was used to obtain the analytical data reported in table III and to establish the accuracy of the measurements. The elements selected in this case were Mg, K, Ca, and Na because of their significance in biochemistry. It is obvious that any combination of elements which can be determined by flame emission and atomic absorption techniques can be chosen. Magnesium was determined in the atomic absorption mode while K, Ca and Na were determined in the emission mode. The calibration was made on eight solutions containing all four elements of known concentrations; Li was used as an internal standard for emission measurements. Each standard solution was run in six replications,

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(*) The name of manufactured products are given for information only and do not constitute an endorsement of the product.

each measurement consisting of the blank and sample run. A solution was then selected from these standards and treated as the « unknown » sample. This solution was run in 3 to 25 replications as indicated in column one from table III, each run consisting of the blank and sample measurements. Columns 2 to 5 show the analytical results obtained for Mg, K, Ca, and Na as well as the percent difference between the concentration found and the concentration taken. In all atomic absorption measurements the computer was programmed to interpolate from a log $\frac{\text{blank}}{\text{sample}}$ versus concentration system, while the interpolation for the emission measurements was made from a sample and blank versus concentration system. In the case described in table III, the internal standard values obtained for lithium were not used to compute and correct the emission measurements. The analytical results obtained demonstrate the accuracy which can be expected from the multichannel spectrometer when simultaneous measurements are made by emission and atomic absorption on four elements.

2.4. *Increasing the Sensitivity of Measurements.*

Various means can be used to increase the sensitivity of measurements in analytical flame spectroscopy, and three possibilities will be discussed.

2.4.1. *Decreasing the Flame Background.*

2.4.1.1. It has been known for a long time that phosphine (H_3P) is one of the impurities of acetylene which is difficult to eliminate. This compound imparts a noxious odor and toxic properties to acetylene. When introduced into the air-acetylene and especially oxygen-acetylene flames, it radiates a strong visible continuous or non-resolved spectrum as illustrated in figure 13 *a* and *b*. This emission can interfere with the determination of the elements, and it is essential to eliminate this contaminant. Since the purification of acetylene was discussed in detail in some of our earlier works ([11, 12]), only the practical aspect will be discussed here. The H_3P can be eliminated from acetylene to an extent that no radiation can be detected in the flames with the instrumentation described in this work. This is done by oxidation to H_3PO_4 using a ferric chloride solution containing an oxidation accelerator, adsorbed on an inert support such as diatomaceous earth. The materials are packed in a stainless steel cylinder 15 in (38.1 cm) long and 2 in (5.08 cm) in diameter which is provided with side tubes. The cylinder is placed between the acetylene tank and the gas monitoring console illustrated in figure 5. Acetylene thus obtained produces a faint blue flame when burned with air, as illustrated in figure 13*b*. Before purification, the flame is seen in figure 13*a* and the corresponding spectrophotometer scannings are given in figure 14.

2.4.1.2. Impurities which can interfere with the measurements are those introduced into the flame

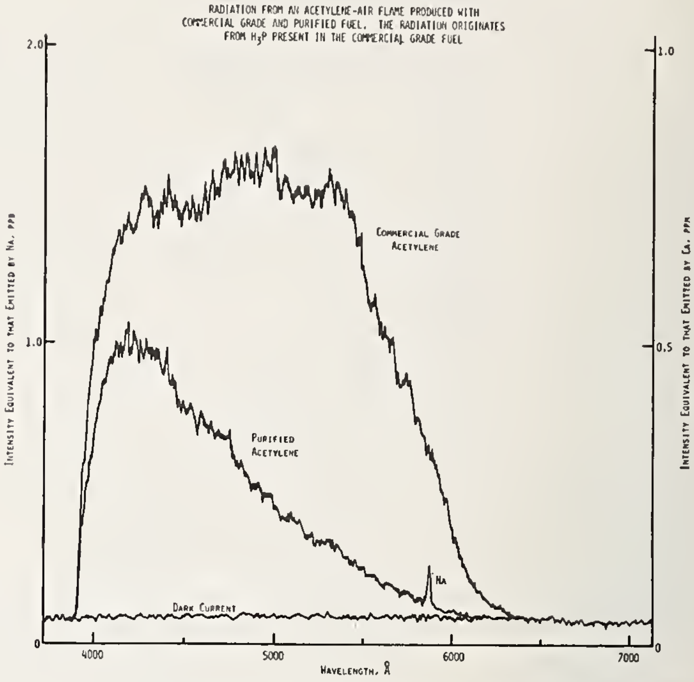


Fig. 14. — Monochromator scanning of the radiations excited in the flame illustrated in figure 13 *a* and *b*.

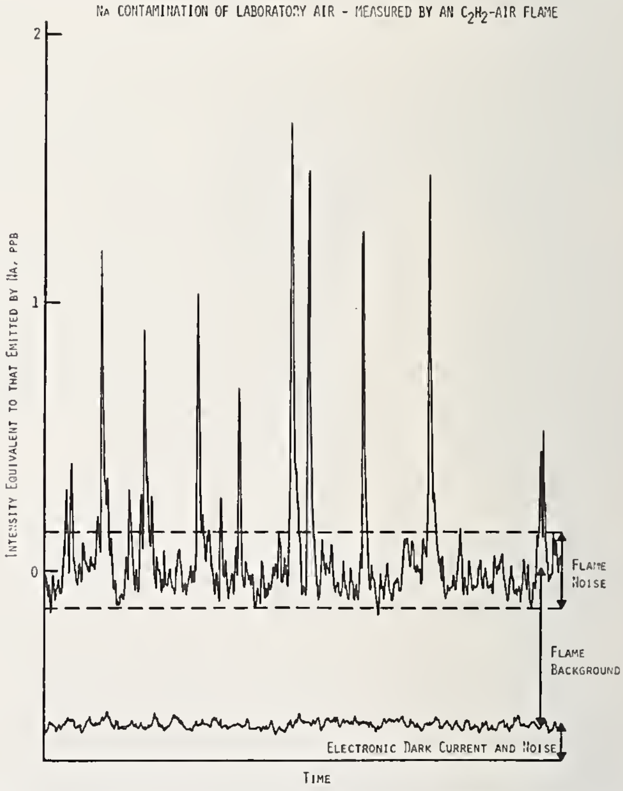


Fig. 15. — Monochromator scanning illustrating the emission of sodium present in the laboratory air surrounding the flame. In this case, the monochromator was set on the sodium emission and the scanning was done in time.

from the surrounding air. Such impurities are sodium and calcium salts which are always present in the laboratory atmosphere. The presence of sodium in our laboratory was determined by monitoring its radiations, which were excited in an acetylene (purified) — air (filtered) flame, using our spectrometer set on the Na wavelength. The results are given in figure 15 and show the recording of Na radiation intensities on the ordinate versus time on the abscissa. The full scale deflection corresponds to 2 ppb Na. As can be seen, the Na content of the air surrounding the flame can be more than 1 ppb. If this element must be determined at the ppb level, it is obvious that the air entering the flame from the atmosphere must be free of sodium contamination. This can be done by working in a clean room or by supplying purified air to the flame.

2.4.2. *Increasing the Optical Pathlength Through the Flame.*

It was demonstrated by Gouy (13) and later by Lundegardh (4) that the emission intensity of the radiations from a flame can be increased by lengthening the optical path; similarly, Walsh (14) has shown that the absorption of a flame can be augmented by increasing its length. This increase can be achieved by producing a longer flame or by increasing the optical path through the flame using multiple reflection arrangements. Both have been used in our work and will be described.

2.4.2.1. *Long Path Flames.*

Figure 16 shows a long path burner head capable of producing a 30 cm long and 1 cm wide flame. Figure 17 gives details on the construction of this burner (7). It is made of stainless steel type 316, tubular sections assembled with appropriate fitting of the same metal welded in a hydrogen furnace. The premixed acetylene-air or propane-nitrous oxide, together with the fine spray of analytical sample, are supplied to the burner head from both extremities to insure the production of an even flame. The air is supplied to the external pneumatic sprayer under a pressure of 39 psi (2.65 atm) and at a rate

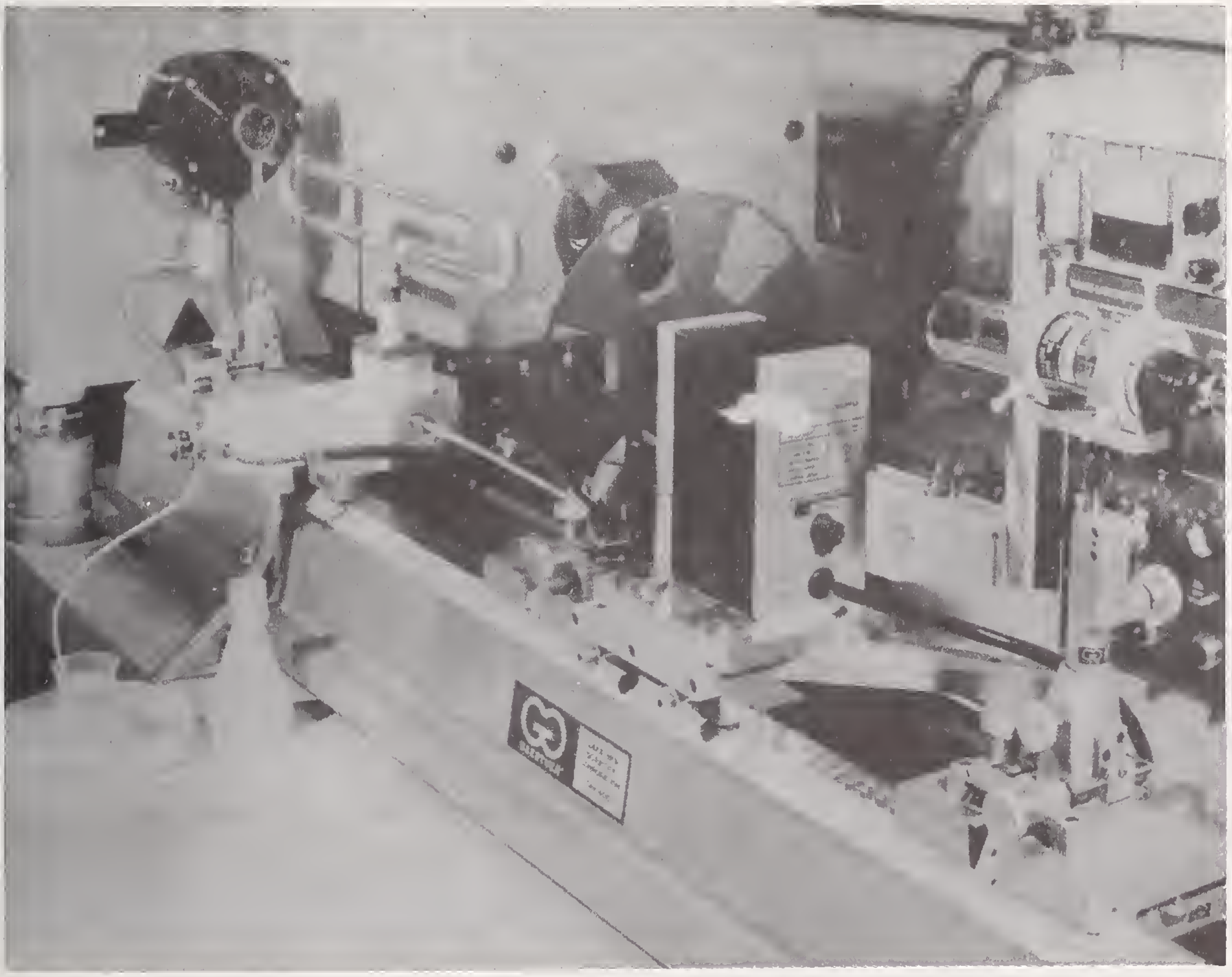


Fig. 16. — Stainless steel long-path premixed acetylene-air burner head adapted to a Teflon spraying vessel provided with a tantalum external variable sprayer.

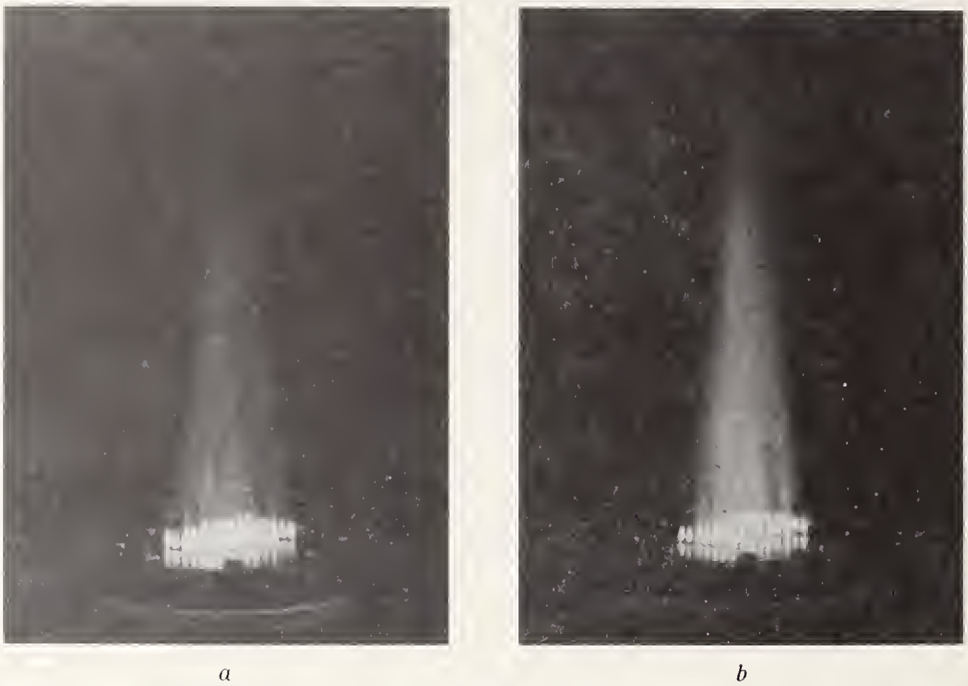


Fig. 13. — *a*, premixed acetylene-air flame produced with purified fuel. *b*, same flame produced with unpurified commercial grade acetylene. Exposure time same as that used for *a*.

Fig. 25. — *a*, appearance of the dual hydrogen flame supplied with distilled water. *b*, same flame supplied with diluted sulfuric acid. *c*, same flame supplied with diluted phos-phoric acid.

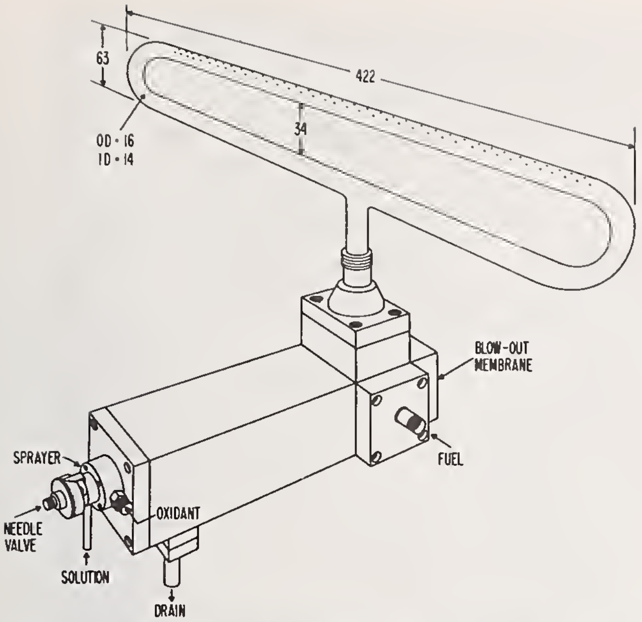


Fig. 17. — Drawing of the unit shown in figure 16. The burner head carries 112 holes of 1 mm in diameter distributed over three parallel rows. The holes from the center row are staggered between those from the two lateral rows. Length of rows, 2.50 mm. Total width, 5 mm (center to center). Distance between rows, 2.5 mm (center to center). Distance between individual holes, 8 mm (center to center). The stainless steel tubing has an inside diameter of 13 mm and an outside diameter of 16 mm.

of 2 200 l/hr. The acetylene was supplied to the burner body through a tantalum nozzle to produce a stoichiometric flame. The consumption of analytical solution in the sprayer 25 ml/mn and the amount of analytical sample solution entering the flame was 1.3 g/mn. The optical system used with this 30 cm flame consisted of two quartz lenses which produce an optical beam having an average cross section of about 10 mm. Under these circumstances, the analytical results obtained when Mg was determined by atomic absorption in conjunction with the scanning electronics described in paragraph 2.2 showed an increase in sensitivity by a factor 3, as compared with a 10 cm path burner.

The optical system using the quartz lenses could be improved by using a two Cassegrain mirror on-axis arrangement as described by MÜLLER-HERGET. This would eliminate the chromatic aberrations characteristic to all lens systems and produce a more adequate optical beam geometry (15).

2.4.2.2. *Triple Pass On-Axis Optical Arrangement.*

This on-axis triple arrangement system (*) can be used for atomic absorption and flame emission measurements and is based on the use of two Mangin-type mirrors with an asymmetric biconvex quartz lens. The principle of the proposed system and the specific dimensions are shown in figures 18 and 19.

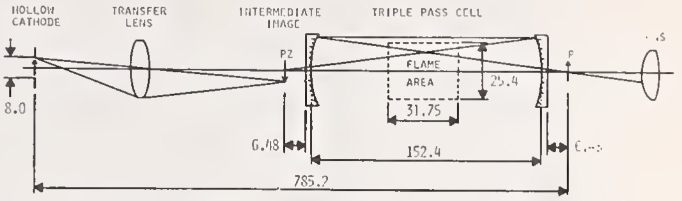
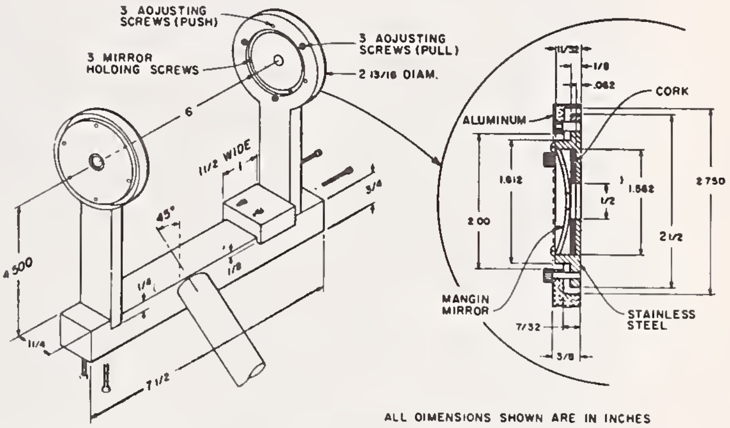


Fig. 18. — Principle of the on-axis triple pass system.



ALL DIMENSIONS SHOWN ARE IN INCHES

Fig. 19. — Drawing of the triple-pass, center bore, Mangin mirrors assembly.

A view of the actual arrangement in working conditions is illustrated in figure 20.

The flame cavity is designed as a concentric triple-pass system with parallel radiations in the second pass. Because of heat and corrosion, it is advantageous to use rear surface mirrors made of fused quartz. The optical elements are Mangin-type mirrors with a center bore. The cavity has been designed to minimize spherical and primary color aberrations in the spectral range 240 nm to 436 nm with the design center at 330 nm. The object at P_z is imaged through the cavity with unit magnification. The conjugated points are both outside, providing 6.48 mm clearance beyond the mirror's back surface. The minimum optical diameters are 6.70 mm for the bore and 35.0 mm for the outside diameter of the mirrors.

The hollow cathode is imaged by an asymmetric biconvex quartz lens at the intermediate image position P_z. It is designed for the same spectral range with the design center at 330 nm. The spherochromatic aberrations have been minimized but are not suppressed in a simple lens. The aberrations of the Mangin cell are only 2 percent of the transfer lens blur. The hollow cathode image is demagnified (1 : 0.635) and is inverse at position P_z and upright at position P.

(*) Designed by W. MÜLLER-HERGET, Philips Laboratories, Briarcliff Manor, New York, 10510, U.S.A.

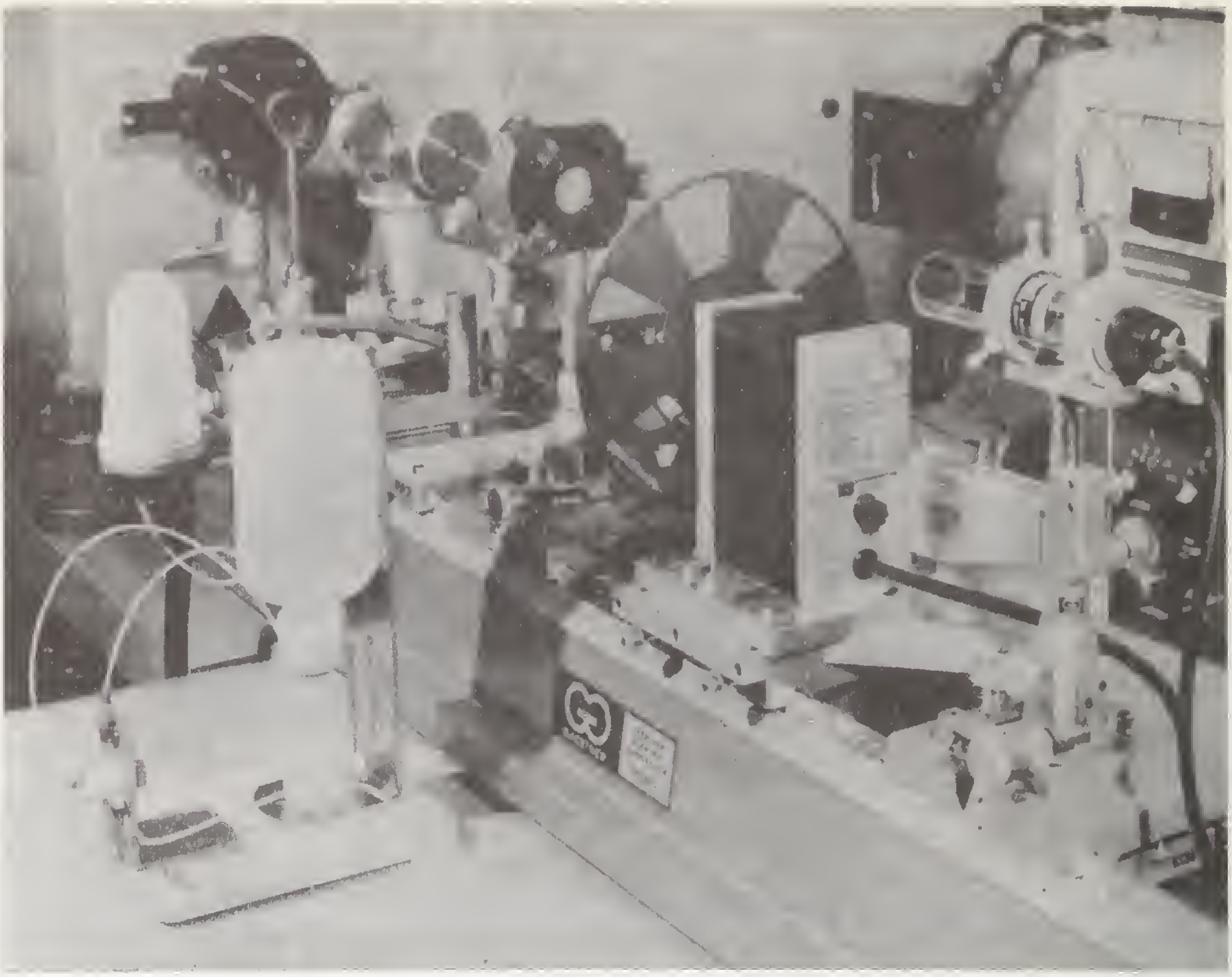


Fig. 20. — On-axis triple-pass system from figures 18 and 19 shown in actual use.

If five passes through the flame are required, both Mangin mirrors may be exchanged for two others of corresponding design, while retaining all previous dimensions. The focal length, *f*, of the mirrors for the five-pass cell will be, in first order approximation: $f = 2.618 \times d = 398.98$ mm for required clearance of $d = 152.4$ mm between the mirrors. The required diameter will be approximately 30 percent larger.

The triple-pass Mangin mirror assembly is placed on the optical bench as illustrated in figure 20, with the analytical flame located symmetrically between the mirrors and at a height selected for best sensitivity. The system was tested in the atomic absorption mode using Mg. An increased sensitivity of 2.7 was observed when measurements were compared with the sensitivity obtained under the same conditions, but without the triple-pass unit.

The triple-pass unit was also tested in emission using sodium. When the rear Mangin mirror was blocked out, an increase in the emission signal of 3.3 percent was observed when compared with the signal obtained without the triple-pass unit. When the front Mangin mirror was blocked out, the increase was 43 percent; when both Mangin mirrors were unobstructed, the increase was 70 percent. Finally, when a flat mirror was placed at the opening of the rear Mangin mirror, the increase in the sodium signal was 158 percent.

The increased sensitivity of flame measurements, using the on-axis Mangin triple-pass mirror system, recommends its use. This system requires careful optical alignment and is somewhat wavelength dependent. This dependence can be eliminated by using reflecting rather than refractive optics in place of the 2 lenses mentioned above.

3. — Discussion of some fundamental excitation conditions in combustion flames.

3.1. *Introduction.*

As a consequence of exothermic combustion reactions, the gases which constitute a flame attain different temperatures, according to combustion conditions, flame structure, and the geometry of the system. The thermal energy in a flame is distributed between particles activated to the various translational energies, and rotational, vibrational, electronic and ionization states. Each state can be defined separately by its own temperature. When this value is identical for all states, the radiation from the flame is in thermal equilibrium. Boltzmann's well-known equation (11), which relates the intensity radiated by a given number of activated particles to the temperature of the excited source, can be applied only in this state of equilibrium. A further limitation to its use is presented by chemical reactions and ionization and self-absorption phenomena occuring in the excitation source. When the temperatures of translation, rotation and vibration are not equal and differ from the electronic and ionization temperatures, the system is not in thermal equilibrium. In a flame, various reactions produce radiations which deviate from thermal equilibrium. We call this process overexcitation. The Boltzmann equation cannot be applied to interpret such emissions, and the notion of temperature loses its meaning. Thermal excitation and overexcitation are thus two widely different types of excitation mechanisms which are both found in flames used in analytical flame spectroscopy, and a study of the temperature distribution related to the flame structure will help to identify the origin of the resulting radiations.

Temperature measurements performed in the outer cone of stoichiometric premixed combustion flames using various procedures and states of excitation (vibration, rotation, and electronic), have produced results in agreement among themselves within the experimental errors and agree also with the thermodynamically calculated value. When similar measurements were made in the inner cone of the same flames, the temperatures differed widely depending to the measuring conditions. From the results, it can be concluded that thermal equilibrium is achieved in the outer cone of premixed flames and the radiation from this zone is of thermal nature (perhaps with the exception of ionization). On the other hand, thermal equilibrium is not reached in the inner cone; the radiations of excited particles in this zone result from various reactions.

It is necessary to mention, however, that whether the radiation of a chemical species excited in a flame is or is not in thermal equilibrium does not preclude its use for analytical purposes. The only condition to be satisfied is that the radiation must be constant and reproducible.

The mechanism responsible for overexcitation was discussed in 1951 by Laidler and Shuler (see ref. 12) who studied the elementary reactions and collision processes involving excited electronic states and then applied the results to various reactions occuring in combustion flames. Some of the reactions listed by Shuler are:

Collisional activation

$$A + B \rightarrow A + B^* \qquad \mathrm{I}$$

Energy transfer

$$A^* + B \rightarrow A + B^* \qquad \mathrm{II}$$

True chemiluminescence

$$A + B \rightarrow AB^* \qquad \mathrm{III}$$

$$A + B + M \rightarrow AB^* + M \qquad \mathrm{III'}$$

Induced chemiluminescence

$$A + B + C \rightarrow AB + C^* \qquad \mathrm{IV}$$

True chemiluminescence

$$AB + C \rightarrow A + BC^* \qquad \mathrm{V}$$

True chemiluminescence

$$AB + C \rightarrow A^* + BC \qquad \mathrm{VI}$$

True chemiluminescence

$$AB + M \rightarrow A^* + B + M \qquad \mathrm{VII}$$

Induced chemiluminescence

$$AB + C \rightarrow A + B + C^* \qquad \mathrm{VIII}$$

The A, B, C, and M may be radicals or molecules as well as atoms. Equations I and II are energy-transfer processes; in the first, the excitation energy of one of the colliding particles comes from translational energy of the other particle. Equations III, III′, and IV are associated reactions; for III′ and IV, a three-body collision occurs; in III′ the third body, M, acts only in stabilizing the product, whereas in IV, it absorbs the energy released by the formation AB. Equations V and VI are metathetical reactions; part of a molecule or a radical is transferred to the colliding particle, and the released energy may be absorbed by the new species (V) or by the remaining part of the dissociated molecule (VI). Equations VII and VIII are dissociation reactions in which the colliding particle splits the molecule AB into two parts; the energy released by the process, if any, is absorbed by a part of the dissociated molecule (VII) or by the colliding particle (VIII) — this latter reaction being very unlikely, due to energy requirements.

Equations III, III′, V, VI, and VII may be termed chemiluminescent since the excited product results from the reaction. Equations I and II enter the category of energy transfers. In equations IV and VIII, the excited partner is a product of the collision, but is not chemically modified; it is acting only to dissipate the energy made available by the process. Such processes may be termed « induced chemiluminescence ».

Distinctions between true chemiluminescence, induced chemiluminescence, and energy transfer processes can be made only when the process is actually known. To distinguish nonthermal emissions from thermal emissions, but without emphasizing the actual process, it is proposed to designate nonthermal emissions as « overemission » and their excitation as « overexcitation » ([12]).

The preferred area of overexcitation is the primary reaction zone or blue cone of premixed flames. Spectroscopic studies have shown that a number of chemical species can be excited to emit specific radiations in this particular zone. This is illustrated in table IV where it can be seen that elements such as Sn, Cd, Ni, Sb, Be, As, Pt, Co, Au, Pd, C, Fe, Ir, Hg, In, Ru, Pb, Bi, Ga. Tl, Mg, are excited preferentially in the blue cone of the premixed acetylene-air or acetylene-oxygen flames with intensities varying from very, very weak (vvV) to strong (S) ([16]). Most of these emissions originate from an overexcitation reaction and can be used for analytical measurements to detect the particular species and to determine its concentration ([17]).

The phenomenon of overexcitation was observed many years ago. George-Louis Gouy was the first to describe the differences in radiations which originate from the blue cone and the outer cone of a premixed city gas-air flame when various chemical species were supplied to the flame ([13]). Detailed studies of this phenomenon were carried out by De Watteville and Hemsalech who, at an early date, made a clear discrimination between thermal and nonthermal excitation of additives in combustion flames. In 1917 Hemsalech wrote:

« The light radiations from vapors in outer mantles of the various flames behave as if governed by the temperatures of these flames.

The spectrum emitted by metal vapours in the region of the blue cone of the air-coal gas flame cannot be accounted for by simple thermal actions, but is probably due to some special chemical process prevailing in the explosion region.

In the case of iron, we established the existence of two distinct groups of lines. One group, some 200 lines, is emitted by the outer mantle of the air-coal gas flame, and the lines merely increase in intensity on passing to flames of higher temperature. We considered them as the fundamental lines of the spectrum, which are easily excited by thermal actions. The other group of over 500 lines, is emitted by the region of the blue cone only, and even in the oxy-acetylene flame we could detect only traces of some of the lines ([18]) ».

TABLE IV

Intensities of Spectrum Lines Rradiated by the Atoms of Various Elements Excited in the Inner Cone (IC) and Outer Cone (OC) of the Premixed Acetylene-Air and Premixed Acetylene-Oxygen Flames.

Excitation Energy (eV)	Wavelength (Å)	Element	Emission observed in C_2H_2 — O_2		Emission observed in C_2H_2 — Air	
			IC	OC	IC	OC
5.84	2 199.3	Sn			vW	
6.03	2 209.7	Sn			vW	
5.18	2 246.1	Sn			wM	
5.89	2 268.9	Sn			wM	
5.84	2 286.7	Sn			vW	
5.42	2 288.0	Cd			vW	
6.77	2 288.1	As			W	
5.41	2 290.0	Ni			vvW	
5.36	2 311.0	Ni			W	
5.36	2 311.5	Sb	wM		M	
5.52	2 312.3	Ni			W	
5.63	2 314.0	Ni			W	
6.42	2 317.2	Sn			vW	
5.51	2 317.2	Ni			W	
5.34	2 320.0	Ni			W	
5.61	2 321.4	Ni			W	
5.49	2 325.8	Ni			W	
5.59	2 330.0	Ni			vW	
5.52	2 334.8	Sn			wM	
5.28	2 345.5	Ni			vW	
5.28	2 348.6	Be	vvW			
6.59	2 349.8	As			wM	
5.47	2 354.8	Sn	W		M	
5.35	2 357.1	Pt			W	
5.15	2 407.3	Co			vvW	
5.24	2 411.6	Co			vvW	
5.31	2 414.5	Co			vvW	
5.36	2 415.3	Co			vvW	
6.19	2 421.7	Sn			wM	
5.11	2 424.9	Co			vvW	
5.10	2 428.0	Au	vW	vvW	W	
5.23	2 429.5	Sn	W		M	
5.20	2 432.2	Co			vvW	
5.26	2 436.7	Co			vvW	
5.18	2 436.7	Pt			vW	
5.31	2 439.0	Co			vvW	
5.08	2 440.1	Pt			wM	
5.06	2 447.9	Pd		vvW	vvW	
5.02	2 467.4	Pt			W	
5.00	2 476.4	Pd		vvW	vvW	
7.68	2 478.6	C	M			
4.99	2 483.3	Fe	vvW	vW	vvW	
5.42	2 483.4	Sn			wM	
4.98	2 487.2	Pt			M	
5.03	2 488.1	Fe	vvW	vW	vvW	
5.10	2 489.8	Fe		vvW		
5.08	2 490.1	Pt			vW	
5.06	2 490.6	Fe		vW		
6.28	2 492.9	As			vvW	
6.03	2 495.7	Sn			W	
5.78	2 495.8	Pt			vvW	

Excitation Energy (eV)	Wavelength (Å)	Element	Emission observed in			
			C_2H_2 — O_2		C_2H_2 — Air	
			IC	OC	IC	OC
5.06	2 498.5	Pt			W	
6.18	2 502.6	Ir			vW	
4.95	2 503.0	Ir			vW	
5.37	2 511.0	Co			vvW	
5.02	2 515.6	Pt			W	
4.92	2 521.4	Co		vvW	vW	
4.91	2 522.8	Fe	vvW	vW	vvW	
4.95	2 527.4	Fe	vvW	vvW	vvW	
6.12	2 528.5	Sb	S		vS	
5.00	2 529.0	Co			vvW	
5.06	2 536.0	Co			vvW	
4.89	2 536.5	Hg	vW	vvW	S	
4.98	2 539.2	Pt			vW	
5.22	2 544.0	Ir			W	
5.10	2 544.3	Co			vvW	
5.38	2 544.9	Co			vvW	
4.87	2 546.6	Sn	W		M	
4.84	2 560.2	In			vvW	
5.89	2 571.6	Sn			wM	
5.84	2 594.4	Sn			W	
5.99	2 598.1	Sb	S		vS	
5.10	2 611.3	Ir			vW	
5.67	2 612.1	Ru			vvW	
5.71	2 613.7	Pb			M	
5.71	2 614.2	Pb			M	
6.13	2 627.9	Bi			W	
4.81	2 628.0	Pt	vvW	vW	mS	
5.64	2 631.3	Ru			vvW	
5.51	2 639.3	Pt			vW	
4.69	2 639.7	Ir			wM	
5.83	2 641.5	Au			vvW	
5.75	2 643.0	Ru			vvW	
4.68	2 646.9	Pt			mS	
4.78	2 650.9	Pt			mS	
5.68	2 651.3	Ru			vvW	
5.48	2 651.8	Ru			vvW	
6.96	2 652.6	Sb			vvW	
4.85	2 659.0	Rh			vvW	
4.66	2 659.4	Pt	vW	wM	S	
4.66	2 659.9	Ga			vvW	
4.87	2 661.2	Sn	W		M	
5.01	2 662.0	Ir			vW	
5.97	2 663.2	Pb			W	
4.65	2 664.8	Ir			wM	
5.70	2 670.6	Sb			W	
4.63	2 676.0	Au	M	mS	W	
4.63	2 677.1	Pt			wM	
4.95	2 694.2	Ir			wM	
6.01	2 696.8	Bi			vvW	
5.35	2 698.4	Pt			W	
4.68	2 702.4	Pt	vvW	W	mS	
4.68	2 705.9	Pt	vvW	W	mS	
4.79	2 706.5	Sn	M	W	S	
5.64	2 709.2	Ru			W	
4.85	2 710.3	In			vW	
5.26	2 718.5	Rh			vvW	
6.85	2 718.9	Sb			W	
4.66	2 719.0	Pt			mS	
4.56	2 719.0	Fe	vW	M	vW	

Excitation Energy (eV)	Wavelength (A)	Element	Emission observed in			
			CH_2 — O_2		C_2H_2 — Air	
			IC	OC	IC	OC
4.61	2 720.9	Fe	vvW	W	vvW	
4.64	2 723.6	Fe	vvW	vW		
5.35	2 729.9	Pt			vW	
4.63	2 734.0	Pt	vW	W	mS	
4.53	2 735.7	Ru			M	
4.64	2 737.3	Fe		vW		
4.61	2 742.4	Fe		W	vvW	
6.77	2 745.0	As			vW	
5.65	2 748.3	Au	vvW		S	
4.50	2 753.9	In			vvW	
5.76	2 753.9	Pt			vvW	
5.75	2 754.9	Pt			W	
4.91	2 761.8	Sn			vvW	
4.49	2 763.1	Pd		W	vW	
4.63	2 763.4	Ru			vvW	
4.48	2 767.9	Tl	wM	M	wM	vvW
5.70	2 769.9	Sb	W		mS	
4.57	2 771.7	Pt		vvW	M	
7.17	2 779.8	Mg			vvW	
5.53	2 779.8	Sn			wM	
6.77	2 780.2	As			wM	
5.87	2 780.5	Bi			vW	
5.52	2 785.0	Sn			W	
5.30	2 788.1	Fe		vvW	vvW	

A medium which is suitable to the production and observation of overexcitation phenomena is hydrogen burning in air or oxygen under various conditions and especially with an excess of fuel. The overexcitation is greatly enhanced when the hydrogen flame is cooled by water. This observation was made more than 100 years ago by Salet who studied the spectra produced by nonmetals in a hydrogen-air flame chilled with water ([19]). Salet studied phosphorus, sulfur, halogens, tin, selenium, tellurium and silicon. Sulfur and phosphorus seem to have retained his particular interest.

The pioneering works of Salet were forgotten for a long time, and it was only during the last 15 years that spectroscopists have shown interest in the use of hydrogen flames to excite nonmetals. At the present time, the literature cites new instrumentation and many applications of this flame to solve particular analytical problems. A recent comprehensive and authoritative review of these works, covering over 200 pages and containing 602 references, together with a complete discussion of the original works, was made by Gilbert ([20]). The nonmetals examined in his review are H, B, C, Si, N, P, As, O, S, Se, Te, F, Cl, Br, and I. We have selected to discuss phosphorus and sulfur due to the particular properties of the two elements. They are easily excited in chilled hydrogen flame and radiate beautiful characteristic molecular spectra; they are also important to environmental pollution problems. Since the excitation of P and S in various hydrogen flames was discussed by GILBERT in the above review (20), we will mention here the original works of SALET (19) together with only a very few essential and more recent contributions. A complete survey of the field is given in Gilbert's review.

3.2. *Experimental Arrangements to Excite Phosphorus and Sulfur, and Discussion.*

The experimental arrangement used by SALET in 1869 and 1871 to excite P and S is illustrated in figure 21. It consists of a hydrogen flame which is produced at the extremity of a glass tube. The flame is chilled by directing it against a water curtain. The hydrogen is supplied with the vapor by passing the gas over the surface of a P or S compound contained in a closed vessel which can be warmed to produce the necessary vapor. SALET describes the blue and green radiations obtained from S and P compounds, and mentions the high sensitivities obtained in detecting these two elements.

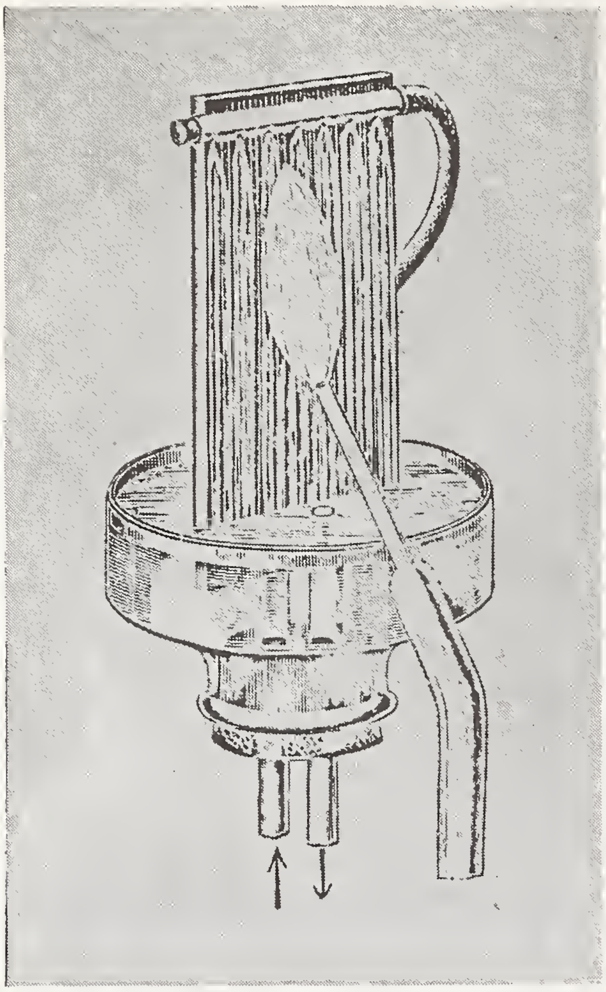


Fig. 21. — Arrangement used by SALET to produce a water chilled hydrogen-air flame.

These observations were used in a patent involving the detection and determination of P and S compounds in gaseous matrices, by the Drägerwerk Company in 1961 (21). The hydrogen flame burns with an excess of fuel and is produced inside a quartz tube cooled with water. The excess hydrogen burns at the extremity of this tube where it comes in contact with the surrounding air. This hydrogen burner is illustrated in figure 22. The detection limits of P or S obtained with this burner were 10^{-8} g of the compound per liter of air (< 0.01 ppm).

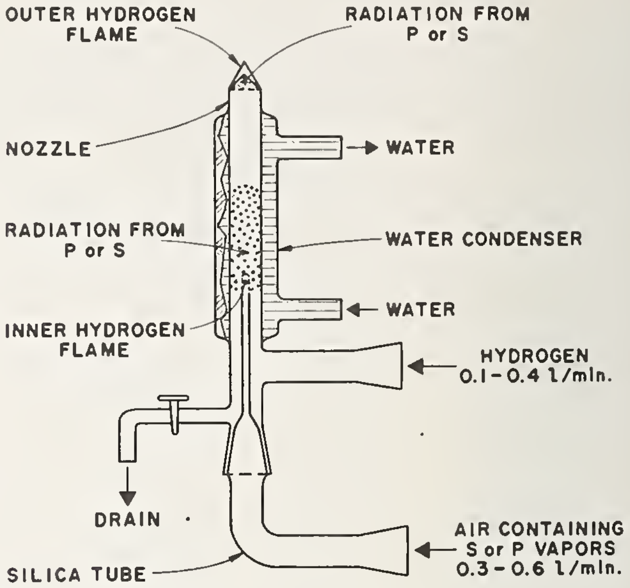


Fig. 22. — DRÄGER burner designed to produce a dual hydrogen-air flame. The inner diffusion flame is water chilled and burns with an excess of hydrogen; the outer flame burns by diffusion with the surrounding air (16). Courtesy Plenum Press.

The water-cooled hydrogen flame of SALET was used in our exploratory work combining the Drägerwerk burner with a sample supplying system similar to that described long ago by GOUY (13). The chilled hydrogen flame can be supplied with solution samples by pneumatic spraying. Argon was used for this purpose. The experimental arrangement is described in figure 23 and a corresponding drawing showing some construction details is illustrated in figure 24.

The horizontal spraying vessel of Teflon is provided at left with an external concentric pneumatic sprayer made of tantalum. The sample solution enters the sprayer through the polyethylene capillary tube. Its supply rate can be varied between 0 and 5 ml/mn through the needle valve and its graduated dial. The argon is introduced into the sprayer through the side tube.

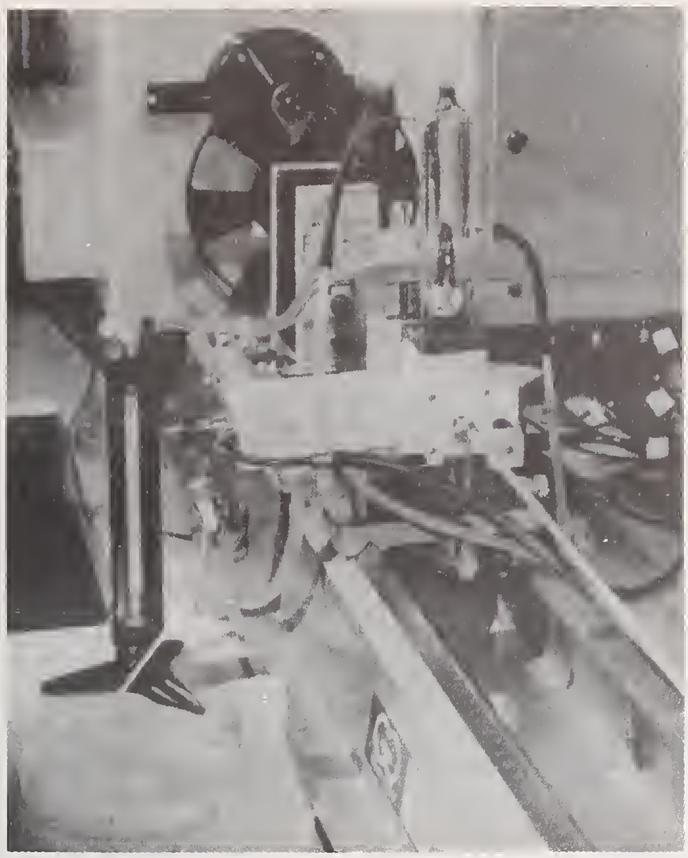


Fig. 23. — Experimental arrangement used to produce a dual hydrogen flame supplied through pneumatic spraying of the analytical solution. The horizontal Teflon spraying vessel with the tantalum external variable pneumatic sprayer is located on the optical bench. The vertical all quartz burner enclosure is adapted to the spraying vessel through an air tight rubber seal.

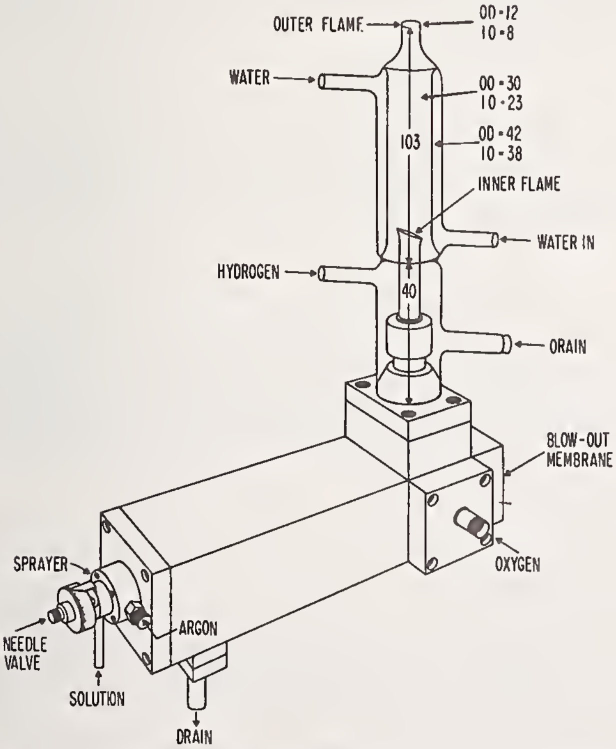


Fig. 24. — Drawing of the unit illustrated in figure 23; dimensions in mm.

The sprayer vessel has a draining tube connected to a hydraulic trap (see fig. 12), and at the right side a rupture disk made of a thin sheet of Teflon. The polyethylene tube, seen at the right side of the spraying vessel, is used to provide oxygen to the argon-sample spray. It is adapted to the tantalum nozzle which extends inside the vessel through a fitting. The oxygen nozzle has a circular opening 0.5 mm in diameter at its extremity. On top of the spraying vessel is a slot-shaped tantalum tube through which the argon, oxygen, and sample spray flows. This tube is surrounded by an all-quartz cylindrical vessel open at both ends and provided with a water cooling jacket. This quartz vessel is adapted to the spraying vessel through a rubber washer which provides an air-tight assembly. The lower side tube at right is used to drain intermittently the water which condenses on the inside walls when the flame burns inside the quartz vessel. The side tube on the left is used to supply the hydrogen which is metered by the flowmeter at left. The entire unit is placed on the optical bench in front of the spectrometer described in Section 2 of this paper, and can be moved in the *x-y-z* direction as required and secured in the chosen position. Discussion of of similar works will be found in reference ([20]). The hydrogen-argon-oxygen flame is produced in the following manner:

The cooling water is turned on and the argon is supplied first to the sprayer at a pressure of 40 psi and at a rate of 300 l/h. Hydrogen is then introduced into the cylindrical quartz vessel and ignited at the upper end of the vessel where it burns by diffusing with the surrounding air. Oxygen is added progressively until the upper hydrogen-air flame flashes back inside the cylindrical quartz vessel and the hydrogen burns with oxygen by diffusion. Sufficient hydrogen is added to supply and maintain both the inner flame and the outer flame. Under these conditions two flames are produced: an inner chilled $H_2 — O_2 — Ar$ diffusion flame which burns with an excess of fuel, hence a reducing atmosphere, and an outer diffusion hydrogen flame which burns with the surrounding air, and hence with an excess of oxidant. The sample solution is supplied as a fine spray to both flames through the pneumatic sprayer. Argon was chosen to operate the sprayer since it has a low quenching cross section. This property should emphasize overexcitation reactions.

Sulphur and phosphorus were supplied to the flame as sulfuric and phosphoric acids, ammonium sulfate, and ammonium phosphate, as well as organic aqueous solutions of dimethyl sulfoxide and hexmethyl phosphoramide.

The hydrogen flames produced under these circumstances are illustrated in figure 25 *a*, *b*, and *c*. Figure 25*a* shows the appearance of the two flames

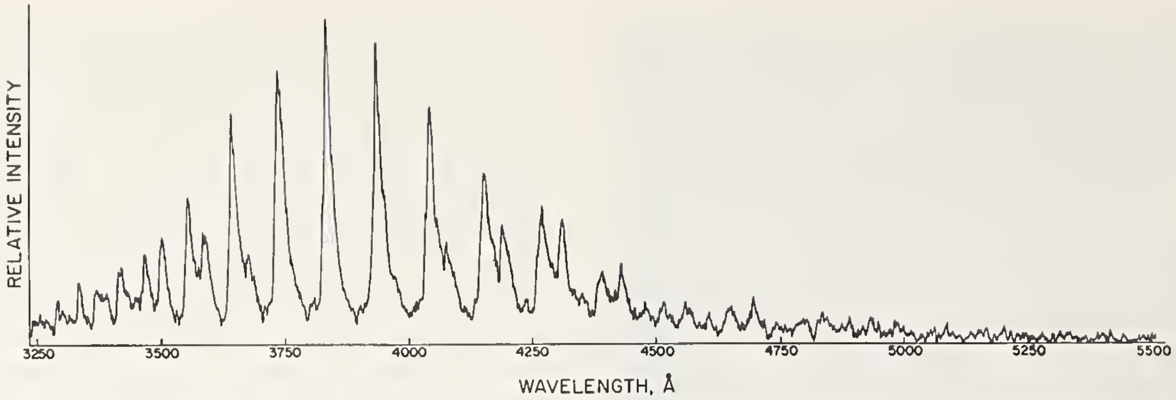


Fig. 26. — Monochromator recording of the inner hydrogen flame supplied with diluted sulfuric acid.

when only distilled water is supplied to the sprayer; figure 25*b* shows the flames supplied with the sulfur containing solution, while figure 25*c* shows the flames supplied with the phosphorus containing solutions. The same types of radiations are obtained with the inorganic or organic bound sulfur or phosphorus. Concentrations of these elements was about 1 percent. The detection limits for both elements are below 0.1 ppm.

The radiations from the inner chilled hydrogen flame supplied with sulphur and phosphorus compounds were examined with the spectrometer in the scanning mode using a grating with 1 200 lines/mm, a scanning speed of 200 Å/mn, and a slit of 0.200 mm (1.6 Å). The recordings of the spectra obtained are given in figure 26 for the sulphur flame and figure 27 for phosphorus flame. As can be recognized from data available in the literature (20), these radiations originate from the S_2 and HPO molecules.

The types and intensities of the radiations excited in the chilled hydrogen flame with an excess of hydrogen depend strongly on the experimental conditions used to produce them. The burner system described in this work is only one of many possible arrangements which can be used to produce these kinds of excitation conditions. Complete and up-to-date information on this subject can be found in reference (20).

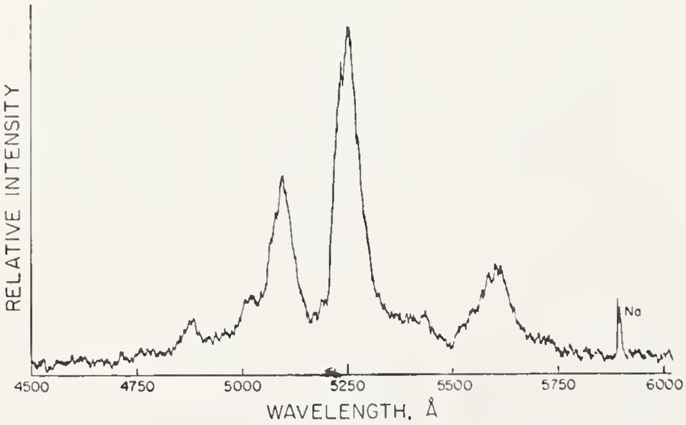


Fig. 27. — Monochromator recording of the inner hydrogen flame supplied with diluted phosphoric acid.

Both S_2 and HPO emissions are characteristic examples of the nonthermal excitation process which we have called overexcitation. Indeed, the thermal energy available in the chilled hydrogen flame is certainly not capable of exciting species such as HPO and S_2 which require about 2.4 and 3.9 eV respectively (*). Various potential reactions have been postulated to account for these nonthermal emissions. Thus, for HPO, Lam Thanh and Peyron considered both reaction (22).

$$H + PO + M \rightarrow HPO^* + M, \qquad (III')$$

and

$$H + PO^* \rightarrow HPO^*, \qquad (III)$$

while Gilbert proposed the chemiluminescent reaction (20),

$$PO + H_2 + OH \rightarrow HPO^* + H_2O. \qquad (III')$$

For S_2, Crone had suggested the chemiluminescent reaction (20),

$$H + H + S_2 \rightarrow S_2^* + H_2, \qquad (IV)$$

which was also postulated by Peyron. Sugden and Demerdache proposed another chemiluminescent reaction (23),

$$H + OH + S_2 \rightarrow S_2^* + H_2O. \qquad (IV)$$

At this stage it seems that further work is needed to elucidate these flame reactions and to arrive at an accurate interpretation of the excitation phenomena occuring in chilled hydrogen flames burning in an excess of fuel.

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

This volume consists of thirteen papers describing the analytical procedures selected at the National Bureau of Standards (NBS) for the determination of Ag, Al, As, Be, Bi, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Pt, Sb, Se, Te, Tl, V, and Zn in biological and botanical materials. These procedures are used at the present time for the certification of various substances issued by NBS as Standard Reference Materials, and belong to the following analytical disciplines: sample preparation, neutron activation analysis, spark source mass spectrometric isotope dilution, atomic absorption and flame emission spectrometry, molecular absorption spectrometry, fluorescence spectrometry, and polarography. Further details on the analytical methods including sample preparation, purity of reagents, and problems associated with blanks are given in sixteen additional papers which are reproduced in the Appendix to this volume.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

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