NBS TECHNICAL NOTE

454

Analytical Coordination Chemistry Section:

Summary of Activities July 1967 to June 1968

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in three broad program areas and provides central national services in a fourth. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, and the Center for Radiation Research.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Standard Reference Data and a group of divisions organized by the following areas of science and engineering:

> Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Cryogenics[2]—Radio Physics[2]—Radio Engineering[2]—Astrophysics[2]—Time and Frequency.[2]

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to methods, standards of measurement, and data needed by industry, commerce, educational institutions, and government. The Institute also provides advisory and research services to other government agencies. The Institute consists of an Office of Standard Reference Materials and a group of divisions organized by the following areas of materials research:

> Analytical Chemistry—Polymers—Metallurgy — Inorganic Materials — Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides for the creation of appropriate opportunities for the use and application of technology within the Federal Government and within the civilian sector of American industry. The primary functions of the Institute may be broadly classified as programs relating to technological measurements and standards and techniques for the transfer of technology. The Institute consists of a Clearinghouse for Scientific and Technical Information,[3] a Center for Computer Sciences and Technology, and a group of technical divisions and offices organized by the following fields of technology:

> Building Research—Electronic Instrumentation — Technical Analysis — Product Evaluation—Invention and Innovation— Weights and Measures — Engineering Standards—Vehicle Systems Research.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center for Radiation Research consists of the following divisions:

> Reactor Radiation—Linac Radiation—Applied Radiation—Nuclear Radiation.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C. 20234.

[2] Located at Boulder, Colorado 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

UNITED STATES DEPARTMENT OF COMMERCE
C. R. Smith, Secretary
NATIONAL BUREAU OF STANDARDS • A. V. Astin, Director

NBS TECHNICAL NOTE 454

ISSUED JULY 1968

Analytical Coordination Chemistry Section:

Summary of Activities July 1967 to June 1968

Edited by Oscar Menis

Analytical Coordination Chemistry Section
Analytical Chemistry Division
Institute for Materials Research

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C., 20402 - Price 55 cents

FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine sections and about 100 technical personnel encompassing some 57 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is a highly important output of our laboratories. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information about our programs. A word is perhaps in order about the philosophy of these yearly progress reports. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication--yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment, etc., which often must be covered in only a line or two of a journal article.

Thus our progress reports endeavor to present this information which we have struggled to obtain and which we feel might be of some help to others. Certain areas which it appears will not be treated fully in regular publications are considered in some detail here. Other results which are being written up for publication in the journal literature are covered in a much abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1968 we plan to issue these summaries for all of our sections. The following is the fourth annual report on progress of the Analytical Coordination Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

Progress made during the past year again reflects the interaction between the needs of the Standard Reference Materials Program and the several competences comprising the Section. While much of the success can be attributed to the development of improved procedures and instrumentation, a relatively large fraction can also be ascribed to the renewed respect for, and a better understanding of, sample dissolution processes. Closed-system dissolutions, especially, have proved invaluable in the areas of titrimetry, gravimetry, spectrophotometry, flame spectrometry and gas evolution methods. In addition, work in these areas has been augmented considerably by the contributions of several guest workers and industrial research associates. This concerted effort has improved significantly the present capability of chemically characterizing both high-purity as well as very complex materials. It has also pointed out the need for developing skills which are applicable to the analysis of micro samples, an area which is discussed only briefly in this report.

While some of the work reported may appear fragmentary and lack detail, it is anticipated that much of it will later appear in journal articles in its entirety. Also, in order to describe experimental procedures adequately, it has occasionally been necessary to identify commercial materials and equipment by the manufacturer's name or label. In no instances does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the particular material or equipment is necessarily the best available for that purpose.

The editorial assistance of Dr. R. W. Burke in preparation of this report is gratefully acknowledged. The assistance of Mrs. Rosemary Maddock and Mrs. Jean Gossard is also gratefull acknowledged. Also, it is a pleasure to acknowledge the invaluable assistance of Mrs. Barbara Keith, Secretary in our Section who performed a wide variety of duties essential to the work in this Section, and for her tireless efforts in typing this report.

Oscar Menis, Chief
Analytical Coordination
Analysis Section

TABLE OF CONTENTS

PAGE

TABLE OF CONTENTS (CONT'D)

PAGE

LIST OF TABLES

TABLE NO.

LIST OF TABLES (CONT'D)

LIST OF FIGURES

ABSTRACT

This annual report outlines the progress made in titrimetry, gravimetry, flame emission, atomic absorption and fluorescence, spectrophotometry, spectrofluorometry and the determination of gases in metals in conjunction with the analysis of Standard Reference Materials. It describes recent developments in instrumentation and in sample dissolution techniques and discusses some unique applications of coordination systems and ternary complexes.

In flame spectroscopy considerable progress was made in the development and testing of electrodeless discharge lamps, Xe-arc continuum sources, a.c. scanning systems, resonance detectors and improved nebulizer-burner combinations. The relative merits of flame emission, atomic absorption and atomic fluorescence were evaluated from theoretical and practical standpoints. Specialized instrumentation was also developed for use in thermal analysis studies and in spectrofluorometry. In the area of gases in metals, a new inert gas fusion apparatus having a unique sampling valve and gas flow system was constructed and coupled to a high sensitivity gas chromatograph. In addition, a new commercial inert gas fusion apparatus was tested and a vacuum fusion unit modified to permit more readily the successive determination of oxygen and nitrogen.

Studies were made of the dissolution of refractory materials containing volatile or easily hydrolizable components. Sealed Teflon-lined bombs and quartz tubes were successfully applied to the determination of trace nitrides in steels and niobium alloys and of antimony at the 10-50 ppm level in ferrous alloys. The latter was prerequisite to the provision of standards for correlating the presence of trace antimony in rotor blades with power turbine failures. Teflon-lined bombs were also used for the dissolution of clays prior to the determination of trace components.

The formation and extraction of ternary complex systems were investigated to provide enhanced spectrophotometric and spectrofluorometric sensitivity for trace metal determination. Improvement in the detection limits of existing procedures were effected by the use of micro-volume techniques. Also, the utilization of recently developed spectrofluorometric chelating agents have yielded significant improvement in sensitivity. Beryllium, for example, was readily determined in resin beads at the 50 picogram level.

Finally, a large number of Standard Reference Materials and potential standards were certified for their major, minor and trace constituents. These included clays, tungsten-molybdenum compacts, neutron flux glasses, aluminum alloys, organo-metallic compounds, ferrous alloys, solder, and high-purity and doped zinc, platinum and gold. Many of the values obtained were confirmed by independent methods.

Key words: atomic absorption and atomic fluorescence spectrometry, differential thermal analysis, flame emission, gases in metals, gravimetry and titrimetry, spectrophotometry and spectrofluorometry, standard reference materials.

1. GRAVIMETRY AND TITRIMETRY

A. Introduction

While research and development in these areas have been relatively limited during the past year, a tremendous amount of work on the other hand has gone into the analysis of a number of important Standard Reference Materials (SRM's). Included in this group are two types of clay, a cobalt glass neutron flux monitor, several metallo-organics, a variety of both ferrous and non-ferrous alloys and, finally, some recently proposed thermal analysis standards.

B. Analysis of Flint Clay, SRM 97a, and Plastic Clay, SRM 98a

The renewal standards for these two clays, which were last certified at NBS in 1931 by Hoffman et al, were analyzed for major components by the general procedures reported by Lundell and Hoffman (1); minor components were determined by a variety of trace methods including flame emission, atomic absorption and solution spectrophotometry. The values obtained by means of these latter techniques are listed in their appropriate sections.

1. Gravimetric SiO_2 Determination

A 0.5-g sample was dried at 140°C for 2 hours and fused with 8 g of anhydrous Na_2CO_3. The melt was dissolved in dilute sulfuric acid (10%), and a double dehydration of the SiO_2 carried out. Finally, the residue was treated with HF and the amount of SiO_2 present was determined from the ensuing weight loss. Soluble silica was subsequently determined in the Al_2O_3 precipitate and added to this value.

2. Gravimetric Al_2O_3

A 2-g sample was dried at 140°C for 2 hours, treated with a mixture of H_2SO_4-HNO_3-HF and evaporated to fumes of H_2SO_4 twice. The insoluble residue was treated with HF-H_2SO_4, fused with Na_2CO_3, filtered, and fused with potassium pyrosulfate. A double precipitation of the aluminum was made with NH_4OH on a 0.4-g portion of the sample, ignited to 1200°C and weighed. This impure Al_2O_3 was corrected for SiO_2 by treating with HF and for Fe, Ti, Zr and V by carrying out a double cupferron precipitation of the latter elements from a second 0.4-g aliquot.

Phosphorus was determined spectrophotometrically in a third aliquot and the amount of P_2O_5 equivalent to a 0.4-g sample was deducted from the initial Al_2O_3 result. Similarly, chromium was determined spectrophotometrically with diphenylcarbazide in another aliquot and the appropriate Cr_2O_3 correction deducted.

3. Gravimetric Determination of Phosphorus

The procedure involved a double precipitation of ammonium magnesium phosphate and ignition to the pyrophosphate.

4. Gravimetric TiO_2 and ZrO_2

Iron, titanium and zirconium were separated from the remaining elements by precipitation with NaOH and the residue redissolved in hot (1+1) HCl. Iron was then precipitated with ammoniacal H_2S and titanium and zirconium precipitated with cupferron. The combined weight of TiO_2 and ZrO_2 was then obtained by igniting to a constant weight. These oxides were then fused with $K_2S_2O_7$, H_2O_2 added to complex titanium and zirconium precipitated with $(NH_4)_2HPO_4$. The precipitate was ignited and weighed as ZrP_2O_7. TiO_2 was finally determined by the difference in weight between the weight of $(TiO_2 + ZrO_2)$ and ZrO_2 (from ZrP_2O_7).

5. Titrimetric Fe_2O_3

A 0.2-g sample was fused with 1 g of lithium metaborate in a carbon crucible at 950°C for 20 minutes. The melt was dissolved by pouring into dilute hydrochloric acid and stirring for approximately 1 hour. Fe^{+3} was reduced with $SnCl_2$, excess Sn^{+2} oxidized with $HgCl_2$ and the Fe^{+2} titrated with standard potassium dichromate. A summary of the gravimetric and titrimetric results obtained on the two clay materials is presented in table 1.

Table 1. Gravimetric and titrimetric determination of major constituents in clay.

SRM No.	Constituent	Weight percent
97a	SiO_2	43.79, 43.78, 43.82
	Al_2O_3	38.58, 38.32, 38.53
	P_2O_5	0.36, 0.34, 0.33
	TiO_2	1.90, 1.85, 1.88
	ZrO_2	0.056, 0.056
	Fe_2O_3	0.47, 0.46, 0.47
98a	SiO_2	49.21, 49.22, 49.13
	Al_2O_3	33.09, 33.04, 33.29
	P_2O_5	0.078, 0.075, 0.075
	TiO_2	1.56, 1.57, 1.55
	ZrO_2	0.044, 0.042
	Fe_2O_3	1.37, 1.37, 1.36

C. Analysis of Solder, SRM 127b and SRM 1131

Titrimetric procedures were used for the determination of tin and antimony in solder. SRM 127b was in a powder form and 1131 was a spectrographic sample.

1. Titrimetric Sn

For the tin determination, the sample was dissolved in H_2SO_4, the Sn^{+4} reduced with lead and then titrated with KIO_3, using starch-iodide as an indicator. To prevent air oxidation the titration was carried out under a CO_2 atmosphere.

2. Titrimetric Sb

For the determination of antimony the sample was dissolved in HNO_3-HF and the lead precipitated with H_2SO_4. Antimony (and arsenic) were reduced with hydrazine sulfate and distilled as the trichlorides from dilute HCl-H_2SO_4. The 110°C fraction containing the arsenic was discarded and antimony was collected in the 160°C fraction. It was freed from chloride by precipitating with H_2S, filtered and then Kjeldahled with HNO_3-H_2SO_4. Sb^{+5} was reduced to Sb^{+3}

with sulfur (sulfur gives lower MnO_4^{-1} blanks than hydrazine sulfate), the excess sulfur filtered off and the Sb^{+3} titrated with standard permanganate.

A summary of the gravimetric and titrimetric results obtained on the two solder standards is given in table 5.

D. Tungsten-Molybdenum Compact

A very homogeneous compact, as ascertained by microprobe analyses, of a nominal composition 80% W and 20% Mo was analyzed to establish an accurate composition value. For this purpose a sample of this compact extruded into a wire with Mo as a surface coating was treated with an acid mixture consisting of equal volumes of HNO_3, H_2SO_4 and H_2O to remove this surface. The final sample which consisted of 0.050 inch diameter wire weighing 0.469 g was analyzed by a procedure described in detail previously (2).

This procedure consists of anion separation in 25% HCl-20%HF. Tungsten and molybdenum were then determined gravimetrically in the eluates by the tungstic acid-cinchonine and benzoinoxime procedures respectively. The results together with data from synthetic samples are presented in table 2. The percentages are corrected for random and systematic error. Independent methods are presently being investigated to check these values and further discussion concerning this analysis is presented in the spectrophotometry section.

E. Gravimetric Determination of Cobalt in Neutron Flux Glass

The gravimetric determination of cobalt in neutron flux glass was undertaken largely as a confirmatory check of the spectrophotometric titration results (see subsequent procedure). As a preliminary study duplicate synthetic samples were prepared containing cobalt, aluminum and EDTA. B_2O_3 and SiO_2 were not added since they were volatilized as fluorides in the dissolution step and Li_2O was not expected to interfere. The results of this study in which cobalt was precipitated with α-nitroso-β-naphthol are shown in table 3.

Table 2. Analysis of tungsten-molybdenum compact.

Material	80W-20Mo wire (1968)	Synthetic Mixt. (1966)	80W-Mo wire (1966)	Synthetic Mixt. (1968)
Sample taken, mg	236.34	46.36 (Mo)	253.5	50.5 (Mo)
	227.49	190.10 (W)	264.0	200.0 (W)
MoO_3 recovered	73.8	66.5	82.2	74.1
	70.9		85.8	
WO_3 recovered	234.7	236.3	250.7	247.1
	225.3		259.9	
% Mo	20.81	18.74	21.64	19.72
	20.77		21.68	
% W	78.85	79.25	78.58	78.22
	78.64		78.117	
Corrected Mo[a]	21.33		21.50	
	21.35		21.63	
Corrected W[a]	78.67		78.50	
	78.65		78.37	

---

[a] Adjusted for total recovery, according to synthetic analysis, and corrected to 100% summation as follows:

$$Mo' = Mo \times \frac{\text{Molybdenum present in synthetic}}{\text{Molybdenum found in synthetic}}$$

$$W' = W \times \frac{\text{Tungsten present in synthetic}}{\text{Tungsten found in synthetic}}$$

Since $Mo' + W' \neq 100$,

$$Mo'' = \frac{100\ Mo'}{Mo' + W'} \quad : \quad W'' = \frac{100\ W'}{Mo' + W'}$$

Where Mo and W are the percentages of the respective metals found in the compact, and Mo', Mo" etc., are successively corrected values.

All factors considered, the gravimetric results represent a much better quality of work than the results would seem to indicate. As is generally the case, considerable blank difficulties were encountered with the use of α-nitrose-β-naphthol

Table 3. Gravimetric determination of cobalt.

Method	Sample	Cobalt found, mg	
		Run 1	Run 2
Ppt. with α-nitroso-β-naphthol→Co_3O_4	25.56 mg Co, 8.0 mg Al, 372 mg Na_2 EDTA	25.62	25.62
Co_3O_4 reduced with H_2		27.0	26.7
Cobalt dissolved and electrodeposited		26.8	26.5
Ppt. with α-nitroso-β-naphthol→Co_3O_4	Cobalt glass No. 1	9.44	9.30
Co_3O_4 + HCl→anion exchange; Co reppt. with α-nitroso-β-naphthol		9.12	9.04
Anion exchange separation; ppt. with α-nitroso-β-naphthol	Cobalt glass No. 2	9.63	9.38

which were further accentuated by the relatively small sample weights involved.

F. Spectrophotometric Titration of Cobalt in Neutron Flux Glass

The need to accurately determine cobalt (approximately 10% CoO) in a doped glass intended for use as a neutron flux monitor suggested the possible application of a spectrophotometric titration. The method ultimately used was an adaptation of a procedure originally proposed by Flaschka and Ganchoff (3). In this method advantage is taken of the exceedingly high stability of the Co(III) EDTA complex in acid solution ($K_f \approx 10^{40}$) to effectively eliminate interferring ions.

1. Procedure

Add excess EDTA to the acidic $Co+^2$ solution. Adjust pH to 11 and oxidize $CoEDTA^{-2}$ to $CoEDTA^{-1}$ with H_2O_2 Acidify to pH 1, add indicator (Pyrocatechol Violet) and sufficient standard $Bi+^3$ solution to complex excess EDTA and also leave reasonable amount for back titration. Adjust pH to 1.0 and titrate excess $Bi+^3$ with standard EDTA at 625 nm. Calculate cobalt from the relationship: moles Co = total moles EDTA - moles Bi.

An important point not discussed in Flaschka's article is the equilibration time required for carrying out the titration at various pH values. For example, although pH 1 or 2 appear equally suited for the precise location of the endpoint (figure 1), the point-to-point equilibration time is of the order of seconds at the lower value whereas 5-10 minutes may be required at pH 2. Obviously instrumental fluctuations occuring during this interval can be disasterous. Therefore, as a compromise between time and sharpness of endpoint, pH 1 was chosen for obtaining the data shown below.

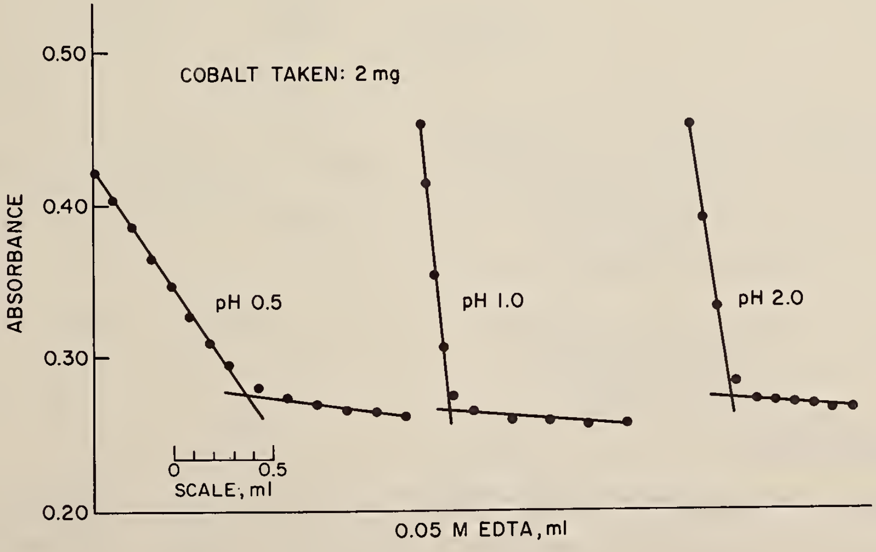


Figure 1. Effect of pH on shape of titration curves near endpoint.

All titrations were carried out in 100-ml beakers, using a Beckman Model B spectrophotometer. Titrant deliveries were made from a 3-ml micrometer syringe, the tip of which had been modified by the addition of a tapered Teflon extension. Titrant was added by lowering this tip below the surface of the sample, adding the prescribed amount and then withdrawing immediately. A lab jack proved quite useful for this manipulation. Solutions were mixed continuously with a motor-driven glass stirring rod.

2. Results

Some results obtained on separate samples of ground glass are shown in table 4.

Table 4. Spectrophotometric titration of cobalt in neutron flux glass.

Sample No.		Weight % CoO
1		9.36
2		9.39
3		9.38
4		9.39
5		9.37
	average	9.38
	SD	0.009%

For two synthetic cobalt glasses the results were as follows:

Synthetic I (9.19% CoO)	9.20
Synthetic II (9.35% CoO)	9.33

3. Discussion

Although the procedure described above is an indirect one with all of the uncertainties falling on the final difference, our experience has been that this system can readily yield both a precision and accuracy of 1 part in a 1000. While milligram amounts of cobalt were employed in these studies, there is no in these studies, there is no reason why the determination can not be extended to include smaller samples as well. The important point is that there be sufficient excess bismuth for a reasonable back-titration.

One other point that deserves mentioning is the compatability of the dissolution procedure with the determination step. Treatment of the glass with either HF-$HClO_4$ or with Na_2CO_3-H_2SO_3 yielded identical results. The accuracy of these results were later confirmed by an independent spectrophotometric method which is described in Section 3.

G. Miscellaneous Gravimetric-Titrimetric Analyses of SRM's

Gravimetric-titrimetric determination of a number of miscellaneous elements in Standard Reference Materials are given in table 5.

H. Differential Thermal Analysis

As described in the last annual report a series of inorganic compounds are being tested as potential standards for calibrating the dynamic temperature scale in differential thermal analysis. This study, an outgrowth of a cooperative effort with the International Conference on Thermal Analysis (ICTA), is being carried out in conjunction with the ICTA Committee on Standards. An initial survey of the data reported by 26 laboratories from nine nations indicates a wide divergence of values for these compounds. With the assistance of Dr. B. L. Joiner of the Statistical Engineering Laboratory a computer program was written to plot transition temperatures of SiO_2 and $KClO_4$ versus those for KNO_3 (after subtracting the values published in the NBS Circular No. 500). Evidence of interlaboratory differences can readily be discerned in the Youden "two sample" plot. The two aspects of interest, the random error and the systematic error can be derived from the scatter of points along a 45° line as shown in figure 2. The vertical distances from that line are indicative of the random error of a given laboratory while the distances along the line provide a measure of systematic error. It is evident from the general 45°

Table 5. Miscellaneous gravimetric-titrimetric analyses of SRM's

Element	SRM	Kind	No. of determ.	%	RSD(1)	Ref.
Al	1075a	Aluminum 2-ethylhexanoate	4	8.07	0.3	4
	1075a	Aluminum 2-ethylhexanoate	4	8.08	0.1	5
Mg	1061b	Magnesium cyclohexanebutyrate	4	6.58	0.2	6
Ni	1065b	Nickel cyclohexanebutyrate	10	13.89	0.07	7
V	1052b	bis (1-phenyl-1,3-butanedione)oxovanadium(IV)	4	13.07	0.4	8
Cu	1080	bis (1-phenyl-1,3-butanediono)copper(II)	4	16.52	0.4	9
Cr	1078a	tris (1-phenyl-1,3-butanediono)chromium(III)	9	9.68	0.04	10
	51	Cast iron	5	0.147	0.1	11
	6g	Cast iron	6	0.361	0.2	11
	6g	Cast iron	6	0.360	0.3	12
	342a	Nodular iron	6	0.0355	0.3	12
Mg	1061b	Magnesium cyclohexanebutyrate	6	6.50	0.6	13
Mn	51	Cast iron	6	0.686	0.5	14
	6g	Cast iron	9	1.067	0.5	14
	30f	Cr-V (SAE 6150) steel	8	0.791	0.4	15
	342a	Nodular iron	6	0.271	0.9	14
Sb	127b	Solder (Pb60-Sn40)	2	0.425		16
	1131	Solder (Pb60-Sn40)	2	0.433		16
Sn	127b	Solder (Pb60-Sn40)	9	39.12	0.2	16
	1131	Solder (Pb60-Sn40)	9	39.40	0.2	16
V	196	Ferrochromium	5	0.097	7	14
V	1052b	bis (1-phenyl-1,3-butanediono)oxovanadium(IV)	16	13.01	0.2	17

---

(1) Relative standard deviation

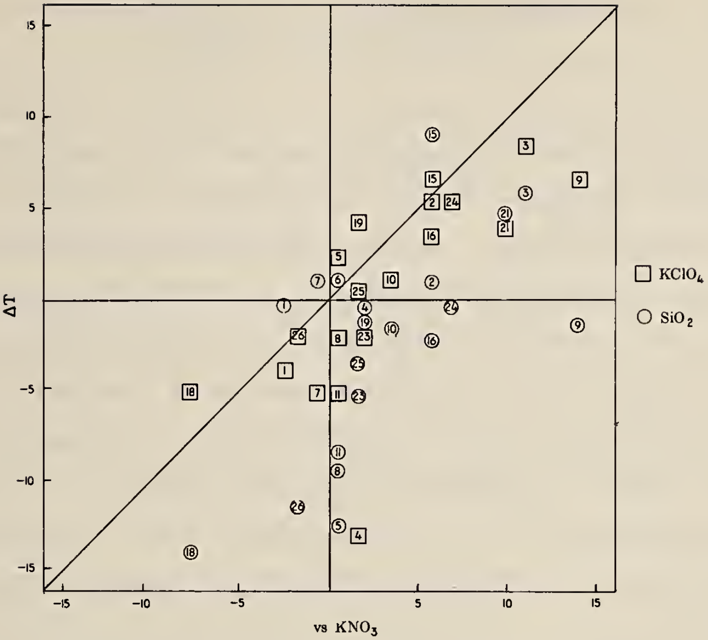


Figure 2. Correlation of interlaboratory DTA determinations by a Youden two-sample chart.

slope of the points that there are substantial systematic differences (or biases) between the 26 reporting laboratories. More formal analyses may be made by the methods outlined in Youden's pamphlet, "Statistical Techniques for Collaborative Tests" [18]. There is some indication in figure 2 that the values for KNO$_3$ and KClO$_4$ tend to agree with one another better than the values for KNO$_3$ and SiO$_2$. In addition, there is evidence that the SiO$_2$ values are on the average lower than the NBS Circular 500 values. The precision of the measurements, as indicated by the magnitude of the departure from the 45° line, seems to be roughly the same for the different laboratories.

This preliminary evaluation points up again the universal need for standards. The program at NBS is motivated by this type of information to make an effort in preparing suitable standards for calibrating the various systems and thus assisting the resolution of interlaboratory differences.

At present, considerable effort is being placed on both the screening of materials which may be suitable as standards and on improving the instrumental procedures for the more accurate measurement of temperatures at the transition points. For this purpose various batches or sources of KNO_3 and SiO_2 are being tested. Also, the instrument described previously (19) is being modified. For this purpose, in place of the X-Y recorder a two-pen recorder with an expanded scale is being used. This should assure a ten-fold improvement in measuring the transition temperatures. In addition, the sample and reference cup have been redesigned. As shown in figure 3 the sample cup was provided with a central inlet for the thermocouple. This modification should assure a direct contact between the thermocouple bead and the sample material. In addition the circuitry was modified to permit the simultaneous measurement of temperature change in the sample compartment and the ΔT of the sample vs reference cell. It is anticipated that these modifications should aid considerably in the more accurate determination of the temperature of transition points of interest.

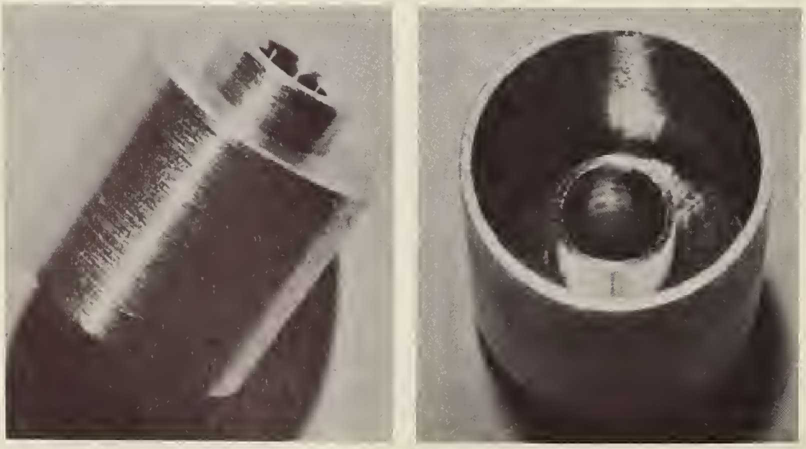


Figure 3. DTA sample cup.

2. FLAME EMISSIONS, ATOMIC ABSORPTION AND ATOMIC FLUORESCENCE

A. Introduction

As in previous years the efforts in this area concentrated on the evaluation of components and the modifications essential for highest precision and accuracy. These studies included the step-wise optimization of the instrumental components and the more careful control of the parameters so that the overall effect was to attain better detection limits and at the same time improve the precision and accuracy of measurements. These investigations included the evaluation of light sources, nebulizer-burners, the selection of oxidant-fuel gases and the careful attention to the optical systems, as well as the application of a.c. scanning techniques. In addition, the methodology in flame emission, atomic absorption and atomic fluorescence are being evaluated from the theoretical and practical standpoint to discover more promising areas for advancement. Finally, the applications to various standard reference and unique service samples point out the wide utility of these methods for determination of micro quantities of components in complex composition matrices.

B. Evaluation of Instrumental Components and Parameters

In a continuing effort to improve measurement techniques in the fields of flame emission and atomic absorption, a number of new approaches were explored during this year. A schematic diagram of the instrumentation used in these fields, as shown in figure 4, shows the relationship of the several components studied. In the absorption mode the instrumental components are as shown while in emission, the instrument is operated without the light source and the chopper is located between the flame and the monochromator. The various components are being evaluated in a search for the optimum conditions so far as the instrumentation is concerned.

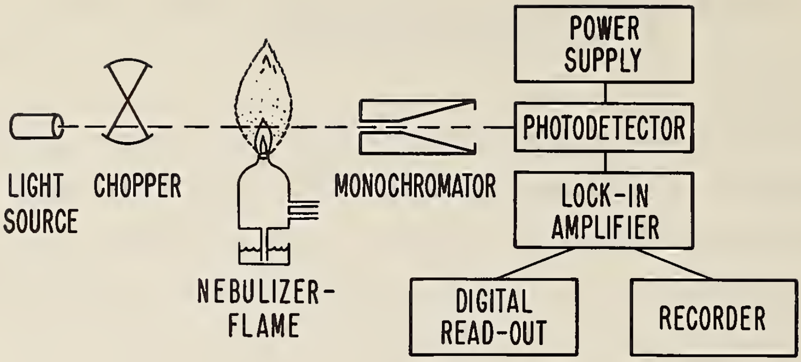


Figure 4. Schematic diagram of atomic absorption instrument.

1. Light Sources

In atomic absorption, the light source must produce lines that are sharp, intense and stable to attain maximum absorption. The line sources which are suitable for atomic absorption spectrometry are the hollow-cathode, Osram discharge lamp, electrodeless discharge lamp and Xe-arc lamp. The hollow-cathode lamps are normally used; however, for many elements the intensity and stability leaves a lot to be desired. In an effort to overcome some of the limitations of the hollow-cathode lamps, various other sources of monochromatic radiation have been explored. Also a continuous light source, a Xe-arc lamp was tested in conjunction with a.c. scanning.

a. Electrodeless Discharge Lamp. In our last report [19] a brief discussion of the electrodeless discharge lamp was presented. During the past year the various parameters associated with these lamps as a source of radiation for atomic absorption have been investigated. This included the effect of lamp size, concentration of metal, pressure of inert gas and means of excitation. The physical dimensions of the lamp will depend upon the source of excitation; however, lamps which were made 15 mm in length and 9 mm O.D. from quartz tubing have proven to give the highest intensity and stability.

i. Construction: The apparatus used in the preparation of these lamps is shown in figure 5. The blanks for the lamps were made from high purity quartz tubing for elements which emit resonance radiation below 2500 A while vycor tubing was used for all elements which emit above 2500 A. The blanks were then connected to the vacuum system by a glass to glass metal connector. The system was evacuated and flushed with argon. The tubing was heated with an oxygen-propane torch to just below the softening point of the quartz or vycor tubing to degas the blank while the system is being pumped out. Argon was then introduced and the blank cooled. After removal of the blank, 1-3 mg of the element as the metal or as the iodide was introduced. In some cases it was necessary to prepare the metal iodide in the blank by reacting the metal with iodine under reduced pressure. The tubes were then evacuated as previously described and flushed with argon. The metal or salt was gently heated to its melting point and evacuated to a pressure of less than 10^{-3}mm of Hg. Then, the tube was filled with argon at the desired pressure and sealed off with an oxygen-propane torch.

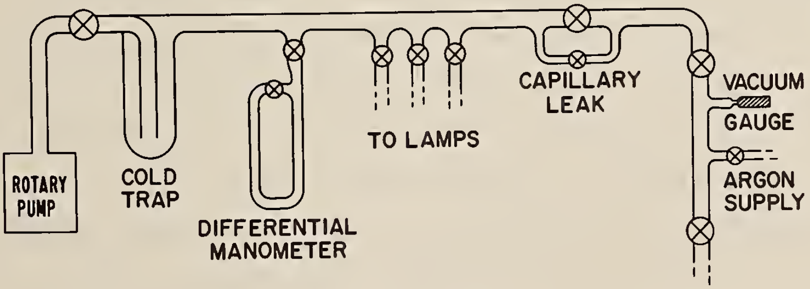


Figure 5. Apparatus for preparation of electrodeless discharge lamps.

ii. Measurement of its Characteristics: The intensity and stability of the lamp was found to be a function of argon pressure as shown in table 6. At pressures of less than 0.1 torr or mm of Hg, the lamp would not maintain a discharge with an Evenson excitation cavity while at pressures above 1 torr the filler gas became the primary source of radiation.

Table 6. Effect of inert gas pressure in electrodeless discharge lamp.

Inert gas press, torr	Intensity, arbitrary units	Drift, %/min.
< .1	0	--
.2	250	<1
.4	1100	1
1.0	200	<1
2.0	1.2	5
3.0	1.2	5
2.0[a]	14	5

---

[a] Commercial Pb lamp.

iii. Excitation Source and Cavity: Since 1950 when Meggers and Westfall first described the construction and excitation of an electrodeless discharge lamp, various types of power sources and cavities have been used [20-22]. 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 tube. One of the more effective cavities which meets these requirements with the greatest efficiency is the Evenson cavity [23]. To match the resonance frequency and impedance of the source the cavity is provided with a coupling slide and tuning screw. To facilitate the tuning a R.F. power meter is placed between the source and cavity. When the resonant frequency of the cavity is tuned to that of the diathermy unit and impedance is matched, the power reflected from the cavity is at a minimum.

To test the operation of this excitation source for atomic absorption a sodium electrodeless lamp was prepared and tested. The data are shown in table 7. It was observed that the lamp increased in intensity with increasing power from the R.F. generator; however, the relative absorption by sodium vapor decreased. By measuring the line width with an interferometer self-reversal was observed to occur for the 5890 A sodium line when the power of the R.F. generator exceeded 15 watts. Strong reversal was observed when the generator reached 50 watts.

Table 7. Absorbance for sodium with electrodeless discharge lamp.

Instrument, 0.5 meter; burner, tri-flame-air/C_2H_2
wavelength, 5890 A; Na, μg/ml-1.0

R.F. generator, W	Line width, A[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	--	0.035
50	--	0.020

---

[a] Inferometer measurement, resolution - 0.012 A.

iv. Comparison of Intensities with Hollow Cathode: A comparison of the intensity of the electrodeless discharge lamps and hollow-cathode lamps is made in table 8. In nearly every case, the electrodeless lamp was more intense than the hollow-cathode lamp, but in no case was the absorption greater (see figure 6). The lower sensitivity for the discharge lamp was attributed to self reversal. At the present time a new power source and cavity are being tested.

T. C. Rains

b. Continuum Sources in AAS. A continuum source Xe-arc lamp, was evaluated under modified conditions as a light source for atomic absorption. It has been previously stated that continuum sources are inferior to line sources in AAS [24]. The chief argument is that the spectral range

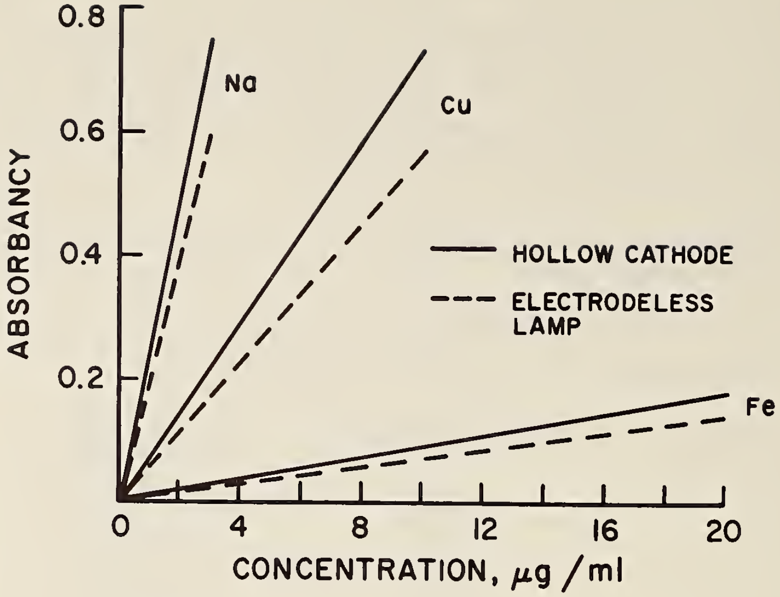


Figure 6. Comparison of sensitivities of hollow-cathode and electrodeless discharge lamps.

Table 8. Comparison of intensity of electrodeless discharge lamp and hollow-cathode lamps.

		Hollow cathode		Electrodeless discharge	
Element	Wavelength, A	Current, ma	I	Power, W	I
Ag	3280	12	1100	30	225
Bi	3068	10	400	30	80
Cu	3247	12	2250	30	8400
Fe	2483	30	200	30	200
Hg	2537			30	5400
Na	5870	15	640	20	900
Pb	2833	12	96	30	1100
Zn	2138	12	14	30	530

---

transmitted through the monochromator is too broad, resulting in a loss in sensitivity and requiring a monochromator with high resolving power. However, when one takes into consideration the relative instability of a light source, it becomes apparent that this instability is the controlling factor. The fluctuations in a light source, considered as the Fouriertransformation of a time-dependent signal, are generally larger at low frequencies (0 to ~100 Hz) than at high frequencies. Some of the causes of instability may be due to irregular wandering of the discharge channel in the source or the fluctuation in the voltage across the discharge which occur at low frequencies. Since the light beam is detected at approximately 1 Hz, even when it is chopped, large fluctuations, of the order of 1/2%, are encountered. This limitation can be overcome by going to higher frequencies until the limiting factor becomes the square root fluctuation of the measured quantity. Under those conditions one can show that there is no loss in signal to noise ratio due to insufficient resolving power of the monochromator. The detection limit expressed as the number of atoms detected per sec., N, then can be calculated from the intensity of the light source, the properties of the apparatus and the line characteristics according to

$$N = 1.58 \times 10^{12} L^{-1} (\lambda_o^2 gf)^{-1} I^{-1/2} (\tfrac{H}{F} DAt)^{-1/2} (\eta\tau)^{-1/2} \text{ cm}^{-3}$$

in which L is the length of the flame, λ_o is the wavelength of the line, gf is its oscillator strength, I is the intensity of the source (in photons per s. sr. cm^2 A), H is the slit height used, F is the focal length, D is the angular dispersion, A is the area of the grating, t is the transmission factor of the apparatus, η is the efficiency of the photocathode and τ is the measuring time [25].

The problem of eliminating the "technical" fluctuations can be overcome by a type of double beam system employing a.c. scanning in which the alternating frequency is larger than the frequencies from the technical instabilities. This approach is now under study.

i. Experimental Setup: In a 0.5 m Ebert monochromator a mirror system was installed between the entrance slit and the exit slit, shown in figure 7. One mirror was vibrated at about 100 Hz in such a way that a small part of the spectrum was vibrating across the exit slit. An absorption line in a continuous spectrum then yields a 200 Hz signal which is detected by a photomultiplier and a lock-in amplifier tuned at 200 Hz. Neither the continuous spectrum itself, nor its first derivative are detected since they yield signals of 0 Hz and 100 Hz, respectively.

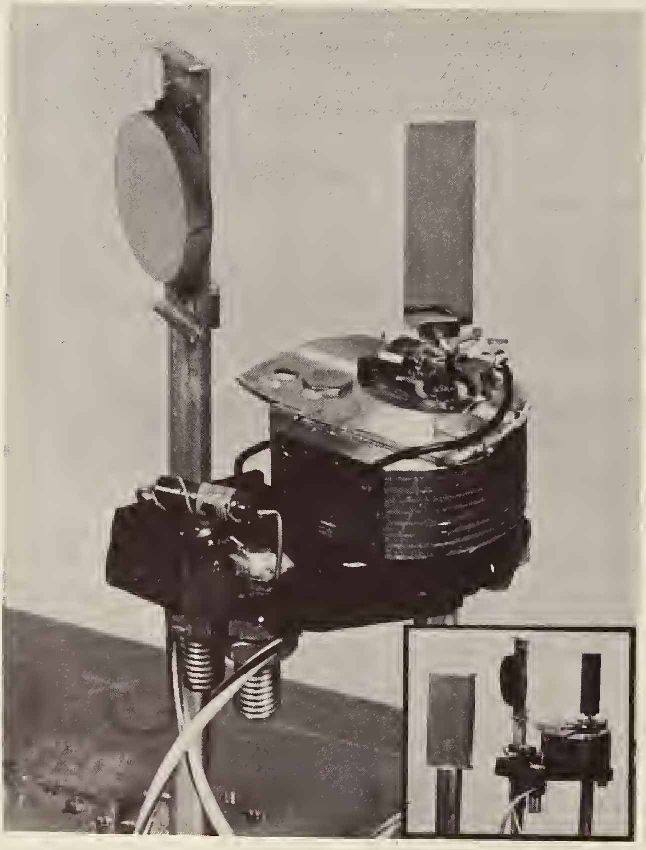


Figure 7. A.C. scanning system.

ii. Results and Discussion: This method of measurement by scanning has been applied extensively in ESR and also in optical measurements [26]. It essentially combines the advantages of a single beam system (identical light paths for two measurements) and a double beam system (fast, repeated comparison of two signals). A comparison of detection limit with the two sources a continuum and a line source was carried out under similar experimental conditions. The data were obtained with a pre-mixed laminar flame under conditions in which all the parameters were not optimized as the purpose of this experiment was to obtain a comparison and not the lowest detection limit. These comparisons are presented in table 9 together with reported literature values. These data indicate considerable improvement in the detection limit with a Xe-lamp operated with a.c. scanning. Currently studies are underway with improved scanning and electronic circuitry to extend the utility of this technique.

Table 9. Comparison of detection limits with chopped and scanned sources.

				Litt. data [6]	
	Hollow cathode	Xe-lamp chopped	Xe-lamp scanned	Hollow cathode	Xe-lamp
Na	0.005 ppm	0.1	0.005	0.005	0.03
Ag	0.1	1	0.1	0.02	0.2
Cu	0.01	0.1	0.01	0.005	0.05
Mg			0.01	0.003	0.01
Ca			0.1	0.01	0.03
Eu			0.5		0.4
Ba			10	1	0.9

Apart from the detection limits, a continuum source in conjunction with a scanning system provides further advantages such as easy correction for continuum absorption due to oxides or hydroxides, means for the measurement of a wide range of concentration and, of course, the main advantage that one lamp can be used for the analysis of many elements.

W. Snelleman

2. Nebulizer-Burner System

The nebulizer-burner system is probably the most important component of the flame emission or absorption instrument. This stems from the fact that the means by which the sample is introduced into the flame will affect the sensitivity, and the type and degree of interference encountered in emission or absorption. The ideal nebulizer should have the following characteristics: (1) high degree of flame stability (2) freedom from any memory effect even from highly concentrated solutions, (3) ease of introducing the sample (4) a fast response time (5) freedom in internal corrosion (6) provide a constant nebulization rate (7) capability of using a wide choice of fuels and oxidants, and (8) the capability of conversion of a large percentage of the solution into fine droplets.

In an attempt to develop a burner with all of these characteristics two new burners were obtained and tested. One, which was fabricated from Teflon except for the burner head, was found to produce a very stable flame; however, the efficiency was very low. A slight modification in design is now underway to increase the efficiency of this system. The other, utilizing pre-mixed gases and a single slot nebulizer-burner system, was found to fulfill most of the above requirements except for flame instability when used with the nitrous oxide-acetylene flame. A slight modification in the burner head in the slot region should overcome this difficulty.

T. C. Rains

3. Choice of Oxidant-Fuel

Many of the interferences which occur in both absorption or emission with analytes forming refractory oxides can be overcome or minimized by the use of the proper oxidant-fuel system. In atomic absorption a burner with pre-mixed air-acetylene is used for many elements. However, it was observed that fuel-rich conditions are required to obtain maximum sensitivity for elements such as Ba, Ca, Cr, Fe and Sr. To overcome some condensed phase, oxide formation type of interferences, the nitrous oxide-acetylene flame was investigated. While the temperature of this flame is slightly lower than that obtained with an oxygen-acetylene flame, the lower burning velocity permits a longer resident time for the production of free atoms. Thus, with the nitrous oxide-acetylene flame the suppression due to phosphate, sulfate and aluminum on calcium or magnesium was overcome up to a ratio of 100:1. For ratios of interferences to alkaline earth elements greater than 100:1, the addition of 500 ppm of lanthanum and 10%(v/v) glycerol is recommended. In flame emission the pre-mixed burner with nitrous oxide-acetylene was found to eliminate the interference of aluminum and also to diminish the interference due to CaO at 5540 A on barium.

Another parameter which must be considered in the selection of the oxidant-fuel is the flame background produced by the gas mixture. When using an oxygen-acetylene or oxygen-hydrogen flame in flame emission, large regions of the visible spectra are adversely affected by C_2 and CH band systems resulting from the decomposition of organic solvents. Any oxidant-fuel system which is known to produce an adverse band system in the region of the wavelength of the analyte should therefore be avoided. These bands are less of a problem in atomic absorption, although they do produce a severe interference in some cases. For example, the resonance lines of arsenic which are located at 1890, 1937 and 1972 A are seriously affected by the flame gases. Various oxidant-fuel systems were tested and the most satisfactory system was an argon (entrained air) - hydrogen flame. This oxidant-fuel system produced a flame with the least absorption of the radiant intensity of the arsenic monochromatic light source as shown in table 10. However, a serious interference was encountered with high concentrations of foreign ion due to scattered light. This necessitated the development of a procedure for the selective extraction of arsenic. The nitrous oxide-propane flame as proposed by Butler [27] was also tested using the Techtron burner with the Boling head. For the several elements tested no improved sensitivity was detected and the head became overheated. As a result, the flame became very erratic and unstable. However, this oxidant-fuel system could be used with the regular nitrous oxide burner with complete safety and had the advantage of a lower temperature. At the lower temperature the interference from the ionization step is minimized.

Table 10. Absorbance of various flame gases at 1937 A.

Burner	Oxidant-fuel	Absorbance
Premix[a]	Air - C_2H_2	1.350
	Air - H_2	.960
	Ar - H_2	.270
Total consumption[b]	O_2 - H_2	.700
	Air - H_2	.290
	Ar - H_2	.210

---

[a] Single pass.

[b] Three passes.

4. Optical Systems

a. Monochromator. Several new additions were made to our optical system during the past year. To secure additional resolution a 0.75 meter Czerny-Turner mount spectrometer was purchased which will extend the resolution capabilities to 0.12 A. This instrument is being used, at present, to evaluate the spectra produced by the electrodeless discharge lamps.

b. Resonance Lamp as a Monochromator. The application of a resonance lamp in place of a monochromator in atomic absorption was investigated. The use of a resonance detector as a monochromator has been discussed by Sullivan and Walsh [28,29]. In a resonance detector a cloud of free-ground state-atoms are produced by a thermal or sputtering technique. The radiation from the resonance line of an analyte will be absorbed by the ground state atoms. Due to the absorption of this radiation some of the atoms will be excited and re-emit resonance radiation (fluorescence) which can be measured. A commercial instrument (AR-200) was tested and compared with our present absorption equipment.

To test the principle with the same electrical circuit, a Ca-Mg resonance detector was obtained. The detector was mounted in place of the 0.5 meter monochromator and compared with the 0.5 meter monochromator. The other components for the absorption or emission remained the same as reported previously [19]. A summary of the results is given in table 11. The sensitivity obtained for Ca and Mg as compared with the present instrument was slightly lower; however, due to the high stability of the resonance detector, the detection limits were of the same magnitude.

T. C. Rains

Table 11. Comparison of sensitivity and detection limits for Mg and Ca.

	Calcium		Magnesium	
	Sensitivity[a] ug/ml/% Abs.	Detection limit,ug/ml	Sensitivity[a] ug/mg/% Abs.	Detection limit,ug/ml
0.5 Meter monochromator	.07	.006	.006	.0003
Resonance detector	.11	.01	.006	.001
AR-200	.23	.02	.012	.001

---

[a] Defined as concentration which will produce 1% absorption.

[b] Defined as the concentration which will yield a signal (2σ) times the background or sample blank.

5. Interferometric Measurements

The widths of and the possible occurrence of self-reversal in the spectral lines from line sources have to be known to evaluate the effective intensity in these lines. Interferometric measurements were made of a number of resonance lines in the visible spectrum. A Fabry-Perot interferometer was used which has a resolving limit of 0.012 A with a spacer of 15 mm. The center of the pattern was used in photoelectric scans by varying the air pressure in the interferometer. Figure 8 gives the results for a number of lines from hollow cathode lamps. The line-width seems to be controlled by Doppler-broadening. The width of the line from an electrodeless discharge (Na) was measured as a function of power input. At low powers, the width (0.04 A) was somewhat larger than the line width from a hollow cathode lamp (0.03 A), but at higher power inputs the line broadened (to more than 0.12 A) and showed considerable self-reversal.

W. Snelleman

6. A System for Modulated Injection

The scanning method cannot be applied to a line source to increase the effective stability as in the case of a continuum source. Therefore, an apparatus for modulated injection was developed [30]. This arrangement may also be useful for differential measurements of samples of high concentrations in emission. Measurements with this equipment are now in progress.

W. Snelleman

C. Comparison of Flame Emission, Atomic Absorption and Atomic Fluorescence

Currently Flame Emission Spectrometry (FES) is sharing the field of interest with the two other methods, Atomic Absorption Spectrometry (AAS) and Atomic Fluorescence Spectrometry (AFS). It is of interest to evaluate the influ-

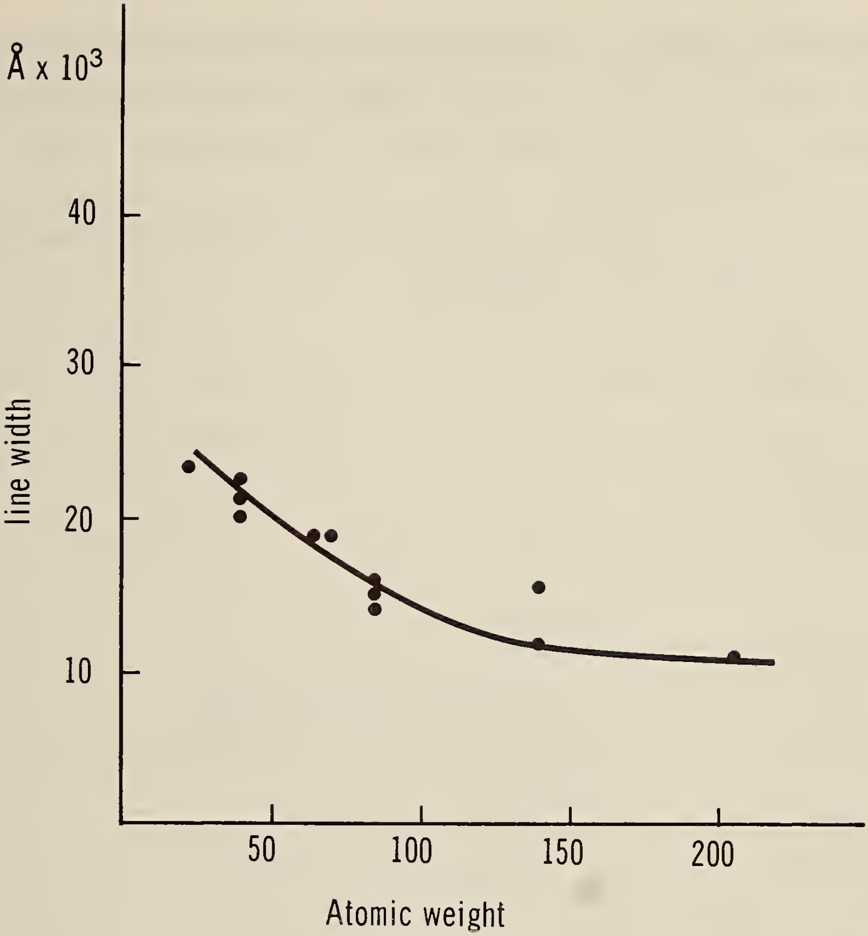


Figure 8. Interferometric measurement of line broadening.

ence of the various parameters in order to find the relative merit of these methods, particularly from the standpoint of optimum detection limits. The main difference between the methods is that in emission the signal is obtained from the small fraction of thermally or thermo-chemically excited atoms, whereas in the other two methods, the signal is obtained from the relatively large fraction of atoms in the ground state, which absorb radiation from an auxiliary light source. In AAS this signal is measured directly, in AFS a small fraction of this absorbed radiation is detected while it is reemitted by the excited atoms. One might say that AAS and AFS are complimentary to FES (excitation by absorption of radiation vs collisional excitation) and that AAS and AFS are competitive methods since they both use the atoms excited by absorption of radiation. In AAS one registers these excited atoms directly, while in AFS one employs the radiation reemitted by these atoms.

For FES, the expression for the magnitude of the signals received by a photo-detector is:

$$I = lN \frac{gA}{Q} \exp[-E/kT]\, h\nu\, \Omega\, S \qquad 10^{-7} Js^{-1} \qquad (1)$$

for AAS:

$$\Delta I = l \int I_\lambda k_\lambda d_\lambda \qquad 10^{-7} Js^{-1} \qquad (2)$$

and for AFS:

$$I_F = \Delta I\, \phi_F\, \Omega_F / 4\pi \cdot W_p / l \qquad 10^{-7} Js^{-1} \qquad (3)$$

in which,

l = length of the flame

N = concentration of atoms in the flame

gA = transition probability of the spectral line

Q = partition function

E = energy of the upper level of the line

ν = frequency of the radiation

Ω = solid angle used in the measurement

S = flame area used in the measurement

I_λ = intensity of primary source at the wavelength λ

ϕ_F = efficiency of fluorescence

Ω_F = solid angle used from the fluorescent radiation

W_p = width of the primary source

The absorption coefficient k_λ can be related to the transition probability A. A convenient numerical example was selected to illustrate these comparisons for the case of the copper line at 3247 A. The properties of the apparatus were chosen as:

$l = 1cm$, $N = 10^9\ cm^{-3}$, $gA = 4.1 \times 10^8\ ss^{-1}$, $Q = 2.4$,
$\Omega = 3 \times 10^{-2}$, $S = 10^{-2} cm^2$, $I_\lambda = 3.3 \times 10^{-3}\ W/cm^2\ sr$,
$\phi_F = 3 \times 10^{-2}$, $\Omega_F = 3 \times 10^{-2}$, $W_p/l = 1$.

With these values from equations 1, 2 and 3 the relative signals in terms of photo-electrons/sec were obtained as shown in table 12. These net signals are detected in the presence of a noise signal. In the case of FES this noise signal generally stems from the emission of the flame gases and/or from the dark current in the photo-detector. Also in AFS these fluctuations are present, but in addition, stray light (light from the primary source that is reflected by particles in the flame) may give an appreciable noise contribution. In AAS the noise signals (from flame background and dark current) are quite negligible as compared to the noise inherent to the primary source itself. Again, a numerical example can best illustrate the influences of these fluctuations. The root mean square (r.m.s.) fluctuations in the dark current of a photomultiplier are taken to be 300 photo-electrons/sec; the signal caused by the emission of an air-acetylene-flame at 3247 A also has an r.m.s. fluctuation of about 300 photo-electrons/sec [31]. In AAS a reasonable noise signal is 0.5% of the primary source intensity, or 5×10^8 photo-electrons/sec. These examples are summarized in table 12.

It can be concluded from these data that while the largest signal by far is obtained in AAS, it also suffers from the greatest noise contribution, and thus the largest random error. It is therefore the signal to noise ratio that ultimately determines the best detection limit. In this example with copper, FES appears to be the best. Of course, other parameters may be encountered which will influence the results of such a comparison. The much larger signals in AAS makes this method less sensitive to optical adjustment, light leaks and other (e.g. electrical) disturbances from outside. This is probably one of the reasons for the current popularity of AAS.

The relation between FES and AAS is also governed by the flame temperature and the height of the upper energy level of the transition (or the wavelength of the resonance line). Fassel [32] compared his FES measurements in an oxygen-acetylene flame with data for AAS from the literature and concluded that the latter is favored when the wavelength is shorter than about 3500 A. From our comparison it follows that FES is favored even down to wavelengths of about 2800 A. This difference probably arises from some practical limitations and interferences which occur in FES because of the very low signal levels (e.g. stability of the electronic set-up and stray light).

In considering AFS one must qualify this generalization using the above example since, the intensity of the available light sources and the influence of stray light varies significantly from element to element. Winefordner [33], in his comparison of AFS and Slavin's AAS data [34], lists the following elements as yielding lower detection limits in fluorescence than in absorption: Ag (50X), Cd (5000X), Hg (5X) and Zn (50X). For copper the detection limits were equal. It seems that only the differences in lamp intensities can account for these large differences.

Ways to improve the methods are evident from the foregoing discussion. For FES the flame temperature is of paramount importance. The use of nitrous oxide mixtures has yielded greatly improved sensitivities. However, ionization phenomena somewhat restrict the advantages of these higher temperatures. For AAS the improvement in stability of the primary source is the main concern. For example, in a signal of 10^{11} photo-electrons/sec (copper electrodeless discharge) the stability is roughly 0.5% or 5×10^9 photo-electrons/sec, whereas the square root fluctuations only amount to 3×10^5. A large gain is therefore theoretically possible. This approach is being investigated.

Table 12. Comparison of FES, AAS and AFS for copper.

	FES	AAS	AFS
Signal[a]	1.3×10^5	1.6×10^9	1.1×10^5
Dark current noise + flame emission noise	500	500	500
Primary source noise	--	5×10^8	--

---

[a] Signals are in photo-electrons/sec at the photo-cathode.

For AFS the development of intense and large sources, of the order of 10^{-1} W/sr within the width of a spectral line, is required, combined with the use of wide-angle optics and non-quenching flame atmospheres. Apart from the improvements discussed above all methods will benefit from a more complete atomization of the sample and from a longer residence time of the atomic vapor in the optical path.

Another area which will affect the future of AFS is the development of high intensity light sources. The high intensity source, required for work in AFS is at present obtained with the aid of electrodeless discharge lamps for some elements, and certainly more will follow. The advantage of a continuum source would, of course, be that it could be used for a large number of element. However, by requiring the same light flux, one would need an output of the order of 300 W per nm, and a total output of many kilowatts. At present, the intensity of even a 1000 W Xe-arc is approximately two orders of magnitude less than that of electrodeless discharges.

W. Snelleman

D. Analytical Application to Standard Reference Materials

1. Determination of Mg, Ca, Sr and Ba in Clays Flint 97a and Plastic Clay 98a

One of the major problems in the determination of minor constituents is the dissolution of refractory materials. The usual procedure for the dissolution of refractory silicates is to use a mixture of HCl, $HClO_4$, and HF which will require 1-2 days of digestion. Frequently, an insoluble residue will remain which may contain some of the trace elements. Another disadvantage of this approach is the possibility of contamination especially for Mg and Ca.

a. New Dissolution Method. A new approach to the dissolution problem was investigated. It has been suggested that the dissolution of refractory silicates can be accomplished with HF in a Teflon lined steel bomb [35]. A drawing [36] of an improved version was obtained and a series of Teflon lined bombs were made and tested. The optimum conditions for the dissolution of a flint and plastic clays were developed.

b. Procedure. Transfer a 200-mg test portion of the sample which had been dried for two hours at 140 °C to a Teflon-lined pressure container. Add 1 drop of HCl, 1 drop of HNO_3 and 4 ml of HF. Seal the container and place in an oven for two hours at 125 °C. Cool, transfer the solution to a platinum dish. Add 5 ml of HF and 5 ml of $HClO_4$. Heat on a hot plate to dense fumes of $HClO_4$. Add 1 ml of HCl and 10 ml of H_2O. Warm the platinum dish to dissolve the salts. Transfer the solution to a 25-ml volumetric flask and dilute to calibrated volume. Then, transfer the solution to a plastic bottle for storage. Time required for complete dissolution is 3-4 hours.

c. Control of Matrix Effect. The older methods available for the determination of trace quantities of the alkaline earth metals in the presence of elements that form refractory oxides leave much to be desired. Among the methods available for the determination of the alkaline-earth metals, flame emission or absorption offers a number of advantages. However, several elements such as aluminum, titanium and zirconium are known to interfere in the conventional flames. The use of releasing agents such as lanthanum or lanthanum plus glycerol is effective in overcoming this type of interference when the ratio of interferent to alkaline-earth does not exceed 100:1. For a higher ratio a method of correction such as standard addition must be applied.

To overcome the condensed phase type of interference, various oxidant-fuel conditions were studied. It was found that with a fuel-rich nitrous oxide-acetylene flame the interference of aluminum, titanium and zirconiun with the alkaline-earth metals could be overcome up to a ratio of 500:1. For higher ratios of interferent to analyte the method of standard addition correction was applied. The only difficulty encountered with this approach was the need for a frequent cleaning of a carbon deposit on the burner head and the necessity for the addition of an ionization buffer (K), to suppress the ionization of the two analytes.

T. C. Rains and T. A. Rush

2. Determination of Magnesium in Ductile Iron

(NBS-SRM 1140, 1140a, 1141, 1141a, 1142 and 1142a)

Atomic absorption offers a fast and precise way for the determination of magnesium in a wide variety of materials. Magnesium was thus determined in ductile iron without any pre-concentration or separation from the iron matrix. The major problem encountered in this determination was the dissolution of the test portion. While a mixture of HCl and HNO_3 will dissolve the major portion of the material, the addition of $HClO_4$ was essential to remove the carbon. Then, dilute HCl was added to dissolve the salts before the determination of the magnesium by atomic absorption using an air-acetylene flame. The data are presented in table 13. The results were in good agreement with the data reported independently by the Spectrochemical Analysis Section.

3. Determination of Na, K and Sc in High Purity Zinc and Doped Zinc

One of the major problems associated with the determination of trace impurities in any high purity material is the preparation of the test portion for analysis. In the determination of Na and K the pretreatment of the test portion becomes an essential part of the procedure for the removal of any surface contamination. In addition one must provide during that process a controlled environment which will yield a minimal and reproducible blank.

The procedure developed for the determination of Na and K in high purity zinc is as follows: Transfer a 0.5-g test portion to a clean 25-ml polyethylene bottle. Add 10 ml of 1:1 HCl and etch the test portion until 10-20 percent is dissolved. Remove the acid and wash the test portion with distilled water. Air dry and weigh. Return test portion to the polyethylene bottle and rinse with dilute HCl and water. Dissolve the test portion with a minimum measured amount of HCl. Dilute to calibrated volume and determine the Na and K concentration by flame emission spectrometry. Carry out blank determinations under similar conditions. See table 13 for results.

4. Service Analysis

A variety of samples from other divisions within the Bureau and outside agencies were analyzed by emission and absorption methods.

a. Trace impurities of calcium and strontium were determined in sodium desoxycholate. The sample was treated with HNO_3 and $HClO_4$ to destroy the organic compound and then the Ca and Sr were determined by flame emission. While the flame background was increased by the radiation of the Na

Table 13. Summary of analyses performed by flame emission and atomic absorption.

NBS-SRM No.	Material	Element	No. of determ.	Conc. %	Std. Dev.	Rel. Std. Dev., %
5k[a]	Cast iron	Cu	23	1.496	0.006	0.4
5l			21	1.010	.002	.2
6k[a]			4	0.243	.003	1.0
6g			7	.499	.006	1.0
97[a]	Flint clay	MgO	7	.217	.004	2
97a			23	.155	.006	4
97[a]		CaO	4	.063	.0007	1
97a			12	.113	.004	3
97[a]		SrO	4	.011	.002	15
97a			16	.174	.009	5
97[a]		BaO	7	.022	.002	9
97a			27	.076	.004	5
98[a]		MgO	15	.708	.025	4
98a			55	.418	.009	3
98		CaO	4	.191	.006	3
98a			12	.312	.006	2
98		SrO	3	.032	.001	3
98a			6	.041	.002	5
98		BaO	8	.087	.004	5
98a			24	.031	.002	6
				Conc. µg/g		
683	Zinc	Na	8	<.2		
		K	8	<.2		
		Sc	8	<.3		
728	Zinc	Na	9	<.2		
		K	6	<.2		
		Sc	6	<.3		
342[a]	Ductile iron	Mg	8	509	8	2
1140			6	184	5	3
1141			6	428	3	1
1142			10	936	17	2

---

[a] Control sample.

ion, the emission intensity of Ca and Sr was only slightly enhanced. The method of single addition was used to correct for any enhancement.

b. Following a series of under sea explosions it was necessary to determine the lithium concentration of the sea water. Since the natural lithium concentration in sea water is less than 0.2 μg/ml, the major problem was the detection of any small change in lithium concentration. The sea water could not be analyzed directly by emission because of the encrustation of the burner. However, because of the high sensitivity of lithium by flame emission (0.005 μg/ml), the sea water could be diluted by a factor of 25 which eliminated this problem. Any deviation of lithium concentration which was greater than 2 parts in 100 ppb could be detected.

c. Iron and cobalt were determined in samples of rolled nickel. The iron was separated from the nickel matrix by solvent extraction using methyl isobutyl ketone and then determined by flame emission. The cobalt was determined by atomic absorption in the nickel matrix. The results for both methods were checked by the single addition method.

d. A number of the other analyses performed included sodium and calcium in a detergent, potassium in a mixed salt of lead and potassium sulfate, sodium in silver sulfate and iron and cobalt in metallurgical stripping solutions.

T. C. Rains

3. SPECTROPHOTOMETRY AND SPECTROFLUOROMETRY

A. Introduction (Spectrophotometry)

Molecular absorption spectrophotometry, although a relatively old and widely used technique, continues to find many new and interesting applications. No other method, with the possible exception of polarography, is applicable to such a wide range of concentrations - from the 100% constituent down to about 1 part per billion, i.e.. about eleven orders of magnitude. This tremendous scope cannot be attributed solely to improved instrumentation although only very recently Müller [37,38] has described some very promising advances. Instead, much of the recent impetus has resulted from a better understanding of coordination chemistry, especially insofar as metal-ligand interactions are concerned. No longer are enhanced extractions attributed to "synergistic effects" but are explained by adduct formation where an additional molecule (or molecules) of acid, base or reagent are bound to the binary complex. In an analogous manner, the addition of a highly absorbing or fluorescent adduct to a relatively simple complex forms the basis for many of the most sensitive and selective spectophotometric-spectrofluorometric procedures presently available. Much of the work subsequently described in this section of the report deals with these types of reactions.

B. Continued Studies Involving Ternary Complexes

The incorporation of ternary complexes into rapid extraction and subsequent absorption-fluorescence measurement systems still hold considerable promise. In general these complexes can be formed over a wide range of acidities - from approximately pH 5 to 10 N acid - while the more familiar binary complexes are frequently limited to dilute acid or even basic solutions. Although some inherent selectivity is obviously sacrificed because of this insensitivity to pH, their overall selectivity is nevertheless generally superior because three species are involved instead of two. Each of these can be manipulated, within readily definable limits, as the analysis demands.

Of the reagents examined to date the most promising have been a series of dyes having either a triphenylmethane (Brilliant Green, Crystal Violet, etc.) or a xanthone-type structure (Rhodamine B, Rhodamine 6G, etc.). An outgrowth of some earlier work on these dyes was the development of a highly sensitive and selective spectrophotometric method for antimony [39]. A further modification of this procedure is described in a later portion of this report. A simple procedure for gold is also included which is quite similar to the antimony method. In this instance interference from antimony is eliminated by converting its hexachloro complex into various benzene-nonextractable hydroxy species ($SbCl_5OH^-$, $SbCl_4(OH)_2^-$, etc.).

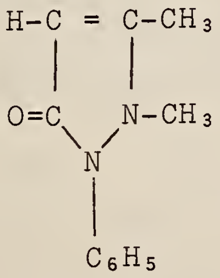
1. Extraction Studies

The extraction of Sb^{+5}, Au^{+3}, Tl^{+3} and UO_2^{+2} with these types of dyes has shown that the most important factor governing extraction efficiency is the polarizability of the solvent. Thus benzene is a more efficient extractant than is toluene which, in turn, is better than xylene, i.e. polarizability $C_6H_6 > C_6H_5CH_3 > C_6H_4(CH_3)_2$. Among the other solvents studied the following general order has been observed: chloroform > hexone > carbon tetrachloride > amyl acetate > isopropyl ether. A novel feature of these types of extraction systems is that their efficiencies can be measured readily without the use of radioactive tracers. The spectra of neutral solutions of aqueous or alcoholic dye are quite similar to the benzene extracts of the metal complexes with only slight shifts in absorption maxima (10-15 nm) being observed. Comparison of the absorbance of standard dye solutions to the absorbance of the organic extracts gives a direct measure of the percentage extracted, provided the stoichiometry of the complex is known. When studying elements having several oxidation states this approach actually may be preferable since the oxidation state of the tracer is not always certain.

The use of high purity solvents is a prerequisite for color stability of the extracts. This effect manifests itself most pronouncedly with those complexes containing metals having redox properties where traces of fatty acid contaminants, such as grease from the stopcock of a separatory funnel, can lead to rapid decomposition of the colored complex. There are, in addition however, inherent differences in the light stability of the various complexes themselves which must not be confused with the effect of solvent impurities. For example, the color of the benzene extract of the tantalum fluoride complex with Butylrhodamine is stable while the color of the same complex with Rhodamine 6G fades rapidly.

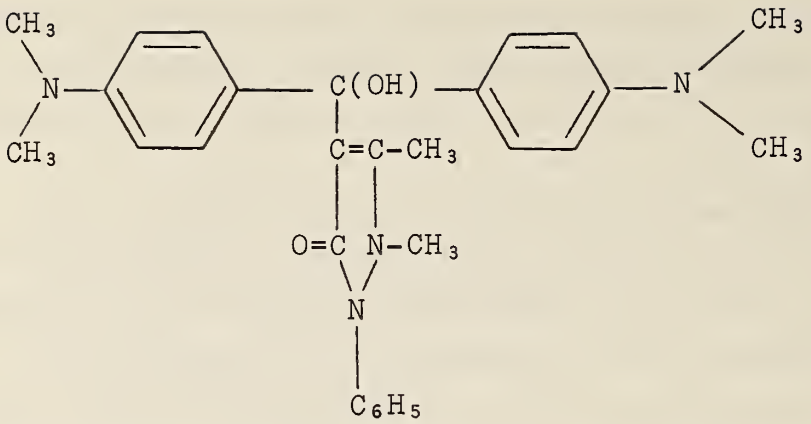
2. New Reagents Under Study

To improve the stability of the triphenylmethane-type dyes in strongly acid media attention has been given to the possibility of substituting heterocyclic radicals into the dye molecule. One of the most interesting modifications and one which Russians workers [40] have investigated considerably involves the substitution of an antipyrine radical (compound I) for a phenyl group.

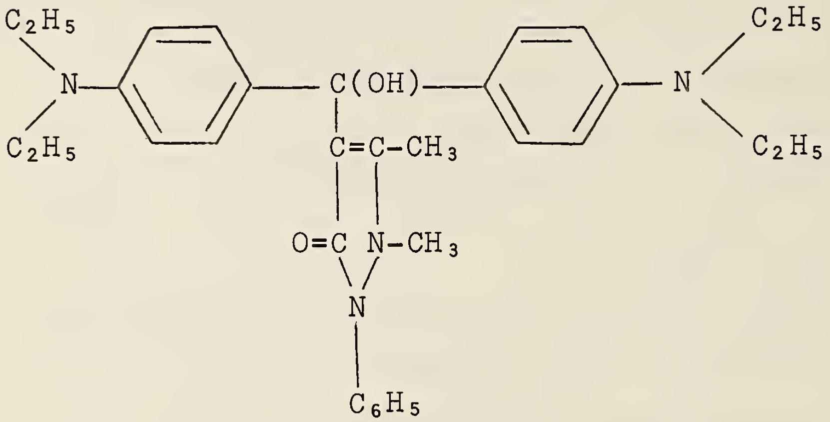


Antipyrine (I)

Compounds II and III shown below have been synthesized recently by condensing antipyrine with the appropriate ketone.



bis(4-dimethylaminophenyl) - antipyrylcarbinol (II)



bis(4-diethylaminophenyl) - antipyrylcarbinol (III)

The extraction properties of these two dyes are now under study.

3. Exchange Properties of Ternary Complexes

For present purposes ternary complex formation can be considered a two-stage reaction consisting of the following steps:

$$M + L = ML \qquad (1)$$

$$ML + R = MLR \qquad (2)$$

where: L is Cl^-, Br^-, CNS^-, etc.

R is a large dye cation such as derived from Brilliant Green, Crystal Violet, Rhodamine B, etc.

In practice selectivity will be controlled primarily by reaction 1 whereas sensitivity will be concerned with reaction 2. The choice of the intermediate ligand, L, is dependent largely on the extent of the following two side reactions:

$$H + L = HL \qquad (3)$$

$$R + L = RL \qquad (4)$$

In those systems where reaction 3 is predominant, little or no extraction occurs; if reaction 4 predominates high blanks are obtained. Depending on the basicity of L there is a more or less narrow region of acidity and ligand concentration where reactions 1 and 2 predominate.

To broaden the scope of ternary complex formation to include ligands of a more basic nature, the possibility of exchanging a weakly chromogenic and/or fluorogenic R group for a strongly absorbing or fluorescent one is being investigated. The desired sequence of reactions are as follows:

$$M + L = ML$$

$$ML + R = [MLR]_{aq}$$

$$[MLR]_{aq} = [MLR]_{org}$$

$$[MLR]_{org} + [R'X]_{aq} = [MLR']_{org} + [RX]_{aq}$$

This approach has been applied to the extraction-spectrophotometric determination of microgram quantities of gold with good success. In this system, chloride was employed as the intermediate ligand, L, tetraphenylarsonium ion as the non-colored R group and Brilliant Green as the strongly colored R' group. The simple binary $AuCl_4^-$ ion was extracted from 1 N HCl into benzene as the tetraphenylarsonium salt, i.e. $[AuCl_4]^- [As(C_6H_5)_4]^+$. Alcoholic Brilliant Green was added to the benzene layer and the excess of the colored dye was back-extracted into water. Variations in acidity from pH 2 to 11 had little effect on the back-wash efficiency. This approach is presently being investigated in those systems where more basic ligands are employed, i.e., thiocyanate, cyanide, benzoate, etc.

C. Modification of the Brilliant Green Procedure for Trace Amounts of Antimony

In an earlier procedure [39] nitrite was the preferred oxidant for antimony even though systems to which it was added exhibited somewhat poorer sensitivity than those utilizing either Ce^{+4} or H_2O_2 oxidation. Also, in the case of nitrite, the absorption peak of the resulting ternary complex was found to shift approximately 15 nm towards shorter wavelengths. Both of these effects are shown in figure 9, curve 4 and are typical of aqueous solutions of the dye. It has since been found that not only are ethanolic solutions more stable but also that the alcohol is quite effective in eliminating the differences obtained with nitrite oxidant (figure 9, curve 3). Recent experiments involving the addition of ethanol at various stages of complex formation suggest that, in its absence, nitrosation of the dye occurs in positions ortho to the activating diethylamino groups. If ethanol is present however when the dye is added, or if the dye is added as an ethanolic solution, then the excess nitrite is apparently converted into the corresponding alkyl derivative (CH_3CH_2ONO). Addition of the alcohol after the dye has been added is ineffective i.e. the spectrum is identical to those obtained when no alcohol is present. Apparently once nitrosation has taken place the reaction is not readily reversed.

D. Extraction - Spectrophotometric Determination of Gold

A simple procedure ($\geq$ 0.01 μg) for the determination of trace amounts of gold have been developed based on the benzene extraction of $AuCl_4^-$ as the Brilliant Green complex. Sb(V) and Tl(III) are the only serious interferences. However, under usual conditions of analysis, Sb(V) rapidly forms hydroxy species which are no longer extractable and therefore its interference can easily be masked.

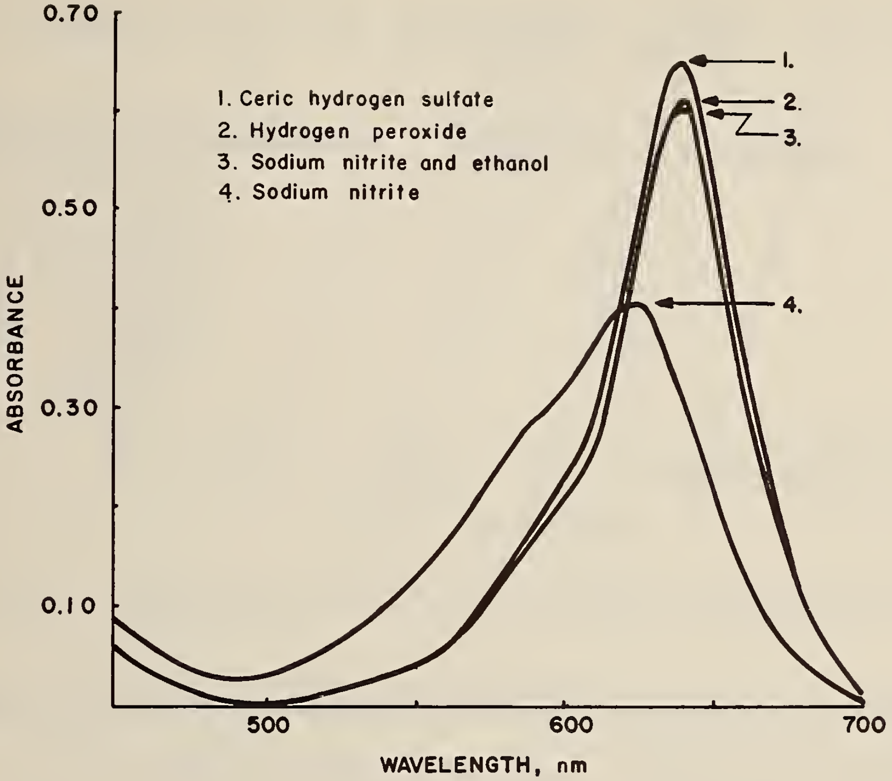


Figure 9. Sensitivity and spectral dependence with choice of oxidant; 4 µg Sb extracted with 5 ml C_6H_6

Extraction of the $AuCl_4^-$ complex is carried out from 1 N HCl, following the addition of alcoholic Brilliant Green solution (5 ml of 0.01%) by shaking approximately 30 seconds with 5.00 ml of benzene. Following phase separation, any remaining droplets of water are removed by filtering through a paper plug inserted into the stem of the separating funnel. In this manner the extract is transferred directly from the funnel to the absorption cell. The method has been applied with good success to the determination of microgram quantities of gold in electrolytic iron and nickel.

These data shown in table 14 were obtained on a Beckman, Model DU spectrophotometer equipped with a Gilford digital readout. Although the gold system exhibits a slight positive

Table 14. Typical calibration data for microgram amounts of gold.

Au, μg	A_s(640 nm); 1-Cm Cell	Sensitivity, A_s/μg/ml/cm[a]
0	0.014	-----
4	0.346	0.415
8	0.684	0.419
12	1.027	0.422
16	1.369	0.424
20	1.722	0.427

---

[a] Corrected for blank.

deviation from Beer's law it is nevertheless quite reproducible.

E. Precise Differential Spectrophotometric Determination of Cobalt

Recent attempts to certify the cobalt content of a series of neutron flux glasses have led to the development of a rapid differential spectrophotometric procedure based on the reaction of Co(II) with 2,3-quinoxalinedithiol. The details of this reaction have been described previously by Burke and Yoe [41]. The present study deals with the modifications essential for high precision work.

1. Procedure

a. Calibration Data. Figure 10 is illustrative of the calibration data obtainable for cobalt over the range from 0-1000 μg. In these runs, 10% v/v aqueous solutions were employed throughout although in the original paper upto 20% water was indicated as permissable. Care must be taken in the procedure as the reagent is slightly unstable to light. Results are satisfactory however when the absorbance is measured against a suitable reagent blank. In the calibration runs shown 5-20 ml of 0.1% reagent were employed per 100 ml of sample. For the range 0-800 μg, measurements were

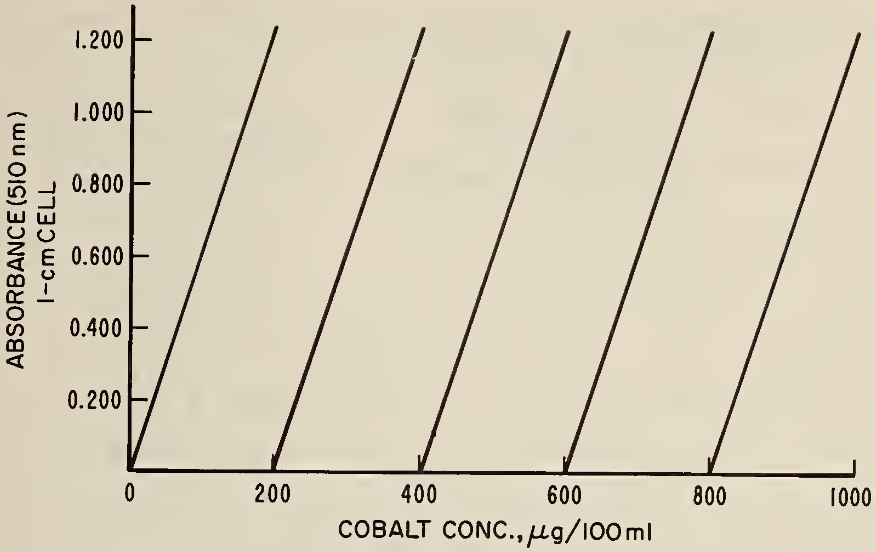


Figure 10. Constancy of slope factor over range 0-1000 mg cobalt.

obtained on a Beckman, Model DU, spectrophotometer modified with a Gilford digital readout. The 800-1000 μg calibration was obtained on a Cary, Model 14, spectrophotometer equipped with a high intensity quartz-iodine source. The average slope calculated from this family of curves is 6.20 ± 0.02 x 10^{-3} A_s unit/μg/100 ml/cm.

2. Results

a. Cobalt Glasses. The results obtained on a series of cobalt glasses are shown in table 15. Fusion with Na_2CO_3 and treatment within $HF-HClO_4$ were both employed for sample dissolution with no significant differences being observed in the results. For comparison results obtained by spectrophotometric titration (described in Section 1) are also shown.

b. Cobalt-Aluminum Wire. In table 16 the results are shown for cobalt in a Co-Al wire. Previous values obtained by two private laboratories indicated a cobalt content of 0.97%; activation measurements suggested that this value was low.

Table 15. Comparative determination of cobalt in neutron flux glass.

Sample No.	Weight % CoO	Weight % CoO
	Differential Spectrophotometry	Spectrophotometric Titration
1	9.34	9.36
2	9.30	9.39
3	9.34	9.38
4	9.33	9.39
5	9.32	9.37
average	9.33	9.38
SD	0.02%	0.009%
Synthetic I (9.19% CoO)	9.22	9.20
Synthetic II (9.35% CoO)	9.30	9.33

Table 16. Comparative determination of cobalt in Co-Al wire.

Sample	Weight % Co	Weight % Co
	Differential Spectrophotometry	Spectrophotometric Titration
1	1.012	1.017
2	1.010	1.013
3	1.004	1.015
4	1.013	1.016
average	1.010	1.015
SD	0.004%	0.002%

F. Spectrophotometric Determination of Molybdenum in an 80W-20Mo Alloy

Molybdenum was determined spectrophotometrically as the thiocyanate complex following reduction with stannous chloride (1 mg iron was added to aid in the formation of the molybdenum thiocyanate complex). Butyl cellosolve (15% v/v) was used to stabilize the color system.

Sample dissolution was effected by fuming gently with H_3PO_4-$HClO_4$. Sulfuric acid was added and the solution was heated to strong fumes. Following dilution to a convenient volume a suitable aliquot was then taken for spectrophotometric analysis. The calibration data were obtained using high-purity molybdenum. The non-interference of tungsten was verified by adding appropriate amounts of tungsten to the molybdenum aliquots. However, when molybdenum and tungsten metal were dissolved together, the apparent molybdenum-thiocyanate color seemed to increase with the age of the original solution. Precipitation of tungsten may have been occurring even though additional sulfuric acid and ammonium citrate were added. Molybdenum was therefore determined immediately after dissolution of the sample. The following determinations were made on samples of crushed rod.

Table 17. Determination of Mo in W-Mo rod.

Sample		Mo, %
1		21.1
2		21.3
3		20.6
4		20.5
5		20.6
6		21.1
	average	20.9%
	SD	0.3%

For use as a microprobe standard, the wire was coated with a thick layer of molydenum and then with a thin layer of tungsten. As a final form, this triple component wire was sliced into thin wafers approximately 1 mm thick. A small cylinder of the 80W-20Mo center was then bored out of the wafers for analysis, (figure 11). These samples which weighed about 5 mg each, were analyzed by means of the above procedure and yielded the following results (table 18).

Table 18. Determination of Mo in microprobe wafers.

Sample	Mo, %
1	21.6
2	21.4
3	21.8
1	21.9
2	21.8
3	22.0
average	21.7%
SD	0.2%

Figure 11. Wafer with the 20Mo-80W core (sample) removed.

G. Modified Indophenol Method for Nitrogen

Historically, both the Nessler and the indophenol reactions for the colorimetric determination of ammonia originated at about the same time. The Nessler procedure, although widely applied, has the disadvantage of yielding large and variable blanks. The indophenol method does not present this problem but there is considerable controversy in the literature as to proper conditions for carrying out this reaction [42,43]. One parameter that has frequently been ignored is the careful control of pH that is required for obtaining reproducible values. As shown in figure 12 the optimum pH is 11.0 ± 0.1. The time required for maximum color development is approximately 40 minutes at this pH while, a few tenths of a pH unit below 11, as long as two hours may be required.

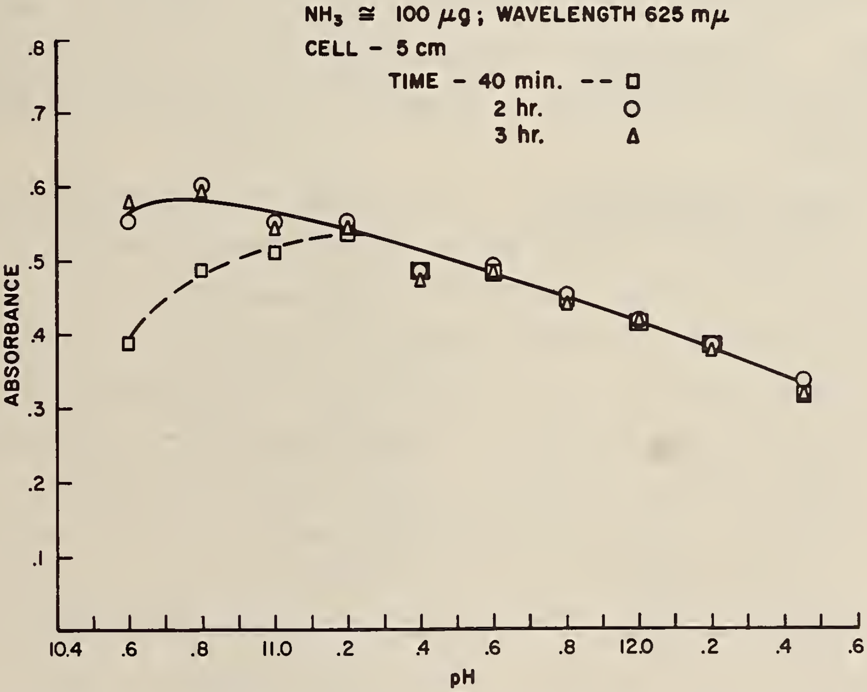


Figure 12. Effect of pH on the absorbance of the indophenol-NH_3 complex.

1. Procedure

Successful application of the indophenol reaction requires strict attention to the preparation of reagents.

a. Sodium Hypochlorite Stock Solution. Dissolve 80 g of NaOH in 800 ml of water and place solution in an ice bath. Bubble Cl_2 gas through the solution until a faint yellow coloration is observed. Fix the free Cl_2 by addition of 20 g NaOH dissolved in 200 ml water and, finally, determine the available chlorine by titrating an aliquot iodometrically, using starch-iodide indicator. From the results of this titration adjust, by dilution with 2.5 M NaOH, to a final available chlorine concentration of about 0.35%.

b. Phenoxide Solution. Dissolve 28 g of NaOH in 100 ml of water and cool under running tap water. Dissolve 60 g of phenol in 20 ml of acetone and 80 ml of methanol. Gradually combine these two solutions by adding small increments of the phenol to the NaOH solution while cooling the latter with tap water. Provided the two solutions are mixed slowly enough, the resulting sodium phenoxide should exhibit only a pale yellow coloration. Prepare this solution immediately before use.

c. Color Development. The amount of hydrochloric acid needed to obtain a final pH of 11 is determined on a blank carried through the distillation procedure by use of a pH meter. This amount is then added to each of the samples comprising a single set of runs prior to the addition of the phenoxide-hypochlorite reagents. When using 100-ml volumetric flasks, the distillates are diluted to approximately 60 ml with NH_3-free water, the pre-determined amount of HCl added, followed by a 16-ml additions of the phenol solution from a buret and 10-ml additions of the sodium hypochlorite solutions. If, by chance, too much acid is added, the sample should be discarded since further addition of NaOH will not readily re-equilibrate the color system. Finally, dilute to volume with NH_3-free water, mix and measure the absorbance in 5 or 10-cm cells at 625 nm. Provided the pH adjustment was satisfactory measurements can be made at any time within a period of 1-3 hours after mixing.

2. Results

The results obtained for nitrogen in a variety of standard reference materials, by the indophenol method are given in Section 4 of this report.

H. Miscellaneous Spectrophotometric Results Obtained on Selected Standard Reference Materials

The spectrophotometric results obtained for a number of miscellaneous elements in standard reference materials are given in table 19. In many instances the particular reagent or procedure used has been either developed or modified at NBS. For detailed information in this respect, the previous three annual reports will be found quite helpful.

Table 19. Summary of miscellaneous spectrophotometric results.

Element	SRM	Kind	No. of determ.	%	RSD[a]	Ref.
As	51	Cast iron	3	≤0.002		44
	6g	Cast iron	3	.043	2	44
Cr_2O_3	97a	Flint clay	3	.028	3	45
Cr_2O_3	98a	Plastic clay	3	.031	3	45
Fe	728	Intermediate zinc	9	.0003		46
		Five 9's zinc	5	.0002		46
Fe_2O_3	97a	Flint clay	9	.453	3	47
Fe_2O_3	98a	Plastic clay	9	1.334	1	47
Mn	30f	Cr-V (SAE 6150) steel	8	0.802	0.4	48
Mo		80W-20M alloy	14	21.7	1	49
Ni	51	Cast iron	5	0.085	1	19
	6g	Cast iron	7	.136	3	
	342	Cast iron	4	.058	1	
	196	Ferrochrome	4	.35	3	
	127b	Solder (Pb60-Sn40)	4	.011	10	
	1065b	Nickel cyclohexanebutyrate	7	13.87	0.2	
Sb	461	Low-alloy steel	4	0.0009		39
	462	Low-alloy steel	4	.0009		
	463	Low-alloy steel	4	.0005		
	464	Low-alloy steel	9	.0018		
	465	Ingot iron	4	.0008		
	466	Ingot iron	4	.0005		
	467	Low-alloy steel	9	.0008		
	468	Low-alloy steel	4	.0010		
TiO_2	97a	Flint clay	6	1.75	0.3	50
TiO_2	98a	Plastic clay	5	1.65	2.1	50

---

[a] Relative standard deviation.

I. Introduction (Spectrofluorometry)

Molecular fluorescence spectrophotometry (Spectrofluorometry) provides the most sensitive means of "wet-chemical" analysis known to date - rivalled only by the related, recently developed technique of Atomic Fluorescence Spectroscopy, and in certain instances, by catalytic methods. However, whilst it has found extensive application to the qualitative and quantitative determination of biological materials, spectrofluorometry is much less popular as a routine tool for trace inorganic analysis. The reasons for this are twofold. Both are outlined below, together with the ways in which the problems underlying them are being solved.

1. Lack of Versatility

In biochemical analysis, use is generally made of the intrinsic fluorescence properties of the analyte, which is normally a large, well-conjugated aromatic molecule. Since the wavelengths of excitation/emission are characteristic of the molecule under investigation, and the intensity of fluorescence proportional to its concentration, fluorometry provides a facile, non-destructive analytical method.

The analysis of inorganic material, however, is based on the formation of a complex between the analyte and a suitable ligand, resulting either in the development or enhancement of fluorescence, or in a shift of the active wavelengths. This places severe restrictions not only on the type of ligand used, but also on the number of inorganic ions that may be analyzed. Thus, because of their paramagnetic character, few transition metal ions form fluorescent complexes. Because of the "Heavy Atom" effect, elements of high atomic number yield only weakly fluorescent complexes. (N.B. Except when the ion itself is fluorescent due to electron subshell transitions eg. 4f transitions in the ions $Sm^{+3} \rightarrow Dy^{+3}$.)

The results of recent investigations of ternary complex systems hold promise for increasing the versatility of fluorescence analysis. By the formation and extraction of such species, in which the ternary adduct is fluorescent, the quenching effects of the paramagnetic and the heavy atom may be obviated [51]. Likewise, the use of indirect methods, involving exchanges between free cations and those incorporated in fluorescent complexes, may further extend the scope of the technique.

2. Lack of Suitable Instrumentation

Spectrofluorometric analysis involves the measurement of a direct signal, and not, as in absorption spectrophotometry, the ratio of two signals. Precise measurement of fluorescent signals necessitates the use of very stable excitation sources, and photomultiplier detectors. The absence, in particular, of suitably stable ultra violet light source has proved a serious drawback in placing the attainment of high precision fluorometric methods.

However, considerable improvements in the design of commercially available spectrofluorometers have taken place during the recent months in an attempt to solve this problem of imprecision. The development of devices for correcting for variation in lamp intensity and photomultiplier response, and of more stable xenon source units, has resulted in an instrumental reliability approaching that of conventional spectrophotometers.

With the prerequisite conditions of versatility and reproducibility fulfilled, spectrofluorometry holds considerable potential as a routine technique in quantitative inorganic analysis. A notable advantage over spectrophotometry is that the greater sensitivity involved (10^2 - 10^4 fold) allows the use of very small samples. Not only does this reduce the consumption of expensive, or not readily available materials, but it also permits convenient separation of the bulk of the matrix, as an alternative to quantitative separation of the desired constituent, by solvent extraction or ion exchange techniques. Unlike the various flame spectroscopic methods of analysis, measurements can be made on less than 1 ml of the final solution. The possibilities of reducing this final volume to a few microliters are currently under investigation allowing the detection/determination of 10^{-13} - 10^{-9}g of the analyte.

In the following sections of this report, the application of fluorometry to SRM analysis has been demonstrated, and a highly sensitive and reproducible method for the determination of beryllium has been developed. This work is part of a general program to establish fluorometry as a routine analytical technique for the determination of trace inorganic constituents, and to investigate means by which the versatility, sensitivity, and selectivity of the method might be improved.

J. Analytical Applications to SRM's

1. Determination of Magnesium in Platinum

Preliminary spectrographic analyses of the proposed platinum standards NBS-680 and 681 indicated the presence of 10 ppm and 0.5 ppm of magnesium in the doped (681) and high-purity (680) materials respectively. A highly sensitive analytical technique was therefore desirable in order to minimize the amounts of sample required.

The most promising method appeared to be that utilizing the fluorescence of the Mg-bis salicylidene - 2,3-diaminobenzofuran complex which was reported capable of detecting as little as 2 ppb (parts per billion) of magnesium [52]. Accordingly, the reagent was synthesized and the procedure investigated.

It was found that the sensitivity of method was limited by the high fluorescence of the reagent. A device was designed to effectively "buck out" the background signals from the reagent and as a result adequate calibration curves were obtained in the 0-3 ppb Mg range with a detection limit of around 0.2 ppb of magnesium at final dilution.

Application of the method to sample analysis required removal of only the bulk of the matrix since none of the other constituents in the platinum was at a sufficiently high concentration to cause interference. The separation was effected by precipitation of platinum as potassium chloroplatinate from 50% 1+1 HCl/ethanol, in which solvent both $MgCl_2$ and $ZrOCl_2$ (see zirconium analysis) are soluble. The potassium chloride solution used as precipitant was rendered free of magnesium prior to use by washing with a solution of 8-hydroxyquinoline (0.1 N) in chloroform.

a. Procedure

i. Doped Platinum (NBS 681). Dissolve the sample (0.2 g) in aqua regia (10 ml), add concentrated hydrochloric acid (10 ml) and evaporate to ∿1 ml to remove oxides of nitrogen. Dilute to 5 ml with 1 + 1 aqueous hydrochloric acid, add 2M potassium chloride solution (1.5 ml) and absolute ethanol (5 ml). Maintain just below boiling for 30 minutes, cool, filter, and wash the precipitate with cold 50% 1 + 1 HCl/ethanol. Evaporate to remove the bulk of the ethanol, transfer to a 50 ml graduated flask and dilute to the mark with distilled water. (Remove 25 ml of this solution, add concentrated hydrochloric acid (17 ml) and dilute to 50.0 ml for subsequent zirconium analysis.)

Take 6 x 2 ml aliquots for analysis, treat with distilled water (∿5 ml), absolute methanol (12.5 ml) and diethylamine/HCl buffer solution (0.5 ml). Dilute to 22 ml with distilled water and allow to cool for 10 minutes. Add 2 ml *bis*-salicylidene-2,3-diaminobenzofuran (0.2 gpl) in dioxan and dilute to 25.0 ml. Measure the fluorescence of the magnesium complex at 560 nm, excitation at 470 nm, using 1 x 1 cm quartz cuvetts. Compare the result with those of a series of standards in the 0-6 ppb range. (N.B. treat each standard solution with 2 ml 'blank' solution, prepared by carrying all the reagents used through the separation procedure.)

ii. High-purity Platinum (NBS 680): Follow the separation procedure as outlined above, taking 2 x 0.7 ml samples for analysis and using triple quantities of reagent solutions. Dilute the analyte solutions to 25.0 ml after removal of the platinum, and take 5 ml aliquots for analysis.

b. Results and Discussion

Table 20. Determination of Mg in platinum

Material	No. of Determinations	Mg found (ppm)	Standard Deviation per Sample (ppm)
NBS 681	21 (3 samples)	15.3	0.7
NBS 680	4 (2 samples)	0.57	0.03

The precision obtained using the procedure described (±4.5% (NBS 681) and ±5.3% (NBS 680)) is good in view of the fact that any trace magnesium determination is prone to contamination by extraneous magnesium from laboratory reagents, atmosphere, etc. It is noteworthy that, in the 681 procedure, 21 separate analysis were performed on a total sample weight of less than 0.3 g, containing about 45 micrograms of magnesium.

2. Determination of Zirconium in Doped Platinum

The well-established fluorescent method using morin (2',4',3,5,7-pentahydroxyflavone) was selected as being most suitable. However, even after purification of the reagent, it was found impossible to attain the sensitivity claimed by Sandell for this method [53] and as a result adequate analyses could be performed on only the doped platinum. A "less than" value was assigned to the high-purity material.)

a. Procedure

i. Reagent Purification: Dissolve the crude material in absolute ethanol, filter to remove inorganic residues, and remove ethanol from the filtrate by evaporation. Dissolve the oily product in sodium hydroxide solution and precipitate the free morin by acidification with acetic acid. Filter, wash with water and dry at room temperature in vacuo.

ii. Analysis: Take 10 ml aliquots of the portion of the filtrate from the platinum separation (see magnesium analysis), add HCl solution (5 ml) and dilute to ∿23 ml with distilled water. Add 1 ml purified morin reagent (0.3 gpl in absolute ethanol) and dilute to 25.0 ml.

Measure the fluorescence at 484 nm (excitation at 410 nm) before and after the addition of ∿10 mg of EDTA. Compare the difference in values so obtained with those from suitable zirconium standards in the 0-0.6 ppm (final dilution) range.

b. Results

Table 21. Determination of Zr in platinum.

Material	No. of Determinations	Zr found (ppm)	Standard Deviations per Sample, ppm
NBS 681	12 (3 samples)	11.5	0.7
NBS 680	2	<0.3	---

3. Spectrofluorometric Determination of Beryllium

The classical fluorometric procedure for the determination of beryllium is based on its reaction with morin. The method enjoys considerable popularity, largely because of its sensitivity (detection limit = 0.02 ppb [54,55]). However, it suffers from a number of disadvantages. (1) The reagent is very unstable, being particularly prone to oxidation even by atmospheric oxygen. (2) The method lacks selectivity, necessitating preseparation of the beryllium either by ion exchange or solvent extraction as the acetylacetonate complex is high (ca 11.5), and beryllium is readily lost by surface adsorption. This factor is particularly critical at part per billion concentrations of the analyte.

The above factors necessitate the use of a carefully controlled, and hence tedious, procedure in order to obtain satisfactory results, and the desire for a simple, but equally sensitive procedure is acute.

A recently published technique for the determination of beryllium utilizes the fluorescence of the 2-hydroxy-3-naphthoic acid complex in solution at pH = 7.5 (figure 13) and claims a detection limit of 0.2 ppb Be [56]. The method has been examined and modified and, as a result, now represents the most sensitive wet-chemical technique for the determination of beryllium.

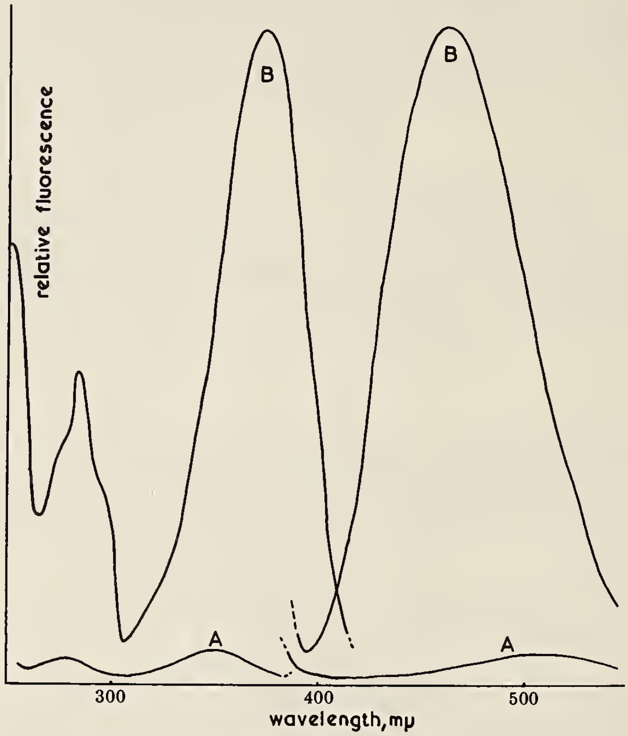


Figure 13. Uncorrected excitation and emission spectra for: A. 2-hydroxy-3-naphthoic acid, 10^{-4} M. B. 1+1 beryllium: 2-hydroxy-3-naphthoic acid, 10^{-4} M.

The major difficulty incurred during development resulted from the loss of beryllium by surface adsorption. Even at the much lower (cf. morin method) pH of 7.5, the loss of beryllium from dilute (10^{-7}M) solutions stored in ordinary laboratory glassware was as high as 50% of the total present over a period of 3 hours. Thus in the time required for the development of maximum fluorescence of the complex (15 minutes) significant losses of solvated beryllium occurred.

Such losses could be reduced significantly by treatment of the glassware with a silicone water-repellent, but results were far from reproducible. The procedure finally adopted involved formation of the complex under acid (pH-3) conditions, followed by increase of the pH to the desired value, and the immediate measurement of fluorescence. Under these conditions, the measured fluorescence was reproducible to within 1.5% for solutions containing 0.1-2 nanograms Be per ml.

Additional modifications to the original procedure included the use of a visual indicator (phenol red) and a more reliable buffering solution thus eliminating the use of a pH meter during the preparation of solutions.

The absolute sensitivity of the method is limited by the fluorescence of the requisite 50-fold excess of reagent over complex. However, by partially "bucking out" the reagent fluorescence a 20-fold increase in sensitivity was obtained. The calibration curves below (figure 14) illustrate the capabilities of this method as developed for the analysis of sub-micro and sub-nanogram quantities of beryllium.

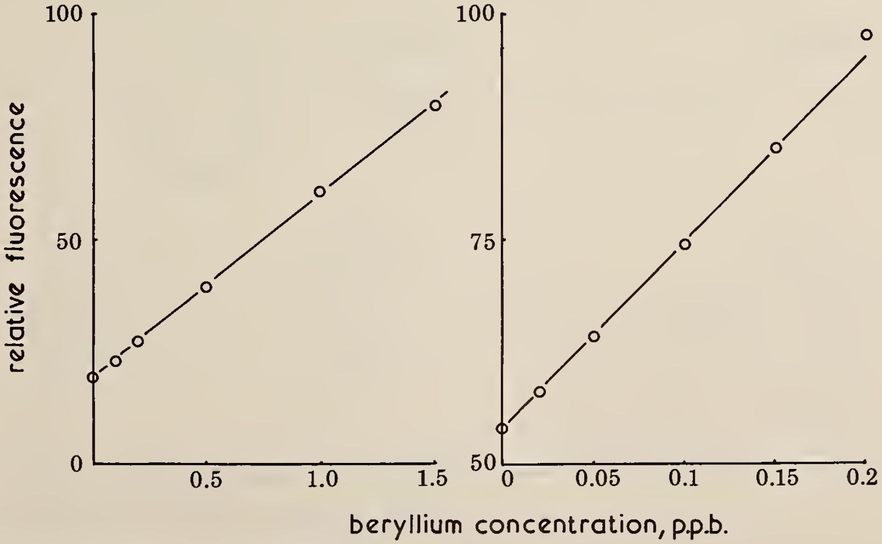


Figure 14. Calibration curves for spectrofluorometric determination of beryllium.

The technique has been applied to the analysis of the beryllium form of sulfonated styrene-divinylbenzene copolymer resins, one of several resins currently under development at NBS for possible use as microchemical standards. The method involved the elution of beryllium with strong, acid calcium chloride solution [57]. Effectively complete (99.95%) recovery of the Be present was confirmed by a procedure involving treatment of the hydrogen form of the resin with known quantities of beryllium (see tables 22 and 23).

b. Results and Discussion

Table 22. Recovery of Be from H-form resin.

	Sample A	Sample B
Wt. H. Form resin, mg	20	20
Be added, μg	50.0	50.0
Be[a] not absorbed, μg	0.153	0.124
Be[a] eluted, μg	49.84	50.62
Be[a] found after wet-ashing, μg	0.0097	0.0226
Total Be recovered, μg	50.007	50.772
% recovery	100.01	101.54

---

[a] Determined spectrofluorometrically using the method described above.

Table 23. Determination of Be in resin samples.

	Sample A	Sample B
Wt. Be resin, mg	11.30	1.58
Be eluted, μg	227.8	158.2
Be found after wet-ashing, μg	0.055	0.095
Total Be, μg	227.9	128.3
Be density, milli-equiv./g.	4.47	4.63

The results above were obtained on relatively large quantities of resin due to the limitations involved in accurately weighed hydroscopic samples. However, provided that single resin beads of known volume can be dispensed satisfactorily, analyses could be performed on samples containing a minimum of 50 picograms of beryllium. On a purely theoretical basis, microvolume techniques will allow the determination of femtogram quantities of the ion. Using 1,2-diaminocyclohexanetetraacetic acid (DCTA) as a masking agent, the cations (at the 1000-fold molar excess level) which interfere with the beryllium determination are as follows: Bi (III), Ce (IV), Cr (III), Fe (II), Fe (III, Sc (III), Sn (IV), Ti (IV, Th (IV). Suitable solvent extraction and ion exchange procedures are available for the separation of Be from these ions.

a. Procedure

i. Calibration Curve: Take 1-4 ml aliquots of beryllium solution (50 ppb, 10^{-3}M with respect to perchloric acid), treat with 5 ml 2-hydroxy-3-naphthoic acid solution (2×10^{-4}M) and one drop phenol red solution (pH - 7.5), dilute to 100.0 ml with distilled water, and measure the fluorescence immediately at excitation and emission wavelengths of 373 and 450 nm respectively (slits at 5 nm and 20 nm) using 1 x 1 cm quartz cuvettes. Compare the fluorescence with that of a solution of quinine sulfate (40 ppb) in 10^{-3}M sulfuric acid at the same wavelengths.

ii. Resin Analysis: Take a 10 ml sample for analysis. Transfer to a microfilter and remove Be by successive elution with 4 x 3 ml aliquots of calcium chloride solution (2M, pH=3). Wash the residue with perchloric acid solution (10^{-3}M) and dilute the filtrate and washings to 1000 ml: with distilled water containing sufficient perchloric acid to maintain the pH of the solution below 4. Dilute 5 ml of this solution to 100 ml with perchloric acid (10^{-3}M) and take 5 ml aliquots for analysis. Compare the fluorescence with that of standard solutions containing 1 ppb of beryllium at final dilution.

Dissolve the residual resin in 1:4 $HNO_3/HClO_4$ (5 ml), evaporate to 2 ml, dilute to 100 ml with distilled water and analyze for beryllium, taking 10 ml aliquots, using the procedure as described under Calibration.

4. GASES IN METALS

A. Introduction

The recognition of the important role trace amount of gaseous constituents have on the physical and mechanical properties of metals and alloys has led to their stringent control. The concentration of these gases range from one part per million in copper to thousands of parts per million in titanium and its alloys. Thus the growing demand for accurate determinations for oxygen and nitrogen has created a need for appropriate standards. These are required not only for calibration of instruments but also for resolving interlaboratory disagreements and providing materials for interlaboratory control.

For the purpose of providing meaningful measurements in this area, the work in this section during the past year has proceeded along several lines. These were: (1) The building and testing of a new analytical apparatus incorporating the basic inert-gas fusion approach with an improved high temperature induction heating gas chromatographic measurement; (2) modification of the vacuum-fusion apparatus to provide greater flexibility to determine both oxygen and nitrogen; (3) studies of the determination of nitrogen and oxygen with a new commercial apparatus; (4) reevaluation of the SRM 1090, 1091, and 1092 for oxygen content by the inert-gas fusion procedure; (5) preliminary studies on new SRM materials for oxygen and nitrogen; (6) certification of new standard reference materials for oxygen content in (a) gold and (b) platinum (doped and pure); and (7) the development of a new chemical procedure for determination of nitrogen. This latter method employed a Teflon lined stainless steel bomb in which the sample was dissolved with the aid of hydrofluoric acid. It was especially useful for refractory metals and nitrides, i.e., materials which are very difficult to decompose by the usual Kjeldahl methods for metals and alloys.

B. A New Inert-Gas-Fusion Apparatus for the Determination of Oxygen and Nitrogen in Metals

The analysis of metals by the vacuum fusion method [50] has certain limitations in comparison with the inert-gas fusion procedure. Some of the more volatile metals are not amenable to the vacuum process. Also, the attainment of higher temperatures in the vacuum is limited by the vaporization of the graphite. Finally, the indirect method for determination of nitrogen in the vacuum system introduces difficulties and errors in the measurement. It was, therefore, decided to build a new apparatus which would eliminate or at least minimize some of these problems.

The new apparatus was designed and built to operate in an atmosphere of helium gas and to analyze the evolved gases by the use of a gas-chromatographic procedure. This apparatus consists of a quartz thimble in which the sample is fused in a graphite crucible insulated with graphite powder. This crucible assembly is contained in a quartz furnace tube through which purified helium is passed at a rate of 1.5 liters per minute. The crucible assembly is heated by means of an induced current supplied by a 2.5 KW, 450 KC, high frequency generator. With this assembly temperatures of about 1900 °C can be attained. Helium flows through the furnace section and sweeps out the gases evolved from the melted specimen. These gases include carbon monoxide, nitrogen and hydrogen. They are passed from the furnace, through a special valve designed and built at the Bureau (shown schematically in figure 15) into a sample collecting loop where they are cooled with liquid nitrogen. This collecting loop or trap is filled with about 5 grams of a molecular sieve (5A) in which the gases CO and N_2 are adsorbed. When all the gases from the sample have been collected (usually about 3 minutes), this special valve is shifted in such a manner as to let the furnace gas vent to the atmosphere and also to permit the carrier gas of chromato-

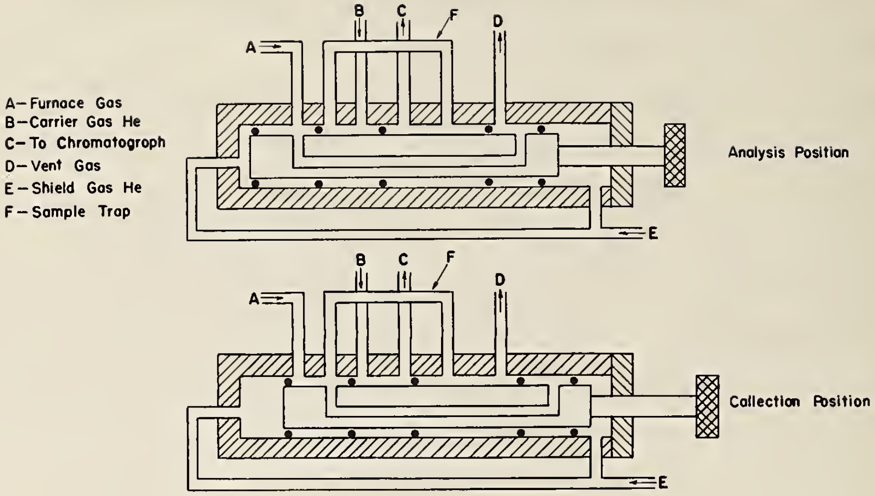


Figure 15. Six-way gas sampling valve.

graph to pass through the sample loop. It is then heated by passing a current through the stainless steel tube from which the loop is constructed. This operation permits the injection of the sample gases into the chromatograph as a concentrated slug.

The gases are then separated by gas chromatography, using a six foot, 1/8 inch diameter molecular sieve (5A) column and detected by means of a thermal conductivity cell. The output from the cell is recorded on a 1-mv strip chart recorder. The latter is also connected to an integrator which measures and prints the area under the peaks due to the CO and N_2. The chromatographic apparatus is calibrated by addition of pure nitrogen or carbon monoxide either through the furnace section or directly into the sample loop. No significant difference was obtained by this variation in the calibration. Variable amounts of the calibration gases were added by means of a standard 1 ml volume in which the pressure and temperature were accurately measured. By varying the pressure in this standard volume it was possible to add known amounts of the gases over a wide range of concentrations.

The apparatus was found to have a sensitivity of 120 counts/μg for carbon monoxide and 122 counts/μg for nitrogen. This similar sensitivity for nitrogen and carbon monoxide is to be expected, as both of these gases have the same thermal conductivity. The sensitivity in terms of weight is then 168 counts/μg oxygen and 98 counts/μg nitrogen. These results were reproducible to at least 20 counts; therefore, a detection limit of 0.2 μg for both oxygen and nitrogen can be conservatively attained. If necessary, this sensitivity can be increased by increasing the bridge current on the thermal conductivity cell. Results for the determination of oxygen in the 1090 series of SRM material are given in Section 4-D.

As will be discussed later, the results for the determination of oxygen in the SRM materials agree quite well with those obtained by other methods. It was found, however, that the determination of nitrogen was not as successful. The indications are that the apparatus as it was originally set up did not provide sufficient power to obtain the high temperatures necessary for the complete extraction of the nitrogen. A 10 KW high frequency generator is being installed, which, with the additional power, should provide the higher temperatures required. It may also be possible to reduce if not completely eliminate the insulation around the graphite melting crucible and thereby reduce considerably the blank values. A single crucible technique is also being adapted for this apparatus which may also facilitate handling large numbers of samples without periodic interruptions.

C. Modification of the Vacuum Fusion Apparatus

The vacuum fusion apparatus has been used quite successfully for the determination of nitrogen in several metals by the use of a spinning crucible furnace [19]. At times, however, it is more convenient to operate the vacuum furnace without the spinning crucible attachment, especially for the determination of oxygen in metals requiring a platinum, nickel or iron bath. It was found that the conversion from the spinning crucible mode to the single, deeper crucible or vice versa took about one or two days. The furnace section of the spinning crucible was therefore redesigned by the addition of a spacing ring, a new heating element and a melting crucible. This modification permits conversion to either mode of operation in 0.5-1 hour. There is a slight decrease in the total capacity of the melting crucible for handling large number of samples but it has proven quite sufficient for all of our applications to date.

D. Evaluations of a New Apparatus for the Determination of Oxygen and Nitrogen

A new commercial apparatus after the design of Koch and Lemm [58] was investigated on several materials at the Bureau in order to explore its applicability to the analysis of SRM for oxygen and nitrogen. The basic method employed in this apparatus involves fusion of a sample in a graphite crucible under a flow of inert gas which releases carbon monoxide, nitrogen and hydrogen. A new crucible is used for each melt so that interference due to the carbon content of preceding samples is excluded. The extracted gases are flushed out of the furnace by a helium carrier gas. The gases are analyzed by means of an infrared absorption analyzer for carbon monoxide content, and hence oxygen. The gases are then passed through a column containing Schutz Reagent to oxidize the carbon monoxide to carbon dioxide. Finally, they are passed through a molecular sieve column to separate nitrogen and hydrogen. Nitrogen is then determined by measurement with a thermal conductivity cell. Results for both the oxygen and nitrogen are displayed on a strip-chart recorder and are also indicated in digital form as the output of an integrating device. The apparatus is calibrated by the introduction of known amounts of pure nitrogen and carbon monoxide. Some of the results for nitrogen obtained on this apparatus for various SRM materials are shown in table 24.

Table 24. Nitrogen by inert gas fusion appartus.

Sample Number	Number of determinations	Nitrogen, ppm		Certified value, %
		Inert gas fusion	Kjeldahl	
3a	3	82.2	86	
3b	6	84.1	84	
3c	3	45.3	46	
4i	3	70.4	70	
4j	3	41.2	37	
5j	6	78.5		
5k	3	101.5		0.009
5l	6	58.2	58	
6f	3	34.4		
8i	3	179.7		.018
10g	10	154.4		.015
30f	3	76.7	75	
32e	3	86.8		.009
55e	3	42.6		.004
72f	3	100.8		.009
101d	3	223.0		.024
125a	6	38.8	40	
129b	3	128.7		.014
163	3	81.4	91	
343	3	733.7		.074
346	3	4525		.441

Samples of SRM 1091 and AISI 431 Stainless steel were also studied with this apparatus. Several conditions such as the use of a bath and chipped or solid samples were investigated. The results of these analyses are given in table 25. These data indicate that the nitrogen content of SRM 1091 is 860 ppm with no significant advantage in using a platinum bath. In the case of the platinum plus tin bath, a lower value for nitrogen was obtained. A slightly higher value was obtained for the nitrogen content for the chipped material, possibly because of nitriding occuring during the cutting process.

Table 25. Effect of sample and bath condition on the determination of nitrogen

Conditions for analysis[a]	Nitrogen ppm	No. of determ.	SD	RSD %
Chips sample size - .01-.08 g	888.7	12	28.8	3.2
Solid sample sample size - .03-.1 g	853.9	12	23.6	2.7
Solid sample sample size - .4 g	861.6	12	9.4	1.1
Solid sample sample size - .4 g bath - Pt; Pt:S=5:1	860.1	6	9.3	1.1
Solid sample sample size - .4 g bath - Pt; Pt:S=5:1 .2 g Sn added before sample and outgassed	828.6	6	10.7	1.3

---

[a] Furnace temperature, 20 seconds at 1850 °C, then 10 seconds at 2050 °C.

E. Sampling Problems

In the course of experiments which were conducted to determine the nitrogen in SRM 1091, it was noticed that a few samples, cut in a manner such that they contained a larger proportion of the outside of the rod, exhibited a higher content of nitrogen. It was, therefore, decided to test this radial inhomogeneity.

Samples of SRM 1091 were prepared by drilling out the center core of the rods with an 1/8 inch diameter drill and adjacent samples were turned down to 1/8 inch diameter rods. Sections of these prepared specimens of approximately the same weight were taken for analysis samples. Analyses of six samples of the cored samples yielded an average nitrogen content of 860 ppm, while six samples of the core material (1/8 inch rod) had an average value of 810 ppm. This data indicates that when this material is certified for nitrogen content it must be specified that a complete cross section be taken as the test sample.

F. Preliminary Investigation of a Low Oxygen Content Material

The trend in a major part of the metal industry is towards the production of metals and alloys with a lower content of interstitial elements. With this in mind a search was made for a homogeneous material containing trace concentrations of oxygen and nitrogen. A plate of maraging steel deemed suitable for this purpose was eventually obtained from United States Steel Corporation.

This material came in the form of a 1/2-inch thick plate approximately 3 foot by 6 foot. Preliminary testing was done on this material by analyzing samples from diametrically opposite corners. Care was taken to obtain samples which were at least 1/2 inch from the edges which had been flame cut during the processing of the sheet. Analysis of this material with the vacuum fusion apparatus indicated an oxygen content of ≤ 5 ppm.

Samples of this material were then alanyzed for O_2 and N_2 with the new apparatus (inert-gas fusion). The designation and the sampling scheme for the homogeneity testing is shown in figure 16. Strips of the maraging steel, approximately 1/2 inch wide, were cut by sawing from either side of the plate. These strips were then hot forged and swaged into rod 5/16 inch diameter and then ground to 1/4 inch diameter. The sample rod from the left side of the plate was assigned the number 1 as the first part of its identifying mark and the rod from the right side of the plate was assigned the number 2. The rod was then cut after preparation into 3 rods and identified as A, B and C and sections of each of these rods were marked 1, 2 etc. the results of

SAMPLING POSITIONS, MARAGING STEEL

Figure 16. Design and sampling scheme for homogeneity testing.

these analyses are given in table 26. As a preliminary test these data indicate good homogeneity.

Table 26. Oxygen determination in maraging steel.

Sample No.	O_2 ppm	N_2 ppm
1A-1	3.7	58.3
1A-2	3.9	58.8
1B-1	4.3	58.5
1B-2	3.0	61.3
1C-1	3.7	61.8
1C-2	3.4	59.3
2A-1	3.4	57.9
2A-2	3.9	58.5
2B-1	3.9	58.4
2B-2	3.2	59.0
2C-1	4.3	57.4
2C-2	3.2	59.0
Mean =	3.7	59.0
Standard Deviation =	.43	1.29
Rel. Stand. Dev. =	11.6 %	2.2 %

It was also decided to check the effect of the addition of varying amounts of the nickel-cerium flux as used in the spinning-crucible technique [19]. The samples used to test the addition of the nickel-cerium alloy were selected randomly from the samples run in the first series of experiments. All samples were analyzed using a furnace temperature program of (20 seconds at 1850 °C and then 10 seconds at 2050 °C). The results of this experiment, summarized in table 27, indicate that the concentration is not critical.

Table 27. Effect of cerium addition on determination of nitrogen in maraging steel.

Sample No.	N_2, ppm	% Ce in final melt
2A-1	62.7	.49
1B-2	64.0	.98
2B-1	60.7	.54
2C	58.6	.77

Notes: Mean N_2 ppm = 61.5 ppm
Standard deviation = 2.4
Relative standard deviation - 3.9%

From the preliminary results it would seem that the maraging steel should make a good standard reference material and it was decided to proceed with further processing of the original plate into 1/4 inch diameter rods.

G. Chemical Method for the Determination of Nitrogen

Traditionally, the Kjeldahl method has been the basis for establishing accurate values for nitrogen in both ferrous and non-ferrous alloys. As reported previously [2,19,59] problems with refractory nitrides lead to the questioning of this procedure and attempts were made to modify the method. In the general method there are three basic steps, (1) sample dissolution, (2) separation of NH_3 by distillation, and (3) analysis of the distillate by either spectrophotometry or titrimetry. Difficulties were primarily encountered in the first and the last steps. The two requirements for the dissolution of the sample are the need to dissolve large solid cross sections (to minimize inhomogeneity problems), and the complete and rapid dissolution of any refractory nitrides. The alternative to the solid cross section is to mill the material into chips. The production of chips by this process, however, always introduced nitrogen from the atmosphere. This contamination can be quite serious when materials low in nitrogen are analyzed. Concomitantly, any dissolution step which is unduly long introduces the danger of ammonia contaminations from the environment. Finally, but equally important, certain nitrides, do not lend themselves to decompositions in typical dissolution (H_2SO_4-H_2O_2) media that are generally used for ferrous materials.

A new procedure based on a pressure-bomb dissolution technique was developed to overcome these difficulties (figure 17). The process involves the dissolution of the

Figure 17. Teflon-lined apparatus for the dissolution of refractory nitrides.

sample in a Teflon pressure bomb [35,36]. It is carried out with aid of an acid mixture of only 3 ml of HF-HCl at ∿150 °C. Under those conditions a typical 0.5-g sample of steel dissolves in 0.5-1 hour. This technique was tested on a variety of materials, especially those which had previously necessitated more drastic treatment. Thus, in the case of SRM 125a which contains refractory SiN, previously only an alkaline fusion under hydrogen gas led to the complete recovery of nitrogen. Similar results were obtained with a niobium base alloy. In this case a cooperative study [60] previously revealed a wide divergence of results. With the new procedure an average value of 36 ppm of N_2 is in good agreement with a recently published value [61]. A summary of results for a large number of SRM's is shown in table 28. On the whole, the

Table 28. Nitrogen values by a pressure-bomb dissolution procedure.

		Nitrogen ppm	
SRM No.	No. of Det.	New Procedure[a]	Previous Values
1090	21	60 ± 5	63
1091	9	932 ± 30	865
1092	6	4 ± 1	10
343	5	814 ± 4	740
125a	14	39.8 ± 5	
3a	3	108 ± 3	86
30f	6	74 ± 4	75
5k	9	86 ± 5	90
51	7	58 ± 5	
6f	6	41 ± 4	50
6g	7	61 ± 3	
4i	3	78 ± 3	70
MAB-FS-85[b]	3	36 ± 4	
Maraging Steel	4	79 ± 4	

---

[a] Pressure bomb-indophenol spectrophotometric method.

[b] See reference 6.

results for these compositions indicate higher recovery for the more complex materials. Only in the case of SRM 1092 are the results significantly lower, indicating that the new procedure assures better control of the environmental contamination at the low, (less than 5 ppm) concentration level.

Additional modifications associated with this analysis were made in the determination step. This was accomplished by a modified spectrophotometric procedure described in Section of this report.

5. REFERENCES

[1] Lundell, G.E.F., and Hoffman, J.I., J. Res. NBS 1, 91 (1928).

[2] Menis, O., Editor, NBS Technical Note 402 (1966).

[3] Flaschka, H., and Ganchoff, J., Talanta 8, 885 (1961).

[4] (NH_4OH Precipitation), NBS Certificate 1075 (1964).

[5] Direct Ignition, NBS Certificate 1075 (1964).

[6] NBS Certificate 1061 (1964).

[7] NBS Certificate 1065 (1964).

[8] NBS Certificate 1052 (1964).

[9] Sweetser, P.B., and Bricker, C.E., Anal. Chem. 25, 253 (1953).

[10] NBS Certificate 1078 (1964).

[11] NBS Misc. Publication 260-6, 43 (1965).

[12] NBS Misc. Publication 260-6, 47 (1965).

[13] Welcher, F.J., "The Analytical Uses of EDTA", D. Van Nostrand, N.Y., 1958.

[14] "ASTM Methods for Chemical Analysis of Metals", 1956.

[15] Lundell, G.E.F., Hoffman, J.I., and Bright, H.A., Ind. Eng. Chem. 15, 1064 (1923).

[16] Scherer, J.S., J. Res. NBS 21, 95 (1938).

[17] Willard, H.H., and Diehl, H., "Advanced Quantitative Analyses", D. Van Nostrand, N.Y., 1943.

[18] Youden, W.J., "Statistical Techniques for Collaborative Tests", The Association of Official Analytical Chemists, 1967.

[19] Menis, O., Editor, NBS Technical Note 424 (1968).

[20] Ivanov, N.P., Minervina, L.V., Baranov, S.V., Pofralidi, L.G. and Olikov, I.I., J. Anal. Chem. of USSR 21, 998 (1966).

[21] Tomkins, F.S. and Fred, M., J. Pot. Soc. Am. 47, 1087 (1957).

[22] Mavrodineanu, R., and Highes, R.C., Spectrochim, Acta 19, 727 (1965).

[23] Fehsenfeld, F.C., Evenson, K.M. and Broida, H., Rev. Sci, Instr. 36 (1963).

[24] Walsh, A., Spectrochim, Acta 7, 108 (1955).

[25] Snelleman, W., Spectrochim. Acta 23B, 403 (1968).

[26] Stauffer, R. and Sakai, H., Appl. Opt. 7, 61 (1968).

[27] Butler, L.R.P., Ahrens, L.H. and Strasheim, A., XIII Colloquium Spectroscopicum Internationale, Ottawa, Canada, June 1967.

[28] Sullivan, J.V. and Walsh, A., Spectrochim. Acta 21, 727 (1965).

[29] Ibid, 22, 1843 (1966).

[30] Hermann, R., Lang, W. and Rudiger, K., Z. Analyt. Chem. 206, 241 (1964).

[31] Zeegers, P.J.T., Thesis, Utrecht (1966).

[32] Fassel, V.A. and Golightly, D.W., Anal. Chem, 39, 466 (1967).

[33] Winefordner, J.D., in press.

[34] Slavin, W., Appl. Spectr, 20, 28 (1966).

[35] Ito, J., Bull, Chem, Soc, Japan 35, 225 (1932).

[36] Bernas, B., Goddard Flight Center, private communication (1967).

[37] Müller, R.H., Anal. Chem 37, 123A (1965).

[38] Müller, R.H., Anal. Chem 40, 109A (1968).

[39] Burke, R.W. and Menis, Oscar, Anal. Chem. 38, 1719 (1966)

[40] Zhivopister, V.P. and Chelnokova, M.N., Zh. Analit. Khim. 18, 148 (1963).

[41] Burke, R.W. and Yoe, John H., Anal. Chem. 34, 1378 (1962).

[42] Bolleter, W.T., Bushman, C.J. and Tidwell, P.W., Anal. Chem. 33, 592 (1961).

[43] Weathenburn, M.W., Anal. Chem. 39, 971 (1967).

[44] NBS Technical Note 424, pp. 64-67 (1968).

[45] Sandell, E.B., "Colorimetric Determination of Traces of Metals", Interscience, N.Y., 1944, p. 191.

[46] Stary, J., "The Solvent Extraction of Metal Chelates", Macmillan Company, N.Y., (1964).

[47] NBS Misc. Publication 206-7, 1965, p. 26.

[48] ASTM 1966 Book of Standards, "Chemical Analysis of Metals", Part 32.

[49] Kapron, M., and Hehman, P.L., Anal. Chem. 17, 573 (1945).

[50] L. Ya. Polyak, Zhur, anal. Khim., 17, 205 (1962), 18, (1963).

[51] Bailey, B., Dagnall, R.M. and West, T.S., Talanta, 13, 1661 (1966).

[52] Dagnall, R.M., Smith, R., and West, T.S., Analyst, 92, 20 (1967).

[53] Geiger, R.A., and Sandell, E.B., Anal. Chim. Acta, 16, 346 (1957).

[54] Sill, C.W., and Willis, C.P., Anal. Chem., 31, 595 (1959).

[55] Sill, C.W., Willis, C.P., and Flygare, J.K., Anal. Chem., 33, 1671 (1961).

[56] Kirkbright, G.F., West, T.S., and Woodward, C., Anal. Chem., 37, 137 (1965).

[57] Crouthamel, Carl E., Ed., "Progress in Nuclear Energy", Series IX, 3, [5-7] p. 191, Pergamon Press, Macmillan Co., N.Y., (1963).

[58] Koch, W., and Lemm, H., Z. Analyt. Chem. 215, 377 (1966).

[59] Menis, O., Editor, NBS Technical Note 275 (1965).

[60] Defense Metals Information Center Report 220 (1965).

[61] Kallmann, S., Hobart, E.W., Oberthia, H.K., and Brienza, Walter C., Jr., Anal. Chem. 40, 332 (1968).

6. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Oscar Menis, Section Chief

Barbara B. Keith, Section Secretary

S. M. Adil
(Guest Worker,
Pakistan)

R. K. Bell
B. B. Bendigo
R. W. Burke
D. H. Christopher
(Temp. Appt. Imperial
College of London)
W. N. Corbin
(Summer Employee)

J. F. Martin
(Research Associate, United
States Steel Corporation)

J. W. Martins
(Guest Worker, Brazil)
T. C. Rains
T. A. Rush
W. Snelleman
(Temp. Appt., University
of Utrecht)
J. T. Sterling
S. A. Wicks

B. Publications

1. Oscar Menis and Theodore C. Rains, Sensitivity, Detection Limits, Precision and Accuracy in Flame Emission and Atomic Absorption Spectrometry. "Analytical Flame Spectroscopy, Selected Topics". Ed. R. Mavrodineanu, Centrex, Eindhoven, in press.

2. Theodore C. Rains, Chemical Interferences in Condensed Phase. "Flame Emission and Absorption Methods". Eds. John A. Dean and Theodore C. Rains, Dekker, New York, submitted to the NBS Review Board.

C. Talks

1. T. C. Rains and Oscar Menis, "Determination of Arsenic by Atomic Absorption Spectrometry with an Electrodeless Discharge Lamp as a Source of Radiation", 154th meeting, American Chemical Society, Chicago, Illinois, Sept. 10-15, 1967.

2. T. C. Rains, "Recent Advancements of Atomic Absorption and Flame Emission Spectrometry in the Modern Laboratory". Richmond Spectroscopy Club, Richmond, Virginia, Oct. 10, 1967.

3. Oscar Menis and T. C. Rains, "Electrodeless Discharge Lamp as a Source of Radiation in Atomic Absorption Spectrometry". 11th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tennessee, Oct. 12, 1967.

4. T. C. Rains, W. Snellemen and O. Menis, "Electrodeless Discharge Lamp with Microwave Excitation as a Source of Radiation in Atomic Absorption Spectrometry". Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 4-8, 1968.

5. T. C. Rains and Oscar Menis, "Comparison of a Resonance Detector and High-Resolving Monochromator in Atomic Absorption Spectrometry". Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 4-8, 1968.

6. T. C. Rains, "An Evaluation of the Electrodeless Discharge Lamp as a Source for Atomic Absorption Spectroscopy". FDA Institute for Advanced Analytical Chemistry-Training Course in Atomic Absorption, Georgetown University, March 22, 1968.

7. T. C. Rains, "Chemical Aspects of Atomic Absorption Spectrometry". ASTM, Symposium on Atomic Absorption. Annual Meeting, San Francisco, California, June 25, 1968.

8. Robert W. Burke, "Accuracy Consideration in the Determination of Trace Quantities of Arsenic". Southeastern American Chemical Society Regional Meeting, Atlanta, Georgia, Nov. 3, 1967.

9. W. Snelleman, "Theoretical Aspects of Atomic Absorption Spectroscopy". Society of Applied Spectroscopy, Hyattsville, Maryland, Jan. 23, 1968.

10. Robert W. Burke, E. R. Deardorff and Oscar Menis, "Precise Determination of Activator Elements in Neutron Flux Monitors". Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 8, 1968.

11. Willem Snelleman and Oscar Menis, "A Modified A.C. Detection Method for Continuous Sources and Line Sources in Atomic Absorption". Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 8, 1968.

12. Oscar Menis and Simon A. Wicks, "Chemical Methods for Refractory Nitrides". Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 8, 1968.

13. J. T. Sterling, "Evaluation of NBS 1090 Series for Oxygen by Vacuum Fusion and Inert Gas Fusion". ASTM at NBS, Washington, D.C., April 4, 1968.

14. Oscar Menis, "Evaluation of NBS 1090 Series for Nitrogen by Dissolution in Teflon-Lined Pressure Bombs". ASTM at NBS, Washington, D.C., April 4, 1968.

D. Committee Activities

Oscar Menis

Member, ASTM - Committee E-3, Div. I, Committee on Gases in Metals.

Member, ASTM - Committee E-10, Subcommittee I, Nuclear Fuel Burnup.

Divisional Representative, American Chemical Society - Program Committee for Middle Atlantic Region.

Editorial Board Member, Chemical Instrumentation, A Journal of Experimental Techniques in Chemistry and Biochemistry.

J. T. Sterling

Member, ASTM - Chairman, Committee E-3, Div. I, Committee on Gases in Metals.

R. K. Bell

Member, ASTM - Committee E-3, Div. N. Committee on Non-Ferrous Metals.

T. C. Rains

Program Subchairman, Society for Applied Spectroscopy - Atomic Absorption and Flame Emission.

NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, chemistry, and engineering. Comprehensive scientific papers give complete details of the work, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Illustrated with photographs, drawings, and charts.

Published in three sections, available separately:

• Physics and Chemistry

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, $5.00; foreign, $6.00*.

• Mathematical Sciences

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, $2.25; foreign, $2.75*.

• Engineering and Instrumentation

Reporting results of interest chiefly to the engineer and the applied scientist. This section includes many of the new developments in instrumentation resulting from the Bureau's work in physical measurement, data processing, and development of test methods. It will also cover some of the work in acoustics, applied mechanics, building research, and cryogenic engineering. Issued quarterly. Annual subscription: Domestic, $2.75; foreign, $3.50*.

TECHNICAL NEWS BULLETIN

The best single source of information concerning the Bureau's research, developmental, cooperative and publication activities, this monthly publication is designed for the industry-oriented individual whose daily work involves intimate contact with science and technology—*for engineers, chemists, physicists, research managers, product-development managers, and company executives.* Annual subscription: Domestic, $1.50; foreign, $2.25*.

*Difference in price is due to extra cost of foreign mailing.

NONPERIODICALS

Applied Mathematics Series. Mathematical tables, manuals, and studies.

Building Science Series. Research results, test methods, and performance criteria of building materials, components, systems, and structures.

Handbooks. Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications. Proceedings of NBS conferences, bibliographies, annual reports, wall charts, pamphlets, etc.

Monographs. Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

National Standard Reference Data Series. NSRDS provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated.

Product Standards. Provide requirements for sizes, types, quality and methods for testing various industrial products. These standards are developed cooperatively with interested Government and industry groups and provide the basis for common understanding of product characteristics for both buyers and sellers. Their use is voluntary.

Technical Notes. This series consists of communications and reports (covering both other agency and NBS-sponsored work) of limited or transitory interest.

CLEARINGHOUSE

The Clearinghouse for Federal Scientific and Technical Information, operated by NBS, supplies unclassified information related to Government-generated science and technology in defense, space, atomic energy, and other national programs. For further information on Clearinghouse services, write:

Clearinghouse
U.S. Department of Commerce
Springfield, Virginia 22151

Order NBS publications from:
Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

U.S. DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20230

OFFICIAL BUSINESS

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF COMMERCE