NBS TECHNICAL NOTE 504

Analytical Coordination Chemistry Section:

Summary of Activities
July 1968 to June 1969

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards ' 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 four broad program areas. 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, the Center for Radiation Research, the Center for Computer Sciences and Technology, and the Office for Information Programs.

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 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 Measurement Services and the following technical divisions:

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

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in the selection, acquisition, and effective use of automatic data processing equipment; and serves as the principal focus for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

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THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System, and provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

> Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information [3]—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

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[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.

NBS TECHNICAL NOTE 504

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Analytical Coordination Chemistry Section:

Summary of Activities
July 1968 to June 1969

Edited by Oscar Menis

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

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 require months to perfect and yet all too 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 more abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1969 we plan to issue these summaries for all of our sections. The following is the fifth annual report on progress of the Analytical Coordination Chemistry Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

The strong interaction during the past year between research and development and the analysis of Standard Reference Materials is again reflected in the work of this section. Particular emphasis has been placed on the development of new or improved methods and the modification of instruments to provide greater precision, accuracy and sensitivity as demonstrated in the analysis of a variety of Standard Reference Materials. Areas of research have included flame emission and atomic absorption, spectrophotometry and spectrofluorometry, thermal analysis and the determination of gases in metals.

The presentation of this material has been arranged to facilitate the use of this information by the reader as it applies to his specific needs or interests. For this reason the topics dealing with the research aspects of the specific competences and the area of Standard Reference Materials are reported separately. In presenting the latter separately, we are able to emphasize the complex nature of the materials and to give proper perspective to the section's contribution to the NBS efforts in chemical characterization. The descriptive information associated with the Standard Reference Materials should assist the reader in making better use of these materials. Even more important, however, we hope it will encourage the reader to communicate with the division to point out the current needs which may have been heretofore neglected and thus be of help in developing a more meaningful program by the Analytical Chemistry Division. Problems related to clinical chemistry have not been discussed in this report; however, a broad program is being initiated involving spectrophotometry, spectrofluorometry, and flame spectroscopy for use in preparing suitable Standard Reference Materials for the clinical chemist. The initial stages concerned the recruitment of appropriate personnel,

the acquisition of special equipment and material, and the development of a program essential in this study. For this reason a full program report will be forthcoming in succeeding reports. While some of the work reported may appear fragmentary and lack detail, it is anticipated that much of it will appear later in its entirety in journal articles or NBS Miscellaneous Publication 260.

In order to adequately describe experimental procedures, it is occasionally necessary to identify commercial products 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 product or equipment is necessarily the best available for that purpose.

The assistance of Mrs. Rosemary Maddock is gratefully acknowledged. Also, we acknowledge the invaluable assistance of Mrs. Mary Pantazis, Section Secretary, who performs 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 Chemistry

James I. Shultz, Assistant Chief
Analytical Coordination Chemistry

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ABSTRACT

Research developments are described in flame emission and atomic absorption spectrometry, spectrophotometry, spectrofluorometry, differential thermal analysis and the analysis and certification of Standard Reference Materials. The application of ac wavelength scanning and second derivative measurements of spectral line intensities serve to overcome broad-band and continuum interferences of matrices in flame emission analysis. It also provides for the analysis of samples as small as 50 µl. In atomic absorption studies of arsenic, basic corrections for spectral interferences are given.

New spectrophotometric methods have been developed for the analysis of multicomponent systems. These include the simultaneous determinations of cobalt, nickel and copper with 2,3-quinoxalinedithiol and of vanadium and iron with β-isopropyltropolone. The extraction of ternary ion association complexes initially containing non-colored or non-fluorescent organic cations, followed by displacement of these groups by highly colored or highly fluorescent dye cations directly in the organic phase, has provided a means of simultaneously improving sensitivity and selectivity in absorption and fluorescence spectrophotometry. The determinations of gold and uranium are described to illustrate the approach. Spectrofluorometric studies of the determination of rare earth elements in synthetic borate glass are also presented.

Instrument modifications and temperature measurement techniques now provide a tenfold increase in the precision of measurements of phase transition temperatures of quartz and potassium nitrate on differential thermal analysis standards.

Procedures, analytical data and background information are presented for Standard Reference Materials of steels, cast and nodular irons, ferrosilicon, high-purity materials,

neutron flux monitor wire, organo-metallic compounds, glasses, and clays. These descriptions include atomic absorption methods for copper in steel, magnesium in nodular iron, impurities in calcium carbonate, high precision spectrophotometric methods for cobalt in aluminum wire, molybdenum and tungsten in microprobe standard, traces of iron and copper in high purity gold and methods for the determination of silica and aluminum in clays.

1. FLAME EMISSION AND ATOMIC ABSORPTION SPECTROMETRY

A. Introduction

The state of the art has grown at a spectacular rate during the past year as indicated by the 300 papers and 4 books that were published during this period. This expanding interest is reflected at NBS by the number of invited lectures, the many requests for assistance and consultation and short courses given on the subjects.

In a continuing effort to improve our competence in flame emission and atomic absorption spectrometry, new instrument designs and techniques were evaluated. These include new sources of monochromatic radiation, nebulizer-burners, gas systems, optical arrangement, electronics and analytical techniques. The technique of ac repetitive scanning of narrow wavelength regions reported previously [1] for atomic absorption has been extended to flame emission. A new design in the optical and electrical components with the ac scan and synchronous detection, provided a versatile analytical tool. The interferences due to a continuum or unresolved band structures are minimized, thus permitting increased detection limits in the presence of relatively high concentrations of matrix ions. Since many analyses required only 50 µl of sample, this technique affords the analyst a unique method for trace analysis in bioclinical and pollution studies.

The successful application of the ac scanning derivative technique to the problem associated with the analysis of Standard Reference Materials and special service analyses attests to its wide utility.

B. Source of Monochromatic Radiation

1. Electrodeless Discharge Lamps

In the two earlier reports [1, 2], our experiences with the electrodeless discharge lamp (EDL) were discussed. To overcome the instability of the EDL, several new approaches

were investigated. The air flow for cooling the cavity was preheated by passing it through a tube furnace. Controlling the temperature of the air increased the radiant intensity and the stability of the EDL. The intensity of lamps containing neon as a filler gas was greater than the argon-filled lamps.

For the first time, a multi-element EDL was prepared. Lamps were prepared containing Pb, Zn and Cd as well as Li, Na and K. The multi-element lamps performed as well as the single element lamps.

Two RF power generators for these lamps with power outputs of 0-100w and 20-200w operating at 2450 MHz were also tested. The stability and radiant intensity of the EDL were similar for both generators. Three new cavities (one - 1/4 wave and two - 3/4 wave) are presently being evaluated.

C. Derivative Flame Emission Spectrometry

The measurement of an atomic line which appears in or on a bandhead due to the concomitants or flame gases, is of interest and concern to flame emission spectroscopists. In an earlier report [1], an ac scanning technique with a continuous source was discussed for atomic absorption spectrometry. The ac scanning of part of the continuum was accomplished by vibrating a mirror within the optical path mounted on the movement of a milliammeter. While the optical arrangement demonstrated the feasibility of the ac scan in atomic absorption work, there were certain limitations due to the development of an improved system which utilizes an oscillating quartz plate and provides an apparatus which is stable and easy to operate. The new optical and electronic arrangement was tested in the flame emission and atomic absorption modes.

1. Experimental Setup

The instrumental system used in this study consists of (a) Czerny-Turner 0.75m monochromator, f/6.5 aperture,

curved slits, exchangeable grating blazed for 3000 and
7500 Å with 1180 grooves/mm, (b) quartz plate mounted on a
rotating mechanical oscillator and (c) associated electronic
controls.   The quartz plate (12x14x2 mm) is mounted on a
rotating mechanical oscillator possessing a variable
amplitude of up to 6° peak to peak, behind the entrance
slit, as shown in figure 1.
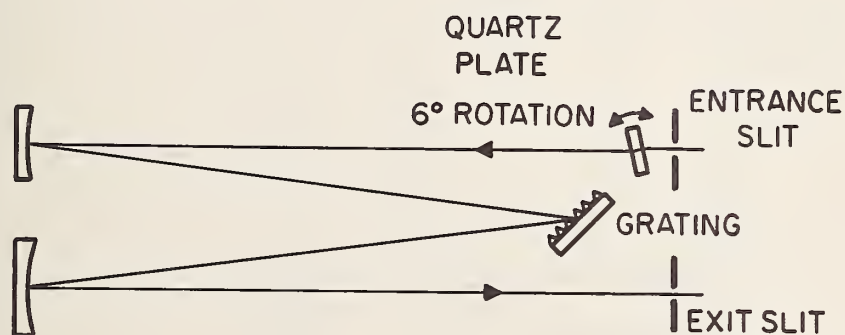
Figure 1.   Location of quartz plate within the
            optical system.

The lateral displacement of the image is proportional to
the thickness of the quartz plate and to the angle of
rotation.   Under the experimental conditions, the displace-
ment of the line was 1 Å.   A larger displacement can be
obtained by using a thicker quartz plate and by increasing
the angle of rotation.   Since the image is defocused at the
exit slit, because of a change in optical path length, the
quartz plate was ground to a slight convex curvature corre-
sponding to a 12m focal length.

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The mechanical oscillator and the associated electronics were designed and built by the Measurement Engineering Division of the National Bureau of Standards.

2. Experimental Procedure

The 5536 Å barium resonance line was scanned using an oxygen-hydrogen flame. The light signal was chopped at 87 Hz using a mechanical disc chopper. The spectrum obtained is shown in figure 2A.
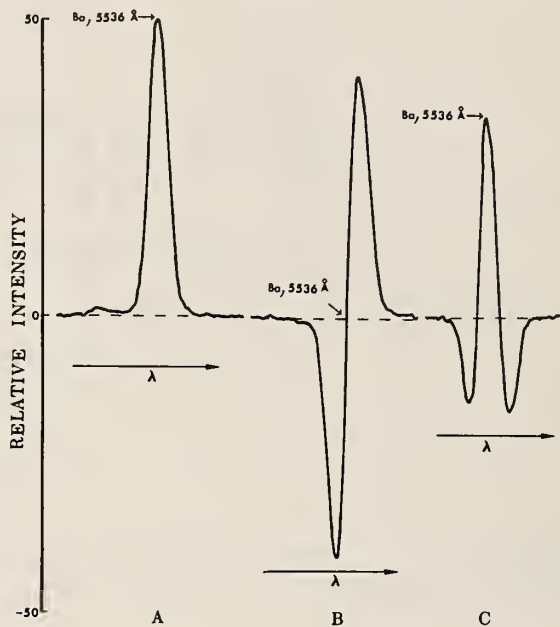
Figure 2. Flame emission spectrum of barium.

The mechanical disc chopper was removed from the system and the quartz plate was placed behind the entrance slit within the optical path. A current was applied to the drive coil which produced an oscillation of the quartz plate. The synchronous lock-in amplifier was tuned to the frequency of the vibrating quartz plate. A wavelength scan of the

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5536 Å barium resonance line was repeated. The resulting spectrum was the first derivative with the peak corresponding to the zero crossing of the X axis. This is shown in figure 2B. While the first derivative has been used in spectroscopy [3] for identifying overlapping band structures, scanning of the wavelength region is required. This offers no advantage in flame emission over the mechanical disc chopper. The experiment was repeated, but the lock-in amplifier was tuned to twice the frequency of the vibrating quartz plate. The spectrum obtained (figure 2C) was the second derivative and is proportional to the analyte concentration.

3. Results and Discussion

Since the CaOH band system over the region of 5520 to 5570 Å interferes in the determination of barium [4, 5, 6, 7], the ac scanning with the second derivative was investigated as a means of reducing this interference. A sample containing equal concentrations of calcium and barium was tested and the calcium did not interfere with the barium. Using the ac scan and taking the second derivative, no continuum or unresolved band structure was detected. By setting on the peak of the barium resonance line and taking the second derivative rather than mechanically scanning the wavelength region, barium can be determined with an air-acetylene flame in the presence of a hundred-fold concentration of calcium, as shown in figure 3. Flames of higher temperatures, such as oxygen-hydrogen or nitrous oxide-acetylene with appropriate burners, permitted the determination of barium in calcium in the ratio of 1:1000.

The resonance lines of copper at 3247 and 3274 Å are located in a region of relatively strong OH emission. The strongest copper line at 3247 Å coincides with a sharp OH bandhead at 3247 Å and the ac scan did not improve the detection limits. However, as shown in figure 4, there are two unresolved OH band-peaks at 3274 Å. With an

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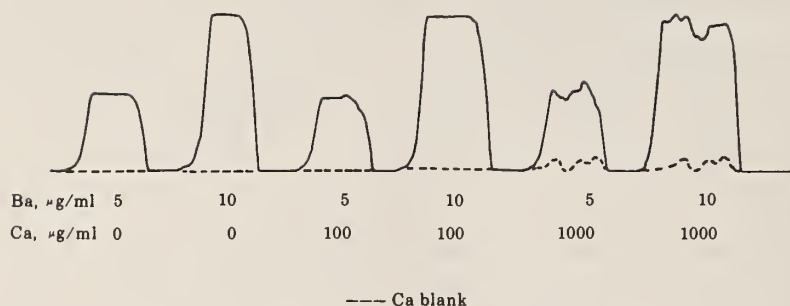
Figure 3.   Effect of calcium on barium in flame
            emission with ac scanning and second
            derivative measurement.

Figure 4.   Spectrum of copper in the region of 3274 Å.

amplitude scan of 1 Å or less, the unresolved OH band peak
is used as a base line. The detection limits measured with
the ac scan and second derivative signal for copper and
several other elements are given in table 1.

Table 1.   Detection limits by flame emission spectrometry
           for ac scan.
           Oxidant and fuel---oxygen-hydrogen
           Burner---total consumption
           Phototube---EMI 9558AQ

Element	Wavelength, Å	Detection limits, μg/ml[a]
Li	6708	0.00002
K	7665	0.0001
Mg	2852	0.1
Ca	4227	0.001
Cu	3247	0.1 (0.1)[b]
	3274	0.03 (0.2)[b]

[a]Detection limit is defined as 2σ of background.
[b]Values obtained with mechanical disc chopper.

The detection limits normally reported for flame
emission spectrometry are generally obtained with pure
water solutions. These values may be very misleading if
applied to samples containing certain cations. The detec-
tion limits obtained using the ac scan for lithium,
potassium and calcium in the presence of 1000 μg/ml of
various matrix elements are given in table 2. The values
are as low as those reported in the literature using pure
water solutions in flame emission spectrometry work.

Another unique feature of this technique is the size of
sample required for an analysis. In normal flame emission
spectrometry, three to five ml of solution are required for
making a scan of the wavelength region of interest. By
setting on the peak of a line and using the ac scan, only
a small portion of the solution is required. For example,
using a total consumption burner and a small bore capillary,

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Table 2. Detection limits by flame emission spectrometry
with ac scanning in the presence of matrix-ions.

Oxidant and fuel---oxygen-hydrogen
Burner---total consumption
Sample size---0.25 ml

Matrix, element 1 mg/ml	Detection limit, ng[a]		
	Li	K	Ca
Li	–	0.2	3.0
Na	0.02	0.08	0.5
K	0.02	–	3.0
Rb	0.02	1.0[b]	3.0
Mg	0.02	0.1	(c)
Ca	0.02	0.03	–
Fe	0.02	0.2	3.0

ng = 10^{-9} grams

[a]Detection limit is defined as 2σ of background.

[b]Rubidium free of potassium not available.

[c]Magnesium free of calcium not available.

lithium was determined in a sodium matrix with only 50 μl of
solution as shown in figure 5. The reproducibility of the
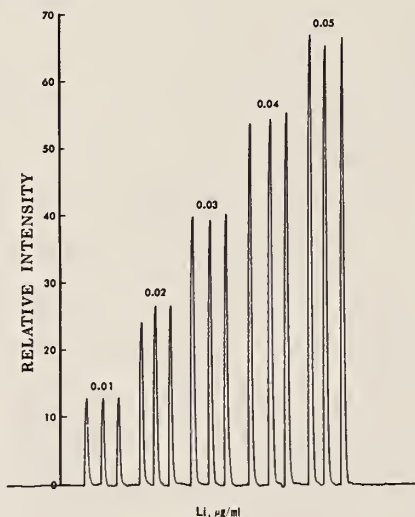
Figure 5. Lithium calibration results by flame
emission with ac scanning and second
derivative measurement.

peak height was better than 2 percent of full scale. The
speed of the recorder pen was the limiting factor for the
required volume of solution.

D. Evaluation of the Atomic Absorption Method for Arsenic

1. Corrections for Physical Interferences

In a continuing effort to improve the precision and
accuracy, reported previously [1], of the determination of
arsenic by atomic absorption spectrometry, several new
parameters were investigated. The absorption of arsenic
at the 1937 Å resonance line varied with different cations
present. While spectral interferences in atomic absorption
are reported in the literature [6], physical interferences
are often present and are associated with the chemical
composition of the matrix. Scattered light which appears
as molecular absorption may be due to high solids or large
droplets produced by the nebulizer. The effects of copper,
and iron on arsenic at 1937 Å are given in table 3. There

Table 3. Effect of copper and iron on the absorption of
arsenic at 1937 Å.

Oxidant and fuel---argon (entrained air)-hydrogen
Burner---total consumption

| | | | 1937 Å | |
Element, mg/ml		As, µg/ml	Abs.	Abs. corrected
Cu	0.0	10	0.267	0.267
	1.0	–	.000	
	1.0	10	.265	.265
	5.0	–	.044	
	5.0	10	.293	.259
Fe	0.1	–	.008	
	0.1	10	.277	.269
	1.0	–	.029	
	1.0	10	.273	.244
	5.0	–	.122	
	5.0	10	.317	.195

is not only scattered light at the 1937 Å line of arsenic,
but iron has a suppressing effect on arsenic in the cool
argon (entrained air)-hydrogen flame. Molecular fragments

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such as CH, C_2 and CN exist in various flame gases and may contribute to the background as well as to scattered light. The major difficulty is the correction for scattered light or molecular absorption. A scan of the arsenic spectrum, figure 6, shows strong neon lines at 1916, 1930 and 1990 Å. Also, a non-absorbing arsenic line is located at 2003 Å. The neon lines at 1916 and 1990 Å may be used to correct for scattered light for arsenic at 1937 and 1972 Å, respectively.
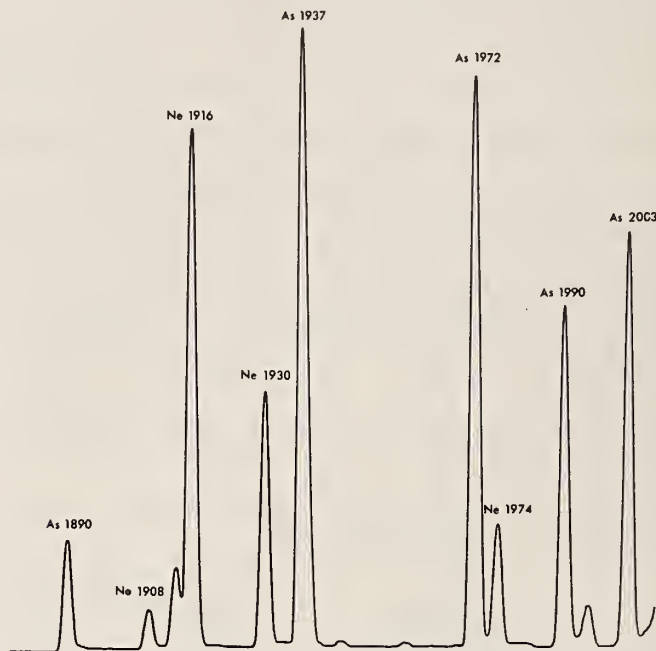
Figure 6. Spectrum of arsenic over the wavelength region of 1880 Å to 2005 Å.

2. <u>Effect of Band Width on Absorption</u>

The major function of the monochromator is to separate the resonance line from the non-absorbing lines which are emitted by the hollow-cathode lamp. If the spectral band width of the monochromator is too large, non-absorbing lines will interfere which appear as a loss of sensitivity and a

bending of the calibration curve. The effect of the band
width on arsenic is shown in table 4. While arsenic is
reported to be relatively free of spectral interferences,
the data would indicate that some non-absorbing lines are
in the region of the arsenic resonance line. As shown in
figure 6, the neon line at 1930 $\overset{o}{A}$ would interfere if the
spectral band width exceeded 7 $\overset{o}{A}$. Also, there is a Ne(II)
line at 1939 $\overset{o}{A}$.

Table 4. Role of spectral band width on the absorption
         of arsenic at 1937 $\overset{o}{A}$.

         Oxidant and fuel---argon (entrained air)-hydrogen
         Burner---total consumption
         Arsenic---100 µg/ml

Spectral band width, $\overset{o}{A}$	Absorbance
0.4	0.229
0.8	.222
1.2	.212
1.6	.202
2.4	.169
3.2	.158
4.8	.158
8.0	.143

E. Analytical Application to Standard Reference Materials

    1. Determination of Copper in Basic Oxygen Furnace
Steel and Chrome-Moly Steel - NBS-SRM 178 and 36b

    In the determination of copper by atomic absorption,
iron was observed to suppress the copper. Various methods
were explored to eliminate the interference of iron on
copper. While the standard addition method was able to
correct for the suppression, the desired precision was not
attained. Subsequently, standard solutions of copper were
prepared containing the same concentration of iron as the
unknown sample. This approach improved the precision and
accuracy of copper in a ferric matrix.

    For NBS-SRM 178 and 36b, a 1-g sample was dissolved in
hydrochloric acid and the solution was transferred to a

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volumetric flask. For 36b the analysis was performed by
atomic absorption without any additional preparation. Since
copper in the basic oxygen furnace steel (NBS-178) was very
low, it was removed from the iron matrix with diethylammo-
nium diethyldithiocarbamate (DDDC). Iron was complexed with
ethylenediaminetetraacetic acid and the solution was
adjusted to pH 7.5-8.0 with ammonium hydroxide. Under these
conditions the copper was extracted with a 0.5 percent
solution of DDDC in chloroform without any interference
from iron. The absorption measurement was then made on
the organic solution. The results are presented in
table 5.

Table 5. Summary of NBS-SRM analyses by flame emission and
          atomic absorption spectrometry.

NBS-SRM No.	Material	Element	No of det'ms	Conc, %	Std dev	Rel std dev, %
178	Basic oxygen furnace steel	Cu	24	0.0327	0.0010	3
36	2 chrome 1 moly steel	Cu	4	.112	.0019	2
36b		Cu	32	.183	.005	3
342	Nodular iron	Mg	10	.0513	.0012	2
342a	"	Mg	17	.0718	.0010	1
1051	Ba cyclohexane-butyrate	Sr	2	.0158	.00014	0.9
1051b	"	Sr	5	.0503	.0010	2
				µg/g		
380	$CaCO_3$	Sr	3	2.1	.12	6
		Mg	3	0.98	.05	6
		Ba	3	<10	–	–
		Li	3	<0.5	–	–
		Na	3	0.4	.1	25
		K	3	<0.5	–	–

2. Determination of Magnesium in Nodular Iron - NBS-SRM 342a)

The determination of magnesium by atomic absorption spectrometry is rapid and precise. The sample is dissolved in a mixture of $HCl-HNO_3$ and then fumed with $HClO_4$ to oxidize the carbon. The solution is transferred to a volumetric flask and diluted to volume with diluted HCl. Magnesium is determined using an air-acetylene flame. The results are given in table 5.

3. Determination of Trace Impurities in Calcium Carbonate - NBS-SRM 380

This high purity material was prepared by J. T. Baker Co. by a method described in the literature [8]. The sample was dissolved in ultra pure HCl and diluted to a calibrated volume. The alkalies, strontium, and barium were determined by flame emission with the ac scan while magnesium was determined by atomic absorption spectrometry. The strontium procedure has been previously described [8]. The major changes in the procedure involved the use of the ac scan and the measurement of the second derivative signal. This new technique improves the precision and accuracy of the analysis. To eliminate the major interference of calcium on barium, the latter was determined using a nitrous oxide-acetylene flame. The interference from the high continuum due to the CaOH band structure was minimized with the ac scanning technique. The magnesium was determined by atomic absorption spectrometry. The gallium line, 2874 Å, was selected to correct for scattered light and molecular absorption.

F. Service Analyses

A total of 74 samples involving 145 analyses were performed by atomic absorption or flame emission spectrometry for other Divisions of the Bureau and other Government agencies. Trace element analyses were made on a wide variety of materials such as metallo-organics, resin beads, laser glass, clinical, book binding material, silver chloride,

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potassium nitrate, rubidium chloride, caffeine, calcium fluoride, and "polymer" water.

a. Trace as well as the major elements were determined in a series of neodymium glasses. The samples were dissolved in a Teflon-lined pressure bomb with HF [1]. Fluoride was removed by repeated evaporations with nitric acid. Cadmium, copper, magnesium and zinc were determined by atomic absorption spectrometry using an air-acetylene flame with a 10 cm slot burner. Calcium, cesium, lithium, potassium, rubidium and sodium were determined by flame emission spectrometry and ac scanning with an oxygen-hydrogen flame, while the nitrous oxide-acetylene flame was used for aluminum and barium.

b. Trace quantities of gadolinium were determined in calcium fluoride crystals. The weight of the crystals varied from 25-50 mg which necessitated a separation and preconcentration. The gadolinium was separated from the calcium matrix by extraction with 2-thenoyltrifluoroacetone in methyl isobutyl ketone [9] and was determined in the organic phase by flame emission using the oxide band peak at 4640 $\overset{o}{A}$.

c. A number of other analyses were performed by atomic absorption or flame emission including potassium and cesium in ^{85}RbCl and ^{87}RbCl; sodium in silver chloride; aluminum and potassium in a portion of old document; alkalies and alkaline earth metals in rubidium chloride; aluminum, calcium, magnesium and potassium in book binding material; and sodium in "polymer" water.

T. C. Rains and T. A. Rush

2. SPECTROPHOTOMETRY AND SPECTROFLUOROMETRY

A. Introduction

The two techniques continue to demonstrate their great applicability and versatility in the accurate analysis of Standard Reference Materials. This accuracy stems primarily from the elimination of systematic errors through a better understanding of the solution and coordination chemistry of these complex materials.

In the following section, work undertaken during the past year is described in considerable detail. In high sensitivity spectrophotometry, the stability and reproducibility of the 2,3-quinoxalinedithiol complexes of cobalt, nickel and copper have permitted the development of a multi-element procedure for the simultaneous determination of these three elements at the 0.1-1 ppm level [10]. In a related study, β-isopropyltropolone has been established as a new and useful reagent for the selective determination of trace amounts of vanadium. General enhancement of spectrophotometric and spectrofluorometric sensitivity has been achieved through continued investigation of ternary ion association systems of the type, $[ML]^-[R]^+$, which are capable of exchanging non-colored or non-fluorescent R groups for highly colored or fluorescent ones directly in the organic phase [11]. The increased precision and accuracy of differential spectrophotometry have been exploited in the development of new and improved methods for the determination of cobalt in cobalt-aluminum neutron flux monitor wire and of molybdenum in molybdenum-tungsten microprobe standards. In addition, a spectrophotometric method has been developed for the simultaneous determination of molybdenum and tungsten in NBS-SRM 480. The determination of air-borne beryllium by solution spectrofluorometry is also described and preliminary data are presented on the in situ spectrofluorometric determination of rare earth elements

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in synthetic borate and silicate glasses. The section concludes with a discussion of the spectrophotometric determination of iron and copper in high-purity gold (99.9999%) and a summary of service analyses carried out during the past year.

B. Research Activities

   1. Development of a Method for the Simultaneous Spectrophotometric Determination of Cobalt, Nickel and Copper

The use of molecular absorption spectrophotometry for multi-element analysis has achieved little success in the past largely because of the broad, and therefore, frequently overlapping band spectra that are characteristic of light absorption in the ultraviolet-visible regions. With either time-shared or in-house computers becoming available in the laboratory, the resolution of complex spectra into their various components has become a relatively simple task. Consequently, greater emphasis should now be placed on the development of additive and reproducible color systems and less concern should be given to the complexity of the spectra involved.

In the method developed, a procedure is presented for the rapid simultaneous determinations of cobalt, nickel and copper based on the color-forming reactions of these elements with 2,3-quinoxalinedithiol in aqueous ethanol. The complexes attain maximum absorbance almost instantaneously, exhibit excellent sensitivity and reproducibility and are relatively stable. More important however, especially for multi-element analysis, the absorbances of mixtures are additive over a wide range of concentrations and compositions.

   a. Procedure. Because the color reactions are performed in aqueous ethanol, the amount of water permissable is governed by the quantity that can be present without precipitating the complexes. Since previous studies [12] have shown that water may be present in amounts up to 20 percent

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(v/v), limiting aqueous volumes of 2 and 20 ml are estab-
lished for final volumes of 10 and 100 ml, respectively.
For the 10-ml volume, 1 ml of 0.1 percent 2,3-quinoxaline-
dithiol is used and, for larger volumes, proportionally
more is recommended. Because the 2,3-quinoxalinedithiol-
metal reactions are quite sensitive at pH 2 [1 ppm solutions
of cobalt, nickel and copper give absorbance readings of
0.635 (510 nm), 0.308 (665 nm) and 0.354 (625 nm), respec-
tively] sample sizes and dilutions are selected so that the
final sample aliquot contains $\leq$10 ppm of each of these
elements.

In practice, two aliquots are required. To one is
added sufficient 1N HCl or 1N NaOH to give a final pH meter
reading of 2.0 ± 0.1 after color development and dilution to
volume with ethanol. To this aliquot, and before the
addition of the alcohol, 5-10 mg of thiourea is added to
reduce Cu(II) to Cu(I), the reactive form of this element.
The sample is diluted nearly to volume with ethanol, the
appropriate amount of the 2,3-quinoxalinedithiol solution is
added (10 percent v/v) and final dilution is made with
ethanol. The absorbance of this solution is then measured
at 665, 625 and 510 nm. It may be read immediately or at
any time up to 24 hours provided it is measured relative to
a 2,3-quinoxalinedithiol reference solution prepared at the
same time as the sample. Fortunately, the absorbance of the
reagent is not sensitive to pH changes at the above wave-
lengths and an appropriate reference can be prepared by
adding 2-3 drops of 1N HCl to sufficient reagent solution
(10 percent v/v) and diluting to volume with ethanol. The
absorbance of the second sample aliquot is also measured
against this reference. Following addition of the acetic
acid-sodium acetate buffer (volume added should be one-
tenth the final volume since tenfold dilution of the pH 4.1
buffer with ethanol gives an apparent pH of 6.0 ± 0.1), the
color is developed in the same manner as the first aliquot,

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but with the thiourea omitted. The absorbance of this solution is measured at 665 nm approximately 5 minutes after color development. The concentrations of cobalt, nickel and copper in the sample aliquots are then calculated by means of simple arithmetic from a series of constants derived from a least squares treatment of the appropriate spectrophotometric data (see Discussion).

i. <u>Analysis of Iron-Base Alloys</u>: For sample sizes of ≤0.5g, dissolve in 10 ml of 1:1 HCl, oxidize Fe(II) to Fe(III) by dropwise addition of concentrated HNO_3 (1 ml) and evaporate the solution to incipient dryness. Dissolve the residue in 8<u>N</u> HCl, cool and transfer to a 60-ml separatory funnel (final acid layer ~25 ml). Extract Fe(III) by shaking for 30 seconds with an equal volume of 1:1 methyl isobutyl ketone (hexone) and amyl acetate previously equilibrated with 8<u>N</u> HCl. Separate the phases and repeat the extraction. Backwash each of the organic layers with 10 ml of 8<u>N</u> HCl and add the latter to the original aqueous fraction. Evaporate this acid fraction to 2-3 ml, add 10 ml of concentrated HNO_3 and 2 ml concentrated $HClO_4$. Evaporate to dense fumes (prior to fuming, HF may be added to decompose any siliceous residue) and dilute to volume. Take suitable aliquots and analyze spectrophotometrically as outlined above.

ii. <u>Analysis of Aluminum-Base Alloys</u>: Dissolve by dropwise addition of 1:1 HCl, add 2-3 drops concentrated HNO_3 and approximately 10 drops of 48 percent HF, if much silicon is present. Add 2 ml of concentrated $HClO_4$ and evaporate to dense fumes. Dilute to volume and take appropriate aliquots for spectrophotometric analysis. A tenfold molar excess of sodium citrate is added if aluminum should hydrolyze at pH 6.

b. <u>Discussion and Results</u>. The absorption spectra of the copper, nickel and cobalt complexes and the reagent are shown in figure 7. At pH 2, distinct absorbance peaks are

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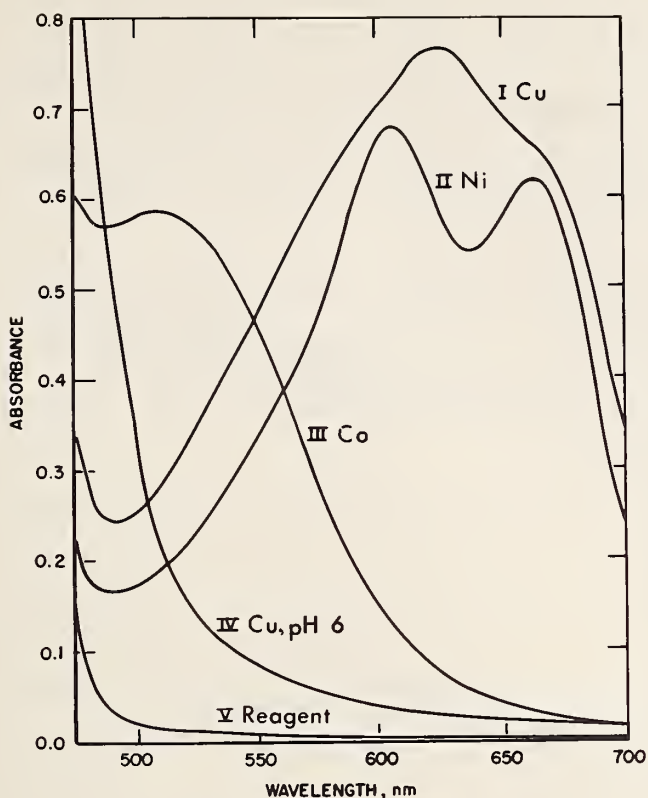
Figure 7. Absorption spectra of the copper, nickel and
cobalt complexes and of the reagent.

apparent at 510 nm (Co), 606 and 665 nm (Ni), and 625 nm
(Cu). Also apparent is the close similarity between the
nickel and copper spectra at this acidity. At pH 6, however,
the copper spectrum is considerably different (curve IV) from
that obtained at pH 2 while the cobalt and nickel spectra
remain relatively unchanged. As will be seen later, this
pronounced pH effect is used to differentiate copper from
nickel. In the latter complex, nickel is present undoubtedly
as the Ni(II) ion while there is evidence favoring both
Co(II) and Co(III) as the reactive form of this element. In
the case of copper, Cu(I) is definitely the reactive species.

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As a result, thiourea and ascorbic acid were investigated as potential reducing agents and the former was found more effective at pH 2. In addition, 2,3-quinoxalinedithiol also reduces Cu(II) to Cu(I). In the pH range of 2-3 the reduction is both acid-catalyzed and light-catalyzed (figure 8).
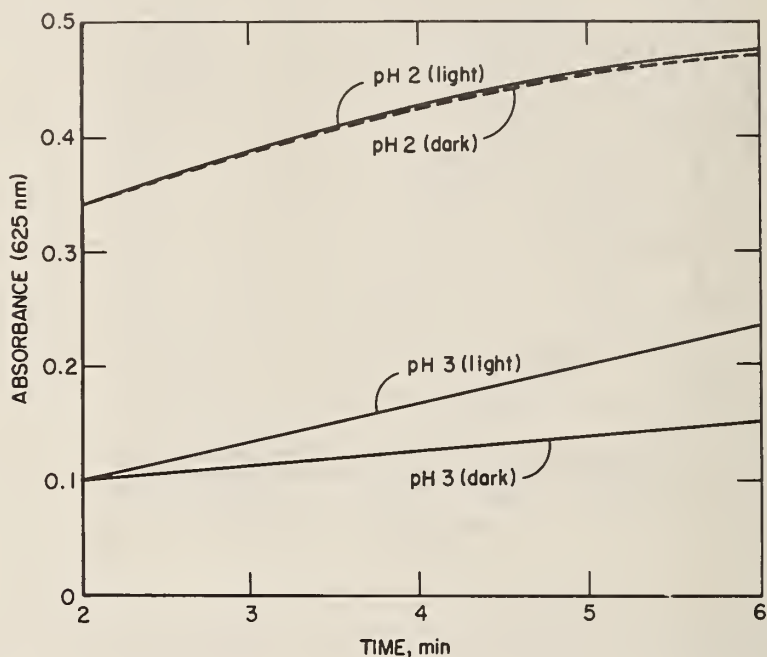
Figure 8. Reduction of copper(II) to copper(I) by 2,3-quinoxalinedithiol.

At pH 2, acid catalysis is the predominant factor; at pH 3, the reaction is preferentially light catalyzed. For these experiments, two solutions were used--one having a pH of 2 and the other a pH of 3 (2.08 ppm Cu in each). During the first two minutes following color development each was exposed to normal fluorescent light of the laboratory. At the end of this period a portion of one was placed into the spectrophotometer and repeated absorbances were measured over a 2-6 minute time interval. During this time the

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sample was in the light path only long enough to obtain a
measurement. Simultaneously, the absorbance of the remaining
portion was measured on a second spectrophotometer. For each
measurement, a new sample (continuously exposed to laboratory
light) was always placed in the absorption cell. The second
solution was treated similarly. The terms "dark" and "light"
in figure 8 refer to these two levels of light exposure.

   i. <u>Effect of pH</u>: The effect of pH on the absor-
bances of the cobalt, nickel and copper complexes is shown
in figure 9. Over this pH range the absorbance of the
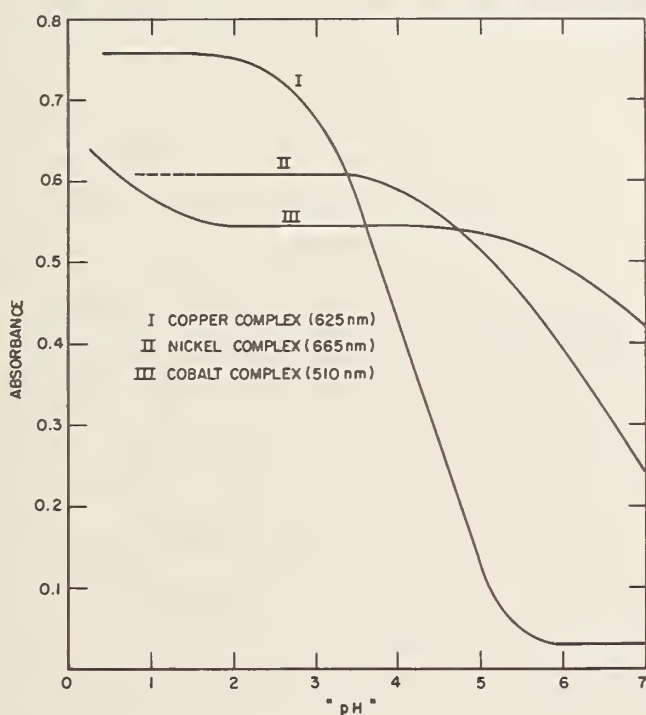
Figure 9. Absorbances of the colored complexes
     at various acidities.

reagent is constant. All pH values refer to meter readings
obtained with glass-calomel electrodes. At relatively
high acidities (pH 2) the apparent pH of aqueous ethanol

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(10 percent v/v) closely parallels that obtained in an all-aqueous system, i.e. tenfold dilution of an acidic sample with water increases its pH by 1 unit. Tenfold dilution of an aqueous sample at pH 4-5 with ethanol, however, gives an apparent pH increase of approximately 2 units.

For the simultaneous determination of cobalt, nickel and copper, two acidities were selected for further absorbance measurements---pH 2.0 ± 0.1 and pH 6.0 ± 0.1. As mentioned previously, because of the similarity of the nickel and copper spectra at pH 2, more information was needed to adequately differentiate between these two elements. Such information is obtainable by making an additional absorbance measurement at pH 6.

The concentrations of cobalt, nickel and copper employed in these studies were 0.87 ppm, 2.00 ppm and 2.08 ppm, respectively. The dotted portion of the nickel curve indicates a region in which this complex may precipitate. Precipitation, however, is not only a function of pH, but also depends on concentration and time. At pH 2 no precipitation was ever observed for nickel concentrations of ≤ 2 ppm. When precipitation did occur at a lower pH, the absorbance decreased rather than increased. This behavior was attributed to the formation of relatively large aggregates instead of the finely divided sols normally observed. The rapid decrease in the absorbance of the copper complex with increasing pH is undoubtedly caused by the inability of thiourea to reduce and/or maintain copper in the +1 oxidation state at these lower acidities.

ii. Reaction Rate and Stability: The pH of the aqueous ethanol (10 percent v/v) can affect both the rate and stability of complex formation. At pH 2 cobalt, nickel and copper react instantaneously with 2,3-quinoxalinedithiol to form highly colored complexes whose absorbances may be measured immediately. Although the reagent undergoes appreciable decompositon with time, especially when exposed

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to laboratory light, the net absorbances of the complexes remain constant for at least 24 hours, provided they are measured against a reagent reference solution prepared and treated in the same manner as the sample. In the analysis of mixtures at pH 6, however, the absorbance at 665 nm increases slowly. In the present work, all measurements at this pH were therefore made within 4-6 minutes after color development.

iii. <u>Interferences</u>: Only iron, platinum and palladium interfere seriously in the present method. Iron(III), however, may be extracted readily with 1:1 hexone and amyl acetate from 6-8<u>N</u> HCl. Even for relatively large amounts of iron, i.e. iron-base alloys, one or two extractions are sufficient. In the direct method, 2 ppm of either Fe(III) or Fe(II) do not interfere. The effects of other cationic and anionic interferences have been investigated in detail previously [12].

iv. <u>Spectrophotometric Equations and Their Solutions</u>: Assuming the absorbances of mixtures of the cobalt, nickel and copper complexes are additive, the following spectrophotometric equations can be obtained by measuring the absorbance of each complex separately at the designated wavelengths and acidities. The 665 nm nickel peak was selected for all subsequent measurements because it has less spectral overlap. In these equations the concentration of each element (denoted by brackets) is in parts-per-million.

At pH 2:

$$0.030 \, [Co] + 0.308 \, [Ni] + 0.310 \, [Cu] = A_s^1 \quad (665 \text{ nm})$$

$$0.081 \, [Co] + 0.290 \, [Ni] + 0.354 \, [Cu] = A_s^2 \quad (625 \text{ nm})$$

$$0.635 \, [Co] + 0.085 \, [Ni] + 0.108 \, [Cu] = A_s^3 \quad (510 \text{ nm})$$

At pH 6:

$$0.018 \, [Co] + 0.185 \, [Ni] + 0.008 \, [Cu] = A_s^4 \ (665 \ nm)$$

$$0.069 \, [Co] + 0.196 \, [Ni] + 0.009 \, [Cu] = A_s^5 \ (625 \ nm)$$

$$0.555 \, [Co] + 0.085 \, [Ni] + 0.112 \, [Cu] = A_s^6 \ (510 \ nm)$$

Since the first four equations are sufficient for differentiating between the three metal complexes, only these were used in obtaining the following least squares equations for estimating the unknown concentrations from the corresponding four A_s readings.

$$[Co] = -0.2452 \, (A_s^1) - 0.2817 \, (A_s^2) + 1.6193 \, (A_s^3) + 0.1058 \, (A_s^4)$$

$$[Ni] = +3.0917 \, (A_s^1) - 2.8384 \, (A_s^2) + 0.0836 \, (A_s^3) + 4.6692 \, (A_s^4)$$

$$[Cu] = -1.3127 \, (A_s^1) + 4.1766 \, (A_s^2) - 0.3517 \, (A_s^3) - 4.2001 \, (A_s^4)$$

In the derivation of the above constants the imprecision in the pH 6 absorbance was assumed to be twice that of the pH 2 values. A discussion of the underlying theory for this treatment of data is given in NBS Handbook 91 [13].

Using these constants, the absorbances are additive for various combinations of metal complexes as shown in table 6. Extreme combinations are listed in which the concentration of each individual element is varied by a factor of 10.

An attempt was also made to determine copper by extrapolation of the time-absorbance curves obtained from the reduction of Cu(II) to Cu(I) by the reagent and thereby reduce the final calculations to solving two equations for cobalt and nickel. With copper only present, the extrapolated absorbance, corresponding to zero time, was never zero but always equivalent to 6-9 percent of the total copper. This behavior was attributed to concentration effects initially present when the reagent was added, but could not be eliminated by rapid injection of the 2,3-quinoxaline-dithiol solution. In addition, there was some evidence that, in mixtures, cobalt could variably alter the reduction

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Table 6. Analysis of synthetic solutions of cobalt, nickel and copper.

Solution	Theory, ppm		Found[a], ppm	Diff., %
A	Co	0.87	0.87	0.0
	Ni	1.00	1.00	.0
	Cu	1.04	1.02	-1.9
B	Co	0.087	0.085	-2.3
	Ni	1.00	.97	-3.0
	Cu	1.04	1.05	+1.0
C	Co	0.087	0.085	-2.3
	Ni	.100	.098	-2.0
	Cu	1.04	1.04	0.0
D	Co	0.087	0.088	+1.2
	Ni	1.00	.99	-1.0
	Cu	0.104	.109	+4.8
E	Co	0.87	0.87	0.0
	Ni	100	.103	+3.0
	Cu	.104	.101	-2.9
F	Co	0.87	0.87	0.0
	Ni	1.00	1.00	.0
	Cu	0.104	0.106	+1.9
G	Co	0.87	0.86	-1.2
	Ni	.100	.101	+1.0
	Cu	1.04	1.05	+1.0

[a]Duplicate aliquots in good agreement.

rate and create additional uncertainty in the extrapolated values. While this approach was temporarily abandoned, there are still reasons to believe it may eventually prove feasible.

v. Analysis of NBS Standard Reference Materials: Cobalt, nickel and copper were determined by the proposed method in three NBS iron-base alloys after extracting the bulk of Fe(III) with 1:1 hexone and amyl acetate from 8N HCl. The extraction procedure is essentially the same as recommended by Claassen and Bastings [14]. An aluminum-silicon alloy was also analyzed. These results are summarized in table 7.

Table 7. Analysis of NBS Standard Reference Materials (SRM's).

NBS-SRM	Type	Present, Wt %		Found, Wt %
462	Low alloy steel	Co	0.11[a]	0.106
		Ni	0.70[a]	0.687
		Cu	0.20[a]	0.207
466	Ingot iron	Co	0.046[a]	0.046
		Ni	0.051[a]	0.051
		Cu	0.033[a]	0.033
55e	Ingot iron	Co	0.007	0.0065
		Ni	0.038	0.037
		Cu	0.065	0.062
87a	Aluminum-silicon alloy	Co	–	~0.01
		Ni	0.57	0.568
		Cu	0.30	0.301

[a]Provisional value.

vi. <u>Summary</u>: In aqueous ethanol, cobalt, nickel and copper react instantaneously with 2,3-quinoxalinedithiol at pH 2 to form strongly colored complexes exhibiting absorption maxima at 510 nm, 606 and 665 nm, and 625 nm, respectively. At pH 6 the reaction of copper can be virtually eliminated while the cobalt and nickel reactions show only small decreases in sensitivity. This combined behavior is the basis of a rapid method for the simultaneous determination of these three elements. The absorbances of the mixed complexes are additive over all possible combinations of elements in which the individual concentrations have been varied from approximately 0.1 to 1 ppm. A least squares treatment of the pertinent spectrophotometric data has provided a series of constants from which the concentration of one, or all, of the elements can be readily calculated. The procedure has been applied to the analysis of complex ferrous and aluminum alloys with excellent success.

2. Development of New Solvent Extraction Systems Designed Especially for High Sensitivity Spectrophotometry-Spectrofluorometry

The advantages offered by the non-aqueous exchange reactions of ternary ion association complexes were outlined in last year's report [1]. Basically, the new technique involves the formation of the complex, $[ML_x]^-R^+$, where R^+ initially is either a non-colored or a non-fluorescent cation. Following extraction of $[ML_x]^-R^+$, a second cation, R_1^+, is added directly to the organic phase which is capable of exchanging with the first R^+ groups. In this instance, however, R_1^+ is purposely selected to be highly colored or fluorescent, thereby producing the highly colored or fluorescent complex $[ML_x]^-R_1^+$. Unreacted R_1^+ is readily back-extracted, leaving only the dye-complex in the organic phase. In the following section the determinations of gold and uranium are described to demonstrate this technique.

a. Experimental.

i. Reagents and Apparatus: Standard solutions of uranium and gold were prepared from high purity U_3O_8 and the metal, respectively. Working solutions were prepared as needed by appropriate dilution of these standards with distilled water.

Dye solutions were prepared by dissolving 30 mg of Brilliant Green (C. I. No. 42040, HSO_4^- salt) or Rhodamine 6G (C. I. No. 45160, Cl^- salt) in 100 ml of absolute ethanol.

The following aqueous solutions were used: $1\underline{M}$ ammonium thiocyanate, $0.1\underline{M}$ sodium benzoate and $0.01\underline{M}$ tetraphenylarsonium chloride.

All other reagents were analytical grade.

Absorption spectra were obtained with a dual-beam recording spectrophotometer whereas measurements at a fixed wavelength were made with a single-beam instrument. Matched 1-cm absorption cells were used in all instances.

Fluorescence measurements were obtained with a single-beam, uncorrected spectrofluorometer.

Extractions were carried out in 60-ml separatory funnels equipped with all-Teflon fittings. A large, industrial-type centrifuge was used to hasten the separation of phases.

ii. Procedure:

Gold-thiocyanate system: The aqueous phase, containing ≤ 20 μg Au^{3+}, is made 0.02$\underline{M}$ in NH_4SCN, 0.002$\underline{M}$ in $\phi_4As^+Cl^-$ and 0.01$\underline{N}$ in HCl. Following extraction with 5.00 ml of benzene for one minute (vigorous shaking), the sample is centrifuged and the aqueous layer is discarded. Approximately 0.5 ml of alcoholic dye solution is added to the benzene fraction, mixed, and the resulting solution is back-washed with an equal volume of 0.01$\underline{N}$ HCl to remove unreacted dye. In this instance a 30-second shaking time is ample. The extract is then analyzed either spectrophotometrically or spectrofluorometrically, depending on the choice of dye. Beer's law is obeyed over the range 1-20 μg Au^{3+}. For Brilliant Green, maximum absorbance is at 640 nm; for Rhodamine 6G the excitation maximum is 525 nm and the emission maximum is 550 nm.

UO_2^{2+} – benzoate system: This is similar to the gold-thiocyanate system except that instead of being 0.02$\underline{M}$ in NH_4SCN, the aqueous phase is made 0.05$\underline{M}$ in sodium benzoate. Also, there is one other significant difference. The $[Brilliant\ Green]^+[UO_2(C_6H_5COO)_3]^-$ complex decomposes with time, but can be stabilized by the addition of acetone. At least 40 percent by volume is necessary. This composition is achieved most readily by diluting a 2.00 ml aliquot of acetone, previously added to a 5-ml volumetric flask, to the mark with the benzene extract.

b. Discussion and Results. From a 0.01$\underline{M}$ CNS^- solution at pH 2, thiocyanate ions can be quantitatively extracted into benzene as the binary complex $[R]^+[CNS]^-$ using either Brilliant Green or Rhodamine 6G as the R^+

group. Consequently, in ternary complex reactions based on metal-thiocyanate-dye systems, the above reaction can yield excessively high blank values since, in both the binary and ternary complexes, the R group is solely responsible for the color and/or fluorescence.

To investigate the possible advantages of the present approach in minimizing the $[R]^{+}[CNS]^{-}$ side reaction, the gold-thiocyanate system was selected for initial study. The absorbances obtained for 10 µg Au^{3+} were 0.902, 0.884 and 0.887 for three independent determinations. Most important, however, the corresponding blank was only 0.003. If the same amount of Brilliant Green had been added to the 0.01$\underline{M}$ CNS^{-} solution directly, the corresponding blank value would have been approximately 0.9, i.e. approximately the same as the sample signal. Thus, instead of having a sample to background ratio of 1:1, the exchange approach gives a ratio of about 300:1, in this instance.

Attempts to extract microgram amounts of UO_2^{2+} as the $[\phi_4As]^{+}[UO_2(CNS)_3]^{-}$ were not as successful as the gold experiments. Although various CNS^{-} concentrations up to 1$\underline{M}$ were investigated, the maximum net absorbance obtained for 100 µg of U^{6+} was only about 0.3 with a corresponding blank also of about 0.3 (for 1$\underline{M}$ CNS^{-}). This magnitude indicated significant amounts of CNS^{-} were being extracted as $[\phi_4As]^{+}[CNS]^{-}$ in the initial extraction and remaining in the benzene phase as $[Brilliant\ Green]^{+}[CNS]^{-}$ following the exchange reaction. Attempts were made to lower the amount of binary-bound CNS^{-} by back-extraction with various metal-ion solutions. Tests with 10 ml of Fe^{3+} (1 mg Fe^{3+}/ml) met with moderate success. In this instance the absorbance of the blank was reduced from 0.3 to 0.09, with an average deviation of ± 0.01 for four repetitive runs.

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The formation and extraction of the red ternary [Rhodamine B]+[$UO_2(C_6H_5COO$]$^-$ was first reported by Feigl [15] and later used by Andersen and Hercules [16] for the quantitative determination of trace amounts of uranium. In the latter work, complete extraction of UO_2^{2+} was obtained only when the aqueous: organic volume ratios were 1:10. In the exchange approach, however, uranium is completely extracted at aqueous: organic ratios of 2:1 and indications are that much larger ratios can be tolerated.

Although Ruzicka and Stary [17, 18, 19] have recently described the analytical applications of chelate exchange in the organic phase, apparently the present work is the first report of exchange reactions involving ternary ion association complexes. The latter technique offers a number of practical advantages in high sensitivity spectrophotometry and spectrofluorometry. First and foremost it opens an entirely new area for formation and extraction of ternary complexes in which relatively basic intermediate ligands (L groups) can now be used. Heretofore, such ligands could not be employed in the normal extraction mode because of the excessively high blanks obtained. In the present procedure these blanks can be kept relatively low irrespective of the intermediate ligand. This capability to further minimize the reagent blank could have considerable impact in fluorescence analysis since, with the single beam instruments normally employed, the blank signal is not subtracted instrumentally. A second and perhaps equally important advantage is that the forward and the back extractions can be carried out in weakly acidic (in contrast to the strongly acidic solutions previously required)

solutions where gross masking agents can be effectively employed. Finally, dye purity and light fastness appear to cause considerably fewer problems in the proposed technique and much smaller quantities of dye are needed.

3. Spectrophotometric Determination of Vanadium and Iron with β-Isopropyltropolone

A new spectrophotometric procedure was developed for the determination of vanadium and the simultaneous determination of vanadium and iron with β-isopropyl-tropolone (IPT). IPT, also know as β-thujaplacin, was first described by Japanese and Chinese workers [20, 21, 22]. The formation of stable complexes by various metals with this reagent has been reported by numerous authors [23, 24, 25, 26, 27, 28, 29, 30]. Dyrssen [23, 24] has studied extensively the extraction equilibria of twenty-seven metal ions in IPT-chloroform system. However, vanadium was not included in that study. He reported that iron-IPT complex formation is very slow, requiring 1 to 4 days to reach equilibrium. In our initial studies, it was observed that vanadium gives a color reaction with IPT and that the rate of formation of the complex is very similar to the Fe-IPT system. However, the procedure was modified to include the addition of an alcoholic solution of IPT to the aqueous medium. Under these conditions, equilibrium was attained rapidly (within 30 minutes). This led to the application of this procedure to the determination of low concentrations of vanadium in steels.

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Vanadium which is an important addition to certain types of steels, high temperature alloys and reactor materials, is generally determined in higher concentrations by titrimetric methods and by spectrophotometry in low or trace quantities. The literature on this subject is ably summarized by Kolthoff and Elving [30]. Its separation and spectrophotometric determination are discussed by Sandell [31]. Currently, hydroxamic acid derivatives have been reported as reagents for the determination of vanadium [32, 33]. A general summary of these derivatives has been described by Bass and Yoe [34]. Most of the procedures lack specificity. Recently, Kakita and Goto [35] reported a more selective procedure using benzophenylhydroxamic acid but indicate some problems with the instability of the complex.

In the present studies, the IPT-complex of vanadium forms a colored chelate which can be extracted from strong acid solutions and, thereby, eliminates a large number of interfering ions. However, in steel analyses, a mercury cathode separation is necessary for the removal of high concentrations of iron and chromium. Complete separation from iron is not essential, since a two-wavelength measurement provides a precise correction. The high molar absorptivity of 11,000, liter mole^{-1} cm^{-1} for vanadium-IPT complex recommends it for the trace determination of this element. NBS Standard Reference Materials of ferrous metals containing traces of vanadium have been used to establish accuracy of the method.

a. Experimental

i. Apparatus: Spectrophotometric measurements were made with a single beam spectrophotometer using 1.00 cm cells. Spectra scanning was carried out with a high precision recording spectrophotometer. The absorption cells were thermostated at constant temperature.

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The spectrophotometer wavelength scale was checked with a holmium glass standard. Measurements of pH were made with an expanded scale pH meter.

ii. Reagents:

Standard Vanadium Solution: Dissolve 0.2295g (V-100 µg/ml of ammonium metavanadate in water and dilute to 1000 ml. Aliquots of this solution were diluted to provide a solution containing 10 µg V/ml.

β-isopropyltropolone (IPT), from a commercial source, was recrystallized twice from petroleum ether. The purity was verified by determining the M.P. (51-52°) and by taking thin layer chromatograms on silica-impregnated plates using butanol, water and ethanol in the ratio of (5:11:4) as the developer. A solution was prepared containing 1.642 gms $(1 \times 10^{-2}\underline{M})$ of IPT in alcohol. The other reagents were reagent grade.

b. Procedures

i. Absorption Spectra of the Reagent: Spectra were taken of $2 \times 10^{-2}\underline{M}$ IPT in chloroform, carbon tetrachloride, benzene and cyclohexane.

ii. Determination of the Absorption Spectra of the Complexes of V(V), V(IV), Fe(III) and Fe(II) with IPT: Transfer an aliquot containing 20 µg of each of the two elements to a 50 ml separatory funnel. Add 0.5 ml of $HClO_4$ and dilute to 5 ml. Extract with 5 ml of IPT/chloroform by shaking vigorously for 2 minutes. Allow the phases to separate and, after 30 minutes, record the spectra of the organic extract.

iii. Rate of Formation of the Vanadium/IPT as a Function of pH: Transfer a 2.0 ml aliquot of the vanadium solution (1 ml = 10 µg) to 50 ml separatory funnel. Adjust the pH of the solutions to cover the range 0 to 7. The solutions were also adjusted to 1 to $6\underline{M}$ in $HClO_4$. Extractions were carried out with 5 ml of IPT solution in $CHCl_3$ and absorbances were taken at 470 nm.

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iv. Effect of Ionic Strength: Transfer 20 µg of vanadium to a separatory funnel and adjust the acidity to 1M in HClO$_4$. The ionic strength was varied from 0.8M to 6M by the addition of NaClO$_4$. Extraction was carried out as above.

v. Effect of Temperature on the Formation of the Vanadium-IPT Complex: To study the effect of temperature, absorbances of the V(V)-IPT extracts were measured at 15°, 25°, 35°, 45°C as a function of time.

vi. Study of the Rate of Extraction of Metal-IPT as Function of Solvent Ethanol: Transfer 20 µg each of vanadium (V) and iron (III) to two separatory funnels. Add 0.5 ml HClO$_4$ and dilute to 5 ml. After adding 2 ml of alcoholic 1x10^{-2}M IPT to the aqueous phase, extract with 5 ml of CHCl$_3$ by shaking for 2 minutes. Measure the absorbances as a function of time.

vii. Determination of V-IPT Species: To 1.0 ml of 1x10^{-3}M vanadium, varying amounts of alcoholic 1x10^{-2}M IPT were added. The acidity was maintained at 1M HClO$_4$. Extract with 5 ml of CHCl$_3$ and measure absorbances at 470 nm.

viii. Calibration and Additive Properties of V(V) and Fe(III): 20-50 µg of vanadium were taken in 1M HClO$_4$, 2 ml of alcoholic 1x10^{-1}M IPT were added and extractions were carried out with 5 ml of CHCl$_3$. Absorbances were measured at the following wavelengths: 470, 540 and 580 nm. Similar sets of experiments were carried out with 20-50 µg of iron as well as with mixtures of vanadium and iron.

ix. Procedure for Steel Analysis: One gram of steel was dissolved in 10 ml of HNO$_3$(3:5). After the reaction subsided, 5 ml of HClO$_4$ was added. The solution was fumed twice to remove the HNO$_3$. Silica was removed by filtration and washed thoroughly with hot dilute HClO$_4$ (1:100). The solution was diluted to 200 ml and electrolyzed with the mercury cathode, using a current of 5A, until the solution gave a negative test for iron. The

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solution was transferred to a beaker, 10 ml $HClO_4$ added, fumed, and then 10 ml HCl was added drop by drop to volatilize chromium as CrO_2Cl_2. After dilution to volume, an aliquot corresponding to 20 µg of vanadium was transferred to a separatory funnel and the acidity was adjusted to $1\underline{M}$ in $HClO_4$. After addition of 2 ml of alcoholic $1 \times 10^{-1}\underline{M}$ IPT, extraction was carried out with 5 ml of $CHCl_3$. After 30 minutes, absorbances were measured at 470 and 540 nm. Vanadium was calculated from a calibration curve. Corrections may be made for residual iron.

       c. <u>Results and Discussion</u>. Dyrssen [23] has pointed out that the Fe-IPT complex takes 1-4 days to reach equilibrium. In the case of vanadium it was found that the absorbance increases with time, as shown in table 8. Even

Table 8. Rate of formation of the colored complex V(V)-IPT in chloroform.

(Vanadium: 20 µg)

Time, hr	Absorbance
1/2	0.402
1	.435
3	.461
25	.494

after 24 hours, a constant value could not be attained. Raising the temperature had little effect. On addition of an alcoholic IPT solution to the aqueous phase, the equilibrium was attained within 30 minutes, both for iron and for vanadium. The spectrum of the iron-IPT complex compares with that of the 1:3 iron complex reported by Dyrssen. In the study of the vanadium complex by the mole ratio procedure, a 1:4 complex was established.

    The spectral characteristics of the reagent do not vary when taken in different solvents such as $CHCl_3$, CCl_4, C_6H_6 and cyclohexane. Finally, chloroform was selected as

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the most suitable solvent since it forms a lower layer that
can be easily removed.

Dyrssen has pointed out that IPT has a high Kd value
(log Kd = 3.37). A high value of 10.41 for pKd + log Kd
favors the distribution ratio of IPT even in strongly acid
solutions. Hence extractions with this reagent were made
at acidities as high as $6\underline{M}$ $HClO_4$. Spectra show that the
same complex is formed at all acidities. Absorbance of
V(V)-IPT is constant between $0-1.75\underline{M}$ and $4\underline{M}-6\underline{M}$. In the
intermediate range of $2\underline{M}-4\underline{M}$, there is an increase in
absorbance, which cannot be explained. Acidity was maintained
at about $1\underline{M}$ in this work. Also, the ionic strength has no
effect on absorbance of the V(V)-IPT complex.

The spectra of the V(V)-IPT complex shows an absorbance
region around 470 nm as shown in figure 10. For the V(IV)-IPT

O. Menis and C. S. P. Iyer
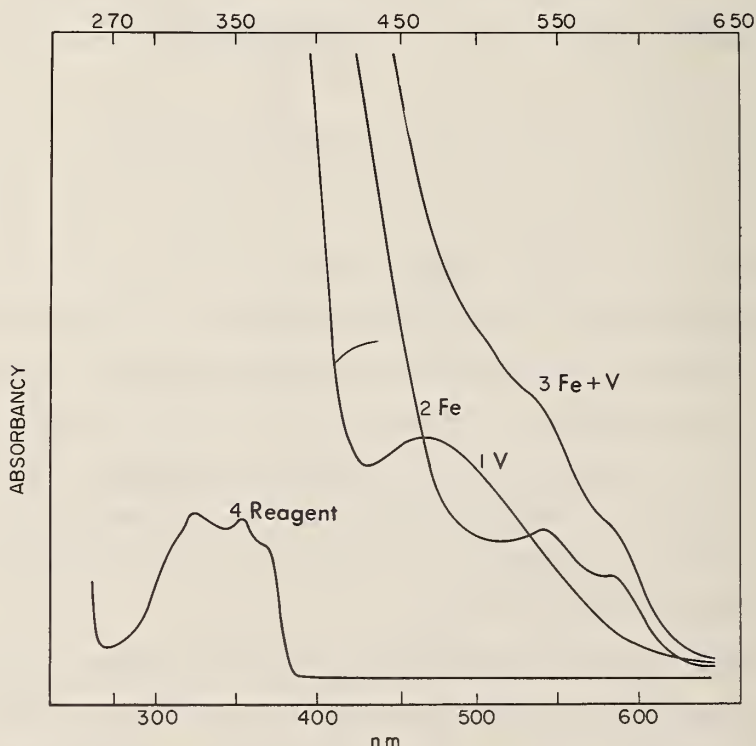
Figure 10.   Absorbance spectrum of the vanadium (V) -
β-isopropyltropolone complex.

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complex there is a continuous decrease in absorbance from 410 nm to longer wavelengths.

In the case of the Fe(III)-IPT system, the spectra of the complex shows two bands in the visible region, one at 540 nm and another at 580 nm as shown in figure 10. In the case of the Fe(II)-IPT systems, there is a continuous decrease in absorbance from 410 nm. This is similar to the V(IV)-IPT complex.

Beer's law is obeyed in the range of 10–50 µg vanadium or iron. For solutions containing both iron and vanadium, the absorbances were additive, table 9.

Table 9. Additive properties of vanadium and iron IPT complexes.

Ion	Conc µg/ 5 ml	A_{470}	A_{540}	A at 470 nm Found	Calc	Diff	A at 540 nm Found	Calc	Diff
V(V)	10	0.177	0.095						
Fe(III)	10	.177	.103						
V(V) and Fe(III)				0.354	0.354	0.00	0.200	0.198	0.002
V(V)	20	.354	.188						
Fe(III)	20	.349	.209						
				.712	.703	.009	.412	.397	.015
	25	.443	.234						
	25	.443	.260						
				.885	.886	.001	.503	.494	.009

To evaluate the method, two SRMs, NBS 464 and 8i, have thus far been tested by this procedure. In ferrous materials, a prior separation with the mercury cathode is required. Chromium, which does not electrolyze completely, should be volatilized as CrO_2Cl_2. Preliminary values obtained for these two standards were 0.275 and 0.0125 percent respectively as compared with certified values of 0.295 and 0.012 percent. The lower value for Standard 464 as also noted from the change of the spectral curve may be due to incomplete separation of chromyl chloride.

Further studies are under way with other materials, in addition to the efforts to resolve the lower values obtained for SRM-NBS 464.

4. <u>Direct Spectrofluorometric Determination of Rare Earth Elements in Synthetic Glasses</u>

The advent of the laser is responsible for renewed interest in the luminescence of rare earth elements in glasses. Likewise, the increasing use of inorganic glasses as matrices for trapped radicals and ions of unusual valences necessitates the development of non-destructive analytical methods for the determination of trace constituents. This interest is extended to the determination of rare earth elements in a proposed series of SRM simulated lunar glasses containing 61 elements in trace quantities ranging from 0.02 ppm to 500 ppm. The determination of europium and gadolinium in sodium borate glasses carried out under a cooperative program at the Hebrew University, Jerusalem, Israel is described briefly and will be published in detail elsewhere [36].

a. <u>Preparation of the Borate Glasses</u>. Dry rare earth chloride, borax and boric acid (wt. ratio 2:1) were placed in plastic vials containing glass balls and mixed for 10 minutes in an electric vibrator. Although these mixtures melted at temperatures below 1000°C, clear transparent samples could be obtained only after heating at 1100°C for at least 15 minutes. All melts were made in platinum crucibles. Drops of the hot melt were allowed to fall directly onto a clean white glazed ceramic surface. The drop was placed within a ring 1 mm thick and then pressed with a second ceramic tile to obtain glasses of uniform (1 mm) thickness. The glasses were inserted into a glass holder containing a 12 mm diameter opening and their excitation and fluorescence spectra were measured at room temperature.

b.   Placement of the Solid Sample in the Light Beam.
To maximize the net fluorescence signal, the proper angular
placement of the glass disc in the exciting light beam must
be established (figure 11).   Based on measurements of gross
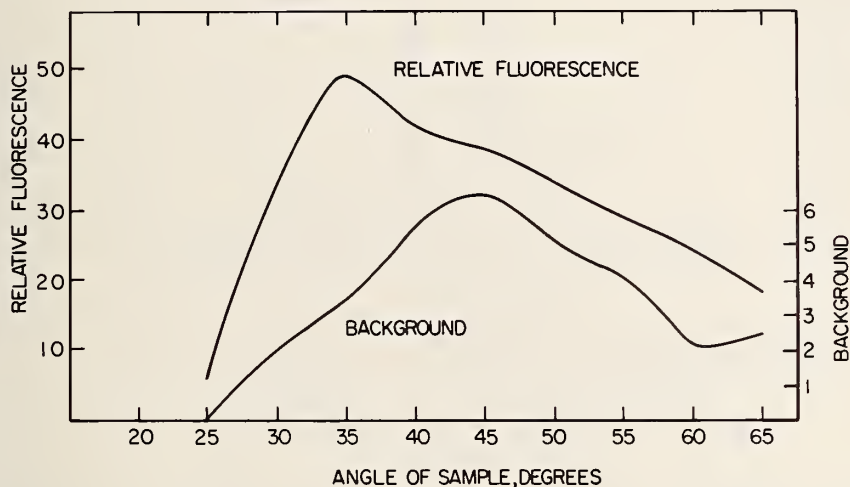
Figure 11.   Optimum angular placement of glass sample
for in situ fluorescence analysis.

fluorescence and of scattered light at various angles (all
angular values refer to the angle between the perpendicular
to the exciting beam and the plane of the sample) an optimum
angle of 35° was established for sample positioning.

c.   Discussion and Results.   The excitation spectrum
of Eu(III) (fluorescence at 617 nm) is shown in figure 12
and consists of a number of sharp lines at 320, 365, 380,
395, 465, 535 and 585 nm and a broad band at 230-290 nm
with a maximum at 260-280 nm.   The strongest peak is at
395 nm.   Figures 13 and 14 show emission spectra excited

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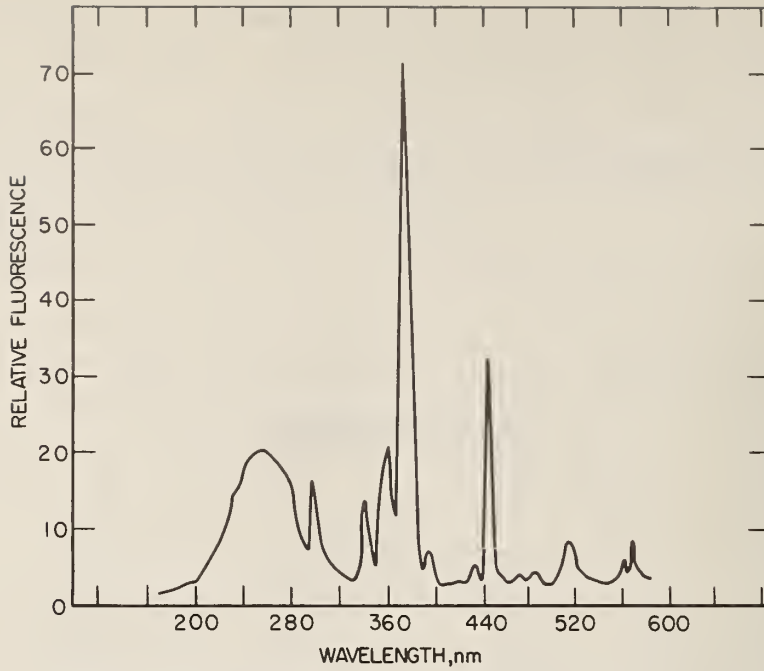
Figure 12. Excitation spectrum of europium (III);
fluorescence measured at 617 nm.
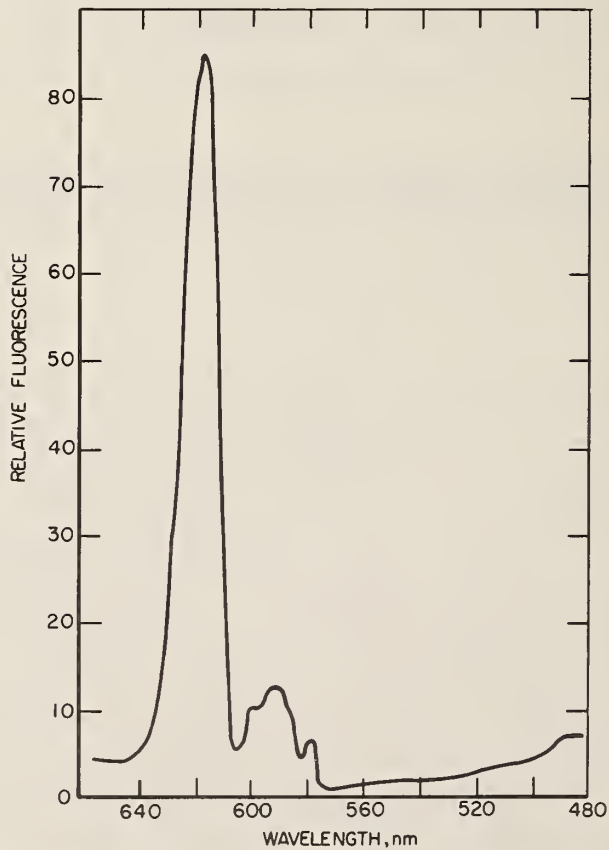
Figure 13. Fluorescence spectrum of europium (III);
excitation at 395 nm with xenon source.

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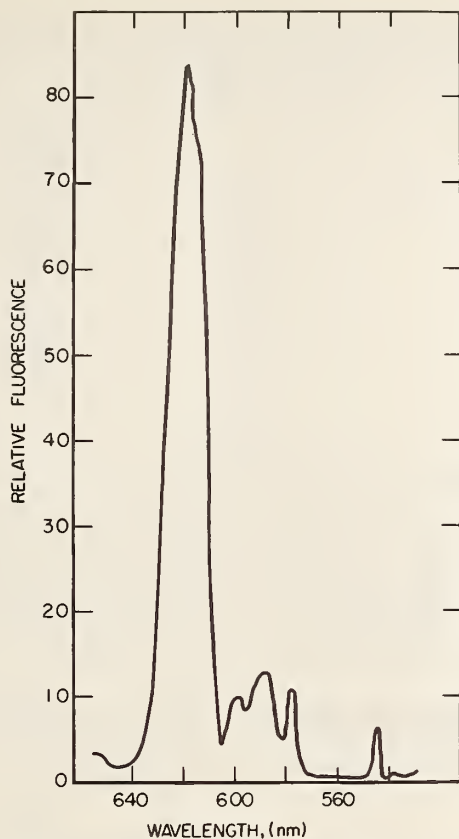
Figure 14. Fluorescence spectrum of europium(III);
255 nm **excitation** with mercury arc.

at 395 nm (xenon arc) and 255 nm (mercury arc), respectively.
The 365 nm excitation gave a similar spectrum, but with
lower intensities. The fluorescence bands observed are
similar at all excitations. Peaks are located at 580, 595,
600, 617 and 655 nm with the highest intensity at 617 nm.
The 545 peak appearing at 255 nm excitation (figure 14) is
due to impurity in the borax.

The fluorescence dependence on concentration was
measured for all fluorescence bands. The most linear
dependence was observed for the 617 nm band. The results
are given for 255 nm excitation. A two- to three-fold
decrease in fluorescence was observed when excitation was
carried out at either 365 or 395 nm.

Table 10. Relative fluorescence, R/F, of various concentrations of europium in borate glass; excitation at 255 nm.

Conc, ppm	R/F
10	27
100	380
2000	1140
4000	1920
8000	2470
10000	3050
13000	3600

For the determination of gadolinium in borate glass, excitation was at 273 nm and the emission was measured at 312 nm. Linear dependence of fluorescence on concentration was observed over the range 10 to 20,000 ppm (table 11).

Table 11. Relative fluorescence, R/F, of gadolinium in borate glass.

Conc, ppm	R/F
10	5
50	24
100	48
500	250
1000	500
2000	1200
4000	2250
5000	2600
6500	3350
8000	4500
10000	4800
13000	6400
20000	10000

To test the effect of the presence of a second rare earth, the fluorescence of gadolinium was measured in a series of glasses containing equal concentrations of samarium. The results are presented in table 12.

Table 12. Relative fluorescence, R/F, of gadolinium as a function of concentration in glass containing equal amounts of Gd(III) and Sm(III).

Conc Gd(III)+Sm(III) ppm	R/F	Ratio $\dfrac{\text{R/F [Gd(III)]}}{\text{R/F [Gd(III)+Sm(III)]}}$
500	180	1.38
1000	390	1.28
2000	720	1.66
4000	1440	1.56
5000	1920	1.36
6500	1980	1.68
10000	2000	2.4
20000	2000	10.0

At concentrations up to 6900 ppm the gadolinium fluorescence decreased by a factor of about one-third and the dependence was linear. At higher concentrations, quenching of fluorescence was observed. It is therefore assumed that a non-radiant energy transfer takes place from gadolinium to samarium.

C. Analysis of Standard Reference Materials (SRM's) and Related Samples

        Throughout the year the spectrophotometry-spectrofluorometry competence has determined numerous elements in a variety of Standard Reference Materials. Although there are many instances where well established procedures can be used, there are numerous occasions where additional development work is necessary before the desired accuracy can be obtained.

        1. Precise and Accurate Determination of Cobalt in Aluminum Neutron Flux Wire (NBS-SRM 953)

        Exact knowledge of the flux and homogeneity of the neutron beam are necessary for absolute counting techniques to be meaningful. One approach to monitoring this beam is through the use of appropriate standards containing neutron-sensitive elements. Cobalt-doped aluminum is such a material and has been proposed as a standard monitor of neutron flux.

For the spectrophotometric determination of 0.1 percent cobalt in aluminum wire, two variations of the 2,3-quinoxalinedithiol method previously described were used. The first was a differential procedure in which the cobalt complex was formed and measured at pH 3. Under these conditions, however, the aluminum matrix hydrolyzed and a subsequent filtration step was necessary. Because of the spread of the differential results and the question of the homogeneity of the sample, some additional work seemed necessary. Further checking with the Reactor Group indicated that the most practical sample size was about 1 cm, i.e. about 5 mg.

The most obvious improvement that could be made to the differential method was to eliminate the hydrolysis-filtration of the aluminum matrix. Initial efforts involved the investigation of various masking agents (fluoride, citrate, tartrate, etc.), none of which proved entirely satisfactory. Next, attention was directed to carrying out the complexation reactions at higher acidities and this modification proved to be the one needed. However, since 5-mg samples had been established as a practical sample size, the differential approach could no longer readily be used (because of sample-volume restrictions) and, conventional spectrophotometry was reconsidered. The results obtained on 15 sections of wire by differential spectrophotometry at pH 3 and conventional spectrophotometry in 1.2$\underline{N}$ HCl are shown in table 13.

In method II, the within-set agreement is better than the between-sets agreement. However, all samples within a set were run as a group and against a common reference solution. With a final volume of 10 ml, it must be realized that variations as small as ± 0.05 ml (1 drop) can create biases of ± 0.5 percent, 10-μg weighing errors, biases of ± 0.2 percent, etc. The fact that the within-set precision

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Table 13. Spectrophotometric determination of cobalt in aluminum neutron flux wire with 2,3-quinoxaline-dithiol.

Method I (differential spectrophotometry); sample size 50-60 mg (∿12 cm)

Sample	Wt % Co		Sample	Wt % Co	
	Set A	Set B		Set A	Set B
1	0.1130	0.1170	9	0.1147	0.1157
2	0.1121	0.1147	10	0.1146	0.1152
3	0.1121	0.1181	11	0.1162	0.1154
4	0.1130	0.1145	12	0.1160	0.1160
5	0.1141	0.1153	13	0.1139	0.1167
6	0.1120	0.1163	14	0.1177	0.1151
7	0.1136	0.1167	15	0.1092	0.1111
8	0.1144	0.1181			

Mean = 0.1151%[a]
S.D. = 0.0017
Rel S.D. = 1.5%

Method II (conventional spectrophotometry); sample size 4.2-5.5 mg (∿1 cm)

Set 1		Set 2		Set 3	
Sample	Wt % Co	Sample	Wt % Co	Sample	Wt % Co
1-1	0.1150	1-2	0.1163	2-1	0.1159
4-1	0.1162	4-2	0.1158	3-1	0.1145
7-1	0.1142	7-2	0.1170	5-1	0.1147
10-1	0.1145	10-2	0.1169	8-1	0.1143
12-1	0.1154	12-2	0.1168	11-1	0.1149
15-1	0.1084	15-2	0.1084	14-1	0.1146

Set 4		Set 5	
Sample	Wt % Co	Sample	Wt % Co
2-2	0.1177	6-1	0.1152
3-2	0.1169	6-2	0.1158
5-2	0.1160	9-1	0.1151
8-2	0.1172	9-2	0.1156
11-2	0.1154	13-1	0.1147
14-2	0.1157	13-2	0.1146

Mean = 0.1156%[a]
S.D. = 0.0011
Rel. S.D. = 1%

[a]Sample 15 not included in means.

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is relatively high, e.g. set 3, the homogeneity of the wire could be 0.1 percent or better at the 5-mg level.

The accuracy of the above method is strengthened by the close agreement between it and a spectrophotometric titration procedure [37], both of which were applied to the determination of 1 percent cobalt in cobalt-aluminum wire [1].

2. <u>Simultaneous and Differential Spectrophotometric Determinations of Molybdenum and Tungsten in Mo-W Compact with Tiron (4,5-dihydroxy-m-benzene disulfonic acid)</u>

The history and preparation of this microprobe standard has been discussed previously [1]. Because of some disagreement in the earlier results, between spectrophotometric thiocyanate procedure and activation analysis, additional results were needed. A brief review of the literature indicated that molybdenum and possibly tungsten, could be determined spectrophotometrically with Tiron.

a. <u>Preparation of Samples</u>. Successively wash each sample core with carbon tetrachloride, acetone, ethanol and water. Dry <u>in vacuo</u> and weigh. Etch the weighed samples with a freshly prepared, equivolume mixture of 1:2 aqueous nitric acid and 1:2 aqueous sulfuric acid (30 ml) for 15 minutes. Remove and retain the supernatant liquid and washings. Dry and reweigh the samples to determine any weight losses (no significant weight loss was observed for any of the samples analyzed).

b. <u>Dissolution</u>.

i. Solvent = 1:2:3 (v/v) $HClO_4/H_3PO_4/H_2O$: Treat 5 mg (100 mg) of sample with 5 ml (10 ml) of the acid mixture and heat gently to fuming. Add 1 ml (2 ml) concentrated perchloric acid and continue to fume until dissolution is complete (∿10 hours). Add 0.5 ml (1 ml) concentrated sulfuric acid and continue to fume for 2 hours to ensure complete oxidation. If precipitation occurs at this stage, redissolve with a few drops of concentrated orthophosphoric

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acid. Dilute to 50 ml (100 ml) with distilled water and
maintain at a temperature of 90°C for 30 minutes. Cool,
adjust the pH to 7.0 by the cautious addition of solid
sodium hydroxide and dilute to 100 ml (500 ml) with distilled
water. Prepare standard solutions by the sample procedure,
using high purity molybdenum and high purity tungsten.

ii. Solvent = HF/HNO_3: Treat 5 mg (100 mg) of
the sample with 5 ml concentrated hydrofluoric acid and add
concentrated nitric acid dropwise until dissolution is
complete. Add 0.5 ml concentrated sulfuric acid and reduce
the volume to 3 ml on a steam bath. Dilute to 50 ml with
distilled water, add phosphate buffer solution, pH = 7.0
(5 ml) and adjust the pH to 7.0 with solid sodium hydroxide
solution. Dilute to 100 ml (500 ml) with distilled water.
Prepare standards in a similar manner, using high purity
molybdenum and tungsten metals.

    c. Analysis

      i. Single-Wavelength Procedure: Take aliquots
containing approximately 1 mg of sample for analysis. Add
phosphate buffer solution, pH = 7.0 (5 ml), and 10 percent
(w/v Tiron solution (10 ml) and dilute to 50 ml with
distilled water. Measure the absorbance (λ = 2 cm) at
380 nm of the solution against a reference solution con-
taining reagent and buffer solution and rendered $3.6 \times 10^{-5} \underline{M}$
with respect to molybdenum (VI) and $7.0 \times 10^{-5} \underline{M}$ with respect
to tungsten (VI). Prepare a fresh reference solution for
each aliquot analyzed.

      ii. Dual-Wavelength Procedure: Proceed as
described under the single-wavelength procedure, but
measure the absorbance at 380 nm (λ = 2 cm) and 475 nm
(λ = 10 cm) against a reference solution containing reagent
and buffer, and approximately the same amount of molybdenum
(VI) and tungsten (VI) as present in the sample. Prepare a
fresh reference solution for each of the sample solutions
examined.   47

d. <u>Results and Discussion</u>. The results obtained
by the two Tiron procedures are shown in table 14. The

Table 14. Simultaneous differential spectrophotometric
analysis of Mo-W compact.

Sample	No.[c]	Aliq./ sample	Solvent	% Mo (±S.D.)[d]	% W (±S.D.)[d]
cores[a]	4	4	$HClO_4/H_3PO_4$	23.90±0.04[e]	76.10±0.04
cores[a]	4	4	$HClO_4/H_3PO_4$	23.76±0.17[f]	73.68±0.26
cores[a]	4	3	HF/HNO_3	23.61±0.09[f]	75.82±0.81
powder[b]	3	4	$HClO_4/H_3PO_4$	21.59±0.02[f]	78.51±0.11
powder[b]	3	4	HF/HNO_3	21.59±0.04[f]	78.5 ±1.4

[a]Five mg cores from center of compact.

[b]Powder Mo-W used in preparation of compact.

[c]Number of independent samples

[d]Standard deviations are per sample deviations based on the
statistical analysis of the sample/aliquot array of results.

[e]One wavelength measurement.

[f]Two wavelength measurements.

analysis of the Mo-W powder, reported in a previous report
[1], was undertaken to check the validity of the new method.
The results obtained compare favorably with the gravimetric
values but are more precise since no preparation of synthetics
was necessary.

In the single-wavelength procedure, both the Mo- and
W-Tiron complexes absorb at 380 nm, but with very different
extinction coefficients. However, it was necessary to make
the assumption that the sample was a binary alloy, since the
presence of a third component, even in relatively small
quantities, could considerably affect both the Mo and W
results. At 475 nm, only the Mo-complex absorbs. The
measurement at this wavelength was only possible after
repeated recrystallization of the reagent.

Alternative dissolution procedures were employed to eliminate possible systematic errors. The 5-mg drillings were less readily soluble in the $HClO_4/H_3PO_4$ mixture than the Mo-W powder. With HF/HNO_3 as the solvent, both forms of the sample could be dissolved in minutes.

The deviations per sample in the analysis of the drillings are greater than expected. Since the weight of the samples can be determined to ± 3 μg, the possibility of inhomogeneity or an inadequate pre-etching procedure should be considered.

3. Spectrofluorometric Determination of Air-Borne Beryllium

A relatively simple spectrofluorometric procedure has been developed for the quantitative determination of air-borne beryllium. Following collection of the sample on a millipore filter, it is dry-ashed at approximately 100°C in an oxygen atmosphere and the residue is treated sequentially with concentrated $HClO_4$ and distilled water and then warmed on a hot plate. The resulting solutions are examined spectrofluorometrically (excitation wavelength-373 nm; emission wavelength-450 nm) for beryllium, using 2-hydroxy-3-naphthaic acid as the chelating agent. Potential interferences are eliminated by addition of a calcium diaminocyclohexanetetraacetate masking agent [1].

This procedure has been applied recently to the determination of beryllium in fourteen samples of air. Detection limits of 0.005 microgram were readily obtainable on sample volumes of 100 ml (0.05 parts-per-billion). Subsequent reduction in the working volumes should permit lowering this limit to at least another order of magnitude.

4. Spectrophotometric Determination of Iron and Copper in High Purity Gold

As a part of the Division's continuing effort to issue extremely high purity metals as standards for use in

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solids mass spectrometry, activation analysis, metrology, etc., it was necessary to determine iron and copper in high purity gold. However, before any spectrophotometric method could be applied, it was necessary that these two elements be separated from the matrix. Also, it was apparent that the gold could be more easily separated from the iron and copper than they could be removed from the gold. However, blanks conceivably could be larger in the former case, since larger amounts of reagents would be required.

Eventually, two approaches were employed to remove the gold. One involved precipitation with SO_2, the other a solvent extraction procedure (removal of macro amounts of gold with ethyl acetate and residual amounts with Brilliant Green). In the former, all operations (precipitation, neutralization and color development) were conducted in a closed system employing the apparatus shown in figure 15.

Figure 15.   Apparatus for dissolution extraction of iron in high purity gold.

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Each gold sample was dissolved and precipitated 3 times to obtain authentic blank (initially, iron-free and copper-free gold) and spiked sample values. In the latter procedure, multiple extractions were readily performed in the same separatory funnel, thus minimizing the risk of contamination.

Irrespective of the procedure used to separate gold, the procedures for the determination of iron were identical, i.e. extraction of the Fe(II) bathophenanthroline complex into n-hexyl alcohol followed by spectrophotometric measurement of the red complex at 533 nm.

In the determination of copper, the same extraction procedure employed for iron was used to separate the gold. Copper was subsequently determined spectrophotometrically by equilibrating the sample solution with an 0.01 percent solution of zinc dibenzyldithiocarbamate in carbon tetrachloride. Under these conditions Cu(II) displaces Zn(II) and gives a yellow complex whose absorption maximum is at 435 nm.

The results obtained are shown in table 15. Sample weights ranged from 0.8 to 1.1g; blank values averaged about one-half the total signal.

Table 15. Spectrophotometric determination of iron and copper in high purity gold.

	Iron, ppm		Copper, ppm	
	Precipitation Procedure	Solvent Extraction		
Wire	0.45	0.36	Wire	0.13
	.47	.44		.12
	.46			.14
Rod	.17		Rod	.13
	.18			

5. Service Analyses

As a supporting service for the various Divisions at NBS as well as other Government agencies, the following analyses were performed during the past year (table 16).

Table 16. Spectrophotometric-spectrofluorometric service analyses.

Element	Matrix	Method	Level
Pd	Epoxy plates	spectrophotometry	1-5 µg
Au	Nickel plating solutions	"	4-6 µg
Sb	Neodymium glass	"	0.60%
Fe	"	"	10-15 ppm
Nd	"	differential spectrophotometry	4-9%
Fe	$MnBe_8$ and $CrBe_8$	spectrophotometry	0.4-0.6%
Co	$MnBe_8$	"	0.15%
Ni	Metallic oxides	"	1.6-4.5%
B	Filter residues	spectrofluorometry	0.01 µg
Fe^{3+}	Ferrous dosimeters	spectrophotometry	1-10 ppm

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3. DIFFERENTIAL THERMAL ANALYSIS

The need for Standard Reference Materials (SRM) for calibration of thermal analysis instruments and procedures, was fully described in NBS Technical Note 454 [1]. This study led to a fivefold increase in the precision in the measurement of transition temperatures for two proposed SRMs, SiO_2 and KNO_3. It involved modification to a commercial instrument, and provision for accurate calibration and evaluation of the homogeneity of the two materials. Also several SRM freezing point standards were tested. In addition, contributions were made in organizing outside scientific groups to provide national leadership in this field. This involved participation, as a charter member of a steering committee, in creating an ASTM task group and formation of a National Society on Thermal Analysis.

A. Modification of Instrument

The commercial instrument initially used in this study was limited in its capability to provide precise and accurate values. This instrument was equipped with thermocouple wires whose cold junction was dependent on the ambient temperature. Thus the temperature measurements would vary several degrees during the day. The hot junction was also located outside the sample compartment. The high programming rate together with a low sensitive recorder were limiting factors of the initial apparatus.

The following modifications were made to ensure its use as a research tool, especially to determine more accurately the transition temperatures of selected compounds for use as standard reference materials:

1. Simultaneous use of the thermocouple for both sample temperature readings and delta-T readings.

2. Insertion of ice bath junctions in all temperature thermocouple circuits for voltage measurements with respect to 0°C.

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3. Simultaneous use of a strip chart recorder for delta T vs time plots. The areas of these thermograms correspond more, in theory, to heats of transitions than do the areas delta T vs temperature plots. Simultaneously, an X-Y recorder was used for convenience for delta T vs temperature plots.

4. Slower scan rates were provided for minimizing gradients between the sample thermocouple and the sample itself, and for approximating adiabatic conditions.

5. Addition of a stable bucking voltage source was provided for use with a sensitive setting of the temperature vs time recorder. This increased the precision of measurement of the sample thermocouple voltage by a factor of ten, by permitting the scanning of 5 millivolts from the thermocouple in ten one-half millivolt recorder spans.

6. Provision for temperature calibration of the apparatus:

a. Replacement of sample thermocouple with calibrated wire.

b. Provision for rapid comparison of calibrated thermocouple with standard voltage source.

c. Construction of non-metallic sample holders for use with metal freezing point standards.

B. Experimental

1. Modification of Commercial DTA - Thermocouple Wiring

The commercial unit was provided with various alloy thermocouples together with a foam insulated box containing cold junction connections for the temperature thermocouple. However, regardless of the intermetallic junctions involved, the voltage of the hot thermocouple was always measured with reference to a cold junction or junctions completing the circuit. The temperature of this thermocouple was thus read with respect to ambient temperature together with the temperatures in the apparatus at the junctions of the alloys. Also, the hot junction supposedly measuring the sample

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temperature was not inside the sample cup (this one was used for the differential measurement only) but was actually the furnace control thermocouple.

The following changes were made:

a. Changes in Thermocouple Arrangement

(1) All thermocouple wiring was removed and replaced with platinum or platinum-10 percent rhodium wires leading to an ice bath (see figure 16). From the ice bath, all copper leads went to the recorders and amplifiers.

(2) The furnace control thermocouple previously used for both the temperature measurement and furnace control was now limited to furnace control. This provided the required flexibility for its optimum placement and avoided interference from the programmer electronics.

(3) The thermocouple in the sample cup was used for temperature measurement (with respect to the ice bath) and differential temperature measurement (with respect to the reference thermocouple). (See figure 16.) This involved having the thermocouples provide a signal for a dc amplifier and four recorder channels simultaneously. Using parallel recorder inputs, as was done here, is not common practice. However, all units were high quality potentiometric devices and did not interfere with one another.

(4) Screw-type terminal strips were provided for direct connections of the thermocouple leads to the ice bath leads of the same metal. Tests with a hot screwdriver showed a slight potential shift due to the small dissimilarities of the Pt and Pt/Rh thermocouples. These shifts, as expected, were small enough to be negligible to ambient temperatures. Since then, the terminals have been replaced with directly soldered connections.

All wiring was external with hookup wire for easy changes. Hum and chatter were suppressed by shielding with wire braid and copper screening and shunting the leads with 0.1 mfd capacitors at the recorder terminals.

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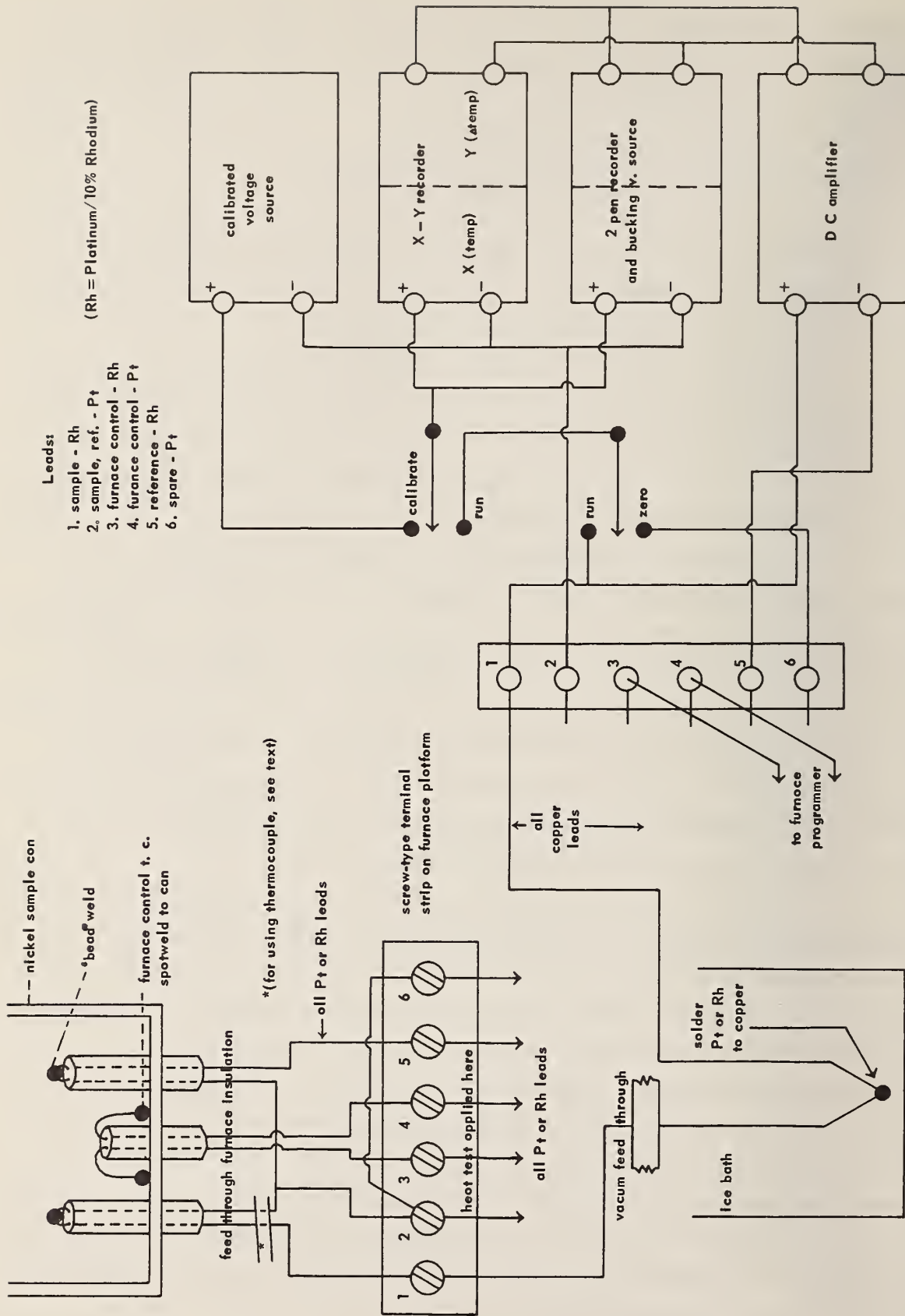
Figure 16. Thermocouple wiring.

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b. <u>Recorder Changes.</u> The two-pen recorder was used to obtain a plot of temperature and differential temperature vs time. To expand the entire temperature scale by a factor of ten, bucking sources were combined with more sensitive scales. Because of the sensitivity due to the scale factor expansion, it was necessary to thermally insulate the bucking voltage divider and associated resistors and dry cells to suppress drift. This was done with plastic packing material. At high sensitivity, the recorder was susceptible to static electric pickup from personnel moving nearby. It was thus necessary to surround the apparatus with grounded copper screening.

Switches were added as shown (figure 16) for setting the recorders to zero degrees centigrade without interference to the differential circuit, and for calibrating the temperature recorders with a standardized voltage source.

c. <u>Lower Scanning Rates.</u> The motor controlling the heating or cooling of the furnace had a reliable speed range of a factor of less than three (see figure 17). Using the
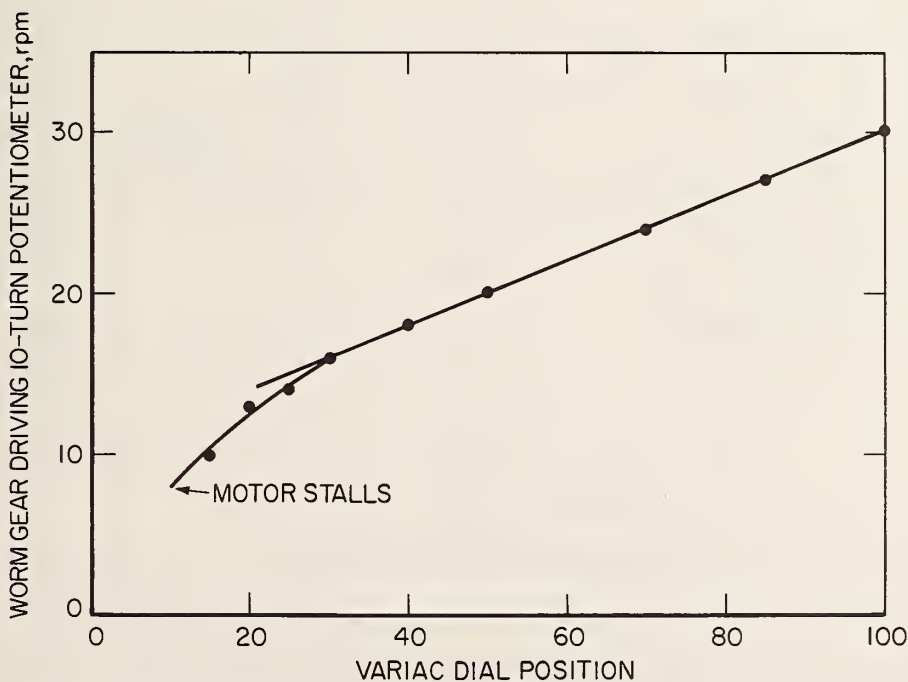
Figure 17. Model B programmer motor speed vs rate dial setting.

lowest reliable setting and the gears provided with the
lowest ratio of potentiometer turns per motor revolutions,
the lowest rate available was about 5 degrees per minute.
Smaller motor gears were made, and the motor was moved to
accomodate them. Also, the electronics in the furnace
programmer were modified to lower the rate of temperature
scan. Because this modification also decreased the tempera-
ture range proportionately, the rate decrease was only a
factor of 2. Using the smallest motor gears, the minimum
heating (cooling) rate was lowered to less than a degree per
minute. However, at the lower heating rates, the feedback
from the furnace sensing thermocouple was slow enough so that
the furnace would cycle above and below the proper tempera-
ture by several degrees with periods of 10 minutes or less.
To speed the feedback, the furnace control thermocouple was
welded to the nickel sample can (figure 17) which was the
closest stable point to the furnace heater windings. Even
with this modification and the optimum adjustment of the
furnace controller, the minimum heating rate that was free
of the cycling was about 1 degree per minute. Moving the
thermocouple outside the can, thus exposing it directly to
the furnace windings has further improved performance.

    d. Automatic Voltage Divider for Bucking Voltage
Source. A bucking voltage source of the following properties
was designed and built (see figure 18):

    (1) Automatic - able to reset the recorder
(temperature) when it went off scale in either direction.

    (2) Isolated from the ac power line and from ground.

    (3) Stable with respect to time and temperature to
within at least 0.1 percent.

    (4) Able to provide 20 increments of approximately
1/2 millivolt each.

The voltage divider was made from 2 percent carbon
resistors and trimmer potentiometers to compensate for the
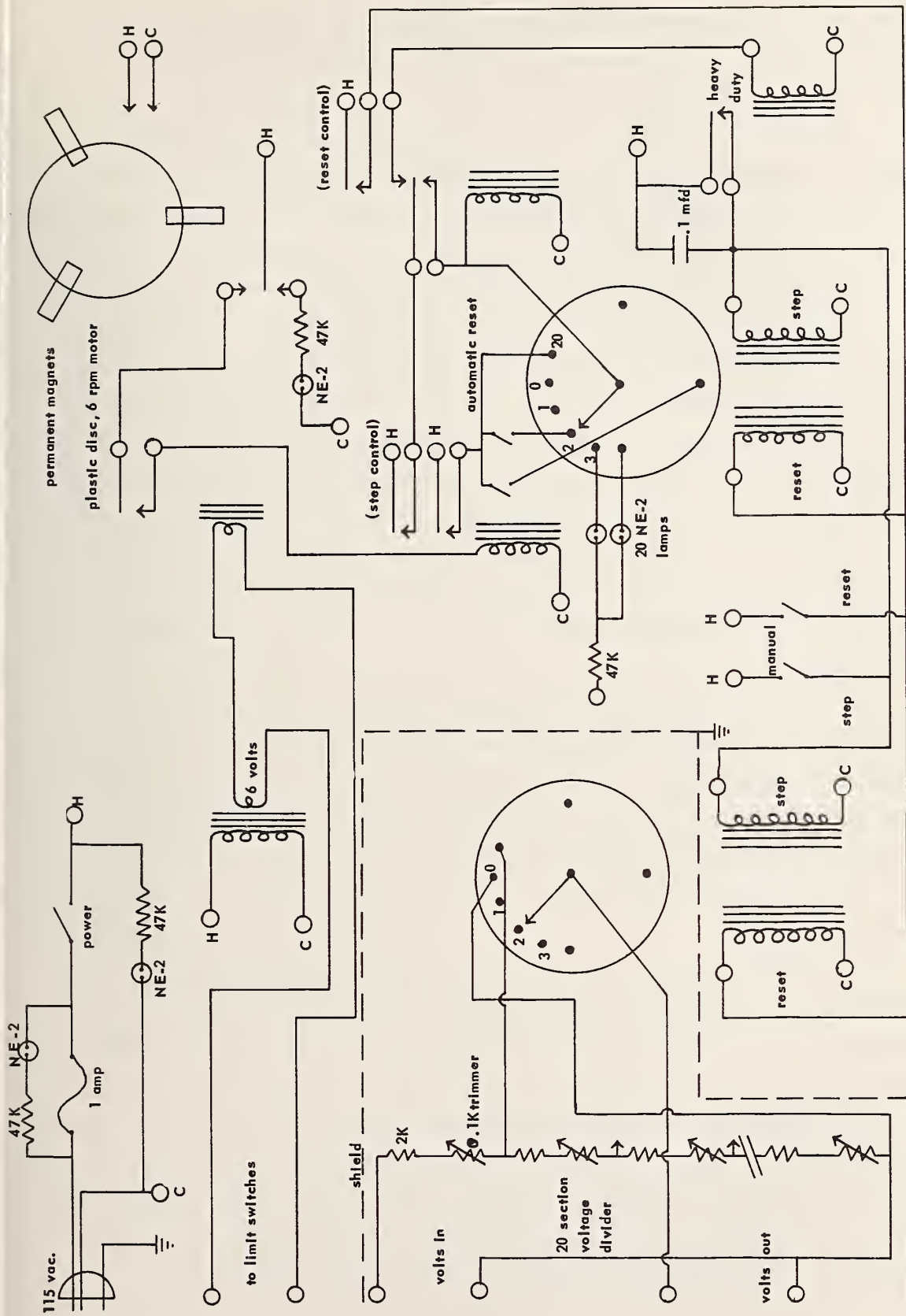
Figure 18. Automatic voltage divider.

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expected 4 percent resistance variation. This portion was shielded from the control circuits, and offered no noticeable hum.

The control circuits were made from relays because space and speed were not at a premium and simplicity of operation was desired. The basic control units were stepping relays that would advance and reset, and a magnetic read switch (whose inherent hysteresis prevented chatter) that was timed to advance the stepping relays once every two seconds. Stepping relays advance or reset continuously until the recorder pen is on scale. Micro switches were added to both ends of the recorder scale, and either would activate the recorder circuit. Additional relays provided power for the steppers to prevent skipping immediately after resetting, and to electrically isolate the limit switches for reasons of safety. Only 6 volts ac were on the limit switch binding posts, and either one could be grounded, if necessary.

The bucker can be set manually to any of its 20 positions and reset from any position. When the limit switch binding posts are connected, the position of the divider will be advanced about once every two seconds (increasing the voltage output) until it reaches the 4th, 9th, 14th or 20th position. It will then reset to the zero position.

Indicator lamps were provided for monitoring the magnetic reed switch (continually driven by the motor and magnets), the position of the voltage divider and a lamp fuse.

Because the bucker was designed for use with a potentiometric recorder or other high-impedance device, it exhibited high impedance (40,000 ohms) and drew very little battery current. It was therefore not expected to supply current. Its purpose was for a voltage source only.

The bucking voltage source was used either with a 1.5 volt dry cell or a mercury cell in series with an 8.2 megohm resistor so that each step would swing a 1/2 millivolt pen recorder almost to full scale.

Because of the scale expansion, the temperature recorder was very sensitive to the drift of the dry cell or mercury cell. The temperature and time stability of dry cells and size D mercury batteries were checked separately with a potentiometer. The performance varied widely except for new cells. All cells were temperature sensitive. The mercury cells performed best, and remained stable to better than 0.1 percent if insulated from ambient temperature by several inches of plastic foam. To suppress further drift, the bucker was enclosed in several inches of insulating material, because of the temperature sensitivity of the carbon resistors in the voltage divider. The bucker-recorder combination seldom drifted over several microvolts per hour. Short term drift was checked and was not apparent. The effect of long-term drift was checked and was not apparent. The effect of long-term drifts (over 20 minutes) on the results was not critical because the entire recorder system was calibrated with a separate potentiometer and was provided with temperature regulated standard cells, which were used frequently for calibration.

C. Temperature Calibration

1. Thermocouple Changes

Platinum and Platinum - 10 percent Rhodium (15 mil) wires were calibrated by the Heat Division at NBS.

The thermocouple over which the sample cup rested was removed, and the calibrated wires were inserted several inches beyond the ceramic tube. The ends of the wires were welded into a bead with an oxy-gas torch, then placed in the same position as those of the previous thermocouple. The reference thermocouple was withdrawn slightly to match the position of the calibrated thermocouple. These pre-

cautions were taken to avoid bending the leads, especially where they enter the bottom of the ceramic tubes and where large heat gradients were expected. The leads were directed to the ice bath containing the copper junction.

2. Calibration Procedure

With the zero-run switch in the operating position, the temperature recorders were switched from the sample thermocouple to a calibrated voltage source which in this case was a high precision potentiometer. The approximate transition temperatures under investigation were known, so the potentiometer could be set to approximately the correct potential. This allowed the fiducial marks to be on scale, within several equivalent degrees of the thermogram. Fiducial marks were taken within minutes before and after the thermogram. Several points gave the correct scale factor for interpolating to the potential reading of the thermocouple.

As a further check on the temperature readings, NBS freezing point standards, lead, aluminum and tin were carefully prepared. Non-metallic cups were used with these materials to avoid alloying with the sample. Graphite rod was chosen because of its availability, purity, and good thermal conductivity. This rod was cut to size, drilled, rinsed several times in acetone, boiled in HCl, and heated to incandescence before use.

3. Sample Cups

Platinum, nickel, stainless steel, aluminum and graphite cups were tested. Stainless steel was unsatisfactory because of oxidation and resultant thermogram. Nickel and aluminum cups were adapted and the thermocouples were inserted directly into the sample and reference. This did not improve the thermograms perhaps because the thermocouple contacted only the small layer of sample immediately surrounding it. This layer acted as an insulator for the remainder of the samples, which were powders or small

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crystals having relatively poor thermal conductivity. This approach was abandoned because the thermograms showed no improvement and since the thermocouple was not protected, the apparatus was more difficult to load and clean.

4. Results

Scanning rates of 1 to 5 degrees per minute were used over the temperature range investigated for potassium nitrate and quartz for use as DTA standards. Temperatures could be determined to a precision of about 0.2 degree (2 microvolts). Data for several melting point standards were within 2 degrees of their certified values. Repetitive temperatures of a given sample were consistent to at least one-half degree for a particular heating rate and at all heating rates.

Typical thermograms of two proposed SRMs, SiO_2 and KNO_3, are presented in figure 19. Those for melting point standards are given in figure 20. The departure point and the transition peak D are marked. These data are summarized in table 17. In all cases, the differential temperature indicates positive deviation on the heating cycle from the thermodynamic data obtained under adiabatic conditions. This is to be expected since in differential thermal measurements the rate of heat transfer is the controlling factor. On the cooling cycle the melting point standards reveal typical supercooling effects. For KNO_3, the cooling cycle reveals the presence of two phase changes dependent on the water overpressure. This phenomenon was recognized and explained early by Kracek in his studies with sealed quartz tubes [38]. It is of interest to note that with the exception of tin, the average values of A (departure point) closely approach the thermodynamic values. The larger deviation of SiO_2 cannot readily be explained and there is a need for calorimetric data to assist in resolving this difference.

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POTASSIUM NITRATE
127.7°

QUARTZ
573°

A
132.3°

A

D

D
135.4°

A
578.2°

D

A

D
580.1°

HEATING

ΔT ↕ 0.4°C ——

T ↕ 2°C — — —

one
↦min↤
time

A – POINT OF DEPARTURE
D – TRANSITION PEAK

121.1°

D

A

D

576.2°

D

A

D

COOLING

A
122.7°

A
577.9°
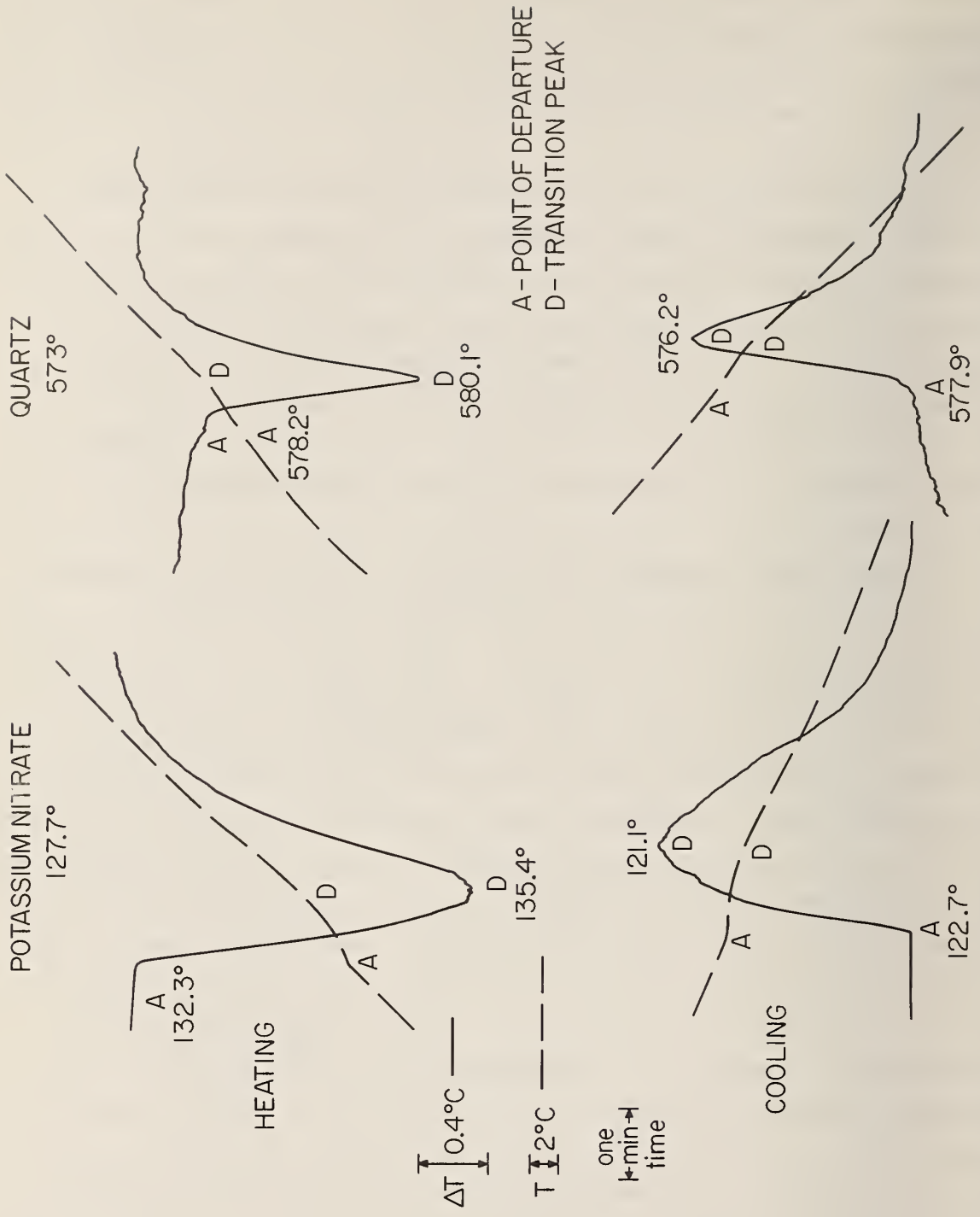
Figure 19. Differential thermal curves – NBS Standard Reference Materials.

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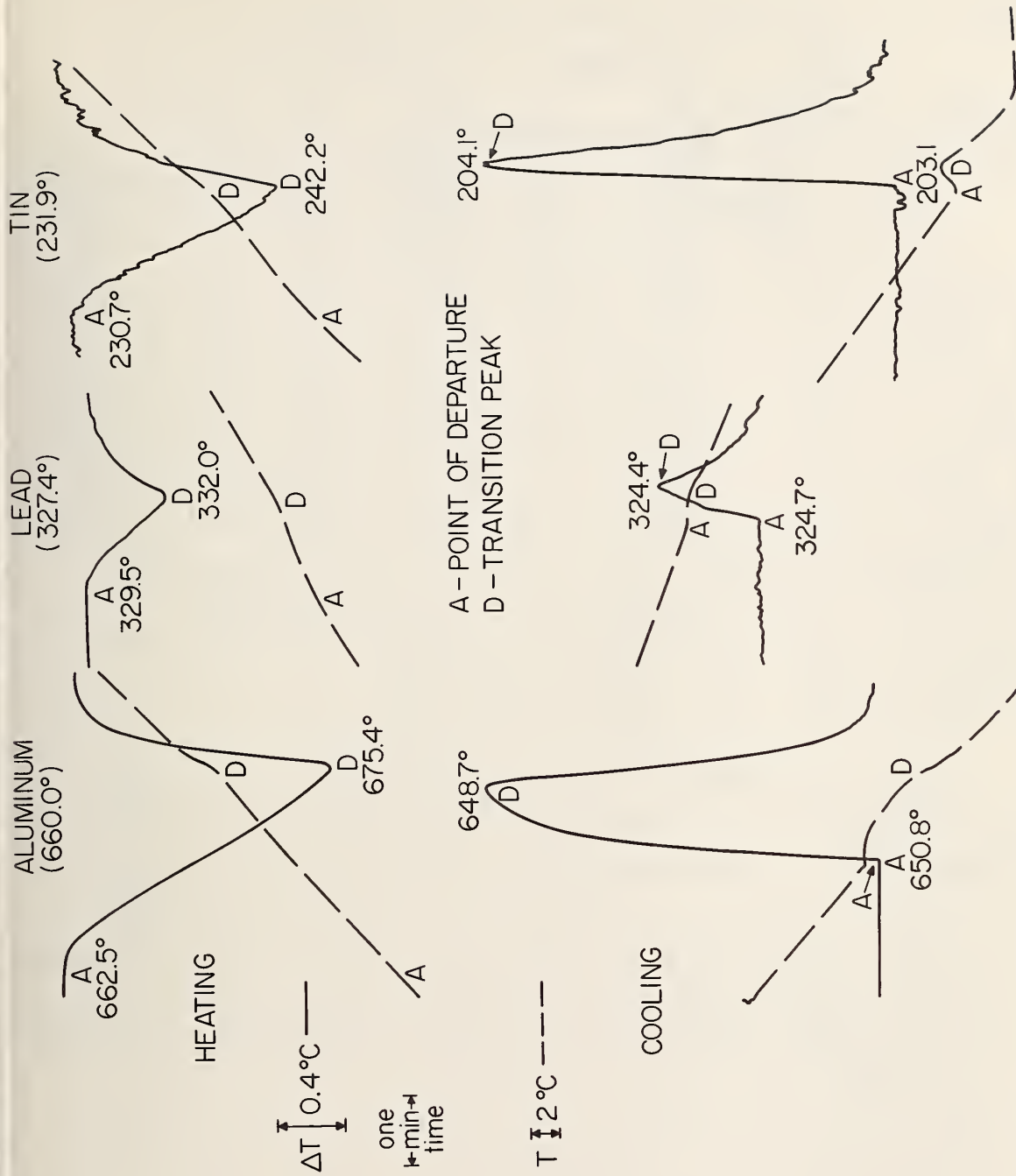
Figure 20. Differential thermal curves - NBS Freezing-Point Standards.

Table 17.   DTA transition point measurements.

Sample[a]	Rate °C/min	Cy[b]	Heating		Cooling		Ave A	Ave D
			A[c]	D[d]	A[c]	D[d]		
KNO$_3$ (127.7°)	5	(1)	131.6	138.6	123.0	121.2	127.3	129.9
		(2)	132.3	135.4	122.7	121.1	127.5	128.2
		(3)	133.4	135.4	122.6	121.2	128.0	128.3
	2	(4)	132.9	137.2	122.8	121.6	127.8	129.4
Sn SRM 42f (231.9°)	5		230.7	242.2	201.1	202.5	215.9	222.3
	1		231.7	236.3	219.2	220.1	225.4	228.2
Pb SRM 49e (327.4)	5		331.1	334.8	324.9	323.2	328.0	329.0
	2		329.5	332.0	324.7	324.4	327.1	328.2
SiO$_2$ (573°)	5		578.2	580.2	577.9	576.2	578.0	578.2
	1		576.5	579.0	579.4	577.0	577.9	578.0
Al SRM 44e (660°)	5		664.2	676.1	654.0	650.5	659.1	663.3
	5		662.2	675.6	656.4	648.8	659.3	662.2

[a]Thermodynamic temperature values from NBS Bulletin 500.
[b]Recycling the same sample below its melting point.
[c]Departure point (see figures 19 and 20).
[d]Transition peak (see figures 19 and 20).

Sample homogeneity, the effect of particle size and recycling through the transition temperature below the melting points of the compounds are summarized in figures 21 and 22. It must be noted that KNO$_3$, in its first thermogram cycle, reveals a large deviation. Subsequent thermograms of the same sample indicate consistent reproducibility. The transition peaks in these figures show a maximum spread of ± 0.5°C which also relates to particle size and source of material. In future work, it is anticipated that adiabatic calorimetric data will be available to support the accuracy of such values. In addition, it is planned to provide other compounds covering a wider range of transition temperatures.

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Figure 21. Homogeneity data on proposed SRM quartz.
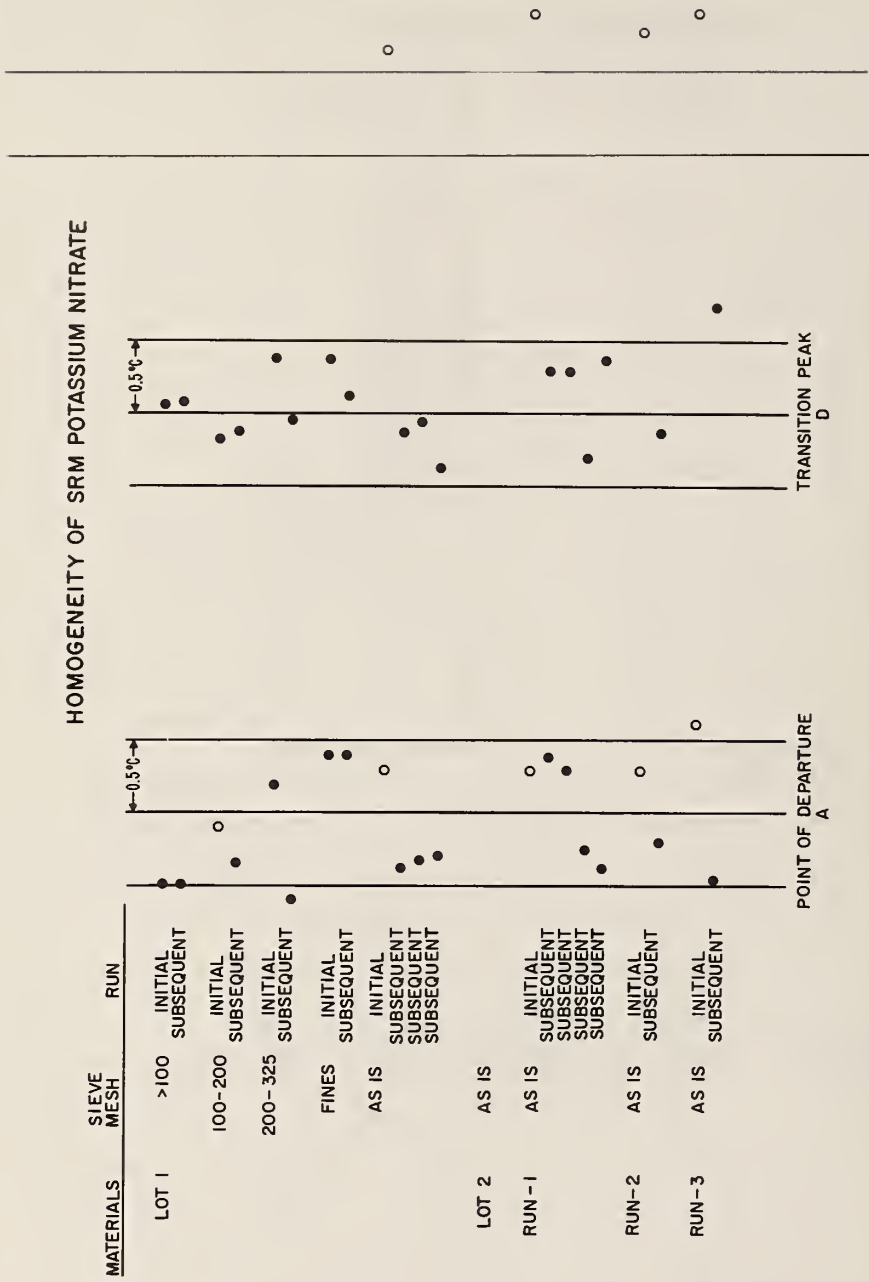
Figure 22.   Homogeneity data on proposed SRM potassium nitrate.

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4. GASES IN METALS

A. Introduction

The continued importance of interstitial elements and compounds on the physical and mechanical properties of metals has been demonstrated by the metal industry's increased adoption of basic oxygen steel making practices, the large scale use of vacuum melting techniques and the continued interest in the determination of gases in metals at increasingly lower levels. There is a real need in the metal industry for analytical methods and reference samples of known gas content at less than 10 ppm level for oxygen. Indeed, with some non-ferrous materials, such as copper, the level of oxygen is less than 1 or 2 parts per million. The nitrogen content is also very important because of its affect on the physical properties of metals; hence, a method which would provide for the simultaneous determination of oxygen and nitrogen is desirable, especially for control analyses. This is important since immediate analyses would be helpful in making adjustments to the composition during the actual production of the materials.

To provide meaningful gas measurements in metals, the work of the section during the past year proceeded along the following lines: (1) testing and improvement of analytical apparatus incorporating the basic inert-gas fusion technique for the extraction of the gases, (2) continuation of studies on a new standard reference material containing oxygen at very low levels and (3) supplemental work on the determination of nitrogen in the 1090 series of SRM's.

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

This new apparatus was discussed at length in the summary of activities, July 1967 to June 1968 for the Analytical Coordination Chemistry Section [1]. However, as indicated in this reference, the nitrogen values obtained

by this procedure needed improvement. The power available
at the time was supplied by a 450 kHz high-frequency
generator and was limited to 2.5 KW, which provided a maximum
temperature of approximately 1900°C. The temperature was
limited by the coupling conditions of the high frequency coil
and by the low power output. A 10 KW, 450 kHz high frequency
converter was installed, with which it is now possible to
obtain temperatures in excess of 2300°C. With this system,
the oxygen concentration was determined on an NBS maraging
steel standard and the results are reported in the following
section.

It was found that by increasing the temperature and by
using a large crucible with the platinum bath, results for
nitrogen were lower than those obtained by the Kjeldahl
method or by the pressure-bomb dissolution techniques. This
is evidenced by values of 124 ppm that were obtained on
samples of SRM 10g certified at .015 percent nitrogen.
Because of this low nitrogen recovery with the large multiple
sample technique, it was decided to modify the apparatus.
The modification involved the use of a crucible for a single
determination, rather than using the same crucible for succes-
sive extractions. The modified crucible was prepared having
the following dimensions: 9/16" O.D., 7/16" I.D. and 3/8" high.
A furnace tube approximately 1" I.D., was fabricated of
quartz. The crucible was supported from the bottom by a
graphite pedestal whose cross section was reduced to minimize
heat conduction. This pedestal was supported by a boron
nitride rod which was held in place by a slip joint fabricated
in the ground glass plug. This was used to close the bottom
of the furnace chamber. With this equipment, it was possible,
after outgassing the crucible for 3 minutes at 2300°C and
using a cycling heating technique, to obtain a nitrogen value
of 147 ppm for SRM 10g which compares favorably with the
certified value of .015 percent. Using this method, the

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crucible is changed for each sample. The necessity for this was demonstrated by the addition of the second and third sample to the same crucible. It was observed that the value of a second sample was lower and the third sample was still lower, indicating incomplete recovery of nitrogen because of a bath build-up in the crucible. The same experiment was repeated with SRM 1091. The initial samples determined gave nitrogen values of 950 ppm as compared with 945 ppm by the pressure bomb solution method. However, on adding subsequent samples to the preceding melt, the values approached 825 and 850 ppm.

A closure for the bottom of the furnace assembly has been designed which employs O-ring seals to permit rapid changing of the crucible. This minimizes contamination of the furnace with atmospheric gases.

C. The Testing of a Maraging Steel for Use as a Low Oxygen Content Standard Reference Material.

As reported in the preliminary study in an earlier summary of activities [1], there was sufficient evidence to indicate that this maraging steel would be sufficiently homogeneous with respect to low levels of oxygen. Accordingly, further testing of this material and preparation for certification as an SRM were undertaken.

The nominal composition of this maraging steel is 12 percent nickel, 5 percent chromium and 3 percent molybdenum. It was supplied in the form of steel plates measuring 1/2"x3'x6' and weighing 300 pounds. Sections 1/2"x1/2" were forged to approximately 5/16" diameter rods and their center ground to 1/4" diameter rods. Samples were taken at the four corners of the plate before the entire plate was cut into strips. The preliminary analysis of this material is described in last year's report [1]. The material reanalyzed consisted of two samples taken from the middle of the sheet. Because the samples taken from the four corners were specially selected and individually

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forged and ground to size, it was decided that those samples
taken from the center portion, marked x and y, were to be
treated exactly as actual production samples. This gave a
check as to whether any appreciable change in the gas content
occurred during the processing of the material.

The very low oxygen content of this maraging material
together with a maximum sample size for analyses, made it
necessary to measure microgram quantities of oxygen. Since
it was possible to measure blanks at the 1 microgram per
minute of collection time for a 1g sample, this presented
no problem.

A set of values obtained for oxygen in the maraging
steel are given in table 18.

Table 18. Oxygen homogeneity in maraging steel.

Sample	Oxygen (ppm)	Mean O_2 ppm
1A1	6.0, 4.0, 3.8, 4.0, 3.9	4.3
1A2	4.0, 4.6, 4.0, 3.9, 5.6	4.4
$1C_1$	4.1, 3.6, 3.8, 3.9, 3.2	3.7
$1C_2$	4.0, 5.6, 4.2, 3.1, 2.5	3.9
2A1	3.8, 5.4, 4.2, 4.1, 2.7	4.0
2A2	4.0, 3.2, 5.6, 5.4, 4.2	4.5
2C1	3.5, 4.3, 4.0, 6.0, 3.6	4.3
2C2	3.1, 3.0, 5.6, 2.6, 3.2	3.5
1x	5.6, 4.1, 6.2, 3.2, 5.1	4.5
2x	3.0, 3.0, 3.4, 2.6, 2.9	3.0
1y	4.0, 3.2, 4.5, 2.6, 3.3	3.5
2y	4.8, 3.1, 4.5, 3.3, 4.8	4.1

All values

Mean   =   4.00
S.D.   =   0.96
Rel S.D. = 24.0%

The values in table 18 were the result of homogeneity
studies and the sample numbers 1A1, 1A2, etc., refer to
the position in the original plate. Samples taken from the
original material were reexamined as were samples selected
randomly from the entire portion of material after forging,

swaging and centerless grinding. Results based on 109 determinations gave a value of 4.5 ppm. The uncertainty of ± 2 ppm includes the variations due to inhomogeneity as well as to the apparatus and operator biases. The final value is based on both inert gas fusion analysis and on the vacuum fusion analysis.

D. The Determination of Nitrogen in Ferrous Materials

The nitrogen content of those ferrous materials currently being issued or in the process of being issued as SRMs were reexamined with the hope that nitrogen as well as oxygen might be certified.

The samples were determined by the spinning crucible technique containing Ni-Ce alloy additions. They were also determined by the inert-gas fusion methods employing a heating cycle in which the sample is heated for 30 seconds at a temperature of 1850°C and then heated for 3 minutes at 2100°C.

The values obtained on these materials by the several methods are given in table 19.

Table 19. Determination of nitrogen ferrous alloys.

Sample	N_2, ppm[a]	Method[b]
1090	60±1	Inert-gas fusion
1091	950±3	" " "
1092	4±1	" " "
1093	3640±76	Spinning crucible
1094	61±1	" " "

[a]Uncertainty represents the standard deviation of a single determination.

[b]Based on use of a single crucible per determination.

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5. ANALYSIS OF STANDARD REFERENCE MATERIALS

A. Introduction

The variety of reference materials that the Analytical Coordination Chemistry Section assisted in standardizing during the last year are listed in table 20. The details of analyses are discussed in subsequent sections.

Table 20. SRM's analyzed by Analytical Coordination Chemistry Section.

Chemical Composition Standards

General Class	NBS-SRM	Type
Steels (Chip)	36b	2 Cr-1 Mo Low Alloy
	125b	3 Si Steel
	131b	Low Carbon (0.0018C)
	160b	19 Cr-14 Ni-3 Mo Stainless
	178	0.4C Basic Oxygen
	1090	Ingot Iron
	1093	Valve Steel
Steels (Spectrographic)	1138	Cast Steel No. 1
	1139	Cast Steel No. 2
	1155	19 Cr-14 Ni-3 Mo Stainless
	1261	0.4C Steel
	1262	0.2C Steel
	1263	0.6C Steel
	1265	Ingot Iron
Cast Irons	122e	Car-wheel (3.5C)
	342a	Nodular Iron (0.07 Mg)
Ferroalloy	59a	Ferrosilicon (50 Si)
High Purity Metals	685	Gold
Clays	97a	Flint Clay
	98a	Plastic Clay
Metallo-Organic	1051b	Barium Cyclohexanebutyrate
	1055b	Cobalt Cyclohexanebutyrate
	1057b	Dibutyltin bis(2-ethylhexanoate)
	1066a	Octaphenylcyclotetrasiloxane
	1069b	Sodium Cyclohexanebutyrate
	1079b	tris(1-phenyl-1,3 butanediono) Iron III
Miscellaneous	480	Electron Microprobe (20 Mo-80W)
	915	Calcium Carbonate
	953	Neutron Density Wire
	1800	Microstandard Ion Exchange Beads

The wide range of materials that the Section was requested to analyze for certification, requires considerable experience, competence and versatility of the staff members. In the course of this work, atomic absorption, spectrophotometric, gravimetric, titrimetric, vacuum fusion and combustion-gravimetric techniques were effectively employed to cover the broad scope of concentrations from the ppm to 80 percent levels. In the certification program, the application of atomic absorption accounts for approximately 25 percent of the analyses, spectrophotometry about 60 percent and gravimetry and titrimetry approximately 15 percent. Analyses by atomic absorption and spectrophotometry occupy positions of increasing importance in the determination of very small concentrations of many elements. We have demonstrated the ability to increase detection limits and to provide high accuracy analyses of the major components of many composition standards by these techniques. A number of the procedures are being adopted, as official methods, by such standardizing bodies as ISO, ASTM and ACS. In addition to their usefulness as general laboratory competences, they are being used quite extensively for high speed analytical control in metal and chemical production. A part of the NBS and Analytical Chemistry Division's wide and varied service to American industry and technology involves the preparation and characterization of many Standard Reference Materials which serve as production bench-marks for many basic industrial products such as steels, irons, ores, ceramics, chemicals, glasses, etc. The materials must be highly stable and homogeneous and are certified as to their composition or their properties. Homogeneity and permanence of material play important roles in the certification of reference standards. The starting material should be homogeneous, but a knowledge of the reference materials' permanence is equally important if the standards are to be useful and meaningful.

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There are at present, approximately 700 standard
materials that are provided by the NBS. The materials are
analyzed carefully by the NBS staff and in many cases, by
selected industrial laboratories as part of a cooperative
program that was established years ago.

The preparation of Standard Reference Materials involves
many factors. In selecting the types and compositions of the
materials to be issued as standards, NBS is guided by the
number and kinds of requests received from potential users
and by the suggestions of those engaged in a particular area
of interest. The majority of the chemical standards are
metals and alloys, that are used extensively for monitoring
thousands of analyses that are made daily in industrial
laboratories, although new standards are being provided in
such expanded areas as clinical chemistry and air pollution.
Standards of chemical composition also serve as guides in
developing new analytical methods or determining the compo-
sition of unknown materials. As industrial and scientific
needs develop, as indicated by requests from interested
parties, new chemical standards are prepared and issued.

Methods of analyses used in the certification program
in the Chemistry Division are selected or designed to give
the best obtainable results. When possible, several methods
for a given element are employed as a cross-check. For
example, copper in steels or cast irons is determined
spectrophotometrically as the carbamate complex, by atomic
absorption and by isotopic dilution and activation analysis
techniques. Values obtained by the various competences are
generally in sufficient agreement to indicate that the best
possible value has been obtained.

B. SRM Information and Summary

The following information on those standards that were
recently issued as Standard Reference Materials or on which
homogeneity studies were conducted, provides background which

may be of general interest. Listed are the elements certified
by the Section members along with brief outlines of the
methods and the data obtained.

1. Steel (2 Cr-1 Mo) - SRM 36b

This steel, first issued in 1941, is one of a series of
low alloy steels and represents a specific type of alloy having
good mechanical properties and high-strength. Typical appli-
cations are found in the automotive industry. Its greatest
use as a reference control standard is in the determination
of carbon, manganese, sulfur, chromium and molybdenum.

Table 21. Composition data for SRM 36b.

Elements	No. Det'ms	Average	Std Dev	Analyst
Carbon	10	0.114[a]	0.0003	JRB
Manganese	8	.0403[b]	–	JRB
Phosphorus	8	.007[c]	.0004	JRB
Sulfur	8	.020[d]	.0002	JRB
Silicon	4	.257[e]	–	JRB
Copper	4	.186[f]	.002	SAW
	8	.183[g]	.005	TAR
Nickel	7	.192[h]	.01	ERD
Chromium	4	2.18[i]	.0002	BBB
Vanadium	4	0.004[j]	.0096	BBB
Molybdenum	4	.995[k]	.004	BBB

[a] Combustion-gravimetric of a 2g sample by induction heating

[b] Manganese oxidized with ammonium-persulfate and titrated
potentiometrically with standard sodium arsenite solution.

[c] Phosphorus determined spectrophotometrically as the ammonium
phosphomolybdate complex.

[d] 1g sample burned in oxygen and sulfur dioxide absorbed in
starch-iodide solution. Liberated iodine is titrated with
standard potassium iodate solution.

[e] Double dehydration with perchloric acid.

[f] Copper determined spectrophotometrically as the carbamate
complex.

[g] Atomic absorption on a 1g sample dissolved in ultra pure
hydrochloric acid.

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[h]Nickel determined spectrophotometrically as the dimethyl-
glyoxime complex at pH 13.

[i]2g sample dissolved in dilute sulfuric acid (1+3), chromium
oxidized with ammonium persulfate in presence of silver
nitrate and titrated with standard ferrous ammonium sulfate
solution.

[j]1g sample dissolved in dilute sulfuric acid. Vanadium
determined spectrophotometrically on an aliquot portion
(0.1g) as the benzoylphenylhydroxylamine complex.

[k]1g sample dissolved in perchloric acid. Molybdenum deter-
mined spectrophotometrically on an aliquot portion (62.5 mg)
as the thiocyanate complex.

2. High Silicon Steel (3 Si) - SRM 125b

The electrical qualities, especially the high magnetic
permeability, of this type of alloy makes it a valuable
material for use in electrical equipment, particularly by
the manufacturers of industrial transformers. Its main use
as a reference standard is in the determination of carbon
(0.03 C), sulfur (0.01 S) and silicon (3 Si).

Table 22. Composition data for SRM 125b.

Elements	Position	Sample No. 1	2	3	4	Analyst
Carbon[a]	Top	0.044	0.031	0.037	0.034	
	Middle	.031	.034	.031	.033	JRB
	Bottom	.031	.031	.029	.033	
Manganese[b]	Top	0.282	0.281	0.286	0.282	
	Middle	.286	.278	.279	.282	SAW
	Top	.280	.277	.277	.277	
Sulfur[c]	Top	0.011	0.010	0.010	0.011	
	Middle	.011	.010	.011	.011	JRB
	Bottom	.011	.012	.013	.013	
Silicon[d]	Top	2.87	2.88	2.87	2.89	
	Middle	2.87	2.86	2.87	2.87	JRB
	Bottom	2.86	2.84	2.81	2.82	

[a]Combustion-gravimetric.

[b]Manganese oxidized with ammonium persulfate and titrated
potentiometrically with standard sodium arsenite solution.

^{c}1g sample burned in oxygen and sulfur dioxide absorbed in starch-iodide solution. Liberated iodine is titrated with standard potassium iodate solution.

^{d}Double dehydration with perchloric acid.

The work to date was to establish the homogeneity of the sample prior to acceptance of the final material. Homogeneity was based initially on 12 test samples taken from 3 positions along a continuously-cast bar measuring 12 feet long, 17 inches wide and 5 inches thick, for carbon, manganese, sulfur and silicon. Additional elements will be determined for final certification. Based on the data obtained above, it was concluded that the material was homogeneous and acceptable for final certification analysis.

3. Low Carbon (<0.002 C) Steel - SRM 131b

This special low-carbon alloy containing between 3-4 percent silicon was first issued in 1949 (131-0.0028 C) and again in 1965 (131a-0.0044 C) at the suggestion and request of the iron and steel industry because of the importance of extremely small amounts of carbon in transformer plate and magnetic materials. It is used as the bench-mark for standardizing and calibrating the many new types of chromatographic instruments specially adapted for low carbon determinations. It also serves as a suitable accelerator or flux in the determination of carbon in metals such as nickel, titanium and zirconium.

Element	No Det'ms	Average	Std. Dev	Analyst
Carbon	10	0.0018[a]	0.0002	JRB

[a]Carbon was determined on composites of four 2.5g samples by combustion in an induction furnace. The evolved carbon dioxide was collected in an ascarite-filled U tube and weighed. Proper blanks were determined and deducted.

4. Stainless Steel (19 Cr-12 Ni-3 Mo) - SRM 160b

The need for this "modified" stainless steel containing 2.5 percent molybdenum was first expressed by the Alloy Casting Institute in 1946. By 1948 the first sample, 160, was issued with a provisional certificate and in 1957 the replacement sample, 160a, was issued. This wrought stainless steel grade has superior corrosion resistance to sea water and other corrodents. It has superior strength at elevated temperatures, is non-magnetic, and has applications for wire-screening, chemical processing equipment, etc. This particular alloy "rounds out" our stock of stainless steels.

Table 23.   Composition data for SRM 160b.

Elements	No Det'ms	Average	Std Dev	Analyst
Carbon	8	0.046[a]	0.0004	JRB
Phosphorus	8	.020[b]	.001	JRB
Sulfur	8	.018[c]	.0005	JRB
Silicon	6	.509[d]	.005	SAW
Nickel	12	12.37[e]	.07	ERD
		12.19[f]		SAW
Vanadium	4	0.047[g]	.0003	JRB
Nitrogen	10	.040[h]	.0003	SAW

[a]Combustion-gravimetric of a 2g sample by induction heating.

[b]Phosphorus determined spectrophotometrically as the ammonium phosphomolybdate complex.

[c]1g sample burned in oxygen and sulfur dioxide absorbed in starch-iodide solution. Liberated iodine is titrated with standard potassium iodate solution.

[d]Double dehydration with perchloric acid.

[e]Nickel determined spectrophotometrically as the dimethyl-glyoxime complex at pH 13.

[f]Nickel determined gravimetrically as nickel dimethyl-glyoxinate on 0.250g sample.

[g]5g sample dissolved in dilute sulfuric acid. Vanadium oxidized with nitric acid and titrated potentiometrically with standard ferrous ammonium sulfate solution.

[h]Sample dissolution in pressure-bomb. Nitrogen determined by distillation-titration.

As an analytical standard, its greatest use is for carbon, chromium, nickel and molybdenum control.

5. Carbon Steel (0.4 C) - SRM 178

This medium carbon steel, the first NBS Standard Reference Material prepared by the Basic Oxygen Furnace method, is one of the most popular carbon steels. It has wide application in the automotive industry, particularly in the manufacture of connecting rods, steering arms, bolts, studs, etc. It makes an ideal reference standard for control analyses for carbon, manganese, phosphorus, sulfur and silicon.

Table 24. Composition data for SRM 178.

Elements	No Det'ms	Average	Std Dev	Analyst
Carbon	30	0.398[a]	0.0018	JRB
Manganese	8	.822[b]	.0008	JRB
Phosphorus	8	.011[c]	.0002	
Sulfur	16	.014[d]	.0003	JRB
Silicon	8	.163[e]	.016	JRB
Copper	24	.033[f]	.003	TAR
Nickel	5	.012[g]	–	ERD
Chromium	4	.015[h]	–	JRB
Vanadium	4	.001[i]	–	JRB
Molybdenum	3	.003[j]	.0002	BBB

[a] Combustion-gravimetric of a 2g sample by induction heating.

[b] Manganese oxidized with ammonium persulfate and titrated potentiometrically with standard sodium arsenite solution.

[c] Phosphorus determined spectrophotometrically as the ammonium phosphomolybdate complex.

[d] 1g sample burned in oxygen and sulfur dioxide absorbed in starch-iodate solution. Liberated iodine is titrated with standard potassium iodate solution.

[e] Double dehydration with perchloric acid.

[f] Atomic absorption on a 1g sample dissolved in ultra pure hydrochloric acid.

[g] Nickel determined spectrophotometrically as the dimethyl-glyoxime complex at pH 13.

[h]Chromium separated from bulk of the iron in a 10g sample by
  precipitation with sodium bicarbonate, oxidized with ammonium
  persulfate and titrated potentiometrically with standard
  ferrous ammonium sulfate solution.

[i]Vanadium separated as in (h), oxidized with nitric acid and
  titrated potentiometrically with standard ferrous ammonium
  sulfate solution.

[j]Molybdenum determined spectrophotometrically as the
  thiocyanate complex.

6.   Ingot Iron and Valve Steel - SRM 1090, 1093

These standards are two of a series of metals that are
certified for oxygen and nitrogen. Because of the importance
of the interstitial gases to the basic properties of metals,
such as ductility and embrittlement, it is vital that the
concentrations of these two elements be firmly established.
In addition to the inert gas fusion technique for the
determination of nitrogen, additional recheck data for this
element were obtained by the distillation-titration and
distillation-photometric methods.

Nitrogen was determined in ingot iron (SRM 1090) by the
indophenol colorimetric method [39].

A 0.5-gram sample was dissolved by the pressure bomb
technique and the nitrogen separated as ammonia by distilla-
tion. The ammonia was reacted with phenolate ions and
sodium hypochlorite to form a quantitative nitrogen indophenol
complex. Forty-five minutes were allowed for completion of
reaction and color formation.

The absorbance of the indophenol complex was measured
spectrophotometrically at a wavelength of 625 nm. The
nitrogen content ranged from 57 to 61 µg with a standard
deviation of 0.0002.   Analytical results are given below:

Table 25. Nitrogen data for SRM 1090.

Sample No.	Material	Element	Conc. %	Analyst
1090	Ingot Iron	N	0.0060	SAW
"	"	"	.0060	
"	"	"	.0057	
"	"	"	.0061	

Average 0.0059%±.0002

Nitrogen was determined also in valve steel (SRM 1093) by the distillation-titration method.

A 0.3-gram sample was dissolved by the pressure bomb technique and the nitrogen separated as ammonia by distillation [40]. The solution was then titrated with standard hydrochloric acid. The nitrogen content ranged from 0.480 to 0.482 percent with a standard deviation of .001. Analytical results are given below:

Table 26. Nitrogen data for SRM 1093.

Sample No.	Material	Element	Conc. %	Analyst
1093	Valve Steel	N	0.480	SAW
"	"	"	.482	
"	"	"	.480	
"	"	"	.482	

Average 0.481%

7. Cast Steels Spectrographic - SRM 1138-1139

The development of these cast steel standards was a joint effort by NBS and the Steel Founders Society to meet the urgent need for calibrating spectrographic instruments for use in production control of cast steels. The two standards represent compositions of a balanced range for the 10 elements that are certified. Although the samples have been issued under a provisional certificate, recheck values were requested for 3 of the elements by techniques other than spectroscopy.

A digital pH meter was used in connection with the titration of small concentrations of vanadium. Increased

precision and a reduction in titration time were noted in evaluating the equipment.

Table 27. Composition data for SRM's 1138 and 1139.

SRM No.	Element	No. Det'ms	Average	Std Dev	Analyst
1138	Chromium	4	0.122^a	0.001	BBB
"	Vanadium	4	$.020^b$	.001	"
"	Molybdenum	5	$.050^c$		
1139	Chromium	5	1.98^d	.002	"
"	Vanadium	5	0.224^e	.0008	"
"	Molybdenum	5	$.503^c$	.006	"

[a]Chromium separated from the bulk of the iron in a 10g sample by precipitation with sodium bicarbonate, oxidized with ammonium persulfate and titrated potentiometrically with standard ferrous ammonium sulfate solution.

[b]Vanadium separated as in (a), oxidized with nitric acid and titrated potentiometrically with standard ferrous ammonium sulfate solution.

[c]Molybdenum determined spectrophotometrically as the thio-cyanate complex.

[d]Oxidation with ammonium persulfate and titration with standard ferrous ammonium sulfate solution.

[e]Oxidation with potassium permanganate and titration with standard ferrous ammonium sulfate solution.

8.   Spectrographic Standards 1261-1265 (Iron and Steels)

These five standards are replacements for the original set of eight NBS spectrochemical standards 1161-1168, that were first issued in 1947. A graded range of approximately 30 elements in each of the five samples will be certified to cover the broad spectrum of steels that will serve as controls for the greater percentage of the world's steel production. In establishing the compositions for these important alloys, the many requests of the steel producers were carefully considered. The samples are intended to serve not only for composition control in the production of iron and steel in this country, but also in customer acceptance.

The initial efforts of the Section were to analyze a number of elements in each of 4 samples for preliminary composition acceptance. To date, the fifth sample has not become available. The list of elements and the preliminary values obtained are given below:

Table 28. Composition data for SRM's 1261, 1262 and 1265.

Sample	Element	Percent found	Analyst
1261	Silver[a]	0.0004	TAR
	Calcium[b]	.0001	"
	Magnesium[a]	.0002	"
	Zinc[a]	.0005	"
	Nitrogen[c]	.0032	JTS
	Oxygen[c]	.0010	"
1262	Sulfur[d]	0.038	JRB
	Silver[a]	.0009	TAR
	Calcium[b]	.0003	"
	Magnesium[a]	.0007	"
	Zinc[a]	.0011	"
	Nitrogen[c]	.0034	JTS
	Oxygen[c]	.0010	"
1263	Carbon[e]	0.62	JRB
	Phosphorus[f]	.026	RKB
	Sulfur[d]	.009	"
	Silver[a]	.003	TAR
	Calcium[b]	.0003	"
	Magnesium[a]	.0005	"
	Nitrogen[c]	.004	JTS
	Oxygen[c]	.0006	"
1265	Carbon[e]	0.010	JRB
	Phosphorus[f]	.002	"
	Sulfur[d]	.008	"
	Silver[a]	0.1 ppm	TAR
	Calcium[b]	1.0 "	"
	Magnesium[a]	0.2 "	"
	Nitrogen[c]	.001	JTS
	Oxygen[c]	.005	"

[a]Atomic absorption.

[b]Flame emission spectroscopy.

[c]Vacuum fusion.

[d]1g sample burned in oxygen and sulfur dioxide absorbed in starch—iodide solution. Liberated iodine is titrated with standard potassium iodate solution.

[e]Combustion-gravimetric.

[f]Phosphorus determined spectrophotometrically as the ammonium phosphomolybdate complex.

A detailed report will be available at a later date, after the final materials have been analyzed and certified.

9. Standard Cast Iron - SRM 122e

This is a replacement standard for the very popular high-carbon cast iron. Preliminary homogeneity data for carbon and sulfur indicated that the material was homogeneous and could be used for final analysis and certification.

Element	No. det'ms	Average	Analyst
Total carbon	39	3.50	JRB
Sulfur	26	0.073	"

A detailed report will be available at a later date, after the material has been analyzed and certified.

10. Standard Nodular Iron - SRM 342a

This unique alloy was first provided by NBS in 1961 at the request of the American Foundrymen's Society. The un-usual properties, high strength with good ductility, of this type iron-base alloy makes it a very popular material for a fairly specialized segment of the metals industry. Because of the inability of the Research Committee of the Ductile Iron Division of the AFS to obtain agreement among various of their laboratories for the contained magnesium, they prevailed on NBS to provide a homogeneous and well-character-ized standard, particularly for the magnesium. The intent of the project was to determine with what degree of reliabil-ity magnesium determinations could be employed as a control of inspection procedure for nodular iron quality.

Its main use as a control standard is in the determi-nation of magnesium, total and graphitic carbon, sulfur and silicon, although the material has been certified for 13 elements.

Table 29. Composition data for SRM 342a.

Elements	No det'ms	Average	Std Dev	Analyst
Total carbon	14	1.84[a]	0.017	JRB
Graphite	8	1.38[b]	.017	"
Manganese	6	0.271[c]	.0025	BBB
Phosphorus	8	.018[d]	.0006	JRB
Sulfur	36	.005[e]	.0008	"
Silicon	4	2.72[f]	.006	"
Copper	3	.134[g]	.001	SAW
Nickel	4	.058[h]	–	ERD
Chromium	6	.035[i]	.0001	BBB
Magnesium	17	.072[j]	.001	TAR

[a] Combustion-gravimetric of a 1g sample by induction heating.

[b] 2g sample dissolved in dilute nitric acid. Graphite filtered onto asbestos pad contained in quartz crucible and dried at 110°C. Carbon dioxide determined by combustion-gravimetric procedure.

[c] Manganese oxidized with ammonium persulfate and titrated potentiometrically with standard sodium arsenite solution.

[d] Phosphorus determined spectrophotometrically as the ammonium phosphomolybdate complex.

[e] 1g sample burned in oxygen and sulfur dioxide absorbed in starch-iodide solution. Liberated iodine is titrated with standard potassium iodate solution.

[f] Double dehydration with perchloric acid.

[g] Copper determined spectrophotometrically as the carbamate. complex.

[h] Nickel determined spectrophotometrically as the dimethyl-glyoxime complex at pH 13.

[i] Chromium separated from bulk of the iron in a 10g sample by precipitation with sodium bicarbonate, oxidized with ammonium persulfate and titrated potentiometrically with standard ferrous ammonium sulfate solution.

[j] Atomic absorption.

11. Standard Ferrosilicon - SRM 59a

This very important ferroalloy has been out of stock for
a number of years, and at the request of the ferroalloy
industry, it has been renewed. To the alloy has been added
approximately 0.1 percent boron, since this element is of
interest to the producers and consumers. Ferrosilicon, like
most of the other ferroalloys, is sold on an "as contained"
basis, hence demands for very accurate control is becoming
of increasing importance.

The following tabulation shows homogeneity data
obtained for silicon on bulk material contained in 5
containers and at 3 positions:

Table 30. Percent silicon obtained on bulk material.

Container No	Position		
	Top	Middle	Bottom
1	48.08	48.06	48.09
	48.11	48.15	48.13
2	48.13	48.04	48.00
	48.03	48.15	48.15
3	48.07	48.11	48.18
	48.15	48.16	
4	48.17	48.13	48.09
	48.12	48.14	48.15
5	48.01	48.11	48.14
	48.17	48.13	48.15

The data for silicon given above indicate that the
material is sufficiently homogeneous for use as a Standard
Reference Material.

Procedures for the Determination of Silicon, Manganese,
Chromium and Iron in Ferrosilicon

a. Silicon. Transfer 0.5g of the sample, accurately
weighed, to a 45-ml zirconium crucible and add about 13g
of sodium peroxide. Mix thoroughly with a platinum rod and
carefully clean the rod of adhering particles by scraping

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with another rod and by rotating the rod in 2g of additional
sodium peroxide used to cover the mixture.

Heat the crucible and contents on a hot plate for 10
minutes to expel water in the peroxide. Carefully fuse over
a Meeker flame by holding the crucible with a pair of tongs
and slowly revolving it around the outer edge of the flame
until the contents have melted quietly, and without spattering.
When the mixture is molten, rotate the crucible carefully so
that the swirling liquid will stir up any unattacked particles
on the bottom or side, the crucible and contents being
maintained at a low red heat. After fusing 3 or 4 minutes,
increase the temperature to bright redness for a minute.

Cover the crucible and allow it to cool to room
temperature. Remove the cover, invert the crucible over a
liter platinum dish, and tap the bottom to transfer the cake.
Cover the dish and cautiously add, in small portions, a total
of 50 ml of water. When the reaction ceases, wash the lid
and crucible with water and add the washings to the dish.
Cool the dish and contents and carefully add 5 ml of sulfurous
acid. Police the crucible, using HCl (1+3), and carefully
add the acid to the dish. Cool the dish and carefully add
HCl until in moderate excess. Heat on a steam bath and, after
effervescence ceases, wash and remove the cover. Evaporate
to dryness on a steam bath.

Cool the dish, drench the residue with 20 ml of HCl,
cover the dish, and heat gently for 5 minutes. Dilute with
200 ml of hot water, digest on a steam bath for 5 minutes,
stir to break up lumps, and filter immediately through an
11-cm medium filter paper. Wash about 8 times with hot HCl
(5+95), twice with warm H_2SO_4(5+95), and 5 times with hot
water. Transfer the paper and contents to a platinum
crucible and reserve.

Evaporate the filtrate and washings to dryness. Cover
the dish and bake at 110°C for 1 hour. Cool, drench with
15 ml of HCl, digest on a steam bath for 5 minutes, add

150 ml of warm water, and stir. Filter immediately and wash 8 times with cool HCl(1+99), twice with cool H_2SO_4(5+95), and 5 times with cool water.

Combine the paper and contents with the reserved paper in the platinum crucible and carefully burn off the carbon, without flaming, by heating slowly to 550°C in a muffle furnace. When the carbon has been completely burned, tightly cover the crucible, gradually increase the temperature to 1150°C, and heat at this level for 45 minutes. Cool in a desiccator for 30 minutes and weigh. Check for constant weight by additional heating periods of 25 minutes at 1150°C.

Carefully add 1 ml of H_2SO_4(1+1) to the crucible to moisten the silica and then add 20 ml of HF (48 percent). Evaporate to dryness in an air bath, ignite at 1100°C for 5 minutes, cool in a desiccator 30 minutes, and weigh. The loss in weight represents SiO_2.

Calculation. Calculate the percentage of silicon as follows:

$$\text{Silicon, percent} = \frac{A \times 0.4675 \times 100}{B},$$

where A = weight of SiO_2, g

and B = weight of sample, g

Manganese, chromium and iron have also been determined on this material. Outlines of the methods together with the results are given:

b. Manganese. Dissolve 1g of sample in 30 ml of HNO_3-HF(5+1) mixture.

Add 30 ml of H_2SO_4-H_3PO_4-HNO_3 mixture and evaporate to fumes of H_2SO_4, cool, add 25 ml of water and add back 8 ml of HNO_3,

Transfer the solution to a 500 ml Erlenmeyer flask, oxidize the manganese with ammonium persulfate in the presence of $AgNO_3$ by boiling the solution for 90 seconds.

Cool the solution to 5-10°C, transfer to a 400 ml beaker, and titrate the manganese potentiometrically with standardized sodium arsenite solution, 1 ml = 0.40 mg Mn.

An average value of 0.747 percent manganese was obtained on 14 determinations.

    c. <u>Chromium</u>. Transfer 5g of sample to a liter platinum dish, cover, and add 40 ml of HNO_3 and 2 ml of HF (48 percent). Warm the dish gently to start reaction. Add 35 ml of HF dropwise from a plastic separatory funnel until the sample is completely dissolved. This requires approximately 25 minutes. Wash the cover carefully with water and add 30 ml of H_2SO_4(1+1). Evaporate the solution to fumes of H_2SO_4 and continue fuming for 5 minutes. Cool, add 100 ml of water and digest on a steam bath. Filter and wash the paper with hot water. Reserve the filtrate. Transfer the residue to a platinum crucible, ignite at 550°C and fuse the residue with 2g of $K_2S_2O_7$. Dissolve the melt in 30 ml of hot water and 1 ml of H_2SO_4. Combine with the reserved filtrate and dilute to 300 ml. Add 10 ml of $AgNO_3$ solution (0.25 percent) and 20 ml of $(NH_4)_2S_2O_8$ (15 percent) and boil for at least 30 minutes to oxidize the chromium. Add 4 ml of HCl(1+1) to destroy the manganese color and boil for 20 minutes to obtain a clear solution. Remove from the heat and cool to room temperature or lower. Titrate potentiometrically with standard $Fe(NH_4)_2(SO_4)_2$ solution (23g/l).

An average value of 0.084 percent chromium was obtained on 5 determinations.

    d. <u>Iron</u>

<u>Reagents</u>

      (a) Mercuric chloride solution: Prepare a saturated solution of $HgCl_2$ in water.

      (b) Sulfuric-phosphoric acid mixture: Mix 150 ml of H_2SO_4 (sp. gr. 1.84) with 300 ml of water, cool, add 150 ml of H_3PO_4 (sp. gr. 1.69), dilute to 1 liter with water and mix.

(c) Stannous chloride solution: Dissolve 150g of $SnCl_2 \cdot 2H_2O$ in 300 ml of HCl (sp. gr. 1.19), dilute to 1 liter with water, and mix.

(d) Sodium diphenylamine sulfonate indicator solution: Dissolve 0.25g of sodium diphenylamine sulfonate in 100 ml of water.

(e) Standard potassium dichromate solution (0.1<u>N</u>): Transfer 4.9032g of SRM 136b, $K_2Cr_2O_7$, to a liter volumetric flask and dissolve in water. Dilute to the mark with water and mix. Determine the iron titer by checking against ingot iron standard 55e.

Transfer a 0.5g sample, accurately weighed, to a liter platinum dish, cover, and add 5 ml of HF (48 percent). Add 2 ml of HNO_3 (sp. gr. 1.42) dropwise at a rate of 4 to 5 drops per minute. Avoid loss by spattering. When reaction ceases, wash the cover and wall with water.

Add 8 ml of H_2SO_4 (1+1) and heat until fumes of H_2SO_4 Cool, add 300 ml of water, and digest on a steam bath to dissolve salts. Neutralize with NH_4OH and add a slight excess. Filter through a 12.5 cm coarse filter paper and wash several times with hot water.

Transfer most of the precipitate from the paper to the dish by washing with water and pour 30 ml of hot HCl(1+2) onto the paper. Wash the paper well with hot HCl(1+99), catching the solution in the dish. Reserve the paper (A).

Dilute the solution in the dish to 100 ml and filter through a 7 or 9 cm fine filter paper to separate a small amount of insoluble residue, catching the filtrate in a 600-ml beaker. Wash the dish and paper well with hot HCl(1+99). Evaporate the filtrate and washings to about 10 ml volume and reserve (B).

Transfer the paper and the reserved paper (A) to a platinum crucible and ignite at 550°C. Cool, add 1g of $K_2S_2O_7$, and fuse the residue. Cool, and dissolve the melt

in 15 ml of hot water and 1 ml of HCl (sp. gr. 1.19).
Combine the solution with the reserved solution (B).

Adjust the volume of the iron solution to about 25 ml
and cool. Add a 2.5 percent solution of $KMnO_4$ dropwise until
a distinct pink or brownish color persists. Heat to boiling,
boil gently for 5 minutes to expel chlorine. Add stannous
chloride solution dropwise while swirling the hot solution
until the color of the ferric iron disappears, and then add
just one drop more. Wash the cover and wall of the beaker
and quickly cool the solution in ice-water. Add at one
stroke 10 ml of the $HgCl_2$ saturated solution, stir, and wash
the wall of the beaker. Allow the solution to stand for 2
to 5 minutes. Add 20 ml of H_2SO_4-H_3PO_4 mixture, dilute to
350 ml with water, and add 5 to 6 drops of sodium diphenyl-
amine sulfonate indicator solution. Titrate with standard
$K_2Cr_2O_7$ solution to a permanent blue or violet color which
does not change upon further addition of dichromate, while
stirring.

Standardize the $K_2Cr_2O_7$ solution by dissolving 0.250g
of SRM Ingot Iron, 55e (99.79 percent Fe) in 10 ml of
HCl(1+1), and continue as directed in the procedure beginning
with heating nearly to boiling and reducing with $SnCl_2$.

Calculation. Calculate the percentage of iron as
follows:

        A = grams of iron used as a standard.

        B = milliliters of $K_2Cr_2O_7$ solution used to
            titrate A. $\frac{A}{B}$ = C.

        C = iron titer, in grams per ml of $K_2Cr_2O_7$
            solution.

        D = ml of $K_2Cr_2O_7$ solution used to titrate the
            sample.

        E = grams of sample used.

Percent Fe = $\frac{C \times D}{E}$ x 100.

An average value of 50 percent iron was obtained on 6 determinations.

In connection with the preliminary determination of iron, consideration was given to the use of various sample sizes, in addition to the need for separating and collecting the iron by precipitation with NH_4OH. The comparative use of $HClO_4$ vs H_2SO_4 for fuming to remove HF and to affect complete solution of the sample was also investigated.

Approximately 26 determinations of iron were made in an effort to establish a procedure that would provide satisfactory results.

12. Metal-Organic Materials

Of the 24 standard metal-organic materials that are provided by NBS, 6 renewals have been analyzed and certified during this reporting period. These materials were developed essentially for use in estimating the degree of engine wear by determining spectrographically the small amounts of metals found in engine crankcase oils.

Listed are the materials certified together with percentages of metal constituents and summary of methods.

Table 31. Certified metallo-organic compounds

SRM No		Det'ms	Average, percent	Analyst
1051b[a]	Barium Cyclohexanebutyrate	9	28.79	BBB
1055b[b]	Cobalt Cyclohexanebutyrate	12	14.87	"
1057b[c]	Dibutyltin bis(2 ethyl-hexanoate)	12	22.92	"
1066a[d]	Octaphenylcyclotetrasiloxane	6	14.13	"
1069b[e]	Sodium Cyclohexanebutyrate	7	12.11	"
1079b[f]	Tris(1-phenyl-1,3 butanediono) iron III	10	10.45	'

[a]Barium determined by wet-ashing a 0.5g sample with H_2SO_4 and HNO_3, dried for 72 hours over P_2O_5 and the resulting insoluble material removed by filtration, ignited at 900°C and weighed as $BaSO_4$.

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[b] Cobalt determined by wrapping the sample in filter paper, covering with oxalic acid and then igniting at 800°C. The resulting oxide was dissolved in HCl, electrodeposited as cobalt from an ammoniacal solution and weighed as the metal. Residual cobalt in the electrolyte determined spectrophotometrically using nitrose R salt to form the colored complex.

[c] Tin determined by wet-ashing a 1g sample with H_2SO_4 and HNO_3, dried for 2 hours over P_2O_5, precipitating the tin with cupferron and converting the precipitate to SnO_2 by ignition at 1000°C. A second method involved preliminary treatment with H_2SO_4 and HNO_3 as above, reduction of the tin with nickel and titrating with standard potassium iodate solution.

[d] Silicon determined by wet-ashing 1g sample with H_2SO_4 and HNO_3, dried for 2 hours over P_2O_5, double dehydration of silica, igniting at 1100°C and volatilizing the silicon with HF.

[e] Sodium determined by wrapping the sample in filter paper, covering with oxalic acid and then igniting. The residue was either converted to sodium chloride and weighed after ignition at 600°C or converted to sodium sulfate and weighed after ignition at 750°C.

[f] Iron determined by wet-ashing a 0.5g sample with HNO_3 and H_2SO_4, dried for 1 hour at 110°C, precipitating with ammonium hydroxide, dissolving the precipitate in HCl, reducing with $SnCl_2$ and titrating with standard $K_2Cr_2O_7$ solution. Determinations were also made by direct ignition to Fe_2O_3 of a 0.5g sample which was wrapped in filter paper and covered with oxalic acid.

13. Clay Standards 97a and 98a

These two clay materials are of interest to the ceramic and refractory industries and will serve as analytical composition standards for flint and plastic clay materials. The graded compositions are necessary to control the physical as well as the chemical properties of the finished products. They will serve as bench-marks for the calibration of many instrumental methods since there have been some marked advances in both instrumental and analytical techniques that are applicable to these complex materials.

To emphasize the complexity of these types of materials and their analysis, Lundell and Hoffman [41] as early as 1928 provided data to show the lack of agreement between analysts

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who assisted in the cooperative analysis of similar materials, and more recently Flanagan [42] of the Geological Survey reiterated that the problem still exists.

In an effort to obtain the best possible values for the 2 major constituents, SiO_2 and Al_2O_3, several methods for each were evaluated. Summaries of these methods are given in the following sections.

a. Gravimetric Methods for SiO_2

Na_2CO_3 Fusion - H_2SO_4 Dehydration. Dry a 0.5g sample at 140°C for 2 hours and then fuse with 8g of anhydrous Na_2CO_3. Dissolve the cool melt in dilute H_2SO_4 (1+9) and dehydrate the SiO_2 twice, with an intervening filtration [4]. Ignite the impure residue at 1200°C, weigh, and treat with HF. Determine the amount of SiO_2 from the loss in weight. Determine spectrophotometrically the soluble SiO_2 in the filtrate by the molybdo-silicic acid butanol extraction method [4] and add to the gravimetric value.

Na_2CO_3 Fusion - HCl Dehydration. Dry a 1g sample at 140°C for 2 hours and then fuse with 5g of anhydrous Na_2CO_3. Dissolve the cool melt in dilute HCl and dehydrate the SiO_2 twice, with an intervening filtration [44]. Ignite the impure residue at 1200°C and weigh before and after HF treatment. Determine spectrophotometrically the soluble SiO_2 in the filtrate and add to the gravimetric value.

$LiBO_2$ Fusion - Ion Exchange Dissolution. Dry a 0.5g sample of SRM 97a, flint clay, and a 0.25g of SRM 98a, plastic clay, at 140°C for 2 hours and then fuse with a fivefold weight of lithium metaborate [45] in a graphite crucible at 950°C for 20 minutes. Swirl the melt gently and then carefully transfer to a Teflon beaker containing 100 ml of water. Grind the solid in an agate mortar, mix with double the MEQ weight of dry cation exchange resin (Bio Rad Ag 50w, X4) required for aluminum and lithium present. Stir the water mixture, sample and resin for 1 hour. Elute the SiO_2 and B_2O_3 with 400 ml of water and reserve for subsequent

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determination of silicon. The $Na_2CO_3-H_2SO_4$ and the Na_2CO_3-HCl dehydration procedures provided the best precision data and gave values that agreed favorably with the certified values for NBS-SRM's 97 and 98 that were used as control standards. The latter work has been temporarily suspended, but will be reactivated at an early date. At that time more details of the procedure, along with analytical data, will be presented.

b. Gravimetric Methods for Al_2O_3

LiBO$_2$ Fusion, Cation-Exchange Resin, Anion Exchange Resin, NH_4OH Precipitation, Al_2O_3. Dry a 0.5g sample of 97a, flint clay, and a 0.33g of 98a, plastic clay, at 140°C for 2 hours. Separate SiO_2 and B_2O_3 on cation exchanger. Separate aluminum from titanium and iron with HCl on an anion exchanger [46, 47] and then precipitate the aluminum with NH_4OH, ignite and weigh as Al_2O_3.

LiBO$_2$ Fusion, Cation-Exchange Resin, Anion Exchange Resin, NH_4OH, Al_2O_3, NaOH-F Titration. Dry a 0.5g sample at 140°C for 2 hours. Pass samples through cation and anion exchange resin as above, but divide the eluate into 2 equal portions. Determine aluminum gravimetrically in one portion as above, and in the second portion add sodium fluoride to react with sodium aluminate to form an alkali hydroxide. Titrate the hydroxide with standard acid. Preliminary results indicate the values run low by the latter method.

LiBO$_2$ Fusion, Acid Dehydration, Anion Exchange, NH_4OH, Al_2O_3. Dry a 0.5g sample of 97a and a 0.3g sample of 98a at 140°C for 2 hours. Remove SiO_2 by double dehydration with HCl. Volatilize boron as methyl borate. Pass solution containing aluminum through an anion exchange resin with HCl. Determine aluminum in the eluant by precipitation with NH_4OH and ignition to Al_2O_3. Residual impurities such as titanium, iron, chromium, magnesium and silicon

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were determined spectrophotometrically and corrections applied to the impure Al_2O_3.

LiBO$_2$ Fusion, Cation Exchange, Anion Exchange Homogeneous Precipitation of Aluminum. Dry a 0.5g sample of 97a and a 0.3g sample of 98a at 140°C for 2 hours and then fuse in a fivefold weight of lithium metaborate. Remove SiO_2 and B_2O_3 by cation exchange. Separate aluminum by an anion exchange in 12N HCl and precipitate homogeneously [48, 49] with succinic acid and urea.

Na$_2$CO$_3$ Fusion, Acid Dehydration, 8-Hydroxyquinoline Precipitation. Dry a 1g sample at 140°C for 2 hours and then fuse in 5g of Na_2CO_3. Remove SiO_2 by double dehydration with HCl [50]. Fuse the residue with $K_2S_2O_7$, leach and dilute to 250 ml. On a 50 ml aliquot portion, precipitate aluminum with 8-hydroxyquinoline in an alkaline solution containing citric acid, hydrogen peroxide and sodium cyanide and weigh.

Mixed Acids Solution, NaOH, NH$_4$OH Separations, 8-Hydroxyquinoline Precipitation. Dry a 0.5g sample at 140°C for 2 hours and dissolve in a mixture of H_2SO_4-HNO_3-HF-H_2O. Fuse any insoluble residue with Na_2CO_3 and combine with main solution. Remove, iron, titanium, magnesium, etc. by separation with NaOH. Separate aluminum by precipitation with NH$_4$OH and finally precipitate with 8-hydroxyquinoline, and weigh. This latter procedure provided the best precision data and gave values that agreed favorably with the certified values for NBS-SRM's 97 and 98 that were used as control standards.

C. ASTM Activities

In cooperative work with ASTM, analyses of various types of iron and steels for sulfur by the Nydahl gravimetric method were made to evaluate its use for a Task Force group in the Ferrous Division of Committee E-3 on Chemical Analysis of Metals. The method consists of adsorption of sulfur as sulfuric acid in a perchloric acid solution on a column

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of alumina, elution with ammonium hydroxide, and gravimetric determination as barium sulfate. The sulfur content of the samples ranged from 0.006 to 0.6 percent. The values obtained were slightly low, ranging from 0.003 to 0.01 percent less than the certified value. The 10 samples tested include wrought iron, ductile iron, white cast iron, carbon steel, tool steel, valve steel, and stainless steel.

If this procedure proves satisfactory, after evaluation by all Task Force members, it will be recommended as the official ASTM method for the gravimetric determination of sulfur (RKB).

J. I. Shultz

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7. PERSONNEL AND ACTIVITIES

A. <u>Personnel Listing</u>

Oscar Menis, Section Chief

James I. Shultz, Assistant Section Chief

Mary B. Pantazis, Section Secretary

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E. R. Deardorff	T. C. Rains
C. S. P. Iyer	T. A. Rush
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B. <u>Publications</u>

1. T. C. Rains and Oscar Menis, "High-Precision Flame Emission Spectrometry", Spectroscopy Letters <u>2</u>, 1 (1969).

2. Oscar Menis and T. C. Rains, "Determination of Arsenic by Atomic Absorption Spectrometry with an Electrodeless Discharge Lamp as a Source of Radiation", Anal. Chem. <u>41</u>, 952 (1969).

3. T. C. Rains, "Chemical Aspects of Atomic Absorption", ASTM Special Technical Publication 443, 1969.

4. T. C. Rains, "Chemical Interferences in Condensed Phase", <u>Chapter in Flame Emission and Atomic Absorption Spectrometry</u>, Vol. 1, John A. Dean and Theodore C. Rains, eds., Dekker, New York, 1969.

5. John A. Dean and Theodore C. Rains, eds., <u>Flame Emission and Atomic Absorption Spectrometry</u>, Vol. 1, Dekker, New York, 1969.

6. Oscar Menis and T. C. Rains, "Sensitivity, Detection Limits, Precision and Accuracy in Flame Emission and Atomic Absorption Spectrometry", Chapter in <u>Analytical Flame Spectroscopy</u>, Selected Topics, R. Mavrodineanu, ed., Centrex, Eindhoven, in press.

7. R. W. Burke and E. R. Deardorff, "Simultaneous Spectrophotometric Determination of Cobalt, Nickel and Copper

with 2,3-Quinoxalinedithiol", Talanta, submitted for publication.

8.   R. W. Burke, "Exchange Reactions of Ternary Ion Association Complexes Directly in the Organic Phase", Talanta, submitted for publication.

C.   Talks

1. D. H. Christopher and Oscar Menis, "The Differential and Simultaneous Spectrophotometric Determination of Molybdenum and Tungsten", 4th Middle Atlantic Regional Meeting, ACS, February 12, 1969.

2.   T. C. Rains and Oscar Menis, "Application of Flame Spectrometry to Simulated Standards for Dust Particulates", 12th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 8-10, 1968.

3.   T. C. Rains, "An Evaluation of Electrodeless Discharge Lamps as a Source for Atomic Absorption Spectroscopy", Eastern Analytical Symposium, New York, N. Y., Nov. 13-15, 1968.

4.   T. C. Rains, "Atomic Absorption Spectroscopy", American Chemical Society Short Course on Atomic Absorption Spectroscopy, Tarrytown, New York, Nov. 16-17, 1968.

5.   T. C. Rains, "Atomic Absorption Spectrometry: Past, Present, Future", Society for Applied Spectroscopy, Baltimore-Washington Section, Silver Spring, Md., Nov. 26, 1968.

6.   T. C. Rains, "Atomic Absorption and Flame Emission Spectrometry for Major Constituents", Twenty-second Annual Symposium on Modern Methods of Analytical Chemistry, Louisiana State University, Baton Rouge, La., Jan. 20-23, 1969.

7.   T. C. Rains, "Atomic Absorption Spectrometry in a National Laboratory", Society for Applied Spectroscopy, Houston Section, Houston, Texas, Jan. 23, 1969.

8.   T. C. Rains and Oscar Menis, "A Critical Evaluation of Some New Techniques for Atomic Absorption and Flame

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Emission Spectrometry", 4th Middle Atlantic Regional Meeting of ACS, Washington, D. C., Feb. 12-15, 1969.

9. Oscar Menis and T. C. Rains, "Derivative Flame Emission Spectrometry", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 2-7, 1969.

10. T. C. Rains, "Atomic Absorption Spectroscopy", ACS Short Course on Atomic Absorption Spectroscopy, St. Paul, Minn., April 12-13, 1969.

11. Oscar Menis and T. C. Rains, "Precise Micro Sample Analysis by Flame Emission Spectrometry", 157th National Meeting of ACS, Minneapolis, Minn., April 13-19, 1969.

12. T. C. Rains, "Recent Developments in Atomic Absorption and Flame Emission Spectrometry", Analytical Group of the American Chemical Society, Delaware Section, Wilmington, Del., May 20, 1969.

13. J. I. Shultz, "NBS Standard Reference Materials" Industrial Management Club of Cumberland County, Vineland, N. J., April 23, 1969.

D. Committee Activities

Oscar Menis

Member ASTM, Committee E-3, Div. I.

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

Editorial Board Member, Chemical Instrumentation, A Journal of Experimental Techniques in Chemistry and Bio-chemistry.

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