NBS

Technical Note 275

QUANTITATIVE SEPARATIONS: TITRIMETRY, GRAVIMETRY, FLAME PHOTOMETRY, SPECTROPHOTOMETRY, GAS EVOLUTION AND ISOTOPIC PREPARATIONS, JULY 1964 TO JUNE 1965

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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ISSUED DECEMBER 27, 1965

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Edited by Oscar Menis
[redacted]
Analytical Chemistry Division
Institute for Materials Research

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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 seven sections and about 85 technical personnel encompassing some 30 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 highly important. In addition, however, it has been my experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information. At the National Bureau of Standards such publications fit logically into the category of Technical Note. In 1965 we plan to issue these summaries for all of our sections. The following is the first annual report on progress of the Quantitative Separation Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

This is the first of a series of annual progress reports dealing with the activities of the Quantitative Separations Section of the Analytical Chemistry Division. In the general reorganization of the Division this section was formed in November 1964. R. A. Paulson was the active section chief until January 1965 and since then O. Menis joined as the chief of this section. The personnel of this section consists of twelve scientists. A roster of this group is presented in the section on personnel.

The work described in this report covers the fiscal period of 1965 and encompasses the following areas of competences: titrimetry, gravimetry, flame spectrophotometry, spectrophotometry, gas components in metals. It includes also areas dealing with uranium and plutonium chemistry. Its major effort during the past year was to establish the most accurate values for the chemical composition of over twenty-five standard reference materials by means of the above listed analytical disciplines. The group performed the analysis and ascertained the accuracy of the methods selected for certifying values for a given composition of the material.

The section's efforts included also assisting in the procurement of these materials, determining their homogeneity, preparing the material in a form most suitable for sampling and finally evaluating the efforts of the outside laboratories which cooperated in checking the values prior to the final certification of the analysis. Some of these functions have been now taken over by the Office of Standard Reference Materials.

In certain areas of competences, or analytical chemistry disciplines, additional efforts are currently being made to improve the accuracy and to facilitate an increased production of standard reference materials. This involved the procurement and installation of additional instrumentation. In the determination of gas components in metals a new instrument makes it feasible to increase the output of samples by a tenfold factor. In the area of spectrophotometry, methods for ultra high sensitivity at the nanogram level, and for high precision spectrophotometry are being developed. For high precision gravimetry, a thermogravimetric analysis apparatus was also obtained and is being tested. Similarly, in flame photometry and atomic absorption, instrumentation has been procured to assist in analysis of trace elements present in a variety of standard reference materials.

While the major effort of this section has been expended during the past year in the certification of standard reference materials, work has been initiated to expand this effort into those areas of study which would also assure greater accuracy and sensitivity in the analysis of new and renewal NBS standards.

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

Oscar Menis, Chief
Quantitative Separations Section

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QUANTITATIVE SEPARATIONS
July 1964 to June 1965

Edited by Oscar Menis

ABSTRACT

This is the first progress report of the Quantitative Separations Section covering the 1965 fiscal period. The report encompasses several areas of analytical chemistry and discusses the activities of this section in relation to the certification of values for standard reference materials. These included a variety of ferrous, copper base alloys, high temperature alloys, titanium base alloys, ceramic, clay, rock and actinide materials.

In the area of titrimetry, problems are discussed that deal with the prior separations associated with the determination of iron and cobalt in high temperature alloy. Also, the application of complexometric titration with a potentiometric apparatus is described. In the gravimetric studies, the application of thermogravimetric procedures to establish a base line for weighing U_3O_8 is illustrated. Current methods which were investigated for the determination of aluminum in feldspar appear to give low results and a need for a new approach is indicated. In another procedure, the partial separation of hafnium from zirconium by an ion exchange separation was achieved prior to a spectrographic determination of this element. An atomic absorption apparatus was installed and tests with the new instrument and a modified flame spectrophotometer are presented. In the spectrophotometric competence, high sensitivity and high precision methods are discussed and applied. Boron and beryllium were successfully determined at the nanogram level of concentration. The differential spectrophotometric method was evaluated for the estimation of high concentration of nickel by the modified dimethylglyoxime procedure. In addition, spectrophotometric methods were applied to the determination of trace elements, As, Be and P in brass B and Zr in cast iron, B in high temperature alloy and nickel in steel and cast iron. An initial investigation of the reaction of the brilliant green reagent with pentavalent antimony indicated that this method can be adapted for the determination of antimony in white cast iron. In the area of gas evolution methods, a new apparatus is described in conjunction with a homogeneity study of oxygen in ingot iron and other materials. Also, the apparatus and procedure is presented for the determination of nitrogen in materials containing refractory nitrides.

Other aspects of the analysis of standard reference materials are discussed from the standpoint of preparation and conversion of the material to a suitable sample form, homogeneity testing, stability, and the cooperative work with outside laboratories. Special fields of analytical interest involving the conclusion of umpire uranium analysis are discussed.

Finally, the isotopic standards preparation program is detailed for the uranium and plutonium materials.

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1. TITRIMETRY

Titrimetric methods were used extensively as shown in Table 1 to establish values for various components of standard reference materials. While in many cases the precision and accuracy of the methods which are listed in this table meet the requirement for the error limits set in the NBS certificates, further reduction of errors is needed especially at the microgram concentration levels. For that purpose studies of potentiometric, spectrophotometric and other techniques for the end point detection are under way.

A. Separation Problems

1. Determination of Cobalt in High Temperature Alloy

In addition, better methods for separation prior to the final titration are needed as they are often the limiting factors in attaining highest accuracy. An example of the latter is the determination of cobalt in a high temperature alloy (NBS 1194) by the ferricyanide titration method. The critical part in the procedure is the gravimetric separation step and the application of a correction for manganese. The separation of cobalt by an alkaline precipitation involves careful neutralization of the dissolved sample and oxidation with bromate. In this case, to improve the current precision as shown in Table 2, an ion exchange separation is being tried.

2. Determination of Iron in High Temperature Alloy

An example of another separation problem was the determination of iron in a high temperature alloy. Iron was determined in a synthetic solution of a high temperature alloy by oxidimetric titration with a standard solution of potassium dichromate in a procedure which involved two different separation schemes. A synthetic solution was prepared based on the following nominal composition of the alloy in per cent: 54-Fe, 25-Ni, 15-Cr, 2-Ti, 1.5-Mo, 0.7-Mn and 0.4-V. In one procedure the iron was separated from the interfering elements by an ammonium hydroxide and next by a sodium hydroxide precipitation. The second procedure involved an H_2S precipitation. In the first procedure the results (shown in Table 3) for iron were found to be low by 0.2 per cent while in the second, were 0.4 per cent high.

Presently, extraction and ion exchange separation are under study to improve the accuracy of this determination.

(R. Bell)

Table 1. Precision of titrimetric methods as applied to analysis in standard reference materials.

Element	Range (%)	Precision ± (%) σ	Oxidation	Titration
			Ferrous Alloys	
Mn	.1 - 0.9 .9 - 1.5	0.003 .01	$(NH_4)_2S_2O_8 + AgNO_3$	$Na_2As_2O_3$
S	.01 - 0.1 .1 - 0.3	.002 .003	Combustion to SO_2	KIO_3
Cr	.01 - 3.0 3.0 - 18.00	.002 .02	$(NH_4)_2S_2O_8$	$Fe(NH_4)_2SO_4$
V	.005 - 0.1 .1 - 0.3	.001	HNO_3	
Sn	.005 - 0.10 .10 - 0.25	.002 .003	Separation with H_2S and NH_4OH	KIO_3
N	.002 - 0.25 .05 - 0.15	.002 .002	Separation with Kjeldahl distillation	Acidimetric
Se	.01 - 0.5	.002	Separated as metal	KIO_3
			Copper Alloys	
Sn	.005 - 1.5	.001 .03	Separate with NH_4OH Fe carrier, Pb reduction	$KBrO_3$
Sb	.005	.001	Separate with NH_4OH Fe carrier reduced with S and distilled	$KBrO_3$ or $KMnO_4$
			High Temperature Alloy	
Fe	50	.1	Separate with H_2S reduced with $SnCl_2$	$K_2Cr_2O_7$
Co	3.0	.02	Separate with NaOH precipitate after oxidation with $KBrO_3$	$K_3Fe(CN)_6$
			Uranium (umpire analysis)	
U	70 - 80	0.03	Separate with H_2S and cupferron extraction Jones Reductor	$K_2Cr_2O_7$

Table 2. Determination of cobalt by ferricyanide-titration method.

Sample No.:	1	2	3	4
	Cobalt (%)			
Test				
1	2.65	2.63	2.69	2.67
2	2.68	2.64	2.65	2.64

Average 2.66
Standard deviation 0.02

Table 3. Comparison of the recovery of iron by two separation methods.

Separation method	Present	Found	Difference
	Iron (mg)		
Two NH_4OH precipitations and one NaOH precipitation	537.4 555.2	536.8 554.0	- .6 -1.2
H_2S precipitation	237.9 257.4 251.2 259.3	237.8 258.7 252.4 260.6	-0.1 +1.3 +1.2 +1.3

B. Complexometric Titration of Calcium and Magnesium

The titration studies are also being extended to supplement the result by gravimetric methods for the determination of calcium and magnesium in standard reference materials of dolomite. In this case, the complexometric titrations with a potentiometric mercury indicator electrode system have been tested [1]. The apparatus is shown in Figure 1. Typical titration curves are shown in Figure 2 for the complexones, ethylene glycol bis-(2 aminoethyl ether)-N, N'-tetraacetic acid, EGTA and ethylenediaminetetraacetic acid, EDTA. As can be noted in Figure 2, the greater stability of Ca-EGTA complex makes it feasible to titrate calcium without the interference from magnesium. On the other hand, with EDTA, Figure 2, both ions substantiate the gravimetric values for the final certification of the dolomite standard.

(K. M. Sappenfield)

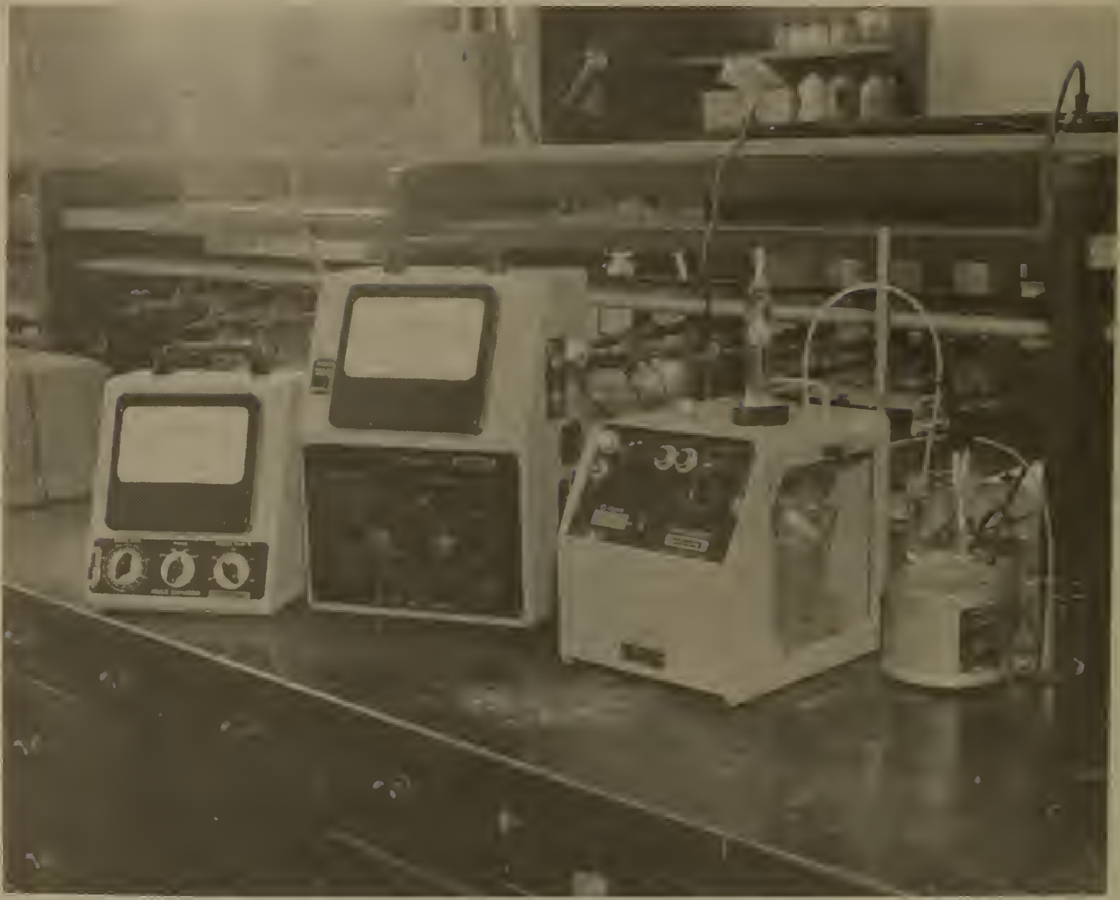


Figure 1. Automatic potentiometric titration apparatus (mercury indicator electrode vs SCE).

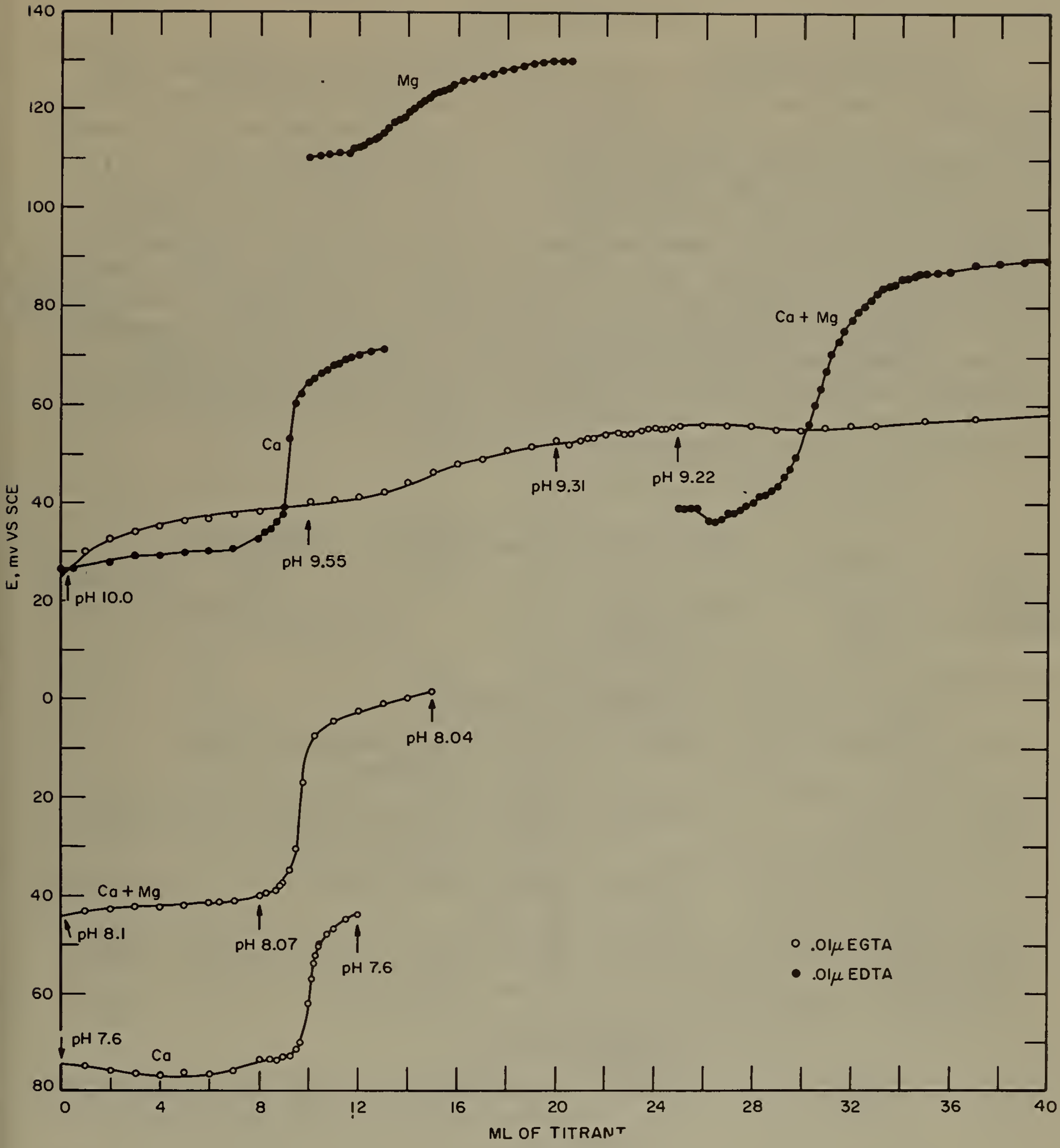


Figure 2. Titration of calcium and magnesium with EGTA (pH checked as indicated). Titration of calcium and magnesium with EDTA (pH 8.5 as adjusted initially). General conditions: Instrument, figure 1; data, manually plotted; mercury indicator electrode vs SCE.

2. GRAVIMETRY

While gravimetric procedures are considered as the classical methods for obtaining accurate values, the "non-ideal" condition when dealing with complex materials leads to relative large errors due to such problems as coprecipitation and absorption. Conditional solubility constants for the solid phase formation may also differ significantly from theoretical values derived in ideal solutions. Finally, the stoichiometry of the final compound will depend on the drying or ignition temperature and on the rate at which equilibrium is reached. To control some of these parameters and reduce errors, better separation schemes, masking and demasking variables and thermogravimetric studies are being carried out. The current applications are summarized in Table 4.

Table 4. Summary of gravimetric methods.

Element	Range (%)	Precision ± (%) σ	Basic method
			Ferrous Alloys
Ni	> .01	0.02	Dimethylglyoxime (DMG) precipitation
Ni	< .01	.003	Extraction of Fe^{+3} with ether; DMG precipitation
C	0.01 - 1.0 1.0 - 4.0	.004 .02	Combustion, absorbed and weighed as CO_2
Si	0.1 - 1.0	.004	$HClO_4$-H_2SO_4 dehydration HF volatilization
			Copper Alloys
Cu	0.05 70.00	.0001 .01	Separation of Sb, As and Sn; Cu by electrodeposition
Pb	4 0.02	.01 .002	Separation by electrodeposition of PbO_2 and lead molybdate precipitation
Ni	.01	.02	DMG precipitation (after Cu electrodeposition)
Al	2	.004	Electrolysis, CN complex 8-hydroxyquinoline

Table 4. Summary of gravimetric methods (cont'd).

Element	Range (%)	Precision ± (%) σ	Basic method
			Feldspar
Si	65	.05	Dehydrated with HCl, corrected for soluble SiO_2 in R_2O_3
Ca	2	.08	Double oxalate precipitation corrected for Ca in $Mg_2P_2O_7$
Mg	.02	.01	Ammonium phosphate precipitation corrected for Ca and Mn
P	.02	.01	Phosphomolybdate separation $Mg_2P_2O_7$
Na	2.5 - 6	.03	J. Lawrence Smith Na-K as chlorides; K as K_2PtCl_6
K	5. - 11	.05	K as K_2PtCl_6
Loss on ignition	.30	.01	Dry at 110 °C; ignite at 1000 °C
			Limestone
Si	5.	.05	Dehydrated with HCl, corrected for soluble SiO_2 in R_2O_3
	40	.03	Evolution weighed as CO_2
Fe	0.9	.02	Precipitate as FeS weighed as Fe_2O_3
Al	1.	.02	R_2O_3 corrected for Fe, P, Ti and Si
Ca	50.	.04	Double oxalate precipitation corrected for Ca in $Mg_2P_2O_7$
Mg	0.4	.01	Ammonium phosphate corrected for Mn and Ca
Loss on ignition	40.	.03	Dry at 110 °C; ignite at 1000 °C
			Dolomite
Si	1.2	.05	(Double dehydration HCl) corrected photometrically
Ca	30.	.05	Four oxalate precipitations corrected for Ca in $Mg_2P_2O_7$
CO_2	40	.04	HCl evolution weighed as CO_2
Mg	21.5	.3	Ammonium phosphate precipitate corrected for Mn and Ca
Loss on ignition	46.	.02	Dry at 110 °C; ignite at 1000 °C

A. Determination of Aluminum in Feldspar

One of the problem areas is the determination of aluminum in feldspar. The aluminum in the samples was determined gravimetrically using three different approaches. In the first procedure the aluminum value of 70a, determined by ammonium hydroxide precipitation which was corrected for iron, silica, phosphorus, and titanium, was (about 0.15 to 0.10 per cent) lower than the cooperators. Aluminum was also determined by the gravimetric 8 hydroxy-quinoline method [2]. The soluble aluminum quinolate in the filtrate was determined photometrically with aluminon [3]. Finally, aluminum was determined by precipitating with ammonium hydroxide after the extraction of aluminum cupferrates with chloroform [4]. The values (based on the summation of the components) are still a little low (0.1 to 0.2 per cent) and additional work is under way to verify whether any loss could occur because of an incomplete dissolution or due to any conditions encountered in these procedures. To resolve these problems, studies involving a new dissolution procedure, ion exchange separation and a homogeneous precipitation technique are under way.

(K. M. Sappenfield)

B. Stoichiometry of Uranium Oxide

Another problem dealing with the stoichiometric composition of uranium oxide is being studied by a thermogravimetric procedure. The details of this evaluation are described in the Uranium-Isotopic Standard Section.

(L. A. Machlan)

C. Thermogravimetric Analysis

A thermogravimetric analyzer attachment for a differential thermal analyzer was received in May. The new instrument is shown in Figure 3. It is expected that this analyzer will be used in such areas of study as: new weighing compositions in gravimetric analysis and their range of temperature stability, studying behavior of materials in atmospheres of various gases, determination of purity and thermal stability of analytical reagents, and automatic gravimetric analysis.

Figure 3. Thermogravimetric and differential thermal analysis apparatus.

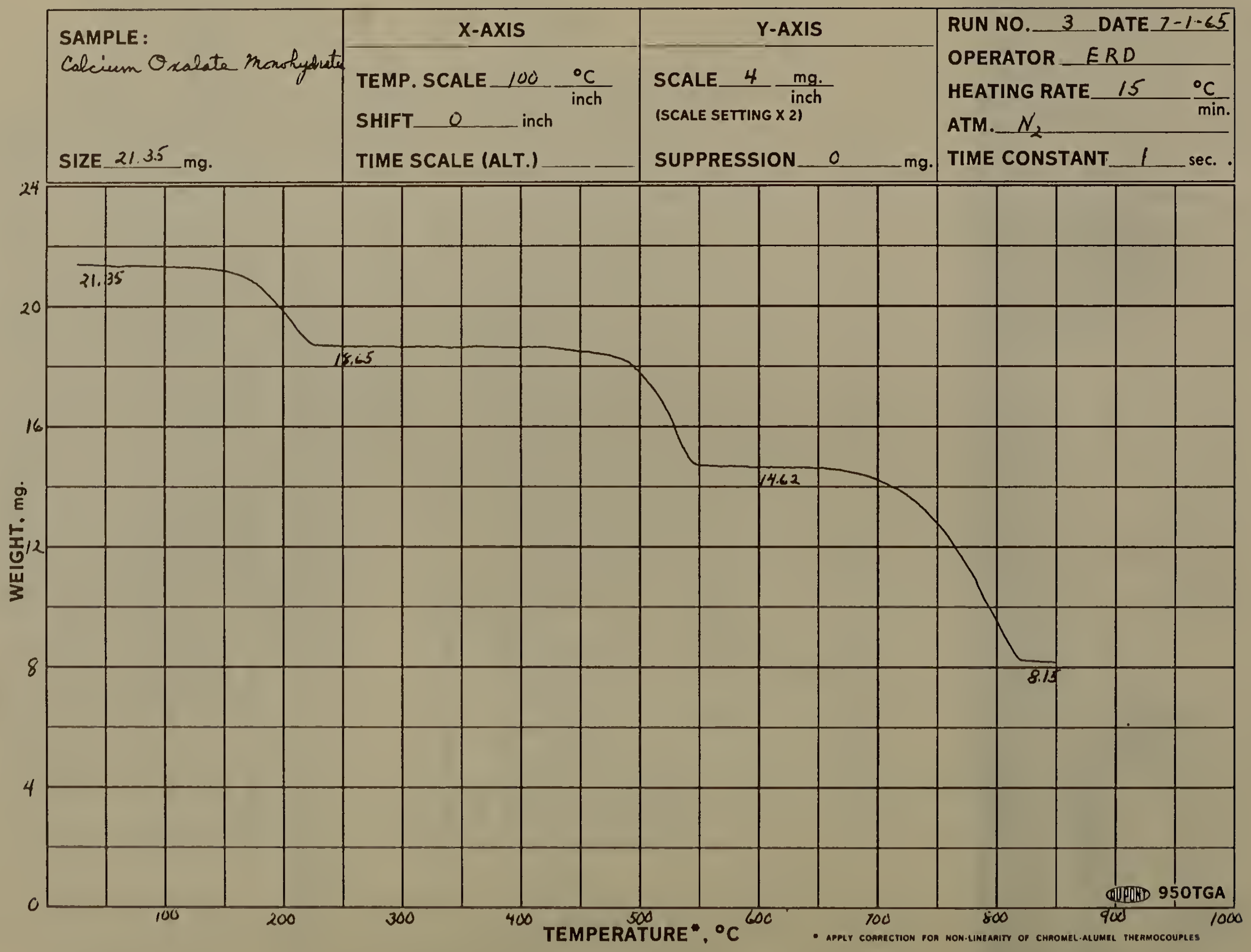
Early work indicates it is possible to obtain a sensitivity of 5 μg with a 100 mg sample load. The corrections for change in weight of a platinum boat on its ignition from room temperature to 1050 °C did not exceed 30 μg. A typical thermogravimetric curve for the decomposition of calcium oxalate is presented in Figure 4. It indicates a relatively "noise" free performance at sensitivity of 0.4 mg per division. The curve, shown in Figure 5 for ignition of NBS 950a U_3O_8 standard reference material in air at sensitivity of 0.02 mg per division again, indicates that a weight change of 5 μg can be readily measured. In this case with a 100 mg load a weight change of 5 parts per ten thousand could be discerned.

(L. A. Machlan, E. R. Deardorff)

D. Preconcentration of Hafnium in Zirconium

The concentration of hafnium, in the range of 40 to 400 ppm, in the standard reference material of zirconium and zircaloy was too low for a direct spectrographic measurement. For that purpose hafnium was preconcentrated by an ion exchange and gravimetric procedure. Hafnium was first separated in a 3.5 M sulfuric acid solution from the bulk of zirconium by ion exchange process. The eluate containing the hafnium and part of the zirconium was then precipitated with cupferron and next with mandelic acid. After an ignition to the oxide it was ready for a spectrographic analysis.

(E. R. Deardorff)



SAMPLE: Calcium Oxalate Monohydrate
SIZE 21.35 mg.

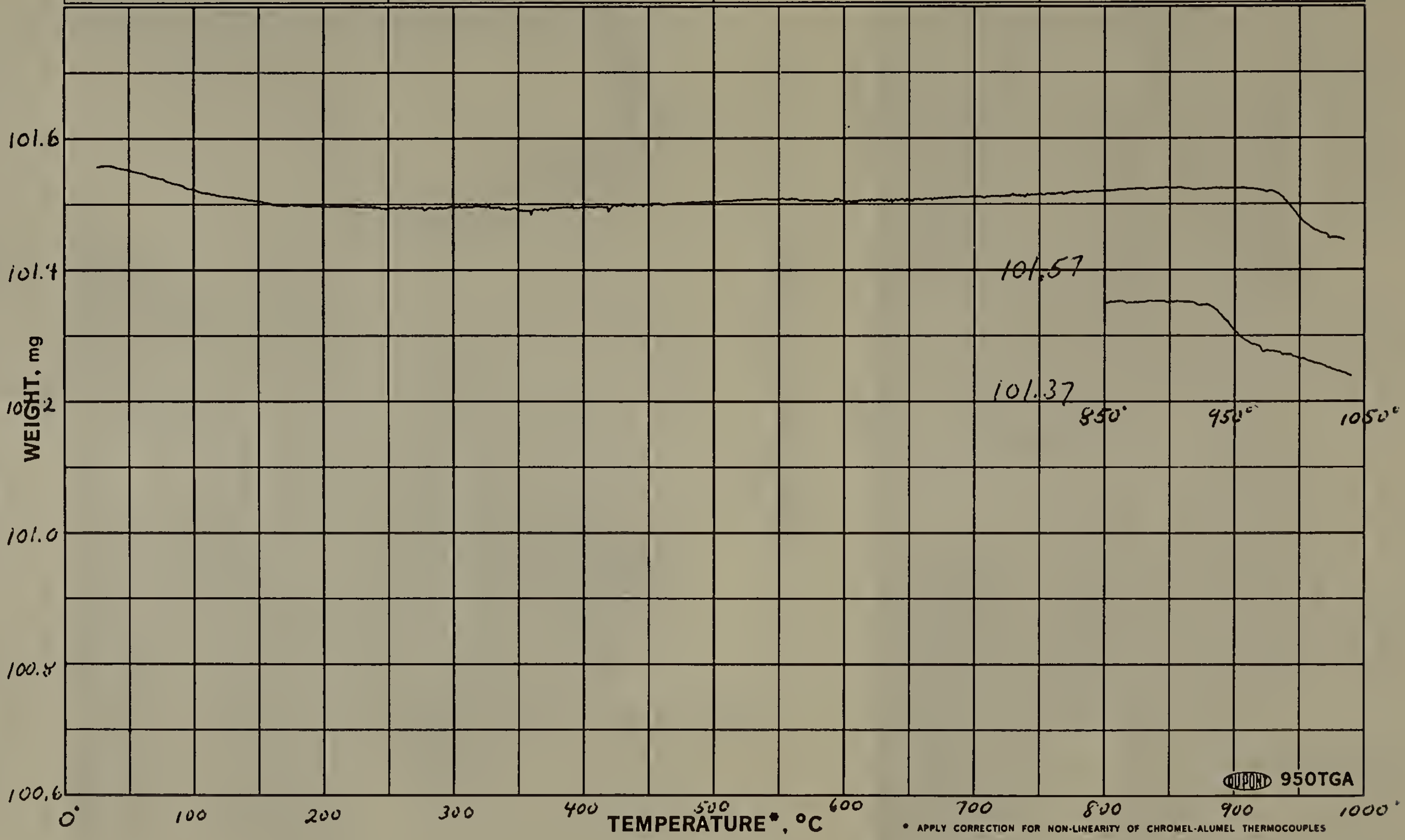
X-AXIS
TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.)

Y-AXIS
SCALE 4 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. 3 DATE 7-1-65
OPERATOR ERD
HEATING RATE 15 °C/min.
ATM. N_2
TIME CONSTANT 1 sec.

Figure 4. Thermogravimetric curve of calcium oxalate monohydrate.

SAMPLE:	X-AXIS	Y-AXIS	
U_3O_8 NBS 950a	TEMP. SCALE 100 °C/inch	SCALE 0.2 mg./inch (SCALE SETTING X 2)	RUN NO. 1 DATE 21 May 65 OPERATOR LAM HEATING RATE 10 °C/min. ATM. air
SIZE 101.56 mg.	SHIFT 0 inch TIME SCALE (ALT.) —	SUPPRESSION 100.6 mg.	TIME CONSTANT 1 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Figure 5. Thermogravimetric curve of U_3O_8.

3. FLAME PHOTOMETRY

The flame photometric competence has the potentialities of yielding accurate values for most of the elements present in trace or relativity low concentration levels. Since one deals in this process with solutions aspirated into a flame source, the chemistry of these solutions plays a dominant role in obtaining best values. Studies are, therefore, under way to determine iron and aluminum in feldspar and calcium and magnesium in dolomite involving solvent extraction, ion exchange chromatography and radiation buffers. The precision of the methods as used on the several materials analyzed during the past year are given in Table 5.

Table 5. Summary of analyses by flame spectrophotometry.

Element determined	Range (%)	Precision ± (%) σ
	Clay 97a and 98a[a]	
Li	.075 - .12	1
Na	.03 - .08	10
K	.5 - 1.0	1
Rb	.002 - .005	20
Cs	.004 - .00	10
	Limestone 1a and Dolomite 88a[a]	
Li	.004	10
Na	.02 - .04	15
K	.14 - .25	3
Rb	.002	20
Cs	N.D.[b]	
Sr	.009 - .14	10

---

[a] All samples were dissolved in 5% $HClO_4$ + HF.
[b] Not detected.

A. New Instrumentation

Further impetus to this work has been made possible by improved instrumentation. Additional components for the two flame photometry instruments were recently installed, adjusted and tested. The instruments are shown in Figures 6 and 7.

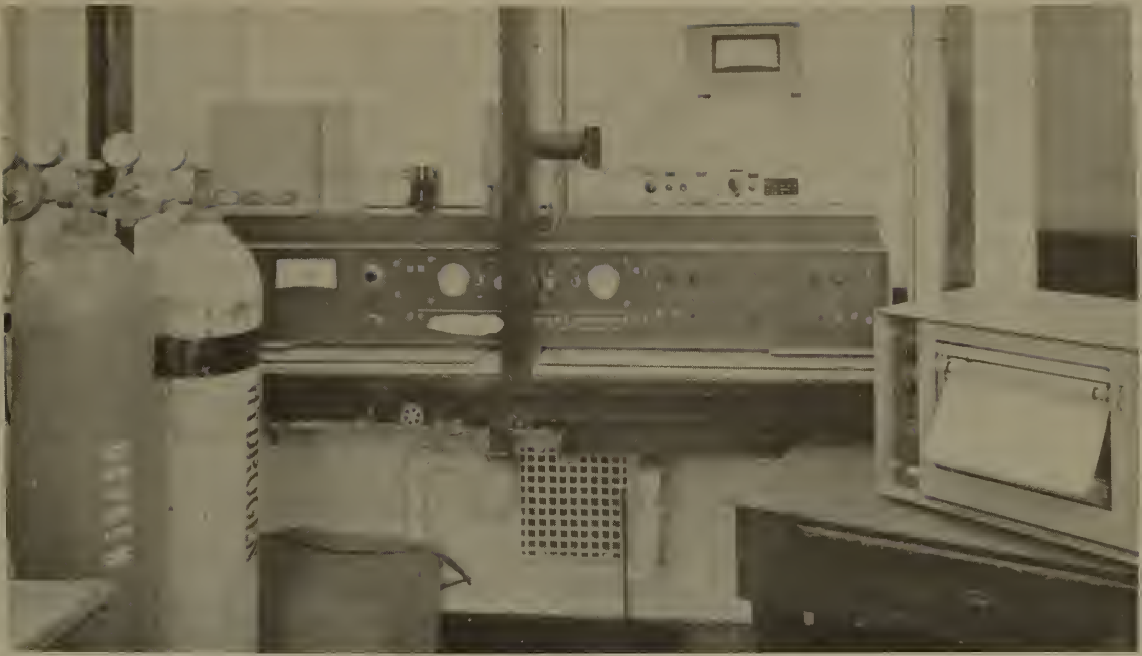


Figure 6. Atomic absorption and flame emission spectrophotometer.

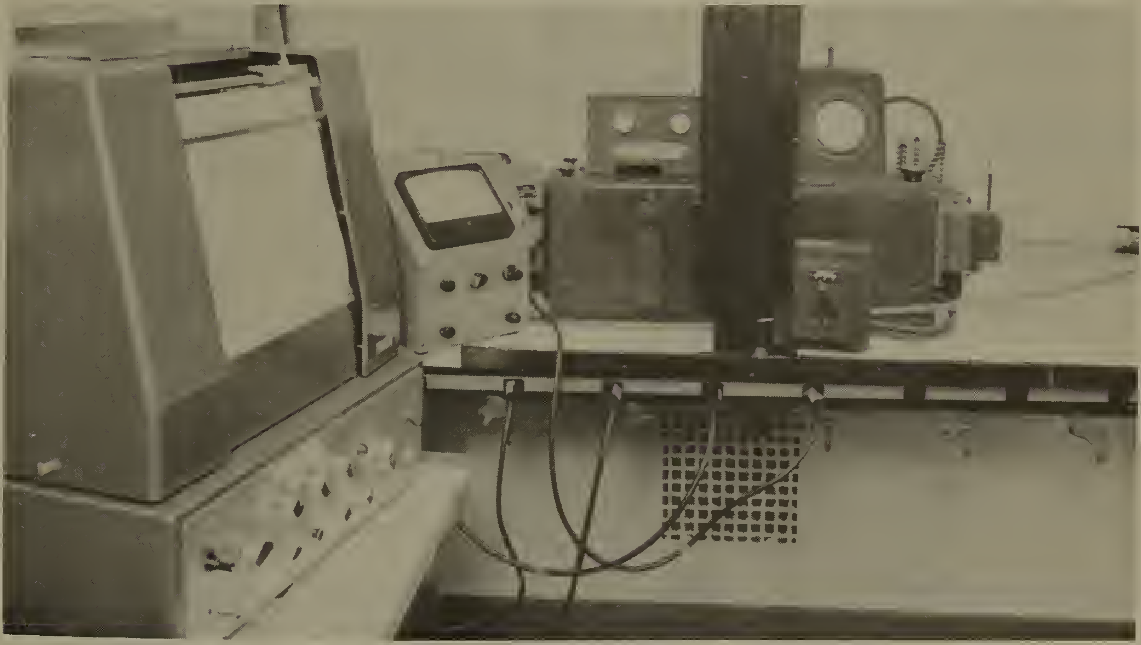


Figure 7. Modified recording flame spectrophotometer.

With the Jarrel-Ash instrument spectra of iron and strontium were recorded and the optimum settings of slit widths, photomultiplier voltage, gain, burner position and fuel to oxygen ratio were evaluated. The emission intensity of the strontium line in the second order at 921 mμ was 40 chart divisions for 3 ppm of Sr. Also, with the new scanning and recording attachment to a modified Beckman Spectrophotometer the spectra of sodium and potassium were recorded. The potassium doublet at 766.5 and 769.9 mμ as shown in Figure 8 was resolved. It is expected that by means of these instruments, the determination of trace elements in standard reference materials will be expedited.

(K. M. Sappenfield and O. Menis)

B. Determination of Alkali and Sr in Clays

In addition to the analytical results on alkali elements for standard reference materials, Flint Clay 97a, and Plastic Clay 98a reported in Table 6, strontium was determined in the

Table 6. Determination of alkali metals in two standard reference materials.

Alkali metal determined	Results (%)	Precision ± (%) σ
	Flint Clay 97a[a]	
K_2O	0.53	1
Na_2O	$.03_5$	10
Li_2O	.12	1
Rb_2O	.002	20
Cs_2O	.004	10
	Plastic Clay 98a[a]	
K_2O	1.06	1
Na_2O	0.07_9	10
Li_2O	$.07_6$	1
Rb_2O	.005	20
Cs_2O	.004	10

---

[a] All samples were dissolved in 5% $HClO_4$ and determined by flame photometry.

Figure 8. Resolution of the potassium doublet at 766.5 and 769.9 mμ. Conditions: 1) instrument, figure 7, 2) slit, 0.02 mm, 3) sensitivity at 15 arbitrary units.

1st curve scanning toward long wavelength, 2nd curve reverse scan.

presence of large concentrations of calcium. A non-aqueous 50% acetone solution was used in this determination. In this case, the sensitivity for the determination of strontium was increased by a factor of two.

C. Determination of Alkali and Strontium in Cements

In cooperation with the Inorganic Building Materials Section, the alkalies and strontium oxide were determined in five Standard Reference Materials Cements by flame photometry. Since only this laboratory determined lithium oxide and rubidium oxide, these values are not certified but are given for added information (see Table 7).

Table 7. The analysis of alkali metals and strontium in cements.

Alkali metal determined	Standard reference material No.					Precision
	1011	1013	1014	1015	1016	(%) σ
Li_2O	0.002	0.001	0.005	0.004	0.012	1
SrO	$.10_1$	$.08_9$	$.25_2$	$.09_9$	$.024_5$	10
Rb_2O	.001	.004	$.006_5$	.005	N.D.[a]	20
K_2O	$.28_1$	$.32_6$	1.02_2	$.89_0$	$.03_8$	1
Na_2O	$.09_1$	$.20_5$	$.24_6$	$.16_5$	$.61_1$	10

---

[a] Not detected.

For this analysis a 0.2g sample is dissolved in perchloric acid, silicon is separated with repeated evaporations with HF and finally, the sample is evaporated to dryness. The residue is dissolved in 5 ml of perchloric acid and diluted with water to a 100-ml volume. In this solution lithium and rubidium were determined flame photometrically by the standard addition method while strontium, sodium and potassium from a calibration curve of synthetic standards.

D. Determination of Alkali Elements in Feldspar (70a)

A 0.2g sample was dissolved in perchloric-hydrofluoric acids and silica was removed by repeated evaporation. The solution was next evaporated to dryness and the residue dissolved in perchloric acid with the final volume adjusted to 100 ml of 5% perchloric acid.

Rubidium and cesium in 70a were also determined flame photometrically by dissolving the potassium chloroplatinate from the gravimetric analysis of potassium in 100 ml of water. The effects of platinum upon the determination of these elements by flame photometry were tested and found to be nil. The values for rubidium and cesium were the same as obtained from the perchloric acid solution of the sample.

(K. M. Sappenfield)

4. SPECTROPHOTOMETRY

During the past year progress in this field can be conveniently divided into two categories: (1) high sensitivity spectrophotometry and (2) high precision spectrophotometry. In addition the general technique has been, and is, finding numerous applications in the characterization of standard reference materials as summarized in Table 8.

Table 8. Precision of spectrophotometric methods as applied to trace element analysis in standard reference materials.

Element	Range (%)	Precision ± (%) σ	Basic method
		Ferrous Alloys	
Mo	0.005 - 0.3	0.001	CNS complex extracted with butyl acetate
	0.3 - 1.5		
Al	.01 - 0.3	.005	Hg cathode separation; aluminon
Ti	0.02 - 0.2	.001	Cupferron precipitation; sodium peroxide
	0.2 - 2.0	.01	
Co	0.001 - 0.1	.001	Nitroso-R salt reagent
	0.1 - 0.0	.005	
Nb	0.004 - 0.2	.001	Cupferron precipitation; anion exchange; hydroquinone
Ta	0.04 - 0.08	.004	Separation as above; pyrogallol
N	0.001 - 0.1	.0005	Kjeldahl; Nessler's reagent
P	0.002 - 0.1	.002	Molybdenum blue complex
	0.1 - 0.8	.01	
Cu	0.002 - 0.1	.002	Citrate + NH_4OH + EDTA; complexation, diethyldithiocarbamate
Ni	20	.02	$K_2S_2O_8$ oxidation; pH 13; dimethylglyoxime (20% Ni by differential method)
		Copper Alloys	
Ni	0.005	.001	Cu electrodeposited; Br_2 oxidation; dimethylglyoxime
Mn	0.03	.002	Oxidized to MnO_4 with KIO_4
Fe	0.3	.005	NH_4OH separation with Al carrier; 1,10-phenanthroline
	.01	.002	
P	0.12	.005	Molybdenum blue complex

Table 8. Precision of spectrophotometric methods as applied to trace element analysis in standard reference materials (cont'd).

Element	Range (%)	Precision ± (%) σ	Basic method
		Limestone	
Ti	0.04 - 0.05	.004	After Al separation; sodium peroxide
Mn	0.15 - 0.20	.001	Oxidized to MnO_4 with KIO_4
		Dolomite	
Si	0.02 - 0.15	.005	Molybdenum blue complex
Al	0.2 - 0.3	.01	Aluminon reagent
Ti	0.01 - 0.02	.002	Sulfosalicylic acid
P	0.005 - 0.01	.001	Molybdenum blue complex
Mn	0.02 - 0.03	.0002	Oxidized to MnO_4 with KIO_4
		High Temperature Alloy	
P	0.004 0.02	.0009 .002	Molybdenum blue complex

A. High Sensitivity Spectrophotometry

1. Introduction

Development work in this area has centered around the investigation of those color reactions which have shown promise of being applicable at the submicrogram level. Although the extension of spectrophotometric to these low levels is inherently difficult, there are certain elements for which sensitivities approaching a few nanograms can be obtained. Boron, nickel, and beryllium have been shown to belong in this group. Cobalt probably does also. The success of such systems depends primarily on a successful pre-concentration step which reduces the final volume of the measured solution. Examination of these concentrates through long path length cells then permits one, in favorable instances, to obtain sensitivities down to the nanogram level.

2. Cell Design

In practical applications a compromise will always have to be made between cell volume and path length. One cannot be increased indefinitely at the expense of the other because of the many problems associated either with handling extremely small volumes or with aligning the long path length cells of very small cross-sectional areas.

A cell design which we have found quite adequate for our present needs is shown in the photograph, Figure 9. These cells were constructed in the NBS shop and the main bodies

Figure 9. High sensitivity spectrophotometric cells.

are made of Teflon. They have a 10-cm light path and an inside diameter of 5.5 mm. Total volume is therefore about 2.3 ml. The silica windows, which measure 1 x 11 mm, are held firmly in place by pressure from a single "O" ring in combination with the screw-on brass end cap. The tapered openings allow these cells to be filled quite readily, the sample being slowly poured down the sides of a hole.

3. Boron-Curcumin System

The first application of these cells to high sensitivity spectrophotometry was to the boron-curcumin system. Although the original color reaction dates back about 100 years, it has received renewed interest in recent years because of the great importance of boron analysis in the nuclear materials field. The British in particular have spent a number of years investigating and refining this procedure [5,6,7]. The preliminary results of our work involving this system indicate that a relative standard deviation of 5% can be obtained in the 10-100 nanogram range. Additional work, however, need to be spent on separation procedures for certain elements when present in large excess before any general applications can be carried out at this level.

4. Beryllium Acetylacetonate

a. Role of blank. A second highly sensitive system which has recently been under investigation is the one formed by the reaction between beryllium and acetylacetone. Strickland and co-workers described the initial work on this system in the early 1950's [8]. The procedure as developed by them is applicable at the microgram level. In their paper, they are quick to point out that, because of the magnitude and variability of the reagent blanks, they could foresee little hope of improving the sensitivity of their method either by pre-concentration techniques or through use of longer absorption cells. We have nevertheless re-examined this system and have found that the absorbances of our reagent "blanks" are at least an order of magnitude less than theirs. Also our precision is better as is seen from Table 9.

Since the method depends upon the measurement of absorbances in the ultraviolet portion of the spectrum, extreme care must be taken to avoid contamination.

b. Determination of nanogram quantities of beryllium with acetylacetonate. The analytical steps in the present procedure are relatively simple. To a sample containing 5-100 nanograms of beryllium, an adequate amount of masking agent is added to complex interferences and the resulting solution is adjusted to a pH of about 7.5 (in practice anywhere in the range 6-10 has been found satis-

Table 9. Absorbance values of acetylacetone "blanks".

Procedures		
Strickland's method	Current method	
	Measured[a]	Calculated
0.08	0.300	0.0060
0.08	0.312	0.0062
0.09	0.310	0.0062
0.08	0.320	0.0064
0.09	0.301	0.0060
0.06	0.290	0.0058

---

[a] These absorbance values were obtained at a 50-fold increase in concentration over Strickland's results.

factory). Two ml of a 1% acetylacetone solution is added and 15 minutes are allowed for complex formation; the solution is then transferred to a small separatory funnel and extracted with successive portions of 2, 1, and 1 ml volumes of chloroform. The combined extracts are diluted to volume in a 5-ml volumetric flask, mixed, transferred to separatory funnel, and then excess reagent is removed by two 15-second backwashes with 10-ml volumes of 0.1 N KOH. The organic layer is drained off through a cotton plug to remove droplets of water and then examined spectrophotometrically at 295 mμ. The beryllium content of the sample is finally determined by aid of a calibration curve.

Acetylacetone is not a specific reagent for beryllium but fortunately the selectivity of the reaction can be vastly improved through the use of masking agents. In practical applications two alternatives exist in eliminating interferences. Either one can separate the beryllium from relatively large amounts of other interfering elements by an electrolysis, batch extraction or the like and then complex any residual interferences with a small amount of masking agent, or else one can add a sufficient amount of complexing agent initially to mask all interferences. The former approach is necessary when analyzing matrices of a low beryllium concentration for example less than 0.1 ppm, while the latter approach (direct masking) may be applicable at higher beryllium levels, especially if the matrix is not too complex.

c. Analysis of NBS samples. Using 1,2-diaminocyclohexanetetraacetic acid as a masking agent, three samples of NBS cartridge brass have been analyzed. In order to test the procedure in the range of 5-100 nanograms of Be, the sample weights varied from 5 to 100 milligrams. The means and standard deviation obtained on these three samples are shown in Table 10.

Table 10. Determination of beryllium in cartridge brass.

Standard reference material No.	Sample wt. (mg)	Weight beryllium (%)	Beryllium (in nanograms) Found	Calculated
1100	5[b]	0.0016	87 ± 2[c]	88
1101	10[b]	0.00055	57 ± 3[c]	55
1102	100[b]	$0.0000 3_3$	29 ± 4[d]	3_3

---

[a] Calculated on the basis of previously reported values.
[b] No separation used.
[c] Four determinations.
[d] Two determinations.

B. High Precision Spectrophotometry

1. Introduction

At its present stage of development differential spectrophotometry has been shown capable of yielding precisions of a few parts in ten thousand [9]; using conventional spectrophotometry, one can achieve at best a precision of approximately 0.2%.

The principle of the differential technique is straightforward and is not confined solely to spectrophotometry. The difference in absorbance between the unknown and a suitably chosen standard is measured. In its simplest form full-scale reading adjustment is made to correspond not to the solvent, as in ordinary spectrophotometry, but to a standard solution of known concentration. There are, however, several possible variations of this general method.

Differential spectrophotometry was first used by Kortum [10] in the 1930's. More recently, it has been advanced by the work of Bastian [11] and Hiskey [12,13,14]. In a purely theoretical treatment Reilley and Crawford [15] have also shown that the ultimate in precision can be obtained by using two reference standards. Their method, however, suffers from the disadvantage of giving a non-linear calibration curve.

Our current investigations in high precision spectrophotometry have thus far been concerned with relatively high concentration and we have, therefore, been using only the single standard technique. The possible application of a differential method to the precise determination of nickel and dysprosium is under investigation. Of the two, the nickel system has been studied much more thoroughly and will, therefore, be presented in some detail.

2. Determination of High Concentration of Nickel

The general procedure for the determination of nickel is based on the method described by Menis [16], except that a differential technique was applied to samples containing high concentration of this element. In this procedure the colored nickel-dimethylglyoxime complex is developed at pH 11 to 13 after oxidation with potassium persulfate.

Initial studies indicate that large amounts of nickel can be determined in less time and with as much precision and accuracy as in the gravimetric method. However, as shown in Table 11, there are still some differences that need to be resolved.

Table 11. Comparison of gravimetric and differential results for several high temperature alloys.

Standard reference material No.	Gravimetric (%)	Differential[a] (%)	Difference	NBS reference No. 1194 (%)	Difference
1193	28.38	28.36	-0.02	28.43	+0.05
1194	24.06	24.10	+ .04	---	---
1195	26.08	26.20	+ .12	25.95	- .13
348	25.88	25.86	+ .02	25.88	.00

---

[a] Versus a standard reference solution of nickel.

The standard deviation calculated on twelve analyses of NBS 1193 (see Table 12) using three different samples and four different nickel concentrations in the reference solution was 0.09%. The accuracy was best in the series of samples measured versus a reference solution of A = 0.400 (see Table 12). These are the results of initial data and variables are being investigated for improving the analyses. A unique feature of this method is that similar alloys can be compared spectrophotometrically for their nickel content. This is demonstrated in Table 11 where the other three high temperature alloys were compared with NBS 1194.

Table 12. The function of absorbance of the reference solution.

	0.005	0.2	0.4	0.6
Sample 1.	28.45	28.23	28.37	28.42
Sample 2.	28.25	28.24	28.37	28.35
Sample 3.	28.29	28.47	28.33	28.43

Other NBS standard materials analyzed for nickel by the differential spectrophotometric method were:

Standard reference material No.	Material	Certified value[a]	Differential method Ni (%)	Differential method Diff. (%)
121c	Cr18-Ni10 (Ti-bearing)	10.51	10.68	+0.17
121c	Cr18-Ni10 (Ti-bearing)	10.51	10.52[b]	+0.01
1175	White cast iron	2.97	2.99	+0.02

---

[a] Based on gravimetric results.
[b] After hexone extraction.

In the case of the white cast iron, the iron to nickel ratio was too great to keep the iron in solution under the high pH conditions of the method. Therefore, most of the iron was separated from the nickel by means of an anion exchange column. Iron may also be the cause for the higher results in 121c, since no separation was made in the first determination.

(E. R. Deardorff and O. Menis)

On the basis of the preceding discussion one might conclude that an unlimited increase in precision can be obtained by employing standard and unknown solutions of sufficiently high absorbance. In practice this increase is limited by two factors. In the first place full-scale readings can be obtained with solutions having a high absorbance only by using relatively wide slit widths. Under these conditions the radiation is no longer monochromatic and all solutes will deviate from Beer's law. The direction of this deviation is such as to decrease the concentrational sensitivity. Secondly, any stray radiation due either to scattering or reflection from optical surfaces makes measurements with solutions of too high an absorbance essentially useless. It may be concluded that for a system to be amenable to differential spectrophotometry, it should (1) form readily and have a high stability, (2) possess a low inherent sensitivity and (3) have a wide characteristic absorption band that is free from interferences.

(R. W. Burke)

C. General Spectrophotometry

1. Determination of Low Concentration of Nickel

The same nickel conditions as used for high precision work can be used to determine small amounts of nickel by direct spectrophotometry. Either an anion exchange column or a methyl isobutyl ketone extraction can be used to separate the iron from the nickel. The methyl isobutyl ketone gave a much faster and cleaner separation than the anion exchange column. Results using such a procedure are contained in Table 13. Preliminary investigation shows that copper does not interfere with this procedure as much as it does with other nickel-dimethylglyoxime methods.

Table 13. Comparison of spectrophotometric values with previous values.

Standard reference material No.	Material	Certified value[a] (%)	Ni determined (%)	Difference (%)
14d	B.O.H. steel	0.041	0.041	0.000
14e	B.O.H. steel	.053	.054	+ .001
55e	Ingot iron	.038	.039	+ .001
152	B.O.H. steel (tin bearing)	.062	.065	+ .003
152a	B.O.H. steel (tin bearing)	---	.057	---
1174	White cast iron	.035[b]	.034	- .001
1174a	White cast iron	.035[b]	.036	- .001

---

[a] Based on gravimetric results.
[b] Not certified.

Future work on this procedure will include determination of the amount of iron that can be tolerated without separation; checking the magnitude of the interferences such as copper, cobalt, and manganese; and use of a variable path cell, see Figure 10, to improve the precision of the differential spectrophotometric measurements. The linearity of this cell's micrometer scale will be evaluated.

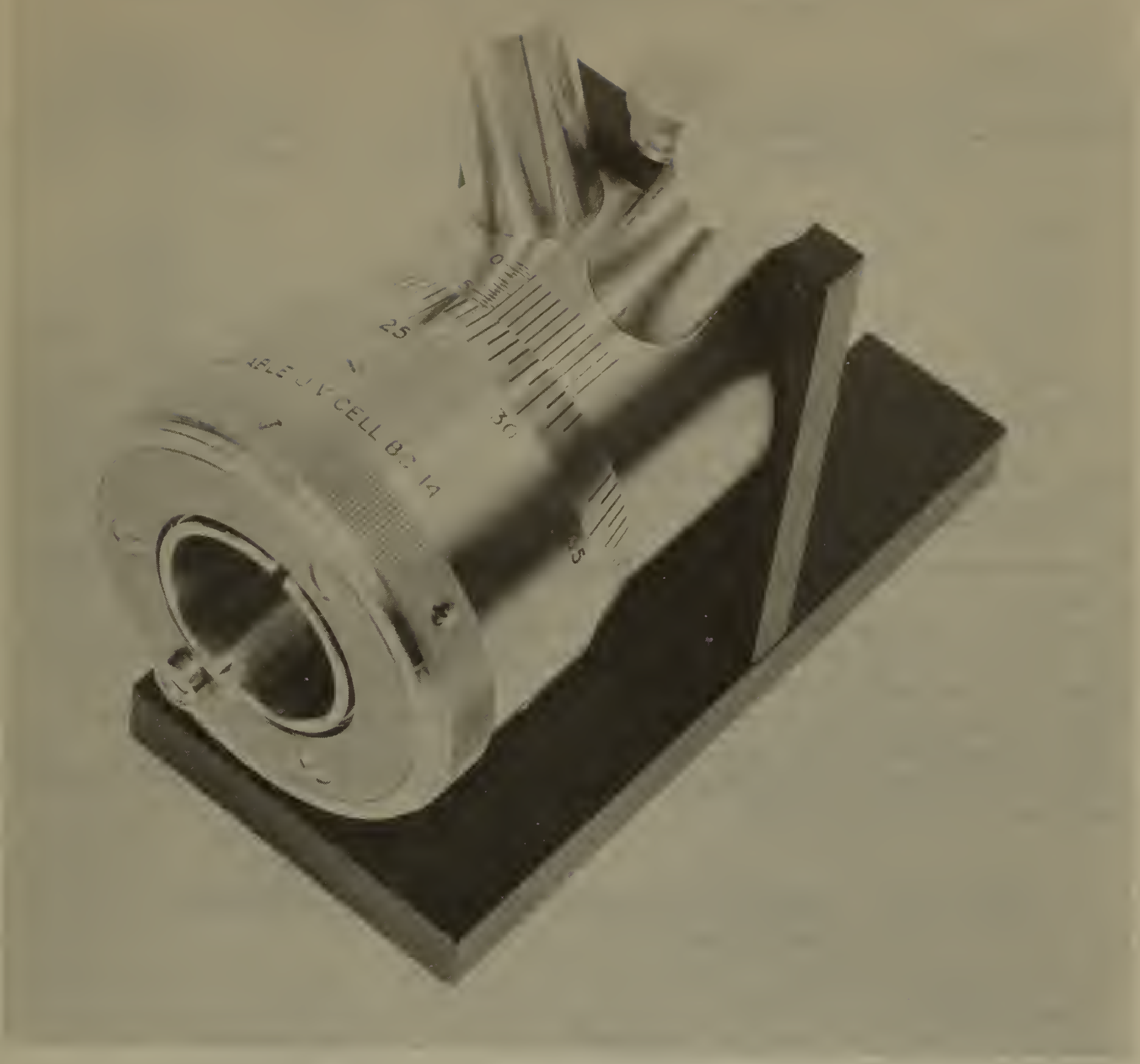


Figure 10. Variable light path spectrophotometric cell.

2. <u>Determination of Trace Elements in Standard Reference</u> Materials.

   a. As, Be and P in brass.
   b. B and Zr in cast iron.
   c. B in high temperature alloy.

The values obtained spectrophotometrically for several trace elements in cartridge brass are given in Table 14. In Table 15 results and the precision are given for boron and zirconium in a number of white cast irons, and in Table 16 for boron in high temperature alloy.

Table 14. Spectrophotometric analysis of cartridge brass.

Standard reference material No.	Phosphorus[a] weight (%)	Arsenic[b] weight (%)	Beryllium[c] weight (%)
C1100[d]	0.010_0	0.020_2	0.0015_9
1101[d]	0.0018_6	0.008_9	0.00055_0
C1101[d]	0.0020_0	0.009_0	0.00054_8
1102[d]	0.0047_0	0.004_5	0.00003_3
C1102[e]	0.0046_7	0.004_5	0.0003_3
Rel. Std. Deviation	3%	4%	1%

---

[a] Phosphorus determined on the yellow phosphovanadomolybdate complex.

[b] Arsenic separated as elemental As by reduction with hypophosphite and determined as the molybdenum blue complex.

[c] Beryllium determined as the acetylacetonate.

[d] Based on three determinations for P and As; based on two determinations for Be.

[e] Based on three determinations for P; based on two determinations for As and Be.

Table 15. Spectrophotometric analysis of white cast iron.

Standard reference material No.	Boron[a] weight (%)	Zirconium[b] weight (%)
1174[c]	0.039	0.011
1174a[d]	0.043	0.020
1175[c]	0.0050	0.039
1175a[c]	0.0043	0.029
1176[e]	0.0008	---
1177[f]	0.025	---
1178[d]	0.114	0.014
1179[f]	0.051	---
1180[e]	0.0020	---

Table 15. Spectrophotometric analysis of white cast iron (cont'd).

Standard reference material No.	Boron[a] weight (%)	Zirconium[b] weight (%)
1182[d]	0.0091	0.0097
1183[d]	0.057	0.125
Rel. Std. Deviation	10%	5%

---

[a] Determined as curcumin complex following separation as the methy borate ester.

[b] Pyrocatechol violet employed as the chromogenic reagent.

[c] Based on two determinations for B and three determinations for Zr.

[d] Based on two determinations for B and two determinations for Zr.

[e] Based on three determinations for B.

[f] Based on two determinations for B.

Table 16. Spectrophotometric analysis for boron in high temperature alloys.

Standard reference material No.	Boron[a] weight (%)
348[b]	0.029
1190[b]	0.093
1193[b]	0.023
1194[b]	0.088
1195[c]	0.0042
1203[b]	0.0062
Rel. Std. Deviation	3%

---

[a] Boron determined as the curcumin complex following separation as the methyl borate ester.

[b] Based on three determinations.

[c] Based on five determinations.

3. Determination of Antimony by the Brilliant Green Procedure

One analysis found especially difficult in studies performed during the past year has been the determination of antimony in cast iron. After attempts by other competences were unsuccessful, recently, by means of the spectrophotometry, the problem now appears to be resolved. Some representative results are shown in Table 17.

Table 17. Spectrophotometric analysis for antimony in white cast iron by the Brilliant Green method.

Standard reference material No.	Antimony weight (%)
1174[a,b]	0.203
1174a[b]	0.203
1175[b]	0.0192
1175a[b]	0.0203
1176[b]	0.33_0
1177[b]	0.200
Rel. Std. Deviation	2%

---

[a] Typical composition of a white iron: C, 2-4%; Mn, 0.3-1.5%; P, 0.01-0.8%; S, 0.02-0.2%; and Si, 0.3-3.5% plus residuals including: Cu, Ni, Cr, V, Mo, Ti, As, Sb, N, Sn, Co, Te, B, Bi, Zr, Pb, and Al.

[b] Based on three determinations.

Briefly, the procedure adopted is as follows: The sample is dissolved in concentrated hydrochloric acid via the sealed-tube technique [17]. By so doing, any possible loss of antimony either as stibine or $SbCl_3$ is prevented. The solution is removed from the tube and diluted to a convenient volume with 1:1 HCl. A suitable aliquot is taken for analysis and the Sb^{+3} is oxidized to Sb^{+5} with sodium nitrite. The sample is then diluted fourfold with a saturated solution of sodium pyrophosphate ($P_4O_7^{-4}$ is used to mask iron interference). An excess of Brilliant Green solution is added, the Sb^{+5} complex is extracted into toluene, and the extract is examined spectrophotometrically at 650 mμ. The antimony content is finally determined by aid of a calibration curve. Once the sample is in solution, a single determination can easily be made in five minutes.

(R. W. Burke)

4. Analysis of Trace Quantities of Manganese and Silicon in Titanium Alloys

Other analyses which have caused some concern during the past year have been the determination of manganese and silicon in titanium alloys. During this period the sensitivity of the periodate method for manganese in these materials has been extended from 50 ppm to 5 ppm. At this lower level a number of outside laboratories have experienced considerable difficulty in obtaining reliable results. This difficulty has now been traced to the presence of organic compounds in the de-ionized water they had employed. By using redistilled water it was demonstrated that a high degree of precision and accuracy can be obtained with this procedure for the determination of manganese at these lower levels.

The ASTM procedure for determining silicon in titanium alloys by the molybdenum blue method indicated no interference from tin [18]. However, in NBS 176, a new titanium standard metallic tin remained undissolved in the dissolution step. The metallic tin reduced the ammonium molybdate reagent and produced a blue color even in the blank solutions. When the sample was oxidized with a few drops of hydrogen peroxide, however, the tin dissolved and did not interfere in the silicon determination.

(E. R. Deardorff)

Also a second method for determining silicon in titanium was also employed. In this procedure the silicomolybdate complex is extracted with butyl alcohol and then the heteropoly blue comples is formed directly in the alcohol extract. By carrying out this extraction step the silicon was separated from interfering elements and consequently the accuracy of the determination was substantially improved.

(R. Bell and E. R. Deardorff)

The precision of spectrophotometric methods as applied to trace element analysis during this period is demonstrated by the results shown in Table 8. As can be seen, suitable methods are presently used for a large number of elements in a variety of materials.

5. Conclusion

Most of the difficulties encountered in spectrophotometry are still due to the complex chemical nature of the sample. The most difficult problems have to do with separation and preconcentration of the desired constituent and with the removal of interfering substances. In the future it is hoped greater use can be made of masking phenomena, extractions and chromatographic separations in an attempt to increase the selectivity of both high sensitivity and high precision studies.

(R. W. Burke and O. Menis)

5. GASES IN METALS

The efforts in the area of analysis of metals for gaseous constituents during the past year centered around the determination of oxygen in ferrous and titanium alloys. A major phase of this work dealt with the homogeneity testing of various metal samples that are to be certified as to the content of the gaseous elements, O_2, N_2 and H_2.

A. Determination of Gases in Ferrous Alloys

1. Types of Materials

Four ferrous alloys are now being investigated for possible use as standards containing certified amounts of gaseous components. The major study at this time dealt with the determination of the oxygen content. The four alloys tested are as follows:

(1) Ingot Iron obtained from the Armco Steel Corp., 1/4" diameter, 12-ft lengths, about 225 rods.

(2) 431 Stainless Steel obtained from the Allegheny Ludlum Steel Corp., 5/16" diameter, 12-ft lengths, about 170 rods.

(3) Vacuum Melted Steel obtained from the United States Steel Corp., 1/4" diameter, 2-ft lengths, 5 lots.

(4) Valve Steel 21-4 N obtained from the Allegheny Ludlum Steel Corp., 1/4" diameter, 10-12 ft long, 250 rods.

All of the above materials were procured through the services of a representative of the AISI.

The ingot iron, 431 stainless steel and the vacuum melted steel have been analyzed in this laboratory and samples of each of these materials have been sent out to cooperating laboratories, the results of which have been received and tabulated.

2. Evaluation of Results

After careful consideration of the results obtained in this section and outside laboratories it was decided that additional tests would be desirable. The new testing program (after consultation with the National Bureau of Standards Statistical Engineering Laboratory) was designed to evaluate the errors due to the inhomogeneity of the material and that due to the method. For that purpose, a sample of some

40 rods out of each lot of material as against the original 12 rods sample is now under way. Four samples are to be taken from a single 12-inch rod in which A and C are opposite ends and B and B' are adjacent middle sections of the rod. These tests are being carried out in a new apparatus which is described in the Apparatus Section. About 1/4 of this reevaluation program of the analysis for oxygen is now completed for the samples of ingot iron. The data from this first test summarized in Tables 18 and 19 indicate that the material could be grouped into two lots containing 525 ± 10 ppm and 475 ± 10 ppm oxygen respectively.

Table 18. Determination of oxygen in ingot iron by CO-Infrared measurement.[a]

Date	Standard reference material No.	Oxygen Found (ppm)	Oxygen Average (ppm)	Standard Deviation (%) σ
6/4	40A-1	525		
	40B-1	511		
	40B'-1	510		
	40C-1	539		
			521.3	2.6
6/4	39A-1	475		
	39B-1	474		
	39B'-1	477		
	39C-1	475		
			475.3	.3
6/4	32A-1	509		
	32B-1	515		
	32B'-1	516		
	32C-1	521		
			515.3	1.0
6/4	12A-3	479		
	12B-3	475		
	12B'-3	471		
	12C-3	476		
			475.3	.7
6/4	31A-1	537		
	31B-1	476		
	31B'-1	528		
	31C-1	536		
			534.8	.9
6/9	11A-1	486		
	11B-1	476		
	11B'-1	479		
	12C-1	515		
			489.0	3.7

Table 18. Determination of oxygen in ingot iron by CO-Infrared measurement (cont'd).[a]

Date	Standard reference material No.	Oxygen		Standard Deviation
		Found (ppm)	Average (ppm)	(%) σ
6/9	30A-1	487		
	30B-1	483		
	30B'-1	483		
	30C-1	481		
			483.5	.5
6/9	29A-1	487		
	29B-1	485		
	29B'-1	501		
	29C-1	483		
			489.0	1.7
6/9	28A-1	484		
	28B-1	478		
	28B'-1	489		
	28C-1	483		
			483.5	.9
6/9	10A-3	553		
	10B-3	534		
	10B'-1	520		
	10C-3	532		
			534.8	2.6

---

[a] Temperature at 1650 °C, Ni-premelt, collection time, four minutes.

Table 19. Segragation of oxygen into two groups in ingot iron samples.

Standard reference material No.	Oxygen (average) (ppm)	Standard deviation (%) σ
39, 12, 11, 30, 29, 28	482.6	2.0
40, 32, 31, 10	526.5	2.4

The estimate of precision as shown by the relative standard deviation (RSD) values in Table 18 is better than previous data obtained with the NRC instrument. Final evaluation of the significance of these values will be made on completion of the tests. A similar study will also be done on the 431 stainless steel and the vacuum melted steel in order to get additional information of homogeneity, as well as obtaining a more accurate value for oxygen content of the materials.

The work on the sample of valve steel was interrupted because of the large error in measuring the oxygen in the presence of the very high concentration of nitrogen. However, it is planned to attack the problem with the new apparatus which eliminates this difficulty.

B. Determination of Gases in Titanium and Titanium Alloys

Four titanium alloys have been acquired through the services of Mr. S. Vigo of the U. S. Army Material Research Agency to be used as standards for gas content.

The materials are as follows:

(1) Unalloyed Titanium obtained from Republic Steel Corp., 511 bars 4" long by 1/2" diameter.

(2) 6 Al-4V - Titanium Alloy obtained from Titanium Metals Corp., 287 bars, 0.435-inch diameter and 7.5 inches long.

(3) 8% Mn - Titanium alloy obtained from Mallory Sharon Metals Corp., 580 bars, 5/8" diameter and 4 inches long.

(4) Titanium Alloy (Cr 10%, V 13% and Al 3%), B120VCA, obtained from Crucible Steel Co. of America, 350 bars, 0.475-inch diameter and 4 inches long.

The preliminary analysis of the unalloyed, 8% Mn alloy and the Al-4V alloy have been completed in this laboratory using a platinum bath, method and the results collected.

Samples of the above material have been sent out to cooperating laboratories and results from most of them have been received. We are now in the process of collecting and correlating these results for a statistical treatment.

Considerable difficulty in obtaining reproducible results with the B120VCA alloy has been also encountered and a method for analyzing this material with some degree of certainty is now being investigated. For that purpose a tin flux and tin bath method is being substituted for the platinum flux.

C. Apparatus

Up to May 1965 only one vacuum fusion apparatus, NRC 912, was available for the analysis of gases in metals.

In this apparatus the metal sample is melted in a graphite crucible and the gases collected and measured using a calibrated McLeod gage. The gases are then separated by means of a differential freezing technique, and the amounts of gas in the metals determined by a constant volume pressure measurement technique.

In May an additional apparatus manufactured by the Bendix-Balzer Corp., Exhalograph EA-1 was received and is shown in Figure 11. In this apparatus the sample is again

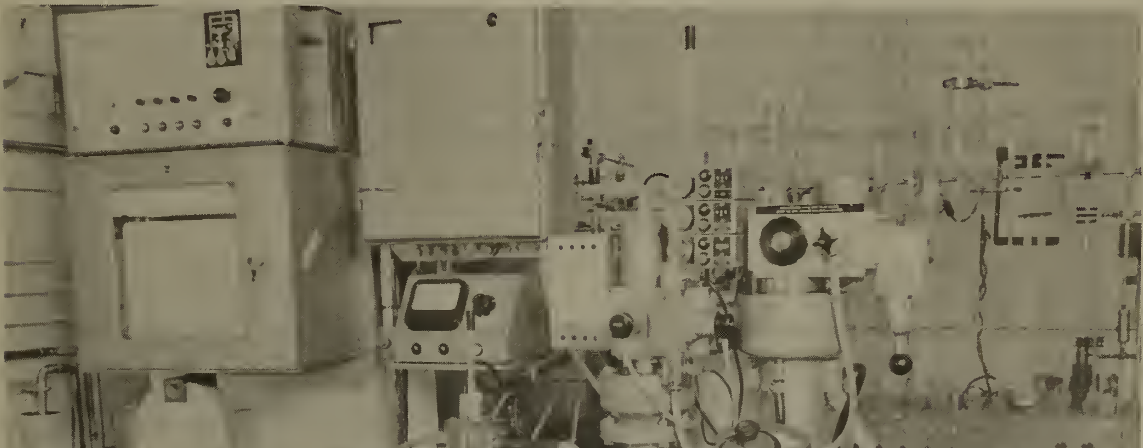


Figure 11. Vacuum evolution apparatus for the determination of O_2, H_2 and N_2.

melted under vacuum in a graphite crucible and the gases given off are collected. The method of measuring these gases, CO (from the reaction of oxygen with carbon), N_2 and H_2 differs, however, and is as follows:

(1) The CO is analyzed with an infra-red analysis apparatus.

(2) The H_2 is analyzed in a thermal conductivity cell.

(3) The nitrogen is analyzed using a pressure difference method.

The particular advantages of this apparatus are that the CO can be determined by a direct method and not by a pressure difference, and also the extreme rapidity with which the samples may be analyzed. For example, recently, with this apparatus it was possible to analyze 40 samples of ingot iron in one day. To analyze this number of samples by the use of the NRC 912, requires 2 or 3 weeks under ideal conditions. It is hoped, therefore, to use this apparatus extensively, especially in the survey of material for homogeneity.

It is also possible to calibrate this apparatus using the pure gases CO, H_2, N_2 admitted to the apparatus by means of a special calibration block. A typical calibration curve for the addition of CO gas under STP condition is shown in Figure 12. This feature is especially desirable as a check whether gettering is taking place in the apparatus, as may happen with certain metals. This checking is accomplished by adding to the furnace section the same amounts of gases which are collected from a metal sample and then repeating the analysis to see whether complete recovery is attained.

(J. T. Sterling, F. Palumbo)

D. Determination of Nitrogen in Ferrous Alloys by Alkaline Fusion

1. Introduction

Two methods, the vacuum fusion and the Kjeldahl, have been extensively used to determine nitrogen in metals. The first method requires complicated and fairly expensive equipment and is not readily applicable for handling large number of samples. Although the Kjeldahl method is used extensively it has been shown to fail when acid resistant nitrides such as those of silicon and boron are present [19].

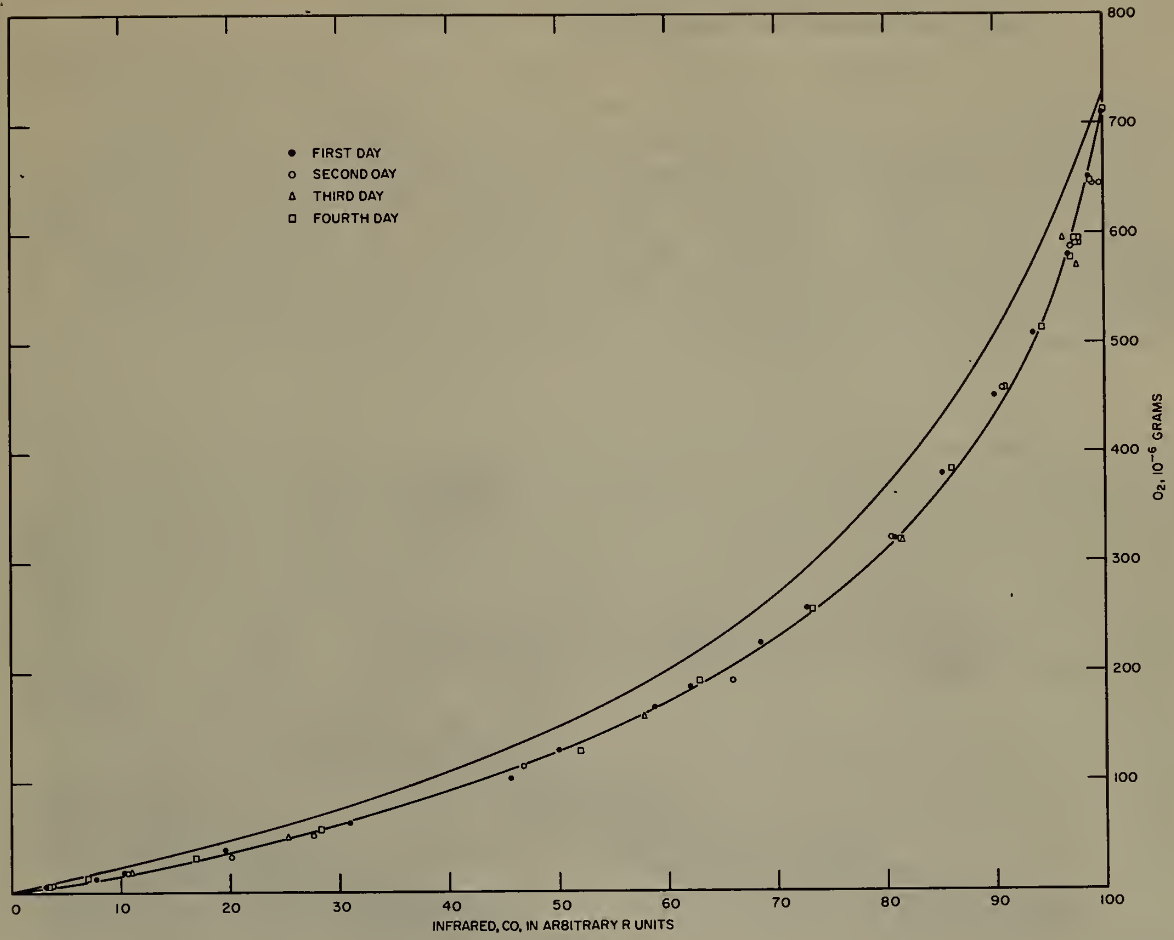


Figure 12. Calibration curve of the infra-red absorbance apparatus for the determination of O_2. (smooth line manufacturer's initial calibration)

When acid resistant nitrides are present, an alkaline fusion method is best suited. Bennett [20] fused samples with an oxidizing mixture consisting of sodium carbonate, potassium carbonate and potassium chromate. The volume of the resulting nitrogen was measured in a nitrometer. Karp et al [19] fused the alloy in an atmosphere of hydrogen with sodium hydroxide containing a little sodium carbonate. The resulting ammonia was absorbed and determined photometrically.

The method suggested by Karp et al will be used to determine nitrogen in the ferrous alloys issued as standard reference materials. These values of nitrogen will be compared with those found by other methods.

. Apparatus and Method

The photograph in Figure 13 shows the apparatus for the determination of nitrogen by the method suggested by Karp et al [19]. The essential part of the apparatus consists of nickel tubing which is heated to 950°C by a split tube furnace. The ends of the nickel tubing are cooled by water by means of wrapped copper coils soldered to the nickel tube. The evolved ammonia is absorbed in water contained in the glass washing bottle. Argon is used to remove the oxygen from the apparatus before the hydrogen is introduced.

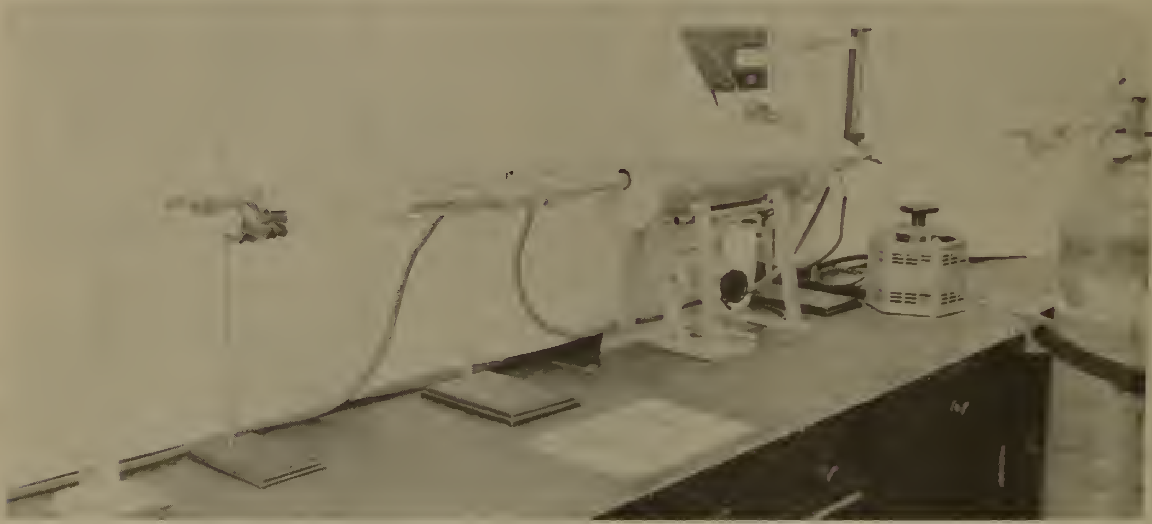


Figure 13. Apparatus for the alkali fusion and hydrogen sweep method for the determination of nitrogen.

3. Initial Results on Nitride Determination

In the first tests with NBS 125a, results comparable to those reported by Karp et al [19] were obtained. These are almost by a factor of two greater than the certified value. The application of this method to check the presence of refractory nitrides in standard reference materials should prove, therefore, of great value.

(B. B. Bendigo)

6. ASPECTS OF ANALYSIS ASSOCIATED WITH STANDARD REFERENCE MATERIALS

A. Introduction

Other aspects of the work of this section relating to the analysis of standard reference materials by one of the competences described previously, deal with the following areas: assistance in procurement of the material, conversion of the material to a suitable sample form, homogeneity testing, selecting and sending samples to cooperating outside laboratories and, finally, evaluating the results of these laboratories and incorporating their values in the certification. Most of these activities have now been assumed by the Office of Standard Reference Materials.

Some of the problems and data relating to this work are described in this section of the report. It deals with the general type of materials of ferrous, non-ferrous, ceramics, limestones, ores, uranium and plutonium. This group represents approximately 25 standard reference samples of the 540 issued by the Office of Standard Reference Materials.

The methods of analysis described in the section dealing with various competences, are selected or designed to give the best obtainable results and depend upon the matrix of the material. In some instances, more than one procedure is employed for an element as a cross-check on both the precision and accuracy of the composition.

The following table, Table 20, gives information on 18 standard iron-base alloys that were either prepared, analyzed and certified since January 1964 or are in the process of analysis.

Table 20. Scope of work in the analysis of ferrous base materials.[a]

Standard reference material No.	Type	Number of cooperators	Elements certified	Number of determinations (NBS)
346	Valve steel	7	C,Mn,P,S,Si, Cu,Ni,Cr,V,N	119
27e	Iron ore	15	Fe,P,SiO_2	40
131a	Low carbon steel	9	C	23
14e	B.O.H., 0.8 carbon steel	5	C,Mn,P,S,Si, Cu,Ni,Cr,V,Mo	88

Table 20. Scope of work in the analysis of ferrous base materials (cont'd)[a].

Standard reference material No.	Type	Number of cooperators	Elements certified	Number of determinations (NBS)
152a	B.O.H., 0.4 carbon steel, tin bearing	6	C,Mn,P,S,Si, Cu,Ni,Cr,V,Mo, Sn	53
12h	B.O.H., 0.4 carbon steel	5	C,Mn,P,S,Si, Cu,Ni,Cr,V,Mo, N	46
1176-1183	Cast irons	5	C,Mn,P,S,Si, Cu,Ni,Cr,V,Mo, Ti,Sn,Co,Al, Pb,Bi,As	335
1174-1174a	Cast irons	2	C,Mn,P,S,Si, Cu,Ni,Cr,V,Mo, Ti,Sn,Co,Al	86
1175-1175a	Cast irons	2	C,Mn,P,S,Si, Cu,Ni,Cr,V,Mo, Ti, Sn,Co,Al	62

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[a] All work completed except for sample 152a.

In addition to the samples listed above, the laboratory completed the analysis of two additional samples.

Standard sample 19g, B.O.H., 0.2% carbon steel is specially noted because it provides a group of residual elements that are becoming of significant interest and importance to the steel industry. The residuals and their certified values are given.

certified values are given as follows:

Elements	Per cent	Elements	Per cent
Cu	0.093	Nb	0.026
Ni	0.066	Sn	0.008
Cr	0.374	Al	0.031
V	0.012	Ti	0.027
Mo	0.013	Co	0.012

The addition of standard sample 339 to the list of standard reference materials represents the Bureau's first attempt at providing a standard sample certified for selenium. This new standard is a stainless steel containing 17 per cent chromium, 9 per cent nickel and 0.25 per cent selenium.

Detailed procedures for the analysis of these types of materials are being published in NBS-260 series.

B. Preparation and Conversion of the Material to a Suitable Sample Form

The preparation of the standard reference materials for use in analyses is important and without which the highest degree of accuracy in analysis cannot be attained. The procedures used for a variety of materials such as ferrous, non-ferrous, ceramics, clays, rocks, actinide elements are briefly outlined here. In the subsequent sections are described the analytical tests employed to establish the homogeneity of these preparations, and the work associated with the cooperators.

1. Steel Samples

For the preparation of standard steel samples, the material which is furnished to NBS by the steel industry, is in the form of round bars about 6 inches in diameter and 36 inches in length and weigh approximately 200 pounds each. Six to twelve bars are generally used for one standard and must be from the same heat and sufficiently homogeneous so that the entire lot can be issued under one certificate of analysis. The outside surface is removed with a heavy-duty lathe and discarded. The bars are then turned into nicked "chips" with a special high-speed tool having a serrated cutting edge. The serrations on the cutting face of the tool control the length of the chips, which are ordinarily 1/4 to 3/4 inches in length, the other dimensions being controlled by the speed of the lathe and the feed. For ordinary steels, the lathe speed is approximately 16 rpm and the depth of cut is 0.011 inch. These may vary, however, depending upon the cutting characteristics of the material.

Cutting is discontinued when the core section approximates 1-1/4 inches. Because it is rarely possible to produce directly the form of chips desired, it is necessary to crush or grind the cuttings in a chilled-iron, Lawrence-type crusher, in order to obtain material of suitable particle size. The material is next sifted and the proper-sized portion, usually that between a No. 16 mesh (1.19 mm sieve opening) and a No. 40 mesh (420 micron sieve opening), is retained for use as the standard sample. The entire sample is then mixed in a large cone-shaped mixer for 1 or 2 hours.

The particles of samples of the metal standards must be comparatively small and be more or less uniform in size, because as is generally well-known the composition may vary with "chip" or particle size.

On a recent 7 bar lot of 14e (B.O.H., 0.8 per cent carbon steel), the following summary shows the recovery of the finished material from the original bar stock.

Standard reference materials No.	Number of bars	Size (inches)	Total weight (lbs)	Final chip sample (lbs)	Number of units
14e	7	6"x36"	2075	1761	4750

The discarded material consisted of the following:

Cores (lbs)	Dust and fines (lbs)	Miscellaneous (lbs)
100	108	106

2. Cast Iron

To prevent undue segregation, cast irons for use in the preparation of standard samples are cast in the form of hollow cylinders approximately 30 inches in length, 12 inches outside diameter with a wall thickness of about 2 inches. The cylinders are machined using a multiple tool consisting of 4 ordinary turning tools clamped together.

The machined material is first sifted to remove the fine particles of iron and free graphite. It is then mixed in a large cone-shaped mixer for 1 hour through which a strong current of air is passed to remove any free graphite. The mixing gives rise to a certain amount of fine material and the mixed sample is, therefore, again sifted to obtain the desired particle size which is the portion that passes a No. 16 mesh sieve and remains on a No. 35 mesh sieve.

3. Spectrographic Samples

Spectrographic samples for chemical analyses vary in types, sizes and composition and are sampled accordingly.

a. White cast iron. These alloys are prepared from 1-1/4-inch square and 3/4-inch thick solid sections by breaking brittle segments cut from the certified portion of the samples, in a hardened iron mortar with an iron pestle. The material is then sized to pass through a No. 14 sieve.

b. Carbon and alloy steels. These alloys are prepared in a variety of sizes (7/32 inch in diameter and 4 inches long; 1/2 inch in diameter and 2 inches long; and 1-1/4 inch in diameter and 1/4 inch thick) and are sampled either by milling the cross section of the accepted material or by lathe-cutting to the desired particle size. Generally, for those samples whose diameters are less than 1 inch, the former technique is used, while the latter procedure is followed for samples whose diameters are greater than 1 inch.

c. Copper-base alloys. Similar processes and preparation tasks were carried out for copper-base and other non-ferrous alloys. The preparation of the spectrochemical standards for which chemical analyses were performed during the past year is described in the NBS 260-2 [21]. Sampling was carried out on rods or bars by cutting with a milling machine or drilling cores at different positions.

4. Limestone and Dolomite

Limestone and dolomite materials were ground with an air reductionizer and screened in a classifier. The final sample was passed through a 200-mesh sieve.

5. Rocks and Ceramics

These materials are crushed, ground and screened through a 100-mesh sieve. The materials are then mixed in a porcelain-lined conic mixer.

6. Actinide Elements

The actinide elements, especially uranium-235 and -233, plutonium metal or compounds such as oxides or sulfates are handled in hoods or glove boxes because of their high toxicity from alpha emission.

C. Homogeneity Studies

A major factor in characterizing standard reference materials involves the establishment of the homogeneity of the sample before it is analyzed for final certification. Depending on the type of material and method of preparation, behavior of a given element during the process of preparation, and the precision of the method used in determining the element, considerable time and effort is expended on this type of investigation. During the past year, homogeneity tests were performed on ferrous-base and copper-base spectrographic standards, and other ceramic or rock materials. In the following sections general characteristics of the materials and the evaluation of their homogeneity are described.

1. Ferrous-Base Materials

a. White cast iron standards. Supplementing the previously analyzed and certified white cast irons (1176-1183) are two additional white irons 1174, 1174a and 1175, 1175a. These standards were developed as replacements for the limited supply of the eight standards (1176-1183) prepared previously and are to serve the long-term need for these types of alloys.

Preliminary homogeneity testing for carbon, phosphorus, sulfur and silicon was considered necessary because of the complexity of the metallurgical structure of white iron. The table shows the data obtained for the 4 elements. The spread of values falls within the error limits of these determinations indicating optimum homogeneity.

Table 21. Homogeneity study of white cast iron, per cent composition.

Standard reference material No.	C	P	S	Si
1174	3.50, 3.51	0.227, .233	0.153, .155	0.288, .292
1174a	3.46, 3.45	0.288, .230	0.157, .156	0.286, .289
1175	1.98, 1.97 2.04, 2.00	0.592, .591	0.016, .017	3.47, 3.46
1175a	2.04, 2.00 1.99, 1.99	0.600, .602	0.017, .017	3.44, 3.44

In addition to the values obtained above, homogeneity testing by spectroscopy indicated the white iron material was sufficiently homogeneous to be used as spectrographic standards.

Other data obtained by this section includes values (by the general methods outlined in the section of this report describing the competences) for the following elements: manganese, copper, nickel, chromium, vanadium, molybdenum, titanium, tin, arsenic, cobalt, bismuth, lead and aluminum.

b. Maraging steels. The maraging nickel steels are a group of relatively new, very low carbon iron-nickel alloys that exhibit ultra-high strength yet possess exceptionally high ductility and toughness. Because of these desirable physical characteristics they are becoming of considerable commercial interest and importance. Two alloys, NBS 1155 and 1156, have been analyzed for carbon, phosphorus, sulfur, nickel, molybdenum and titanium to establish homogeneity. Whether or not the material can be used for standard samples will depend upon additional data being supplied by spectrochemical analyses.

c. High-temperature alloys. Three (3) nickel chromium-iron alloys (NBS 1193, 1194 and 1195) referred to as Discaloys, have been analyzed for carbon and sulfur for homogeneity prior to their analysis at NBS and before being sent to selected laboratories for cooperative analysis. The carbon content ranges from 0.007 (1195) to 0.028 (1193) per cents and the sulfur ranges from 0.014 (1195) to 0.083 (1194) per cents, in these three materials.

Of interest, are data that were obtained in connection with homogeneity studies during the cutting operation of standard sample 19g, 0.2 per cent carbon steel. Samples were taken from different positions on two bars and analyzed for carbon and sulfur.

The figures below represent cross-sections of each of two bars and show the distribution and relative values obtained for the two elements at three positions. From the data in Table 22, it was concluded that the variations were not significant enough for rejection; hence, the material from the two bars was processed for standard sample use.

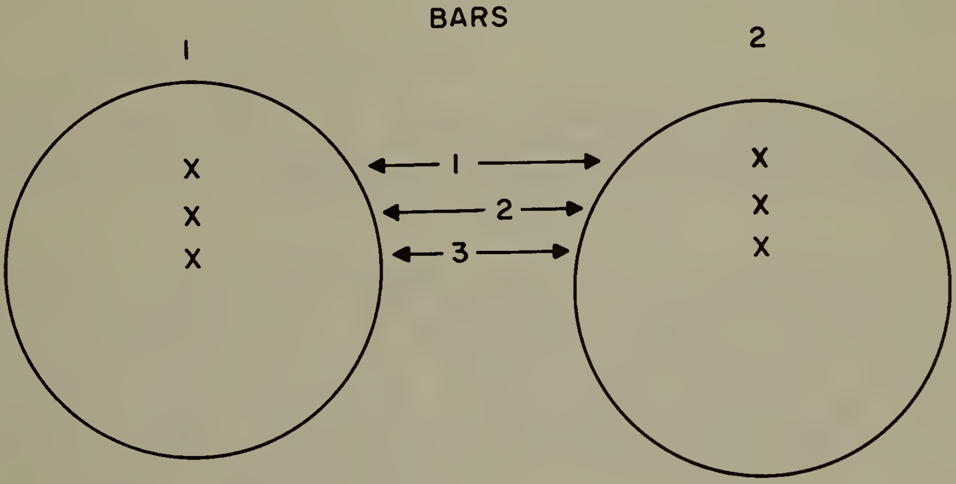

Figure 14. Sampling positions from bars of discaloy.

Table 22. Distribution of carbon and sulfur in high temperature alloy.

Bar	Position	Distribution	
		Carbon (%)	Sulfur(%)
1	1	0.224 0.225	0.031 0.031
	2	.228	.032
	3	.236	.034 .034
2	1	.232	.032
	2	.229 .227	.032
	3	.240 .242	.033

After final processing of the material, the final certified values for the two elements, carbon and sulfur, are 0.223 per cent and 0.033 per cent, respectively.

In a stainless steel high temperature alloy trace elements, Ti, Zr, Nb and Ta were also determined and are summarized in Table 23.

Table 23. Homogeneity and precision of trace components in spectroscopic standard of high temperature alloys of stainless steel.

Sample	Set	Weight	Distribution			
		(g)	Ti (%)	Zr[a] (%)	Nb[b] (%)	Ta[b] (%)
1152	1	5	0.117	0.026	0.203	0.080
		10	.116	.029	.201	.083
	2	25	.124	.030	.202[a]	.088[a]
		30	.116	.030	---	---
		Average:	0.118	0.020_8	0.202	0.0837
		Standard Deviation:	0.004	0.002	0.001	0.0044
1154	1	5	0.473	0.020	0.260	0.043
		10	.465	.021	.259	.044
	2	10	.487	.020	.251[a]	.044
		15	.486	.020	.251	.045
		Average:	0.478	0.0202	0.255	0.044
		Standard Deviation:	0.01	0.0005	0.005	0.0008

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[a] Gravimetric values.
[b] Spectrophotometric values.

(R. K. Bell)

2. Copper Base Materials

The compositions of seven principle copper-base alloys: cartridge, free-cutting, naval red and aluminum brass; gilding metal and commercial bronze of nominal, high and low compositions were tested for homogeneity.

Some of the homogeneity data for these materials, representing chill-cast and extruded standard reference materials are given in the following tables: in Table 24 data on the distribution of copper, aluminum and phosphorus in aluminum brass; in Table 25 data for arsenic by two methods, in Table 26 data for antimony; and, data in Tables 27 and 28 on the distribution of copper and phosphorus in free cutting and red brass.

Table 24. Homogeneity and precision of analysis of extruded aluminum brass (major components).

Standard reference material No.	Element	Position					Std. Dev.	Bulk					Std. Dev.
		A3	B2	C2	D4	Avg.						Avg.	
1118[a]	Cu	75.054		75.054	75.062	75.056	0.013	75.044		75.040	75.075	75.053	0.013
	Al	2.789		2.784	2.780	2.784	.006	2.783		2.792	2.794	2.789	.006
	P	0.132		0.132	0.133	0.132	.001	0.131		0.132	0.131	0.132	.001
1118[b]	Cu	75.052	75.054		75.056	75.054	0.006	75.050	75.040		75.044	75.045	0.006
	Al	2.784	2.785		2.785	2.785	.004	2.788	2.787		2.796	2.790	.004
	P	0.132	0.133		0.133	0.133	.001	0.131	0.132		0.131	0.131	.001
1119[a]	Cu	77.149		77.137	77.172	77.153	0.013	77.150		77.135	77.149	77.145	0.013
	Al	2.109		2.111	2.113	2.111	.004	2.116		2.118	2.119	2.118	.004
	P	0.068		0.068	0.067	0.068	.002	0.072		0.068	0.068	0.069	.002
1119[b]	Cu		77.134	77.131	77.158	77.141	0.012						
	Al		2.110	2.113	2.112	2.112	.001						
	P		0.072	0.071	0.071	0.071	.001						
1120[a]	Cu	80.148		80.138		80.143		80.141		80.136		80.138	
	Al	1.439		1.435		1.437		1.439		1.442		1.440	
	P	0.019		0.189		0.019		0.0188		0.0190		0.019	
1120[b]	Cu		80.156			80.156			80.144			80.144	
	Al		1.435			1.435			1.437			1.437	
	P		0.019			0.019			0.019			0.019	

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[a] Extruded 1.
[b] Extruded 2.

(R. K. Bell)

Table 25. Comparison of two methods in the homogeneity analysis of cast and extruded aluminum brass.

		Arsenic (%)				
Material (cast)	Set	As[a]	Average	As[b]	Average	Standard deviation
C1118	1	0.0061				
	2	.0066				
			0.0064			
C1119	1	0.0365				
	2	.0376				
			0.0370			
C1120	1	0.0779		0.0754[c] .0875[c] .0904[c]		
	2	.0822	0.080	0.0876[c] .0888[c] .0892[c]		
					0.0865	0.0124
(Extruded)						
1118	1	0.0067				
	2	.0067				
			0.0067			
1119	1	0.0387				
	2	.0384				
			0.0386			
1120	1	0.0847		0.0815[d] .0877[d] .0911[d]		
					0.862	.03
	2	.0850	0.0848	0.0877[d] .0877[d] .0886[d]		
					0.0898	.002

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[a] Distillation and titration (sample weight 14, 5 and 2.5 g respectively).

[b] Spectrophotometric (sample weight 0.2, 0.3 and 0.4 g respectively).

[c] Different position in rod.

[d] Different extrusions.

(R. K. Bell)

Table 26. Homogeneity and precision of analysis of extruded and cast aluminum brass. Minor constituent antimony.

Material	Set	Sb	Antimony (%) Average	Standard deviation
(cast)				
C1118	1	0.0118		
	2	.0105		
			0.0112	0.0009
C1119	1	0.0533		
	2	.0539		
			0.0536	0.0004
C1120	1	0.1091		
	2	.1034		
			0.1062	0.0040
(extruded)				
E1118	1	0.0113		
	2	.0093		
			0.0103	0.0014
E1119	1	0.0523		
	2	.0484		
			0.0504	0.0028
E1120	1	0.0994		
		.1008		
			0.1001	0.0010

(R. K. Bell)

Table 27. Homogeneity and precision of analysis of extruded free-cutting brass (major components).

Standard reference material No.	Element	Position C9	Position D12	Average	Standard deviation
1105	Cu(%)	63.725	63.726	63.725	0.006
	P (%)	0.001	0.001	0.001	0.001
		Bulk			
1105	Cu(%)	63.714	63.719	63.716	0.006
	P (%)	0.001	0.001	0.001	0.001

(R. K. Bell)

Table 28. Homogeneity and precision of analysis of extruded red brass (major components).

Standard reference material No.	Element	Position						Average	Standard deviation
		A	B	D	A6	B2	D9		
1109	Cu(%)	82.249	82.244	82.247				82.244	0.005
	P (%)	0.0057	0.0058	0.0058				0.0058	0.0008
	Cu(%)				82.248	82.276	82.192	82.251	0.032
	P (%)				0.0058	0.0055	0.0073	0.006	0.0007
		Bulk							
1109	Cu(%)	82.235	82.243	82.249				82.244	0.005
	P (%)	0.0057	0.0058	0.0058				0.0058	0.0008
	Cu(%)				82.254	83.251	82.283	82.251	0.032
	P (%)				0.0061	0.0054	0.0060	0.0058	0.0007

(R. K. Bell)

3. Limestone, Dolomite and Clays

a. Limestone-homogeneity. After the material was screened through a 200-mesh sieve homogeneity tests were performed on the fines, coarse and the sample fractions. The tests included hydrochloric acid insoluble SiO_2, total SiO_2 (corrected for soluble SiO_2) and loss on ignition. The test results are summarized in Table 29.

Table 29. Homogeneity data for limestone.

Test	Fines (%)	Coarse (%)	Sample (%)
Insoluble in HCl	7.15, 7.29	5.43, 5.40	6.35, 6.29, 6.35
SiO_2	5.37, 5.29	4.29, 4.25	4.91, 4.91, 4.79
Loss on ignition	40.54	41.10	40.90, 40.89, 40.86

b. Feldspar-stability. Most of the homogeneity tests and analyses have been completed on Standard Reference Materials 1a and 88a. Moisture tests and the determination of CO_2 were conducted on feldspars, 70a and 99a, to determine their stability during storage. While this is not strictly a homogeneity test, it provides an index of stability of the material on prolonged storage. The samples were dried at 110 °C and the carbon dioxide and hydrogen were determined by combustion in a micro C and H apparatus at 750 °C or by a Meeker Burner. To be certain that the carbon dioxide and the hydrogen were evolved quantitatively, various fluxes were used during combustion. The data are summarized in Table 30.

Table 30. Direct determination of carbon dioxide and water (hydrogen) in feldspar.

Flux	Sample weight (g)	Heating time (min)	70a CO_2 (%)	70a H_2O (%)	99a CO_2 (%)	99a H_2O (%)
WO_3	0.25	15[a]	0.035 .029 .022	0.408 .448 .410	0.106 .104 .120	0.230 .269 .231
WO_3	.5	45[a]	.031	.414	.106	.237
V_2O_5	.15	10	.024	.378	.135	.243
No flux	.25	10	.032	.402	.135	.226

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[a] Carbon and hydrogen apparatus at 750 °C.
[b] Meeker burner.

c. Clay. Similar tests were performed on flint clay, 97a and plastic clay 98a. In these tests, the drying condition at two different temperatures was evaluated and is summarized in Table 31. Drying at 140 °C produced a constant weight loss. These data are being checked by a thermogravimetric procedure.

Table 31. Drying conditions for flint clay, 97a and plastic clay, 98a.

Test	Conditions	Loss in percent 97a	Loss in percent 98a
Drying	132 hrs. at 110 °C; additional 92 hrs. at 140 °C	0.86	1.77
		.18	0.25
	Total	1.04	2.02
Drying	66 hrs at 140 °C	1.09	2.05
Loss on ignition	1.5 hr at 1000 °C	13.18[a]	12.11[a]

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[a] Dried basis.

D. Cooperative Work with Outside Laboratories

Until now the Quantitative Separations Section through direct contacts with outside industrial or scientific laboratories had obtained their cooperation in checking analytical results prior to the issuing of a certificate for the standard reference material. Presently this function is in the process of being transferred to the respective coordinators in the Office of Standard Reference Materials. From a list of several hundred laboratories, a score or less, representative establishments, whose experience in the analysis of these materials is well-established, were selected and after the homogeneity tests were completed, samples of the materials were sent to them. The results from these cooperators were evaluated statistically and are also based on the experience of the analyst and the accuracy that might be expected from a given method. Those values falling within the pre-established limits of errors of the methods are incorporated in the certificate.

Whenever disagreement is encountered, consultation follows to ascertain the cause of the bias. An example of this was the case of the iron ore SRM (NBS 27e) in which the reported values for iron and silica were outside the accepted error limits. As shown in Figure 15, the initially scattered and biased values after they were rechecked fell in line with those established at the Bureau. The error in the iron determination was eliminated when the laboratories used the NBS dichromate as the primary standard in place of a "pure" iron wire. In the case of silica a double dehydration step yielded the corrected values. In another example, the difficulty encountered by the cooperating laboratories in obtaining agreement for trace amounts of manganese was eliminated when the cooperators used redistilled water instead of demineralized water in their sample solution step. Traces of organic matter from the resin bed caused the reduction of permanganate and lead to low results. The current problem under study is the determination of aluminum for which values obtained in this section are 0.1 per cent lower than reported by the cooperators.

(J. R. Shultz and O. Menis)

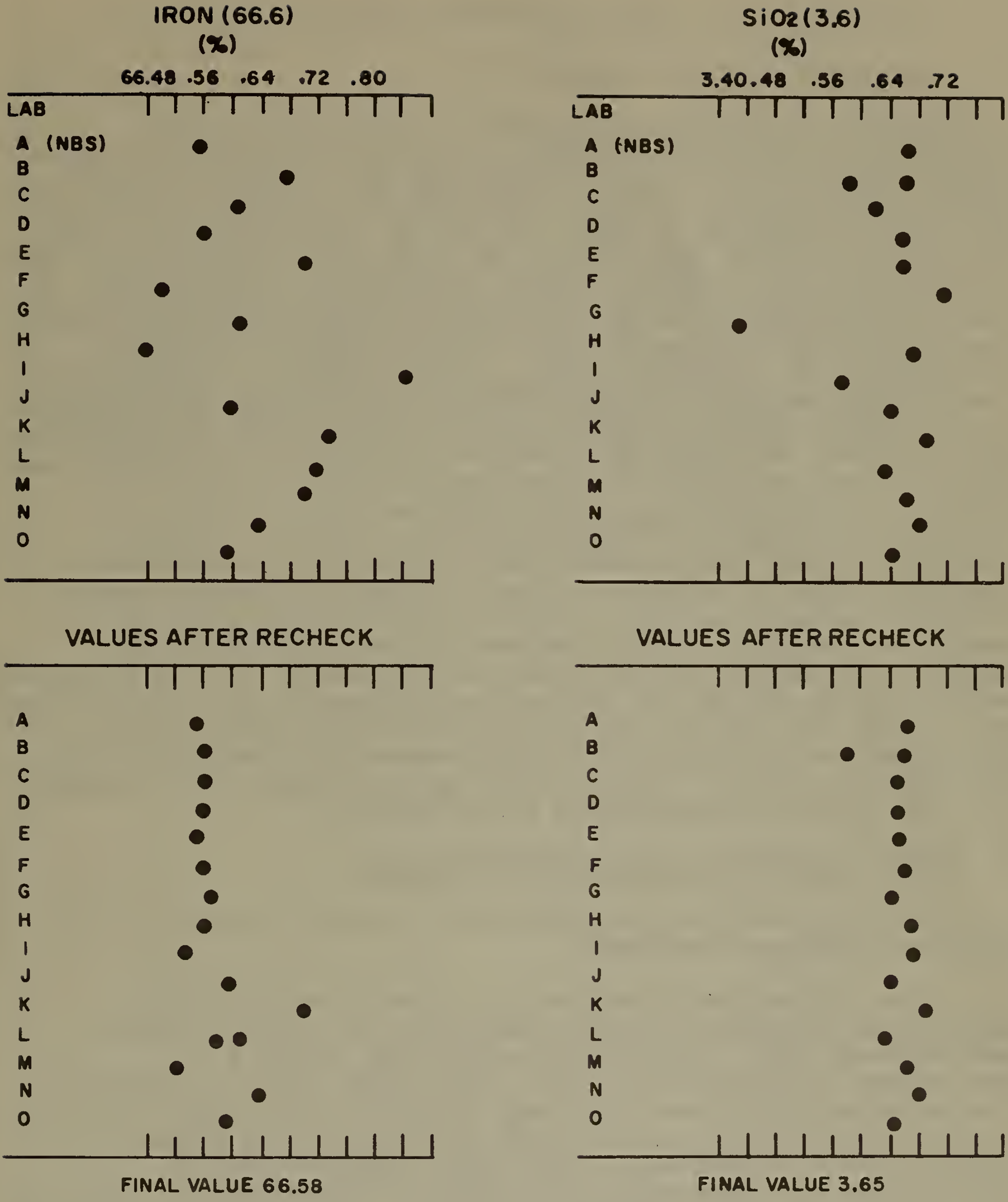

Figure 15. Correction of bias between cooperating laboratories (results before and after reevaluation for Fe and SiO_2 determinations).

7. URANIUM UMPIRE PROGRAM

A. Status of Current Program

Since 1949 NBS has performed the umpire analyses required by the USAEC uranium procurement program. Improved understanding and control of sampling and analysis problems have brought about a marked decline from the peak of about 900 umpire requests in 1959, to 110 in 1965 and led to the narrowing of acceptable limits of error in uranium assays to less than 0.20 per cent. These circumstances plus the approaching expiration of the existing AEC foreign contracts designating NBS as the umpire, obviate the need for an uranium umpire program at NBS. Consequently a close-out of the program was initiated in 1964. Because the experience at NBS on a variety of materials over a long period of time has provided the accepted standard by which the uranium industry has evaluated its performance, NBS continued to provide umpire analyses, with a planned cut-off date of July 1965, while also taking action to assure continued availability of NBS uranium assay "know-how". Duplicate determinations of uranium in each of the 110 umpire samples received between July 1, 1964 and May 15, 1965 will be completed in June. These include 9 foreign samples in addition to those from 15 domestic producers. A comprehensive and detailed account of the umpire program at NBS was written as a guide for the use of future umpires and other groups analyzing uranium, and is being prepared for publication in the NBS 260 series. Also, twenty extra samples were assayed for use by AEC in qualifying a new umpire.

B. Participation in the AEC-GAE Program

Participation in the AEC General Analytical Evaluation Program (GAE) was continued.

The GAE program, designed to permit laboratories performing analyses for the Commission to evaluate their performance, and coordinated by the Commission's New Brunswick Laboratory, dealt with four types of uranium concentrates each year from Aug. 1961 to Sept. 1964. In the current (fifth) year the program involves the analysis by each of four laboratories (NBS, NBL, MCW and LPI) of 54 GAE samples representing 3 types of concentrates. Half of the samples are AEC reference samples. Every three weeks each cooperating laboratory receives three samples, in any combination of materials and including both production and disguised reference samples. These GAE samples are independent of the umpire samples received by NBS.

All GAE results have been evaluated in NBL reports. The general reproducibility is illustrated in Figure 16, taken from an NBL report showing deviations from the average for the Homestake-Sapin reference material between Sept. 1963 and April 1965. Each point represents the assay of one bottle of material. The inner, solid lines represent 95 per cent probability limits for the laboratory average and the outer, dashed points represent 95 per cent probability limits for a single plotted point. Bottling reliability has greatly improved since the 1950's, but the variability of the Dawn reference material (Sept. 1963-Aug. 1964) indicated that unsuspected sampling variations may still occur, and emphasized the continued need for basing assay evaluations on a standard of known composition, such as NBS No. 950a. The effect of variations in composition on assay is still determined by adding approximate amounts of appropriate impurities to known amounts of the high purity standard uranium.

(M. S. Richmond and J. R. Baldwin)

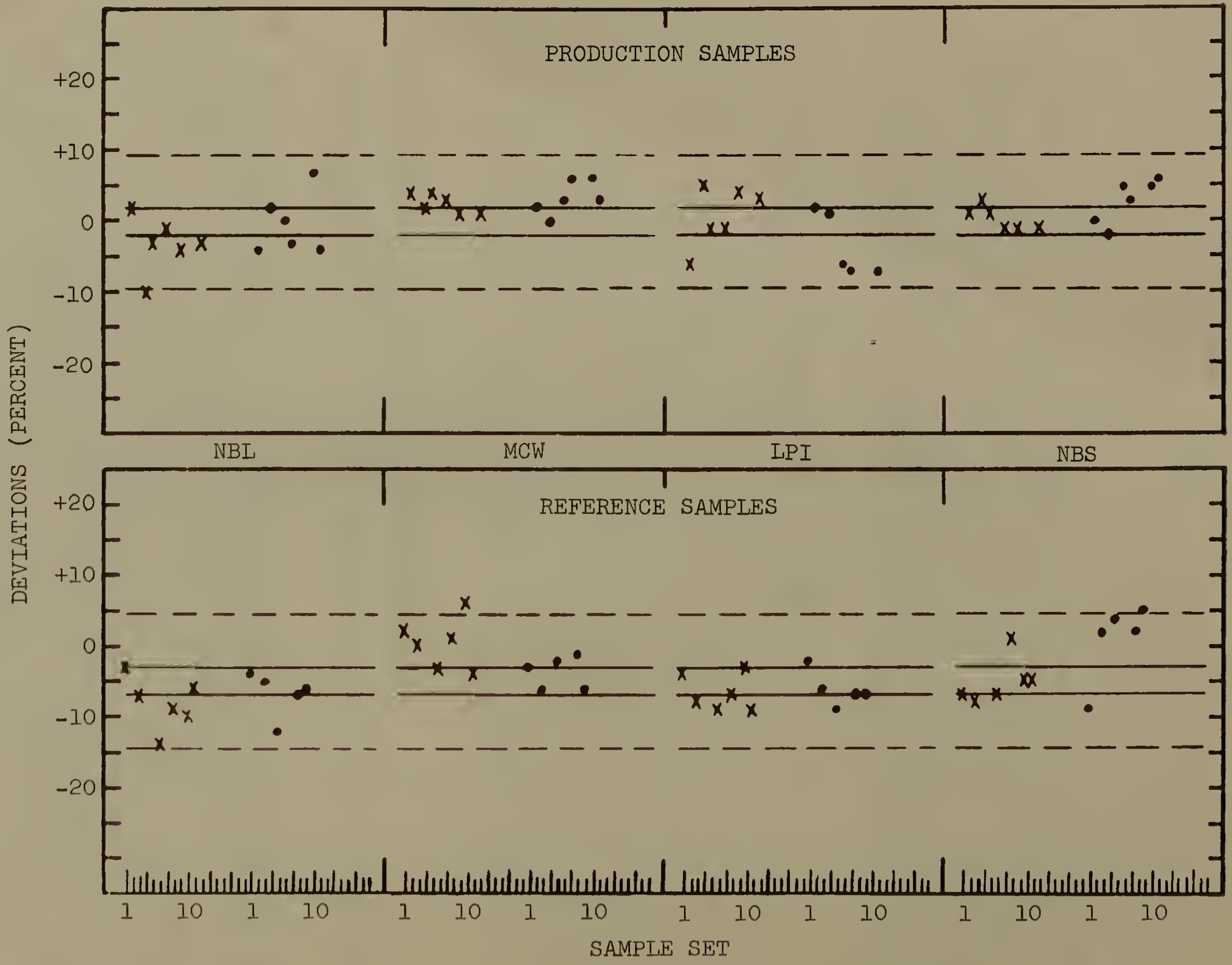

Figure 16. Deviations from average U_3O_8, for Homestake-Sapin material in 1963-5.

8. URANIUM AND PLUTONIUM ISOTOPIC STANDARDS

A. Introduction

To meet the need of accurate isotopic uranium and plutonium standards for industry and science in the atomic energy field, a program of preparing synthetic mixtures of these isotopes was undertaken.

Sixteen uranium isotopic standards, supplied by Oak Ridge National Laboratory, are being re-evaluated by preparing known mixtures of isotopes for mass spectrometer calibration. For the determination of U-235 and U-238, solutions were prepared from the primary enriched U-235 and either the primary* or secondary* standard of depleted U-238 to calibrate the mass spectrometric measurements for the Mass Spectrometry Section. For the determination of U-234 and U-236, the standards are spiked with high-purity U-233 to give favorable ratios for mass-spectrometric measurements.

B. Assay Process of Uranium Oxide Prior to Blending of Isotopes

In order to blend the depleted U-238 and enriched U-235 and to spike the standards, it is necessary to know accurately to better than one part in ten thousand the amount of uranium in each isotopic component. The stoichiometry of U_3O_8 used as the starting material depends on the method of preparation and on ignition conditions. An ignition procedure was developed for U_3O_8 to give a reproducible oxide for weighing prior to its analysis. These standards were then analyzed for uranium by constant current coulometry in Section 310.05.

The following ignition cycle for the oxides was developed: one hour at 900 °C in air (to correlate with previous work), overnight at 1050 °C in air, followed by 1 hr in oxygen at 850 °C. The ignitions were conducted in a quartz tube and the samples were protected from water and carbon dioxide in the air by weighing them in small glass desiccators

The following Table 32 shows the ignition loss of the isotopic standards, the depleted U-238 samples, and the

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*The primary and secondary designations differentiate between a higher purity isotope available in smaller quantities and a less pure secondary isotope standard.

Table 32. Reproducibility of the ignition loss of U_3O_8 samples.

Loss of weight for U_3O_8 after an ignition cycle[a]

Sample	Number of runs	Average loss (%)	Standard deviation
U-005	6	0.0394	0.001_8
U-010	6	.0392	$.001_8$
U-015	3	.0307	.0007
U-020	5	.0484	$.001_2$
U-030	3	.0507	$.002_2$
U-050	6	-.0058[b]	$.002_8$
U-100	5	.0319	$.002_1$
U-150	3	.0287	$.000_8$
U-200	3	.0280	$.001_1$
U-350	3	.0377	$.003_4$
U-500	5	.0971	$.003_4$
U-750	3	.0373	$.001_8$
U-800	3	.0398	.0007
U-850	3	.0471	$.003_1$
U-900	3	.0676	.0004
U-930	3	.0639	$.000_9$
Secondary depleted	22	.0481	$.003_0$
Primary depleted	8	.1037	$.003_8$
Primary enriched	20	.779	$.03_5$

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[a] Initial sample weight minus final weight at 850 °C.

[b] A modified procedure was used in the preparation of this material by ORNL.

enriched U-235 sample. The primary enriched sample contained a relatively high percentage of water and appeared to be absorbing additional moisture as the ignition loss of individual samples increased with time. Based on the calculated values of standard deviation of replicate samples taken through the ignition cycle, the largest error introduced in the weight of a gram of the final oxide was less than 4 parts per hundred thousand. In most cases, it was smaller by a factor of two. A thermogravimetric analyzer has recently been acquired and its use will enable us to understand better the stoichiometry of U_3O_8 and to help check the accuracy of the ignition procedure (see Gravimetry Section). It should be feasible then, by means of a reduction and oxidation cycle to determine both the stoichiometry and concentration of the uranium in the sample, and thus, eliminate the need for the coulometric titration.

In cooperation with Section 310.05 work is in progress to determine the assay of uranium oxide prepared by different procedures and ignited by the preceding procedure.

C. Preparation of Isotopic Mixtures

Mixtures of enriched U-235 and depleted U-238 samples were prepared to enable a mass discrimination factor to be determined on the mass spectrometer. Five mixtures were prepared with a U-235 to U-238 atom ratio of 8.95 to 9.05, five mixtures with a ratio of 0.99 to 1.01 and five mixtures with a ratio of 0.110 to 0.112. The primary depleted U-238 was used in preparing the mixtures with a ratio of 0.99 to 1.01 and the secondary depleted U-238 was used to prepare the others.

Each sample was ignited, by the ignition procedure developed to give reproducible oxides, using the calculated weight of sample to give the desired ratio. The platinum boat and U_3O_8 sample were carefully transferred to a 250-ml teflon bottle. After both the depleted and enriched samples had been ignited and transferred to the bottle, sufficient HNO_3 (1+1) was added to the bottle to give a HNO_3 (1+19) and 5 mg U per milliliter solution when diluted with sufficient water. The bottle was sealed with a teflon-lined cap and the sample dissolved by heating on a steam bath. After cooling, enough water was added to give a HNO_3 (1+19) solution.

Known amounts of U-233 were also added to the uranium isotopic standards to determine their U-234 and U-236 content. This was done by adding weighed amounts of U-233 solution to solution of the samples. Two sets of samples were spiked with two separate U-233 solutions of approximately 0.1g each. To one sample of each kind, U-233 was added to make it approximately 1% more than the estimated U-234 content and to the other sample of each kind, U-233 was added to make it approximately 1% less than the estimated U-234 content. Additional samples were spiked at each change of U-233 dilution, to check whether any errors were made in the dilution procedure.

Each sample was ignited by the ignition procedure developed to give reproducible oxides. The platinum boat and U_3O_8 sample were carefully transferred to teflon bottles. The samples were dissolved in HNO_3 (1+1) by heating on a steam bath. After dissolving, enough water was added to make the solution approximately HNO_3 (1+7). The U-233 sample was dissolved last and it was diluted to approximately 1 mg of U_3O_8 per gram of solution HNO_3 (1+19) . The cap on the U-233 bottle was replaced with a similar cap containing a piece of polyethylene tubing shaped for use as a squirt bottle. The U-233 was then added by squirting U-233 solution into the sample bottles. By weighing the U-233 bottle before and after the addition the amount of U-233 added can be calculated. The sample solutions were diluted with water to obtain a HNO_3 (1+19) solution containing 5 mg U per ml. The "spiked" solutions were then submitted for mass spectrographic analysis.

Based on this study a table of "best estimate" values has been sent to all purchasers of uranium isotopic standards.

(L. A. Machlan)

D. Plutonium Isotopic Standard 948

1. Preparation of Plutonium Isotopic Standards

The plutonium isotopic standard was prepared by the New Brunswick Laboratory of the Atomic Energy Commission in the form of plutonium sulfate tetrahydrate from metal. The standard was bottled and samples for homogeneity testing by the 310.04 personnel at New Brunswick. The samples were packaged in 2R containers as required by ICC regulation and after transfer to NBS the screw caps and joints were coated with plastic "Seal-Stop". Preliminary measurements by mass spectrometry indicated the material was isotopically homogeneous, and the sample was distributed to a selected group of cooperators.

2. Separation of Americium

The plutonium standards which were to be certified for Pu-239, Pu-240, Pu-241, and Pu-242 isotopic composition required a separation of Am-241. The Pu-241 decays to Am-241 which interferes with the mass-spectrometry measurement for Pu-241. A procedure was adapted for the separation of americium from plutonium by anion-exchange. The sample was dissolved in 8N nitric acid and added to a small column of Dowex 1 x 4 resin (1.3 cm high by 4.5 mm diameter). The americium was removed by elution with 8N nitric acid and the plutonium was then removed with 0.3N nitric acid. Section 310.06 then carried out mass-spectrometry measurements on these solutions. Values obtained on duplicates of three samples taken at the beginning, middle, and end of the bottling are given in the following table.

Table 33. Atom per cent corrected to June 1, 1964.

Sample	Pu-239	Pu-240	Pu-241	Pu-242
1	91.3693	7.904_2	0.6937	0.0327
1_2	91.3599	7.911_9	.6950	.0331
3	91.3620	7.9100	.6949	.0330
3_2	91.3661	7.9063	.6945	.0330
5	91.3625	7.910_4	.6940	$.033_0$
Average:	91.3649	7.9074	0.6946	0.0330
Standard deviation:	0.0041	0.0040	0.0007	0.0001

(M. S. Richmond and L. A. Machlan)

E. Miscellaneous

1. Bottling and Packaging Radioactive Samples

Because of the radioactivity of the material, all bottling of uranium isotopic standards was done in the "hot lab". Approximately 1300 samples have been bottled in the past year. Approximately twelve thousand additional samples are yet to be bottled.

Approximately 180 plutonium metal standard 949a were packaged in 2R containers as required by ICC regulations and, in addition, the screw caps and joints were coated with plastic, "Seal-Stop".

Of the uranium oxide 950a for chemical assay, approximately 650 samples were bottled for sale.

2. Distribution of Uranium and Plutonium Standards

In order to ensure observance of health and safety regulations applicable to the distribution of source and fissionable materials, an experienced chemist was directly responsible for each shipment until March 1965. By then packing details had been standardized as shown in the attached drawings, Figure 17a and 17b, and also the procedures for processing orders were written; subsequently, responsibility for strictly clerical aspects of handling orders of these materials were assumed by the Office of Standard Reference Materials. However, personnel of this section continue to be the vault custodians, supplying standard reference materials and maintaining inventory records; and to serve as the consultants providing the shipper with radioactive shipment details that aim to insure (and coordinate) compliance with NBS, AEC, ICC, carrier and receiver regulations.

3. Clean-Up Program

The changing program of the section has resulted in considerable moving or disposal of materials and equipment. This included the entire contents of one large laboratory (Rm. 306) and most of one small laboratory (Rm. 316). The isotopic uranium group made 3 shipments effecting the transfer of 800 kg of Congo ore, 28 kg of high-grade pitchblende, and nearly 11 kg of three highly enriched materials, from NBS to AEC storage sites. Surplus and waste U-233 oxide from three lots including two lots last used in 1959 were accounted for and disposed of.

(M. S. Richmond)

PACKING DETAILS FOR NBS NO. 948 (ISOTOPIC STANDARD)

Material: PLUTONIUM sulfate tetrahydrate
Emitted Radiation: Alpha
Specific Activity: 76 mCi/g
Unit Net Weight: 0.25g (Pu)

Unit Legal Weight: 21 oz (includes sealed pipe)
Commodity Code Number: 5150020
Outside Shipping Container: ICC Specification 12B fiberboard box

Size	10" x 10" x 5" for:	1 unit,	to	6 units,
	Estimated Gross Weight:	5 lb,	to	12 lb,

or 12" x 12" x 12" for: 7 units (15 lb) to 16 units (30 lb gross)

Labeled for: Radioactive Material, Class D poison, Group III

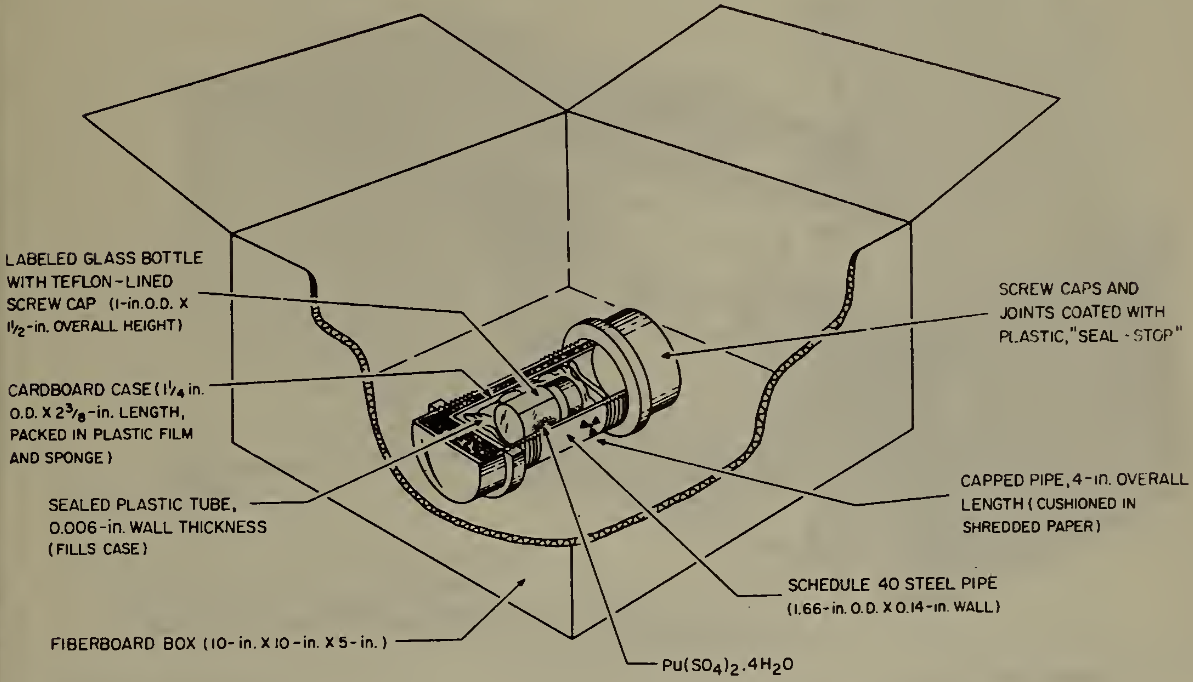

Figure 17a. Packing details for plutonium NBS Standard Reference Materials.

PACKING DETAILS FOR NBS NOS. U-010 THROUGH U-930

Material: U-235-ENRICHED U_3O_8, with U-235 abundance of 1% (in U-010) to 93% (in U-930)

Emitted Radiation: Alpha

Specific Activity: up to 0.07 mCi/g (depending on enrichment)

Unit Net Weight: 1.0g (U)

Unit Legal Weight: 1 oz (includes cardboard case)

Commodity Code Number: 5150020

Container: The material is packed as shown below and, except for domestic shipments of less than 1.35 mCi, the material is further packed in an ICC Spec. 12B fiberboard box (10" x 10" x 5", for up to 32 units, with an estimated gross weight of 4 to 6 lb).

Labeled for: Radioactive Material (according to activity range)

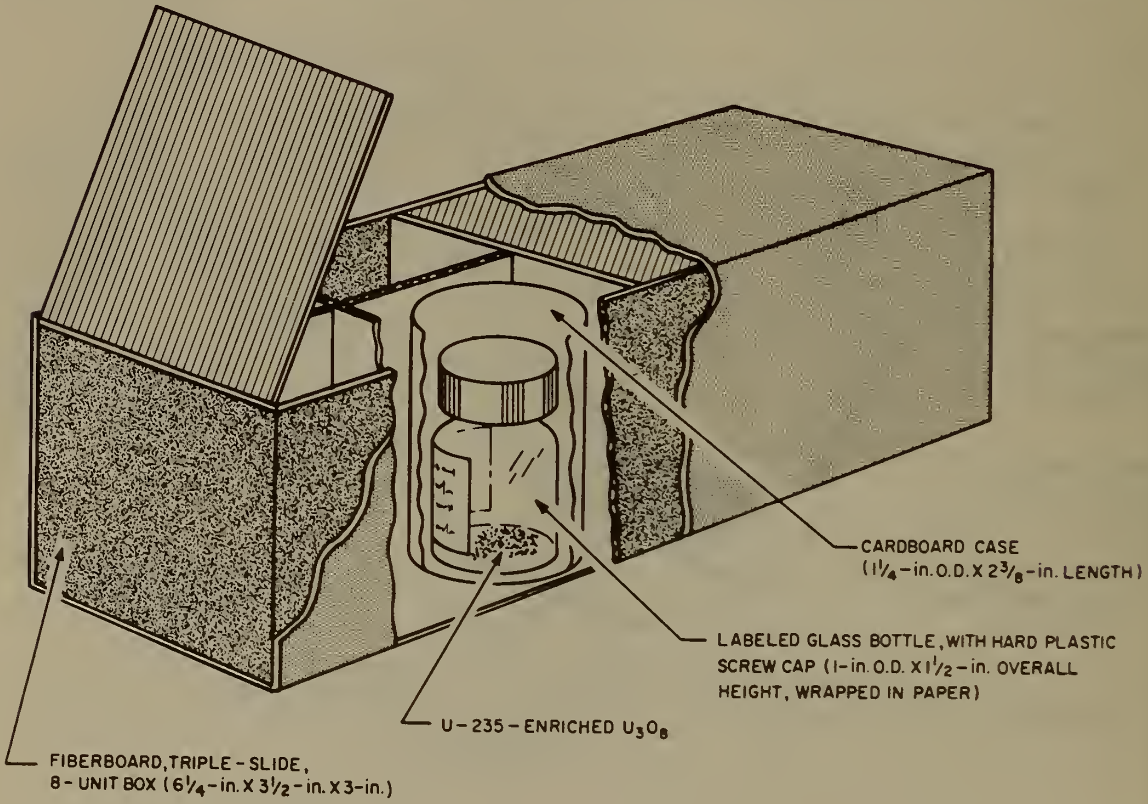

Figure 17b. Packing details for uranium NBS Standard Reference Materials.

9. PERSONNEL AND ACITVITIES

A. Personnel List

Quantitative Separations Section, Oscar Menis, Section Chief
Mrs. M. Pantazis, Secretary

J. R. Baldwin

R. K. Bell

B. B. Bendigo

R. W. Burke

E. R. Deardorff

L. A. Machlan

F. J. Palumbo

M. S. Richmond

K. M. Sappenfield

J. I. Shultz

J. T. Sterling

B. Talks

R. W. Burke, A.C.S. Meeting in Miniature at U. of Maryland, May 7, 1965, "Application of Spectrophotometry to Trace Element Analysis at the Submicrogram Level - Determination of Nanogram Quantities of Beryllium".

C. Committee Activities and Education

E. R. Deardorff

Attended Thermoanalysis Institute, Fairleigh Dickinson University.

L. A. Machlan

Member, Board of U. S. Civil Service Examiners.

Completed course, "Electronics for Scientists", 3 weeks at U. of Illinois.

O. Menis

Co-chairman of the Chemistry Program for the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1965.

Chairman of Symposium of "Burnup Analysis" at the ANS Meeting, Gatlinburg, Tenn., 1965.

M. S. Richmond

Completed course, "Radiochemistry", N.B.S. Graduate School.

J. I. Shultz

ASTM Activities

Chairman of Lundell-Bright Memorial Award Committee.
Member of Advisory Committee of Committee E3 (Chemical Analysis of Metals).
Vice-Chairman of Division F (Ferrous Materials) of Committee E3.
Chairman of Task Force for revising and rewriting ASTM methods of analysis for ferrous materials.
Member of Divisions M and G of Committee E3.

NBS

Chairman of the Suggestion Program Subcommittee on Technical Procedures.

D. Publications

Shultz, J. I., Standard Reference Materials: Methods for the Chemical Analysis of White Cast Iron Standards, NBS Misc. Publ. 260-6, July 1965.

Bell, R. K., Standard Reference Materials: Methods for the Chemical Analysis of NBS Copper-Base Spectrochemical Standards, NBS Misc. Publ. 260-7, In Press.

Richmond, M. S., Standard Reference Materials: Analysis of Uranium Concentrates at the National Bureau of Standards, NBS Misc. Publ. 260-8, In Press.

10. ACKNOWLEDGEMENTS

The Quantitative Separations Section acknowledges the help of Rolf A. Paulson who was the acting chief in the first half of the period covered by this report. The section also wishes to thank Mr. John Hague for his guidance and discussions of the various aspects of standard reference materials, especially of the isotope standards program.

The section acknowledges Mrs. R. S. Maddock's assistance in preparing this report. Special appreciation is expressed to M. Pantazis as the section's secretary for her tireless efforts in getting this report typed.

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