NBS TECHNICAL NOTE

402

Analytical Coordination Chemistry: Titrimetry, Gravimetry, Flame Photometry, Spectrophotometry, Gas Evolution and Isotopic Preparations July 1965 to June 1966

Edited by Oscar Menis

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

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Analytical Coordination Chemistry Section
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 nine sections and about 100 technical personnel encompassing some 45 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 our 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 a Technical Note. In 1966 we plan to issue these summaries for all of our sections. The following is the second annual report on progress of the Analytical Coordination Chemistry Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

Since the issuance of the last report the title of the Section has been appropriately changed from Quantitative Separations Section to Analytical Coordination Chemistry. This new name reflects more accurately the activities and goals of this group. In four out of the five competences covered in this report - titrimetry, gravimetry, spectrophotometry and flame photometry - the ligand-metal ion and the associated competing reactions lend themselves to the same basic treatment. These problems are best resolved with the aid of modern coordination chemistry, as applied to complex ions or coordination compounds in a given solution or solvent. Thus, whenever one studies the selection of the best counter ion in a homogeneous precipitation, the relative stability of metal chelates and indicators in titrimetry, the formation of ternary complexes in spectrophotometry, or the use of "releasing agents" in flame spectrometry, the theoretical aspects of these reactions are interrelated. This should lead to the common goal of improving selectivity, accuracy and sensitivity of the respective techniques.

This report stresses the initiation of these efforts in the several competences mentioned. In titrimetry, greater application of spectrophotometric and coulometric titrations are described. The use of various complexing media are discussed from the standpoint of their ability to shift formal potentials. In the case of gravimetry, considerable progress has been made through greater application of homogeneous precipitations. The use of thermogravimetric analysis has been extended to obtain information on the stoichiometry and mechanism of reaction. In spectrophotometry, the simultaneous analysis of a multicomponent system and application of a ternary system have been successfully completed. In flame photometry, progress is reported on use of improved instrumentation and on studies of solution conditions. Finally, in the field of the analysis of gases in metals, a series of new standard reference materials have been certified. At the same time, this year, approximately seventy percent of this Section's efforts have involved the analysis of standard reference materials. In addition this report includes one section dealing with special problems in plutonium and uranium analysis, and a summary of special analytical services performed for other Divisions. Other topics such as extraction, ion exchange, pyrohydrolysis and thermogravimetry are appropriately discussed with whatever competence they were associated. Also a subject of general interest, mamely, the move from Washington to Gaithersburg, is not covered in this report. It will be reported when all the arrangements and final distribution of work in the given laboratories are completed.

This Section wishes to express their appreciation to Mrs. R. S. Maddock, Administrative Assistant for the Division of Analytical Chemistry in Charge of Publications, who assisted in preparing the report for publication.

Necessarily, in the application of various instrumental methods, commercial components have largely been employed. The identification of these by the manufacturers' name does not indicate that they were selected because of their special quality or imply any preference but is offered only for general information.

Oscar Menis, Chief
Analytical Coordination Chemistry

TABLE OF CONTENTS

PAGE

LIST OF FIGURES

FIGURE NO. PAGE

LIST OF TABLES

TABLE NO. PAGE

LIST OF TABLES (CONT'D)

ANALYTICAL COORDINATION CHEMISTRY
JULY 1965 TO JUNE 1966

Edited by Oscar Menis

ABSTRACT

Studies in four areas of analytical chemistry: titrimetry, gravimetry, flame emission and atomic absorption, and solution spectrophotometry, are described from the standpoint of analytical coordination chemistry and applications to NBS standard reference materials. In the first two competences these investigations dealt with spectrophotometric titrations and homogeneous precipitation methods. Advances are described in the latter two areas through the unique applications of ternary complexes, displacement reactions in metal-ligand systems and the use of complexing media as "releasing agents". This approach is described for the determination of nanogram quantities of Sb, Cu, Ni and Au in very high purity zinc by both spectrophotometric and flame procedures. Also in flame emission and atomic absorption a current table is presented for the detection limits of 70 elements. Progress of a new method is reported for the simultaneous determination of Ni, Cu and Co by the dimethylglyoxime method. Descriptive tables of results are also given for ferrous, non-ferrous and ceramic materials which were analyzed by one of the four competences. In another analytical area dealing with the analysis of gases in metals results of homogeneity and precision studies lead to certification of three new ferrous SRM's for their oxygen content. Also reported are the initial investigations of pyrohydrolytic separations of fluoride, nitrides and boron, separations of molybdenum from tungsten, controlled potential coulometric titration of molybdenum, and a description of improved instrumentation in flame emission and atomic absorption. Finally data are given on the preparation of stoichiometric mixtures of uranium oxide of varied isotopic composition and a list describing the variety of special analyses is included.

Key words: spectrophotometric titration, controlled potential coulometric, molybdenum, homogeneous precipitation, aluminum, beryllium, thermoanalytical standards, tricalcium silicate, spectrophotometry, antimony, high precision determination of nickel, simultaneous determination copper, cobalt, "releasing agents" in flame emission and atomic absorption, magnesium, ferrous SRMs, stoichiometric mixtures uranium oxide, isotope ratio determination

1. TITRIMETRY

By following the concepts briefly enumerated in the last report [1], additional progress has been made in instrumental applications of endpoint determination to the general field of titrimetry. Ringbom [2] has described the possibility of extending the precision and accuracy of determining both macro and micro quantities of a given element. This can be achieved from a knowledge of the conditional equilibrium constants and from the magnitude of the change in instrumental readout at or near the stoichiometric endpoint. The intent of the present work is to find systems which can provide optimum conditions, maximum equilibrium constants, more sensitive endpoint detections and freedom from interferences when applied to a given matrix. Progress along these lines has been made in providing the standards of high accuracy needed in technology and in basic science.

The current efforts in this area have dealt largely with the analysis of complex matrixes as represented by standard reference materials with and without prior separations and reflect some improvement in precision and accuracy. This report describes studies of the recent efforts involving instrumental methods, pyrohydrolytic separations of nitride, boride and fluoride from refractory materials and a summary of results on recently certified materials.

A. Spectrophotometric Titrations

1. Introduction

Under proper conditions spectrophotometric titrations have been shown to yield precise results for both macro and micro quantities of a given element [3]. This technique also was shown by Menis et al. [4], among others, to be applicable to automatic titrations of microgram quantities. The chief requirements are a stable instrument, accurate delivery of relatively concentrated titrant and an appropriate choice of

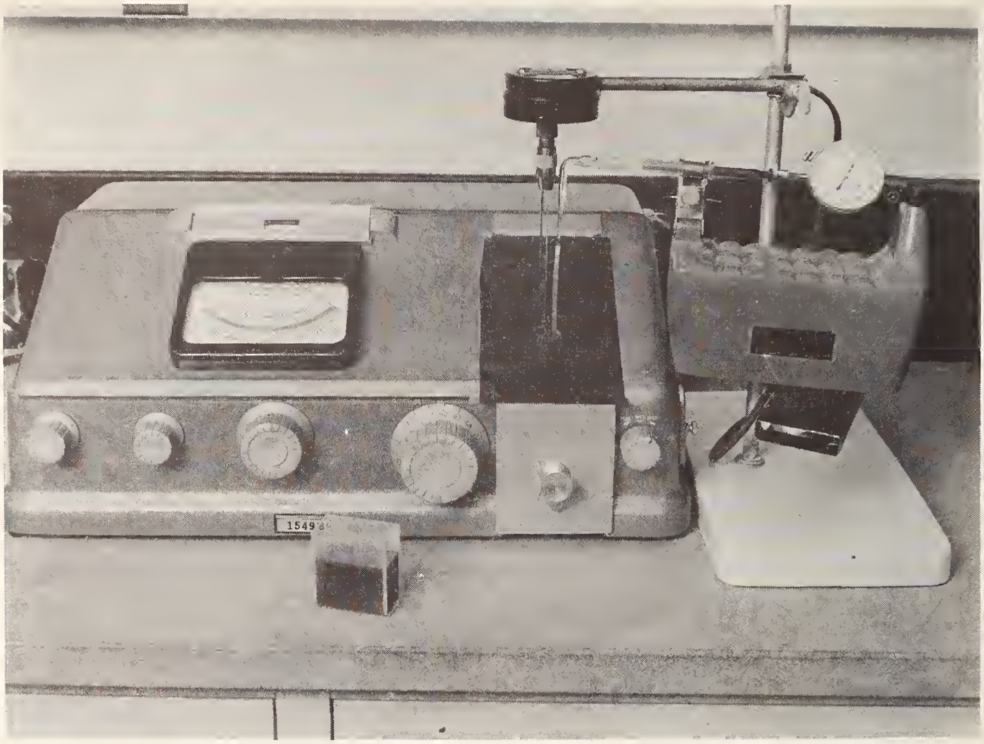

Figure 1. Spectrophotometric titration apparatus.

system for the element in a given matrix. The first requirement was achieved by the arrangement shown in figure 1 and is described in the Experimental Section. Examples of several reaction systems with their characteristic titration curves are shown in figure 2. Curves 2a and 2b are representative of the "step-indication" type titrations. In the first example, Eriochrome Black T served as the metalochromic indicator for the titration of magnesium with EDTA; in the second, Mg-Eriochrome Black T was used as an indirect indicator for calcium determination. In curves 2c and 2d a slope type titration is obtained. An acid-base titration, as shown in 2c, is carried out with the mixed indicator, Methyl Purple, which exhibits a color transition between pH 4.8 and 5.4. In the photometric titration, a small color transition can be measured and the inflection point more precisely determined. In curve 2d the absorbance of excess titrant is measured directly as is exemplified in this instance by the redox titration of Ce (III) with Mn (VII).

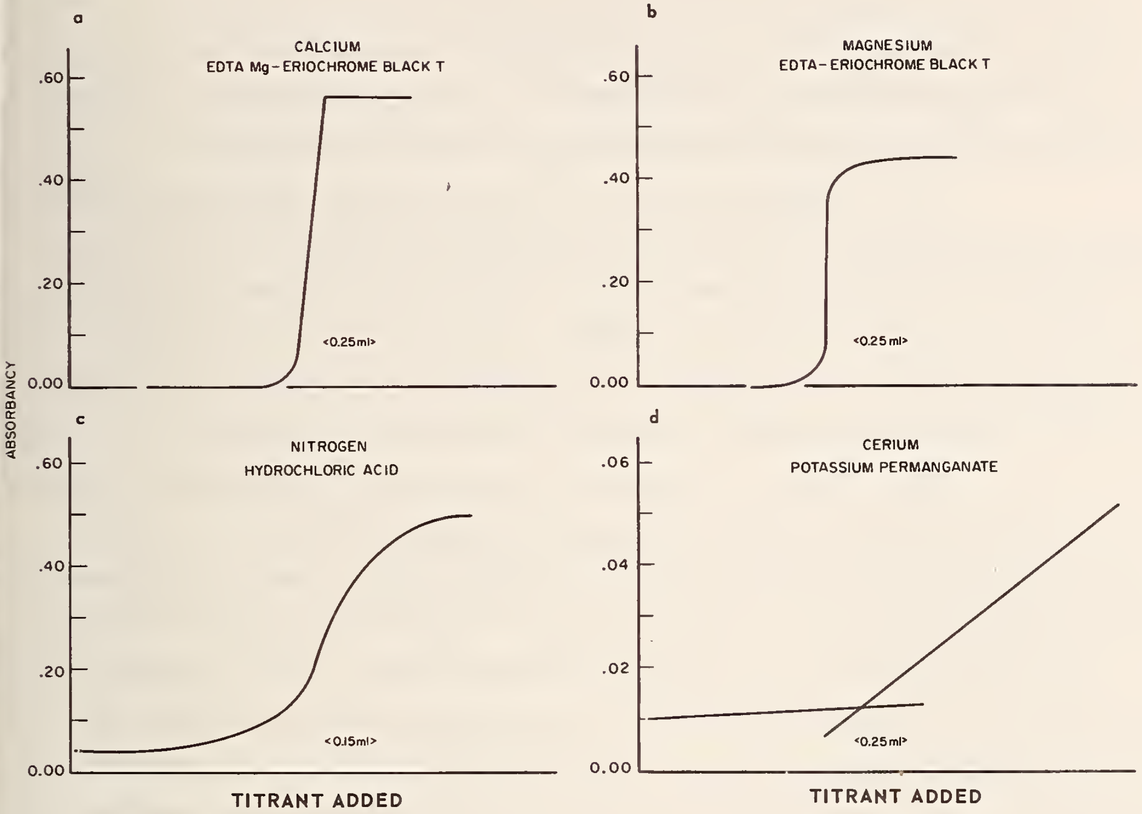

Figure 2. Spectrophotometric titration curves.

2. Experimental

a. Complexometric titration. A spectrophotometric endpoint for the complexometric titration of magnesium or calcium after an ion exchange separation offers a rapid method for the analysis of these elements in silicate rocks. The potentiometric endpoint detection, described in the last report, could not be readily applied in this analysis since the solutions from the ion exchange separation contained high concentrations of chloride which interfere in the detection of the endpoint with a mercury indicator electrode. For that reason an indicator method in conjunction with a spectrophotometric procedure was adapted. In this procedure 50 ml of solution was titrated in the modified spectrophotometer shown in figure 1. An 80-ml cell with a 5-cm light path (shown in front of the instrument) was placed in the spectrophotometer compartment. A light-tight cover with an opening for stirrer and the tip of a micrometer buret was placed over it. By means of a syringe-buret combination, microliters of titrant were accurately measured.

(1) Magnesium was titrated in an ammonium chloride-ammonium hydroxide buffer solution at pH 10. Using Eriochrome Black T as the indicator, the titrations were carried out at a wavelength of 650 mμ. The replicate titrations of five 50-mg samples of magnesium and eight 5-mg samples of magnesium, the relative standard deviation was 0.1 percent.

(2) Similar determinations were carried out for calcium. The indirect Mg-Eriochrome Black T indicator system was used in this spectrophotometric procedure. The relative standard deviation in titrating 100 mg of calcium was 0.1 percent. To ascertain the precision and accuracy of the method, when applied to silicate analysis, calcium was determined in SRM 88a, dolomitic limestone. A relative standard deviation of 0.2 percent was obtained for five analyses and the results agreed, within the error limits, with the gravimetric method.

Since the calcium content of silicate materials varies extensively, further trials extending into the microgram range were also made. The relative error for 700, 100 and 10 μg was 2, 10 and 17 percent, respectively. These error limits, at the levels tested, compare favorably with other methods.

An extension of this method to the determination of 10 μg of calcium in a steel sample was also attempted. In this instance iron was removed by extraction with methyl isobutyl ketone (hexone). The calcium was then extracted from the raffinate solution with glyoxal-bis (2-hydroxy-anil) in 1:1 hexone-sec-octyl alcohol [5,6]. It was subsequently found that because of the partial solubility of the organic solvents in the aqueous phase, the endpoint could not be detected. Eventually, a flame photometric method provided a more suitable analysis.

(3) For the purpose of determining small amounts of fluoride in rock materials, another type of complexometric indicator titration was evaluated. The titration curves of fluoride by the thorium-Alizarin Red S reaction [7] are very similar to that shown for the oxidimetric titration (figure 2d). In the titration of 100 μg of fluoride, the relative standard deviation was 3 percent.

b. Redox titration. A study was conducted of the spectrophotometric titration of cerium in low-alloy steels in the range of 1 to 10 μg. The method is based on the oxidation of cerous ions with a permanganate solution at 525 mμ [8]. A relative standard deviation of 5 percent was obtained in a series of tests with 10 μg of cerium.

c. Acidimetric titrations. In the determination of nitrogen in steel via a Kjeldahl distillation, the feasibility of improving the precision and accuracy by a spectrophotometric method was tested. The usual procedures involve the use of either a colorimetric method or a pH titration. In this study the change in the transition color was followed at 520 mμ. With concentrations of 100 μg and 10 μg of nitrogen in 50 ml of distillate, the relative standard deviation was 3 and 12 percent respectively. The results of titration of two NBS standard reference materials are compared with other methods in table 1. The best precision was obtained by the spectrophotometric titration.

Table 1. Comparison of methods for nitrogen determinations

Method	Number of determinations		Rel. std. deviation, %
SRM 1090, Ingot iron			
Spectrophotometric titration	8	0.0064	6
pH titrations	96	.0063	12
Nessler's reagent (color)	16	.0062	8
SRM 1092, Vacuum-melted steel			
Spectrophotometric titration	4	0.0008	10
Nessler's reagent (color)	32	.0011	27

K. M. Sappenfield and O. Menis

B. Controlled Potential Coulometric Titration - Molybdenum

1. Introduction

In the lower concentration range molybdenum can readily be determined by spectrophotometric methods and in the higher ranges by gravimetric methods. In the intermediate concentration range, however, a more accurate method is needed. Controlled potential coulometry offers a means for precise and accurate determinations if interferences can be eliminated and a suitable electrolyte system can be found. This requires an electrolyte system in which molybdenum can be reduced with 100 percent current efficiency and in which the matrix components of the molybdenum sample will not interfere.

2. Study of redox systems

In order to eliminate the interference from iron several inorganic as well as organic complexing electrolyte systems were investigated to determine their relative ability to shift the formal potential of the molybdenum VI to V redox couple to more negative potentials. In the initial tests it was found that the reduction in these systems proceeded beyond a one electron change. In a sulfuric acid-pyrophosphate electrolyte system used by Pantani and Migliorira [9] in a polarographic study, the reduction of molybdenum VI to V proceeded with a 100 percent current efficiency. Optimum potential at which to carry out the reduction was determined as -0.2V vs SCE. The accuracy of the method was checked by calibrating the instrument with an NBS standard resistor and calculating from Faraday's law the theoretical equivalents to be titrated from the known amounts of molybdenum. The results in table 2 indicate that the method was accurate for molybdenum solutions to within one to two parts in a thousand.

3. Study of interferences

Because the determination of molybdenum in steels is of importance, the presence of iron in large quantities was checked. Iron added as ferrous ammonium sulfate did not interfere in the determination, although it did cause a somewhat higher background

Table 2. The accuracy of molybdenum titration in a pyrosphosphate electrolyte.

Mo Added mg.	Instrument readout in volts[a]	
	Calculated	Found
2.00	0.0530	0.0536
2.00	.0530	.0532
2.00	.0530	.0531
5.00	.1325	.1327
5.00	.1325	.1324

---

[a] The integrated current is converted to a readout in volts.

current. A second experiment involved partial oxidation and reduction of iron before attempting to reduce the molybdenum. Because phosphate media shift the reduction potential of iron to approximately the same value as the molybdenum, it was necessary to pre-reduce the ferric iron in a sulfate medium and then add pyrophosphate to reduce the molybdenum. Data in table 3 indicate that iron does not interfere if it is pre-reduced in a sulfate medium at +0.15V.

Table 3. Molybdenum recovery in the presence of iron.

Fe[a] (mg)	Potential Fe III/Fe II, V, vs SCE	Mo added (mg)	Instrument readout in volts[b]	
			Calculated	Found
40	+0.20	2.00	0.0530	0.0571
40	.15	2.00	.0530	.0532
40	.15	2.00	.0530	.0531

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[a] Approximately 1/3 of the Fe++ was coulometrically oxidized to Fe+++ before the reduction was begun.

[b] The integrated current is converted to a readout in volts.

To see if this new coulometric method could be applied to a new standard reference material of maraging steel, SRM 1156, several samples were analyzed. This high nickel-cobalt alloy also contains Mn, Cu, Cr and Ti among other trace elements.

The average of six runs yielded a mean value of 3.14 percent. These results were higher than those obtained by gravimetric methods. The precision was also considerably poorer than that obtained on synthetic samples of molybdenum and iron. The small percentage of copper in the sample interferes under the present experimental conditions. Other possible interferences, as well as the reason for the relatively poor precision, are currently being investigated.

L. A. Machlan and O. Menis

C. Pyrohydrolytic Separations

1. Introduction

Prior to the determination of nitrogen, boron and fluoride by a titrimetric procedure, it is essential to separate them quantitatively from refractory materials. This represents a challenging analytical problem, especially in cases requiring a high degree of precision and accuracy. In one such important problem, 20 percent boron had to be determined in a synthetic glass intended as a neutron flux monitor. For that purpose a precision and accuracy of better than 0.1 percent relative error is required.

Similar precision and accuracy are required in the determination of fluoride present in fluorspar, a standard reference material. Normally, 95 percent or better of this material is composed of CaF_2. On the accurate determination of CaF_2 hinges a 50 million dollar import business, since the duty restrictions are high at 0.2 percent below the 95 percent value. The present legal procedure, based on an NBS initial certificate, is dependent on a relatively empirical method. This procedure requires the determination of the soluble portion of the fluorspar and then the determination of calcium in the insoluble portion. Fluoride concentration is calculated from the latter calcium value. A direct determination of fluoride would obviously provide a more accurate answer.

Lastly, certain nitride compounds in steel are not readily decomposed by the classical Kjeldahl process and lead to low estimation of nitrogen in this type of material. A newer approach has therefore been undertaken which can appropriately be classed as a pyrohydrolytic separation.

The use of pyrohydrolytic techniques to separate elements such as nitrogen [10], boron [11,12,13] and fluoride [14] from refractory materials have been described in the literature. However, in most instances the studies have not been definitive and the methods are applicable only to specific materials. The role of fusion fluxes reported by Menis and Powell [14] need reevaluation to establish some of the reaction mechanisms and to test the quantitativeness of separation of macro quantities of volatile constituents.

2. Separation of nitrogen from refractory nitrides

The methods and apparatus for the determination of nitrogen were described in the last annual report of this Section [1]. In general, the process can be classified as a fusion-pyrolysis separation.

The results of analyses of several ferrous alloys for nitrogen are shown in table 4. The results for high silicon steel agree with those reported by Karp et al [10] and reflect a more complete decomposition of the nitrides. Similarly good agreement with previous values was obtained for cast iron and ingot iron samples. The method failed, however, when attempts were made to analyze ferrous alloys of high chromium and nickel content. At present, this procedure serves well as a check for the presence of refractory nitrides which, in a Kjeldahl method, may be overlooked.

3. Separation of boron

Boron has been separated from glass, ferrous alloys and other materials by pyrohydrolysis at temperatures in the range of 1100-1300°C [11,12,13]. Most of these procedures, based on steam pyrohydrolysis, require the collection of as much as a liter of condensate. Analogous to the conditions established

Table 4. Nitrogen by fusion pyrolysis.

SRM	N, % Certificate	N, % Found
125a (high silicon steel)	0.002	0.0041 ± 0.0002
7g (cast iron, high P)	.004	.0049 ± 0.0006
55e (ingot iron)	.004	.0044 ± 0.0005
160a (19 Cr-14 Ni-3 Mo steel)		incomplete decomposition

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for fluoride separation, it was hoped to separate boron by means of a fusion flux, with only a small partial pressure of water and at a much lower temperature.

a. Variables studied. The initial parameters investigated are summarized as follows:

Flux: Na_2O_2, $NaHSO_4$ (fused), $NaHSO_4$ + NaF, NaOH + SiO_2 (fused)

Temperature: 400 to 600°C

Time: 0.5 to 1.5 hr.

Oxygen flow: 4 liters/min.

Temperature of scrub water through which oxygen flows: ambient, 50° and 60°C.

Samples: NBS-SRM 1177 (0.024 B), and B_2O_3.

Scrubbing solution: dilute NaOH or H_2SO_4 solution.

b. Observations. The amount of boron recovered under these conditions varied from none to about 50 percent. These incomplete recoveries cannot be attributed to the inefficiency of the scrubbing solution but must be due to the incomplete decomposition and volatilization of the boron complex. Further studies will therefore be carried out at higher temperatures and with modified fusion fluxes.

4. Separation of fluoride from CaF_2

Powell and Menis described a method for the separation of microgram quantities of fluoride from refractory materials [14] in an apparatus shown in figure 3. The current studies deal with the effort to extend it to macro quantities of fluoride found in fluorspar. Initial data with a sodium tungstate flux indicate that temperatures higher than the 850°C, recommended for the dissociation of sodium fluoride, are required to decompose this material. After 1-1/2 hours of pyrohydrolysis at 860, 937, 982, 1018 and 1090°C, approximately 60, 68, 78, 86 and 100 percent, respectively, were recovered. From visual indications it was evident that at higher temperatures the flux decomposes in the presence of fluoride and contributes to the high results. In thermogravimetric tests with only the flux material, no loss of weight was noted even at 1000°C. This would lead one to postulate that the observed decomposition product is a WO_2F_2 intermediate, which could account for any tungsten coming over into the scrubbing solution. Plans for testing other flux materials are under way.

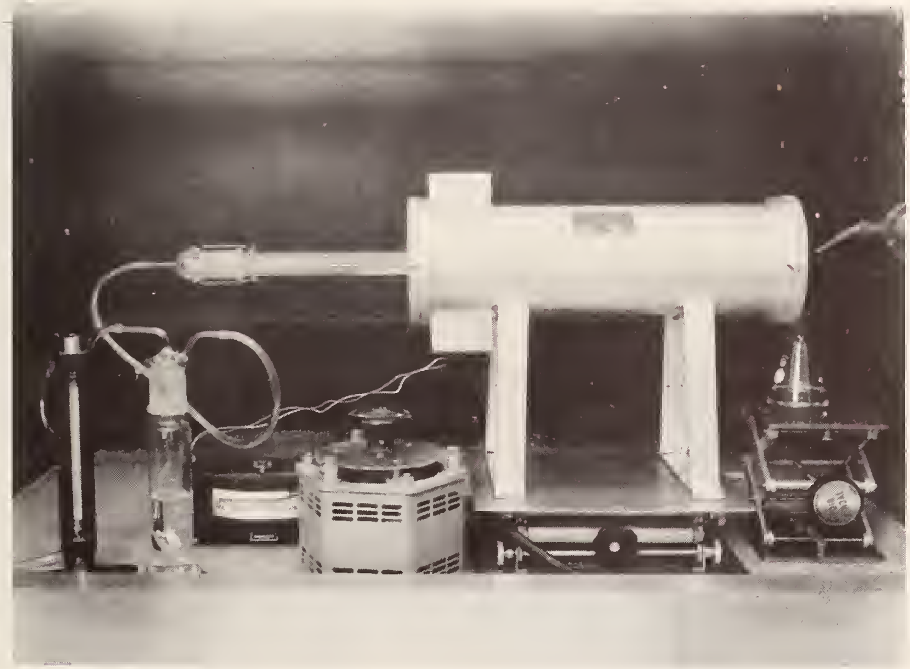

Figure 3. Pyrohydrolysis apparatus.

B. B. Bendigo and O. Menis

D. Summary of the Titrimetric Results

In table 5 data are summarized for some of the work completed on standard reference materials. These data indicate that the new application of complexometric titration to the determination of the calcium compares favorably with the much more time-consuming gravimetric procedure. Theoretically, it offers a more accurate method, since it is subject to fewer systematic errors than in the latter method. Again, a significant improvement in the determination of nitrogen can be noted, 6% vs 12% relative error, when a spectrophotometric procedure instead of the potentiometric method was applied. The more classical potentiometric titration of chromium, manganese and vanadium reflect the normal trend in precision. It is evident that vanadium at very low concentrations has the poorest precision and that another method, such as activation analysis, may be more suitable. Of the newer approaches, the spectrophotometric or coulometric titrations in conjunction with appropriate selection of complexation chemistry should lead to better precision and attainment of stoichiometric reactions.

Table 5. Titrimetry - summary of SRM analyses.

Element	Standard reference material No.	Kind	Number of determinations	Percent found	Rel. std. deviation
Ca	88a	Dolomitic limestone	5	30.11[a]	0.2
Ca	1074a	Calcium 2-ethylhexanoate	20	12.54[b]	.2
Cr	12h	Basic Open Hearth, 0.4C steel	10	0.0774[c]	.2
Cr	73c	Stainless steel (Cr13) (SAE 420)	4	12.846[d]	.3
Cr	82b	Nickel-chromium cast iron	10	0.335[c]	.1
Cr	152a	Basic Open Hearth, 0.5C, 0.04 Sn steel	9	.0467[c]	.5
Cr	1156	Maraging steel	3	.2002[e]	.2

Table 5. (Continued)

Element	Standard reference material No.	Kind	Number of determinations	Percent found	Rel. std. deviation
V	12h	Basic Open Hearth, 0.4C steel	10	.0020[f]	5
V	73c	Stainless steel (Cr13) (SAE 420)	4	.0278[g]	2
V	82b	Nickel-chromium cast iron	10	.0261[f]	0.5
V	152a	Basic Open Hearth, 0.5C, 0.04 Sn steel	9	.0006[f]	40
Mn	13g	Basic Open Hearth, 0.6C steel	9	.856[h]	0.2
Mn	15g	Basic Open Hearth, 0.1C steel	32	.485[h]	.5
Mn	82b	Nickel-chromium cast iron	32	.745[h]	.2
N	73c	Stainless steel (Cr13) (SAE 420)	6	.0368[i]	3
N	1090	Ingot iron	8	.0064[j]	6
N	1090	Ingot iron	96	.0063[i]	12
N	1091	Stainless steel (AISI 431)	14	.0865[i]	1
N	1092	Vacuum-melted steel	4	.0008[k]	10

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[a] 2.5g sample, Ca separated by ion exchange, 50/250 aliquot, titrated spectrophotometrically with EDTA and Eriochrome Black T indicator [15] [16].

[b] 1g sample ignited to CaO, dissolved in $HClO_4$, titrated with EDTA and mercury indicating electrode [15].

[c] 10g sample, $NaHCO_3$ separation, $(NH_4)_2S_2O_8$ oxidation, titrated potentiometrically with $Fe(NH_4)_2(SO_4)_2$ [17].

[d] 0.5g sample, $(NH_4)_2S_2O_8$ oxidation, titrated potentiometrically with $Fe(NH_4)_2(SO_4)_2$ corrected for vanadium [17] [18].

Table 5. (Continued)

[e] 2g sample $(NH_4)_2S_2O_8$ oxidation, titrated potentiometrically with $Fe(NH_4)_2(SO_4)_2$ [17].

[f] 10g sample, $NaHCO_3$ separation, HNO_3 oxidation, titrated potentiometrically with $Fe(NH_4)_2(SO_4)_2$ [17].

[g] 3g sample, HNO_3 oxidation, titrated potentiometrically with $Fe(NH_4)_2(SO_4)_2$ [17] [18].

[h] 1g sample $(NH_4)_2S_2O_8$ oxidation, titrated potentiometrically with Na_2HAsO_3 [19].

[i] 0.5g sample, ammonia steam distilled from alkaline solution titrated with HCl using pH meter [20].

[j] 0.5g sample, ammonia steam distilled from alkaline solution, titrated spectrophotometrically using Methyl Violet indicator [20].

[k] 1g sample, ammonia steam distilled from alkaline solution, titrated spectrophotometrically using Methyl Violet indicator [20].

2. GRAVIMETRY

A. Introduction

Gravimetric methods play an important role in many of the determinations used in standard reference materials. Gravimetry has a major advantage in that the final product of known stoichiometric composition can be isolated. It, therefore, serves as a direct means for estimating the accuracy of the determination. The main disadvantages of the gravimetric procedures are the potential systematic errors due to solubility, coprecipitation and absorption phenomena. In many procedures advances in the use of chelating or masking reagents serve to prevent effectively the coprecipitation of interfering elements. Similarly, the applications of homogeneous precipitation in gravimetric methods offer a means of eliminating errors due to absorption of interfering elements. Another important factor in broadening the scope of gravimetric methods has been the utilization of separation schemes. Again, with the advent of newer extraction and ion exchange procedures, the lack of specificity in gravimetric methods can be overcome. It is claimed that the gravimetric methods are more time consuming, but it can also be readily demonstrated that, under proper conditions, they provide values of higher accuracy.

During the past year, much emphasis has been placed on studies of homogeneous precipitations, the use of masking reagents, and extraction and ion exchange separations. The current work dwells on some of the problems connected with the analysis of standard reference as well as with other potential SRM materials. Studies are also included on the progress of the determination of molybdenum and tungsten in a sintered compact.

Thermogravimetry and differential thermal analysis provided means for verifying the stoichiometry of final composition and the presence of impurities. As a result of this application the potential need for a standard Reference Material in the field of Differential Thermal Analysis is currently under study. Some criteria for a suitable standard are discussed and a preliminary investigation with tricalcium silicate is described.

B. Analysis of Standard Reference Materials

As shown in table 6, gravimetric procedures offer the best approach for certain element . In this table, values are shown for silicon, phosphorus, cobalt, aluminum, calcium, magnesium, molybdenum, nickel, copper, and beryllium in a wide variety of materials. In these determinations, accuracy of the values is ascertained by analyzing simultaneously a material of similar and certified composition, or by synthetic samples prepared from high-purity reagents.

The highly accurate gravimetric methods for the determination of silicon dioxide have been widely used for these materials. In the Bessemer steel sample, a low value for silicon was obtained because of the greater solubility of SiO_2 in a perchloric acid medium. To assure the greatest accuracy, it is necessary to determine and correct for the soluble silica in the filtrate by spectrophotometric analysis [21]. A relative precision of 0.1 to 1% was attained with the actual value depending on sample size and complexity of the matrix. Phosphorus was also determined by the gravimetric method. While the percentages of phosphorus are low and large samples are required, good accuracy can still be claimed for this method. In certain instances the degree of accuracy is extremely high. For example, in the electrogravimetric method for copper it is one to two parts in ten thousand. Cobalt was also determined electrogravimetrically following an ion exchange separation. A precision of three parts in ten thousand was readily obtained. Nickel, as the dimethylglyoxime chelate, also yields a precise and accurate value of five parts in twenty thousand. In a sample of a complex matrix, however, it should be pointed out that the accuracy of this method depends on carefully controlled conditions which are influenced by the type of material and the experience of the operator.

The determinations of aluminum and beryllium will be discussed in subsequent sections.

Table 6. Gravimetry

Element	Standard reference material No.	Kind	Number of determinations	Percent found	Rel. std. deviation
Si	13g	Basic Open Hearth, 0.6C steel	8	0.355[a]	0.6
Si	15g	Basic Open Hearth, 0.1C carbon steel	8	0.0957[a]	0.3
Si(lot 2)	10g	Bessemer steel	4	0.0224[b]	
Si(lot 2)	10g	Bessemer steel	4	0.0195[c]	2.
Si	82b	Nickel-chromium cast iron	8	2.096[d]	0.1
Si	73c	Stainless steel (Cr13) (SAE 420)	4	0.179[a]	0.6
Si	1170	Selenium-bearing steel	3	0.163[a]	0.6
Si	1156	Maraging steel	3	0.186[a]	0.5
Si	16e	Basic Open Hearth, 1.0C steel	4	0.202[a]	1.
P	15g	Basic Open Hearth, 0.1C carbon steel	4	0.00056[e]	0.6
P	1156	Maraging steel	2	0.0105[e]	1.
Co	1156	Maraging steel	3	7.259[f]	0.2
Al	70a	Feldspar	6	17.84[g]	0.3
Ca	88a	Dolomitic limestone	4	30.19[h]	0.4
Mg	88a	Dolomitic limestone	4	21.35[i]	0.4
Mg	88a	Dolomitic limestone	6	21.36[j]	0.2
Mo	1156	Maraging steel	10	3.04[k]	1.0

Table 6. (Continued)

Element	Standard reference material No.	Kind	Number of determinations	Percent found	Rel. std. deviation
Ni	1156	Maraging steel	5	18.994[m]	0.05
Cu	A[1*]	Beryllium-copper alloy	4	97.460[n]	0.02
	B[1*]	Beryllium-copper alloy	4	97.430[n]	0.01
	C[1*]	Beryllium-copper alloy	4	97.116[n]	0.01
Be	A[1*]	Beryllium-copper alloy	8	1.95[o]	1.0
	B[1*]	Beryllium-copper alloy	8	1.78[o]	1.1
	C[1*]	Beryllium-copper	8	0.46[o]	2.2

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[a] 5g sample, double dehydration with $HClO_4$, HF residue correction [19,22].

[b] 5g sample, double dehydration with H_2SO_4, HF residue correction [19,22].

[c] 10g sample, double dehydration with $HClO_4$, HF residue correction [19,22].

[d] 2.5g sample dissolved in aqua regia, double dehydration with $HClO_4$ [22].

[e] 12g sample, molybdate-magnesia method [22].

[f] 2g sample, anion-exchange separation and electrodeposition, 1g of SRM 1187 and 1g of SRM 553 as synthetic control, Co present, 0.2092g; Co found, 0.2100g [23].

[g] 0.5g sample, fusion with Na_2CO_3, SiO_2 dehydrated with HCl and volatilized with HF, Al precipitated homogeneously with succinic acid and urea. Fe in Al_2O_3 correction [24,25].

Table 6. (Continued)

[h] 2.5g sample dissolved in HCl, Ca separated by ion-exchange in 50/250 aliquots precipitated with $(NH_4)C_2O_4$, ignited to CaO [K. M. Sappenfield, unpublished work].

[i] 2.5g sample dissolved in HCl, Mg separated by ion-exchange in 50/250 aliquot, precipitated with $(NH_4)_2HPO_4$, ignited to $Mg_2P_2O_7$.

[j] 2.5g sample dissolved in HCl, Mg separated by ion-exchange in 50/250 aliquots, precipitated with 8-hydroxyquinoline.

[k] 1g sample dissolved in HCl, Mo precipitated with α benzoinoxime, ignited to MoO_3 [26].

[l*] Sample not certified.

[m] 2g sample, dimethylglyoxime precipitation in 50/250 aliquot, drying at 150°C [22].

[n] 5g sample, HNO_3 solution, electrodeposition with total current of 0.5 ampere, gravimetric. No SRM available, used synthetic sample as control [21,27].

[o] 1g sample in aliquot of electrolyte, dehydration of SiO_2, added EDTA for complexation, NH_4OH, ignition, gravimetric BeO. Used synthetic sample as control [28,29].

C. Studies and Application of Homogeneous Precipitations

1. Determination of aluminum

The determination of aluminum in a Standard Reference Material of feldspar, 70a, was reinvestigated in order to establish its value and resolve the difference between NBS results and those of the cooperating laboratories. By a procedure based on the precipitation of aluminum with ammonium hydroxide, results at the Bureau were 0.1% higher than those reported by cooperators. Since homogeneous precipitation offers the advantage of a purer and more easily filterable precipitate, this technique was tested in rechecking the results. As shown in table 6, a relative precision of 0.3% was obtained, which represents a two-fold improvement over the classical procedures. While the mean of the revised value is 17.85 percent, it is within one sigma value of the previous average of 17.90 percent. These new data therefore support the previous values obtained.

2. Determination of beryllium

Determination of beryllium in a copper-beryllium alloy is under investigation in an effort to improve the precision and accuracy of establishing its value. The initial results (table 6) which were based on an ASTM procedure [19] indicate a large relative error of about 1%. Spectrographic analysis later revealed the presence of impurities in the ignited precipitate. For this reason, homogeneous precipitation by the hydrolysis of urea in the presence of hexaminetetramine was studied as a means of homogeneously increasing the pH. The effect of several counter ions and complexing agents was also studied. A basic sulfate medium markedly improved the particle size of the precipitate. Also, thermogravimetric data are being recorded for the new precipitates. This problem is now under investigation to evaluate the optimum condition for a gravimetric method and to resolve some of the conflicting recommendations for the final ignition temperature which is required to obtain a stoichiometric product. The details of this study will be published on completion of this investigation.

D. Separation of Tungsten and Molybdenum

1. Introduction

As part of the program for new standard reference materials, R. E. Michaelis, Metal Standards Coordinator of the 302 Division, submitted a compact of 80 percent tungsten and 20 percent molybdenum powder for the determination of the major components. This material was found by microprobe examination to be homogeneous and an accurate analysis of its composition was needed to establish its stoichiometry. Provided a quantitative separation could be achieved, gravimetric procedures could then be readily applied to the accurate determination of those two elements.

2. Separation of molybdenum and tungsten in a sintered metallurgical rod

For this purpose two methods seemed to be appropriate; one involving liquid-liquid extraction and the other an ion exchange method. The liquid-liquid extraction is based on a study reported by Kimura [30] in which the separation factor of molybdenum from tungsten (D_{Mo}/D_W) in hydrochloric acid was reported to be 130. This is insufficient in a batchwise extraction for quantitative separation. Therefore, a study was undertaken to establish whether by use of suitable complexing media such as HF a more favorable separation factor could be obtained. For that reason a study of mixed acids of HCl-HF was instituted. Since HF forms a much stronger tungsten complex, it was hoped that through preferential complexation the separation factor could be increased to a 1000 or better.

a. Experimental. In the initial test, experimental conditions were varied to study the effect of different concentrations of mixtures of HCl-HF on the distribution of molybdenum between the aqueous and organic phase.

Since, initially, radioactive tracers were not available, this study was carried out through individual extractions of molybdenum and tungsten. Aliquots of a stock solution containing 10 mg of Mo or 0.5 mg W were pipetted into a 60-ml separatory funnel. The volume was adjusted to 10 ml with the appropriate acid mixture. Then 10 ml of 1 to 1 bis (2-ethylhexyl) orthophosphoric acid-toluene was added. The two phases were allowed to stand for approximately 10 minutes and then separated. One ml aliquots of the aqueous phase were analyzed spectrophotometrically. For Mo and W, NaCNS-butyl acetate and the dithiol methods, respectively, were used. On the basis of this analysis the distribution ratio was estimated. The data are presented table 7. In a second group of experiments, ^{99}Mo tracer was added to solutions containing both molybdenum and tungsten. Relatively higher concentrations of tungsten were used to simulate the conditions that would be encountered in the 20 percent molybdenum - 80 percent tungsten rod. Unfortunately no W tracer was available and the data represent only molybdenum distribution. In the general procedure, it was found that tungsten precipitates at higher concentrations. Thus with 40 mg of tungsten, the aqueous phase had to be increased to 20 ml, while 80 mg of tungsten required a higher concentration of HF. The variable conditions and results are presented in table 8.

Table 7. Effect of HF and HCl concentration on the distribution coefficient, $D = \frac{M_{(org)}}{M_{(aq)}}$.

Normality of HF:	0	0.05	0.1	0.2	0.3	0.2	0.2
Normality of HCl:	1	1	1	1	3	0.5	1
$D = \frac{Mo_{(org)}}{Mo_{(aq)}}$:	600	110	50	18	10	---	10
$D = \frac{W_{(org)}}{W_{(aq)}}$:	20	0.1	0.033	0.01	0.006	0.04	---

b. <u>Results</u>. From the data in tables 7 and 8 it is evident that the role of HF is quite important in this separation. With increasing concentration of this acid, the distribution of molybdenum is decreased but at the same time less tungsten is also extracted. With larger quantities of tungsten, 40 mg in 20 ml, at least 0.12 $\underline{N}$ HF is required to keep the tungsten from precipitating. However, under these conditions

Table 8. The effect of HF or H_3PO_4 on the extraction of Mo in the presence of W from 1 N HCl into HDEHP[a].

Complexing acid	media conc. (N)	Elements Mo (mg)	W (mg)	Activity, A, cts/2 min organic	aqueous	$D = \frac{A_{(org)}}{A_{(aq)}}$	% E[b]
HF	0.05	10[c]	10[c]	7515	108	70	
					13[d]	170	99.6
	0.1	10[c]	10[c]	6966	590	12	
					57[d]	82	99.0
	0.05	25[e]	--	3752	187	20	95.
	0.1	10[e]	40	7306	599	12	92.
	0.12	10[e]	40	5481	958	5.7	
					226	24.2	96.
		10[e]	40	5290	993	5.3	
					249[d]	21.2	95.
	0.2	25[e]	80	3530	1266	3	
					627[d]	5.6	85
H_3PO_4	0.4	10[e]	40	5721	2236	2.5	71

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[a] HDEHP bis (2-ethylhexyl) orthophosphoric acid = 50% v/v in toluene.

[b] $\%E = \frac{D}{D+1} \times 100$ = percent extracted.

[c] Volume ratio: org/aq = 10/10.

[d] Second extraction.

[e] Volume ratio org/aq = 25/25.

over 95% of molybdenum can be removed by two successive batch extractions. This would indicate that it should be feasible to achieve a separation by a counter-current extraction process. In a more thorough investigation tracer studies will be undertaken. As shown by the data in table 7 the distribution ratio does not agree with that reported by the initial investigator. It is suspected that the purity of the organic reagent, HDEHP, may contribute to this and will have to be tested.

3. Ion exchange separation of Mo-W in the sintered compact

Another appraoch to the separation of molybdenum and tungsten is by means of ion exchange. This type of separation was investigated for molybdenum and tungsten in the sintered compacts by taking advantage of the stability of their respective fluoride complexes.

a. Experimental procedure.

i. Preparation of sample: Thin slices were cut from the rod and pulverized in an agate mortar until the sample passed through a number 80 sieve. A 0.25 g sample was weighed into a plastic beaker and dissolved in 30 ml of 50% HCl-10% HF plus about 25 drops of nitric acid by warming overnight on a steam bath.

ii. Ion exchange procedure [31,32]: The sample was transferred to a plastic anion exchange column 1 inch in diameter and 6 inches long, and filled with Dowex 1x8 resin finer than 270 mesh. The first fraction containing the tungsten was eluted with 465 ml of 50% HCl-10% HF solution.

iii. Gravimetric determinations: The first eluate, containing W, was transferred to a platinum dish, sulfuric acid was added, and the solution was evaporated to fumes of SO_3. The evaporation was repeated three times. The remainder of the procedure is described in the literature [31,32]. To the second eluate (25% HCl-20% HF), containing the Mo, 70 g of H_3BO_3 were added and an α-benzoin oxime precipitation was carried out [26]. The efficiency of boric acid complexation was checked with a synthetic solution carried through the same procedure.

b. Results and observations.

The initial values from two samples of the rod for Mo and W were 21.65, 21.68, 78.49, and 78.07%, respectively. These results would indicate that a 100.14 and 99.75% summation was achieved. Acceptance of the method will depend on the collection of more data to enable one, statistically, to evaluate the accuracy of a method which requires a relatively long eluation process.

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E. Differential Thermal Analysis

1. Introduction

The thermoanalytical methods, particularly differential and thermogravimetric analyses, are being reviewed to find a useful standard reference material to assist the workers in this field in calibrating the variety of instruments now available from commercial sources, and to check their techniques. It is realized that a selection of suitable calibration standards would be desirable, but there are special problems inherent to the differential thermal analysis process which limit the utility of many standards. The data obtained by this technique depend on a large number of independent variables. These variables are affected by such instrument characteristics as the cell geometry, cell size, the materials of which the sample holders are constructed, the rate of heating, atmosphere and the preparation of the sample. In addition, there are inherent physico-chemical properties of the materials such as changes in heat capacities and thermal conductivity at higher temperatures, phase and crystaline modifications, as well as their emissivity at high temperatures, which influence the shape of the differential curves. It is the latter factors which make the selection of one suitable calibration standard extremely difficult. In order to be of service to the individual, a standard should have physical properties similar to those of the unknown; otherwise interpretation by comparison of the two may be misleading. One possible solution to the problem would be to enlarge the number of standard samples to include a variety of materials whose overall characteristics would cover a range of these properties, and then one could select an appropriate one for a given test sample. This type of screening is essential in order to make these reference standards of general value. In addition, other properties such as particle size, purity and history of preparation have to be carefully controlled, recorded and made available as essential information.

2. Differential thermal analysis of tricalcium silicate

In the preliminary screening of materials as potential standards for differential thermal analysis the DTA data on tricalcium silicate, as reported by Mazieres [33],were of interest. He reported four transition temperatures which might be useful for calibration purposes.

a. Experimental.

The sample of tricalcium silicate was received in a sealed vial from the old files of the Cement Division. Unfortunately, the history of the preparation of the sample was not available. The vial was cut open and the sample was transferred to a weighing bottle. The sample weight was 9.30 grams.

Two half-gram samples were weighed into bottles and placed in a desiccator containing P_2O_5. Two additional 500 mg samples were placed in a desiccator containing a solution of saturated sodium chloride which provides an atmosphere of 75% relative humidity. These four samples were weighed daily. In four days the weight of the two samples over P_2O_5 remained constant and the two samples in the 75% humidity gained 1.2 and 1.5 mg. The samples were then switched to the opposite desiccators. The samples moved from the 75% relative humidity to the dry P_2O_5, lost 0.2 mg and then remained constant at a net weight gain of 1.0 and 1.3 mg. The two samples moved from the dry atmosphere to the 75% relative humidity continuously gained weight; each gained a total weight of approximately 6.5 mg in thirty one days. The conclusion can be drawn is that tricalcium silicate very slowly picks up moisture and does not release this moisture to P_2O_5.

DTA thermograms were run on small samples (2 mg) of the tricalcium silicate. Samples were run with the intermediate temperature cell 850°C and the high temperature cell 1200°C. A comparison of our results with those in the literature [33] is shown in the following table 9.

Table 9. Endotherm temperatures, °C for tricalcium silicate.

Heating	(a)	600	915	980	990
	(b)	656	923	981	none
Cooling	(a)	560	905	970	985
	(b)	none	876	955	none

(a) Mazieres
(b) NBS

The endotherm peaks were very small, 0.03 to 0.15 °C, and very difficult to measure. The intermediate temperature cell was heated at a rate of 15°C/min with a detection limit of 0.2°C/in. In order to be able to detect the thermal changes it was necessary to run the high temperature cell at 50°C/min with a sensitivity of 0.2°C/in. during heating and 0.5°C/in. during cooling. The faster heating gives greater sensitivity but less accuracy.

The failure to reproduce Mazieres' data may be attributed to lack of sensitivity in our instrument and to the sample size. His instrument required only a microsample which markedly increased the sensitivity of DTA curves.

F. Conclusions and Future Considerations

Further work is essential in the field of coordination chemistry and thermal analysis. By means of masking, choice of counter ions and selective precipitation reagents, liquid-solid phase separations can be achieved which are free from contamination. The stoichiometric composition of the final product also needs to be checked. Thermogravimetric analyses in conjunction with differential thermal analyses should provide useful information not only about the stoichiometry but also of the type of binding in the solid phase. In addition, it may provide a very sensitive guide for the relative purity of the compound.

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3. FLAME SPECTROPHOTOMETRY AND ATOMIC ABSORPTION

A. Introduction

As indicated in the general introduction, analytical coordination chemistry plays an important role in flame photometry and atomic absorption. As solutions are aspirated into the flame and evaporated, the ease of dissociation of compounds and complexes varies depending on the composition of the solution. In the current studies with the phosphate, aluminum, calcium and magnesium systems, as well as, in the studies of chelate systems for the analysis of high purity zinc, the chemistry of the solution played an important role in attaining high accuracy and low detection limits. In this respect, a very effective means for the elimination of interferences from phosphate and aluminum in the measurement of calcium was the utilization of a "releasing agent". Another analytical development involved initiation of studies for the determination of copper in steel and high purity zinc. The latter represents a special challenge since it dealt with a six nine purity (99.9999) material and the problem of finding less than 1 ppm of impurity imposed unique difficulties.

The other efforts during the past year involved setting up new instruments and testing their performance. The components which were evaluated included atomizer-burner systems, the use of integrator and a stable power supply with the photomultiplier tube. In addition, in setting up new laboratories a new hood design and installation was required for the flame spectrophotometers. For this work it is intended to operate in two laboratory modules connected by an internal door. One module will be reserved for instrumentation under controlled conditions to minimize environmental contamination and the other will be used for sample preparations. The facilities have as yet not been completed but the major features and major components have been installed.

B. Scope - Detection Limits

The wide scope of application to over seventy elements for the estimation of microgram and nanogram amounts makes the method attractive and fast growing in applications. In the current years we have accumulated data, shown in table 10, indicating some of the limits of detection for approximately fifty elements.

Table 10. Sensitivity limits for various elements obtained by flame emission and atomic absorption spectrophotometry.

Element	Wavelength, (A)	Detection Limits[a], μg/ml Flame Emission	Atomic Absorption
Ag	3383	.02[b]	
	3281		.005[c]
Al	3962	.1[b]	
Au	2676	.5[b]	.01[d]
B	547_0	.3[b]	
Ba	5536	.05[b]	.2[c]
Bi	2231		.1[d]
Ca	4227	.001	.005[c]
Cd	2288		.001[d]
Co	3527	.01[b]	
Cr	4254	.01[b]	
Cs	8521	.002	
Cu	3248	.1	.007[c]
Dy	573_0	.1[b]	
Er	504	.1[b]	
Eu	4594	.05[b]	
Fe	3720	.01[b]	
Ga	4172	.05	
Gd	464_0	.1[b]	
Hg	2537		.2[d]
Ho	566_0	.1	
In	4511	.01[b]	

Table 10. (Continued)

Element	Wavelength, (A)	Detection Limits,[a] µg/ml Flame Emission	Atomic Absorption
K	7665	.0002	
La	743_0	.1[b]	
Li	6708	.0002	
Lu	468_0	.05[b]	
Mg	2852	.02	.005[c]
Mn	4031	.008[b]	
Na	5890	.0001	.01[c]
Nd	700_0	.2[b]	
Ni	3525	.01[b]	
	2320		.05[c]
Pb	4058	.1[b]	
	2833		.02[d]
Pd	3635	.04[b]	
Pt	2659		.5[d]
Rb	7800	.001	
Rh	3692	.5	
Ru	3727	.07[b]	.5[d]
Sb	2176		.1[d]
Sc	607_0	.01[b]	
Sm	652_0	.1[b]	
Sr	4607	.002	.005[c]
Tb	535_0	.1[b]	
Te	2143		.02[d]
Tl	3776	.0005[b]	
Tm	494_0	.1[b]	
Y	597_0	.02[b]	
Yb	3988	.01[b]	
Zn	2139		.001[c]

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[a] Detection limit = 2 x σ of background

[b] Organic solvent

[c] Laminar flow burner with preheater

[d] Quartz tube

C. Instrumentation

Modifications and additional components for the atomic absorption and flame emission instrumentation have been obtained since our previous report. The present atomic absorption equipment, as shown in figure 4, consists of a 0.5 meter Ebert mount monochromator, with replaceable gratings blazed for 3000 and 7500A. The hollow-cathode power supply and tube holder remains the same as received with the original equipment. To this was added the electronic circuit which is used for both atomic absorption and flame emission. It consists of three units and a chart recorder. The three units are (a) the 0 to 2100 V multiplier phototube power supply, (b) the selective amplifier and synchronous detector and (c) the dc-amplifier, integrator and timer section. The multiplier

Figure 4. Atomic absorption equipment.

phototube power supply is a John Fluke Mfg. Co., Inc., Model 412B* and has a current capability of 30 mA. The selective amplifier and synchronous detector is a Princeton Applied Research Corporation Model JB-4 'Lock-in Amplifier'*. The third unit, containing the dc-amplifier, integrator and timer, was built by the Measurement Engineer Division of the National Bureau of Standards and is a modification of the design by Jones, Fisher and Kelley [34], [35].

A new flame housing was added to the flame emission equipment, as shown in figure 5. In order to use the selective amplifier and synchronous detector, a light-beam-chopper disk was placed between the flame housing and the monochromator. By means of the integrator from the electronic circuit, flame emission detection limits for many elements can be extended.

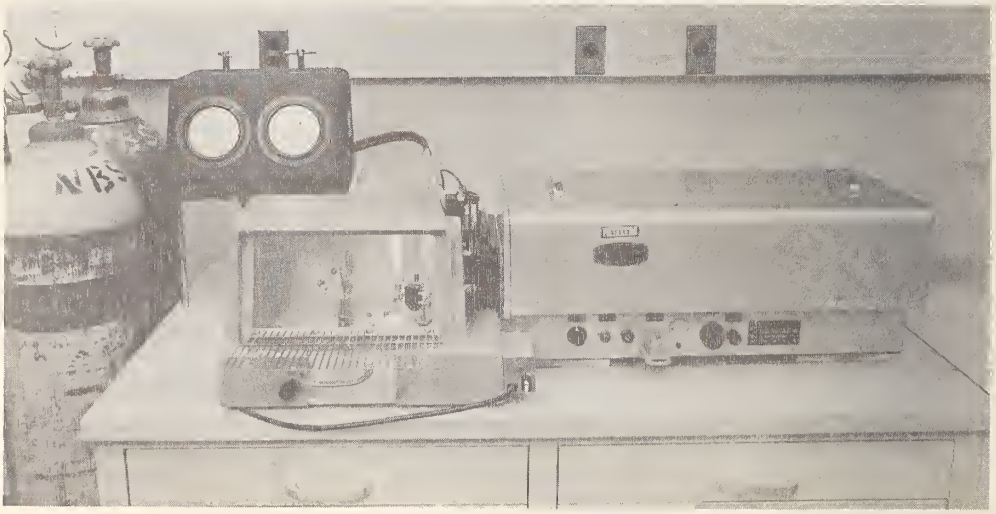

Figure 5. Flame emission equipment.

At present, an EMI/US QB* multiplier phototube is used in flame emission to span the wavelength range from 2500 to 8300A. A combination of phototubes has been used in the atomic absorption work.

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*See note in preface.

A variety of burners, both of the total consumption and premix type, are being tested. These studies include the evaluation of their relative sensitivity, optimum precision and effect from the matrix.

D. Determination of Magnesium in Various Materials by Atomic Absorption

The sensitivity of magnesium by atomic absorption (AAS) is sufficient for most purposes (0.0005 μg/ml in aqueous solutions). However, in the presence of phosphate and aluminum, a severe suppression is observed. This led to studies of ways for overcoming these interferences. This investigation involved both atomic absorption and flame emission spectrophotometry and included the following parameters: (a) the effect of different types of burners and fuel systems, (b) burner height, and (c) the use of releasing agents.

1. Effect of phosphate

The relative effect of phosphate on magnesium in atomic absorption with and without releasing agents for the different types of burners shown in figure 6. It is observed that the suppression of magnesium is far greater in the total consumption type of burner (figure 6C) with an oxyhydrogen flame than in the two premix type burners using air-acetylene. A similar effect is also observed in flame emission.

Also, if the phosphate is added as diammonium hydrogen phosphate (figure 6B), the suppression is greater than in the presence of phosphoric acid. It is postulated that the increased adverse effect of the diamonium hydrogen phosphate is due to its rapid conversion at high temperatures to pyrophosphoric acid. The pyro acid has a much greater ionization constant than the ortho acids [36] and leads to the formation of refractory pyrophosphate compounds. Pyrophosphoric acid is also produced when orthophosphoric acid is evaporated at elevated temperatures; but, the reaction proceeds more readily when a monohydrogen phosphate is present.

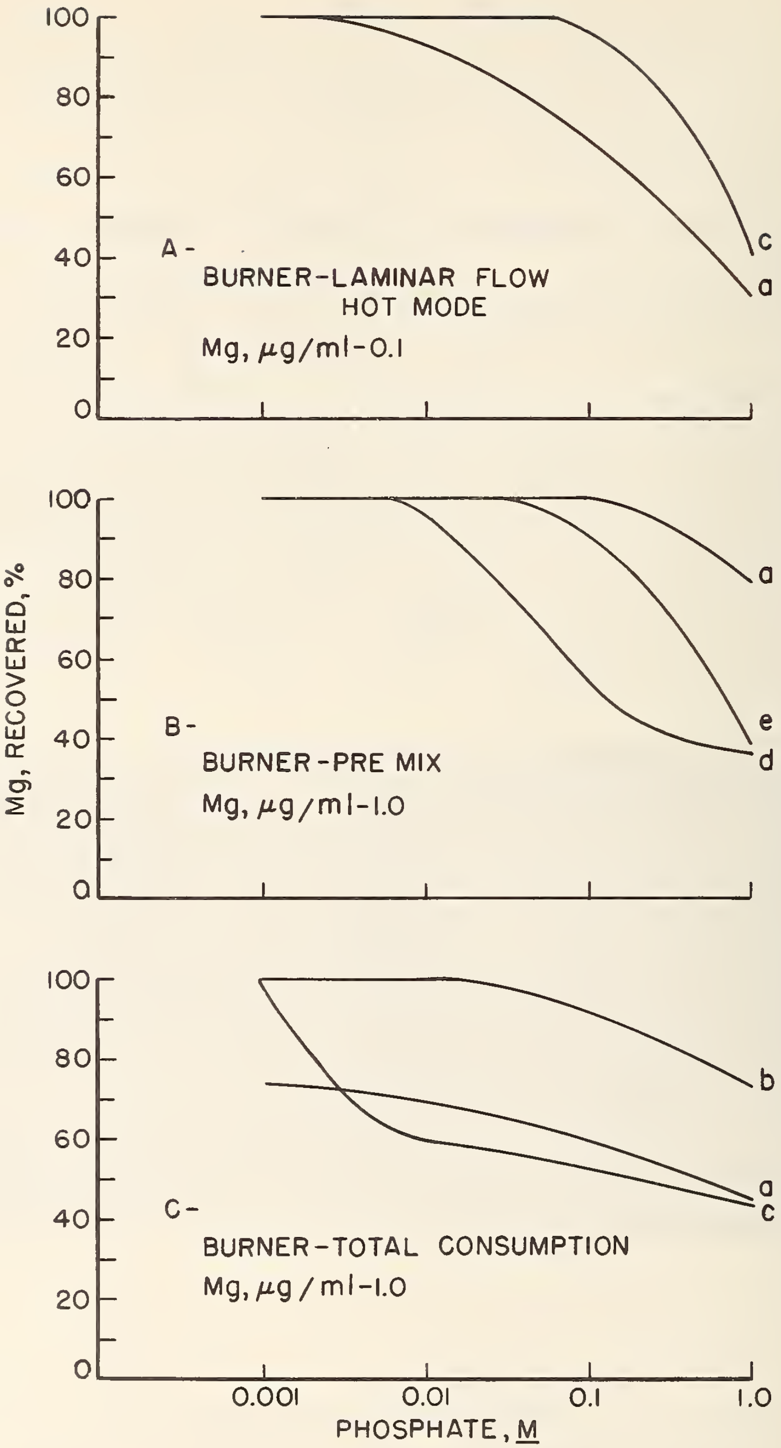

Figure 6. Effect of phosphate on magnesium by atomic absorption spectrophotometry with three different burners. a. H_3PO_4; b. Glycerol, 10%; $HClO_4$, 0.1 M; c. La, 1 mg/ml; d. $(NH_4)_2HPO_4$; e. $(NH_4)_2HPO_4$; Glycerol, 10%; $HClO_4$, 0.1 M.

Several methods proposed by others for preventing the interference of phosphate on the alkaline earth metals [37], [38], [39] were studied. It was established that the suppression of magnesium due to phosphate in a total consumption burner can be best minimized by the addition of glycerol and perchloric acid. In the laminar flow burner with the preheater in the hot mode of operation, lanthanum yielded the best results. The glycerol in this case became charred on the hot chamber walls of the premixed gas burner and failed to reach the intercone gases. Disodium ethylenediaminetetraacetate was found to be less effective than glycerol or lanthanum.

2. Effect of aluminum

A similar study was made investigating the effect of aluminum on magnesium in AAS as shown in figure 7. In this case, lanthanum was the best releasing agent. It was established that if the weight ratio of lanthanum to aluminum is 10:1, aluminum has no effect on the absorption of magnesium. However, this high concentration of lanthanum produces burner clogging when the aluminum concentration is greater than 100 ppm. If, however, glycerol is used in conjunction with the lanthanum, a weight ratio of only 2:1 is necessary for a complete recovery of magnesium, and thus eliminated this problem.

3. Effect of flame region

In the process of studying flame conditions, the effects of phosphate and aluminum on the atomic absorption of magnesium in the various regions of the flame were tested. It was observed that the influence of phosphate on magnesium is lessened in the upper region of the flame. The suppression of the magnesium in the presence of aluminum on the other hand was essentially constant over all the regions. From the standpoint of the role of releasing agent, it was observed that the efficiency of glycerol and perchloric acid was increased,

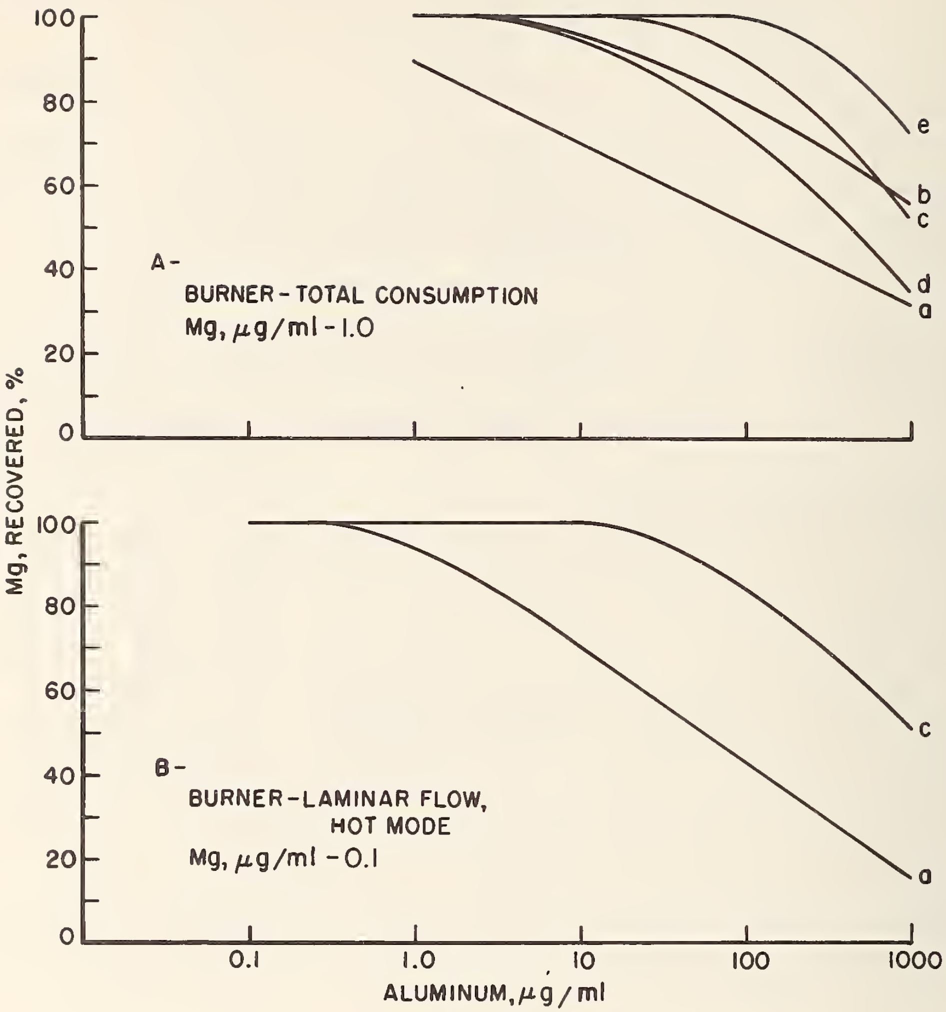

Figure 7. Effect of aluminum on magnesium by atomic absorption with and without releasing agents.

a. Al; b. Glycerol, 10%; $HClO_4$, 0.1 $\underline{M}$;
c. La, 1 mg/ml; d. EDTA, 0.05 $\underline{M}$;
e. La, 1 mg/ml; Glycerol, 10%; $HClO_4$, 0.1 $\underline{M}$.

especially for aluminum, when absorbance measurements are taken in the region of 6 to 10 cm above the top of the burner. Therefore, this portion of the flame should be observed when aluminum is present.

The precision of, the method for several materials analyzed during the past year is given in table 11.

Table 11. Determination of magnesium in various types of material.

	MgO, %			
	Gravimetric[(a)]		Atomic Absorption	
NBS SRM	Range	Av.	Av.	Relative Standard Deviation, %
1a Limestone	2.11 -2.26	2.19	2.17	3
70a (K) Feldspar	.01 - .04	-	.039	6
98 Plastic Clay	.69 - .75	.72	.74	5
99a(Na) Feldspar	.014- .028	.02	.013	7
120a Phosphate Rock	.25 - .30	.26	.27	4

(a) Range of values reported by the different cooperating laboratories.

E. Determination of Magnesium by Flame Emission

The effect of phosphate and aluminum on magnesium by flame emission is shown in figures 8 and 9. With the total consumption burner, the effect of these ions on magnesium was found to be less than those observed in atomic absorption (figures 6 and 7). However, the sensitivity of magnesium by atomic absorption is so much greater than by flame emission that the former method is still prefered for the determination of magnesium in various types of standard reference materials.

F. Determination of Copper in SRM Steel Samples

The determination of copper by atomic absorption offers a method which is inherently more rapid than the spectrophotometric diethyldithiocarbamate procedure. To check the

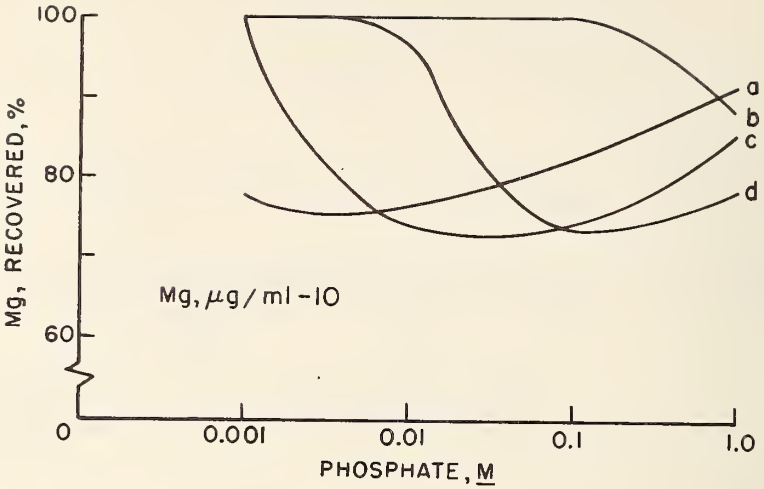

Figure 8. Effect of H_3PO_4 on magnesium by flame emission spectrophotometry with and without releasing agents. a. H_3PO_4; b. Glycerol, 10%; $HClO_4$, 0.1 M; c. La, 1 mg/ml; d. EDTA, 0.05 M.

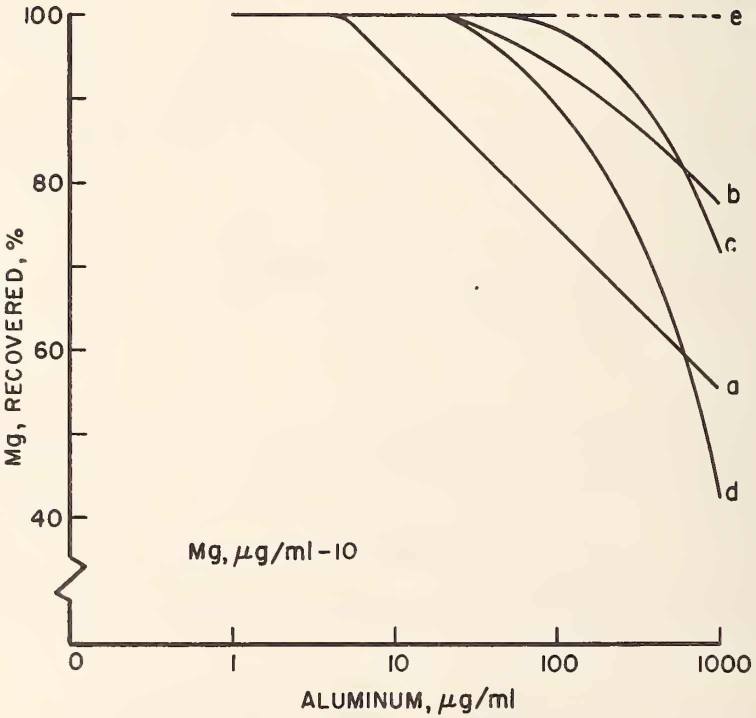

Figure 9. Effect of aluminum on magnesium by flame emission spectrophotometry with and without releasing agents. a. Al; b. Glycerol, 10%; $HClO_4$, 0.1 M; c. La, 1 mg/ml; d. EDTA, 0.05 M; e. La, 10 mg/ml.

precision of the atomic absorption determination of copper in steel samples, two SRM steel samples were analyzed for copper without any preliminary separations. The results are shown in table 12. The precision is comparable to the colorimetric method. The value obtained by AAS for a SRM-11g of 505 ppm which was certified at 510 ppm attests to the accuracy of the method.

Table 12. Determination of copper in steel

Standard Reference Material No.	Cu	Average µg/g	Standard Deviation	Relative Standard Deviation, %
11-g	499, 515			
	502, 505	505	8.5	2
1156	256, 244			
	252, 251			
	243, 260			
	237, 243	248	7.7	3

G. Determination of Trace Elements at the Submicrogram Level in High Purity Zinc

The determination of various elements at the submicrogram level in high purity zinc is under investigation. For the purpose of these determinations by flame emission or atomic absorption, the zinc matrix offers a unique advantage because solutions of zinc containing 150 g/l can be prepared in hydrochloric or nitric acid. Concentrations of zinc of 100 g/l can be readily aspirated without causing any burner clogging. By atomic absorption and flame emission, the detection limits for silver, magnesium, cadmium and potassium are 0.05 µg per gram of zinc while the copper and lead are 0.1 and 1 µg per gram, respectively. As a check for any enhancement or suppression due to the viscosity of the zinc sample, the standard addition technique is used to correct for any suppression by the more viscous sample solution. To further increase the detection limit of copper in zinc, the copper is extracted with 0.1 M 2-thenoyltrifluoroacetone in hexone from an acetate buffered medium and then aspirated into the flame. Additional work is planned to improve the detection limits of lead.

H. Conclusion

While considerable progress has been made during the past years in instrumentation, more effort is needed to evaluate the nebulizer-burner system in order to improve the precision of the method which at present, in most cases, is of the order of 1% relative standard deviation. The other aspects involve the further study of the mechanism of "releasing agents" as they affect complex mixtures. Finally, more effort is needed to establish the role of scattered light encountered in atomic absorption and methods of overcoming the interference compensation.

T. C. Rains and T. A. Rush

4. SPECTROPHOTOMETRY

A. Introduction

Spectrophotometric methods, as indicated in a current survey [40], are still very much in the forefront of analytical chemistry. This leadership stems from such advantages as sensitivity and precision, comparative simplicity of operation, speed and relatively inexpensive instrumentation. During the past year, this competence has been extensively relied upon for the determination of minor and major components in the standard reference materials summarized in table 13. Newer efforts in this area deal with the development of a more accurate procedure for trace quantities of antimony and for the simultaneous determination of nickel, copper and cobalt. In the latter case the continuation of the study of high precision determination of nickel, which was previously reported [1], permitted a simultaneous determination of these three elements in a single sample. Other applications which are included in this report involve the determination of boron and zirconium. Finally, some initial studies are described for the determination of calcium in maraging steel and for the analysis of six-nines purity zinc.

B. Spectrophotometric Determination of Antimony

The determination of antimony at the microgram level in ferrous and non-ferrous materials has, in the past, presented many difficulties. Losses due to volatilization, uncertainty in oxidation state and various other side effects have frequently lead to low and erratic results.

Of the many reagents proposed for the spectrophotometric determination of antimony, those having either a xanthone-rhodamine or a triphenylmethane structure have appeared the most promising. The present study has been concerned with a critical evaluation of the use of one of these dyes, namely

Table 13. Spectrophotometric analysis of standard reference (SRM) materials.

Element	Standard reference material No.	Kind	Number of Determinations	Percent found	Rel. std. deviation
B	1156	Maraging steel	7	0.0022[a]	14
Cu	82b	Nickel-chromium cast iron	8	0.038[b]	1.9
Mn	13g	Basic Open Hearth, 0.6C steel	8	0.851[c]	0.4
Mn	15g	Basic Open Hearth, 0.1C carbon steel	10	0.486[c]	0.6
Mn	16e	Basic Open Hearth, 1.1C steel	8	0.381[c]	0.1
Mn	73c	Stainless steel (Cr13)(SAE420)	8	0.330[c]	0.3
Mn	1156	Maraging steel	6	0.208[c]	1
Mo	73c	Stainless steel	4	0.089[d]	2
N	1090	Ingot iron	16	0.0062[e]	8
N	1092	Vacuum-melted steel	16	0.0011[e]	27
Ni	73c	Stainless steel (Cr13)(SAE 420)	2	0.248[f]	0.8
Ni	82b	Nickel-chromium cast iron	9	1.22[f]	1.6
Ni	1156	Maraging steel	11	18.98[f]	0.2
Ni	1174a	White cast iron	7	0.034[f]	0.6
P	16e	Basic Open Hearth, 1.1C steel	4	0.021[g]	2
P	73c	Stainless steel (Cr13)(SAE 420)	4	0.020[g]	8
P	1170	Selenium-bearing steel	3	0.110[g]	0.9
Sb	55e	Ingot iron	5	0.0010[h]	5
Zr	1156	Maraging steel	5	0.0044[i]	2

---

[a] Methyl borate distillation, curcumin in ethyl acetate (540 mμ) (Section 4G).

Table 13. (Continued)

[b] Diethyldithiocarbamate, butyl acetate extraction (565 mμ) [41].

[c] Periodate oxidation, MnO_4^- (545 mμ) [19].

[d] CNS^-, butyl acetate (540 mμ) [19].

[e] Ammonia distillation, Nessler's reagent (440 mμ) [20].

[f] $K_2S_2O_8$, pH of 13, dimethylglyoxime (465 mμ) (Section 4C).

[g] Phosphomolybdate reduced with hydrazine sulfate (650 mμ) [42].

[h] $NaNO_2$ oxidation, Brilliant Green, benzene (625 mμ) (Section 4B).

[i] Trioctylphosphine oxide extraction, pyrocatechol violet (655 mμ) (Section 4D).

Brilliant Green. A summary of the important steps in the procedure thus developed is outlined below.

1. Dissolution of sample $\longrightarrow Sb^{+3}$
2. $Sb^{+3} \xrightarrow[HCl-H_2SO_4]{\text{oxidant}} SbCl_6^-$
3. $SbCl_6^- + R^+ \longrightarrow (RSbCl_6)_{aq}$
4. $(RSbCl_6)_{aq} + \text{excess } R^+ \xrightarrow[\text{extraction}]{\text{benzene, toluene, etc.}} (RSbCl_6)_{org}$

In the first step, the hydrolysis and formation of a non-reactive antimony species was avoided by dissolving the sample in a sealed tube in a non-oxidizing acid [43]. In this manner only Sb^{+3} is formed. In the second step a study of a large number of oxidants lead to the selection of sodium nitrite in preference to ceric ion, whose concentration was critical, or to hydrogen peroxide which reacted with the chloride solution. The third step involving the addition of the dye presented problems because of reducing impurities in the commercialgrade reagents. This difficulty, however, was eliminated by a chromatographic separation of the impurity on silica gel. Finally, by means of Sb^{125} tracer, it was demonstrated that the ternary complex was extracted quantitatively into the organic phase. Since the method has been published [44], a full discussion and details of this procedure is not included in this report except for the results obtained on the following samples (table 14).

Table 14. Antimony values in SRM, by the new method.

Standard reference material No.	Kind	Antimony present	Antimony found
55e	Ingot iron	--	0.0010
63c	Phosphor bronze	0.52	0.526
124d	Ounce metal	0.17	0.173
C1100	Cartridge brass	0.018[a]	0.020
1101	Cartridge brass	0.012[a]	0.013
C1101	Cartridge brass	0.012[a]	0.013
1102	Cartridge brass	0.005[a]	0.0048

---

[a] Provisional value.

C. A Highly Precise Nickel Method in the Presence of Copper and Cobalt.

1. Introduction

A modification of the persulfate-dimethylglyoxime method for nickel was briefly described in an earlier report [1]. Considerable progress has been made since that time in developing a better understanding of the many experimental variables associated with this reaction. The important aspects of the high precision method which have been studied are the effect of high pH, the role of ammonia, control of the concentration of persulfate and the tolerance of interfering ions. Attention has been given also to the correction for the interference of copper and cobalt and the possible simultaneous determination of nickel, copper and cobalt. Heretofore, the latter two elements constituted serious interferences for which reliable correction factors were not easily determined.

In order to expedite a more rapid dissemination of this method an extensive description of the new procedure is presented at the end of the discussion. The results of a detailed study will be published on completion of the study of the mechanism of the several reactions.

2. Observations and discussion

a. The optimum conditions. The conditions finally adopted require a pH of 13 or greater, citrate ions, a controlled amount of ammonium ions and a large excess of persulfate as oxidant. The stabilizing effect of high pH on the color of the oxidized nickel dimethyglyoxime complex has been mentioned in the literature [45]. Color development was very slow and difficulties were encountered in applying these procedures to the direct determination of nickel in a variety of ferrous and non-ferrous alloys [46]. It was found, however, that the addition of citrate ions leads to a rapid development of color. This ion further aids in preventing the hydrolysis of other diverse metal ions. Either sodium citrate or the ammonium salt may be used. The latter is preferred in the presence of copper ions as it assists in controlling the interference of this element. Potassium persulfate is the most effective oxidant for forming the stable (~24 hours) water soluble complex. A large excess, at least a mole ratio of 30:1 of persulfate to nickel, is necessary in order to obtain satisfactory stability. However, when the ratio exceeds 250:1 the color formation will be inhibited in a solution containing only nickel. This effect is less apparent when other metal ions are present.

b. Explanation of interferences (table 15). Up to one milligram of iron does not precipitate in the proposed system. In the case of very low nickel alloys, where this amount is exceeded, the iron can be easily extracted with methyl isobutyl ketone (hexone).

Table 15. Tolerance of interfering elements and correction factors.

Element	Tolerance max. µg[a]	Range Ni µg	Interference and correction factors
Fe	1000	unlimited	ppt; extracted with hexone
Mn	250	unlimited	ppt; corrected by blank
Cr	unlimited	unlimited	corrected by blank
Cu	2000	20-300	1 µg Cu ≅ 0.0065 µg Ni
Co	200	20-300	none; 15 min.
Co	1000	100-300	1 µg Co ≅ 0.01 µg Ni, 30 min.
Co + Cu	100-1000 + 200-2000	20-200	Co equivalent + twice Cu equivalent

---

[a] Final valume 50 ml.

The manner in which copper, cobalt and copper plus cobalt interfere can be noted from the absorbance curves shown in figures 10, 11 and 12. The interference of copper is a linear function of its concentration up to 2 milligrams. Above that concentration it leads to the decomposition of the nickel complex (curve d in figure 10). From an independent analysis of copper, an appropriate correction can be applied. The simultaneous determination of nickel, copper and cobalt will be discussed in a subsequent section.

Cobalt interferes after 15 minutes only if it is present in excess of 200 µg. Above that level a correction factor can be applied in the same manner as for copper. This correction holds for all cobalt levels below 1000 µg. At higher values, the complex is decomposed (curve f, figure 11).

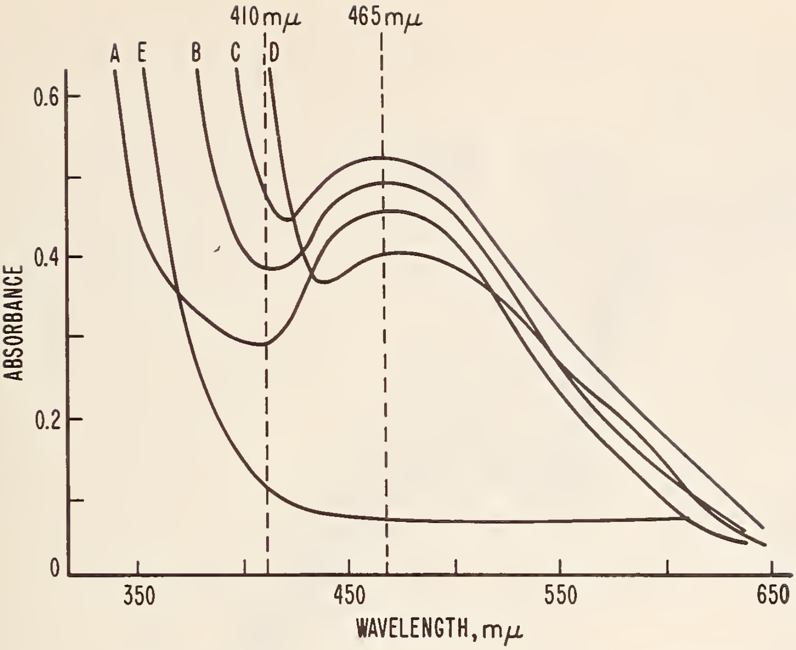

Figure 10. Spectral shift of Ni DMG complex in presence of copper. A. 100 μg Ni; B. 100 μg Ni + 1000 μg Cu; C. 100 μg Ni + 2000 μg Cu; D. 100 μg Ni + 4000 μg Cu; E. 400 μg Cu.

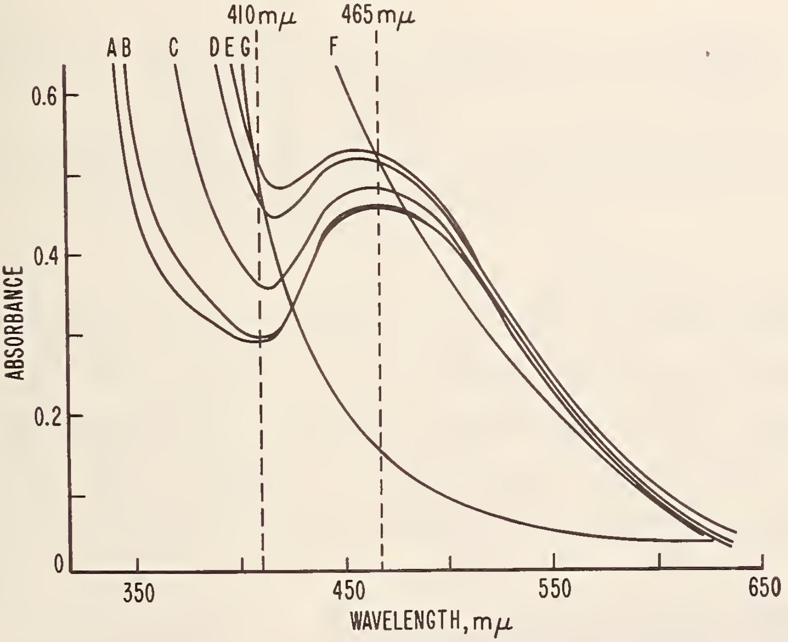

Figure 11. Spectral shift of Na DMG complex in presence of cobalt. A. 100 μg Ni; B. 100 μg Ni + 80 μg Co; C. 100 μg Ni + 400 μg Co; D. 100 μg Ni + 800 μg Co; E. 100 μg Ni + 1000 μg Co; F. 100 μg Ni + 3000 μg Co; G. 1600 μg Co.

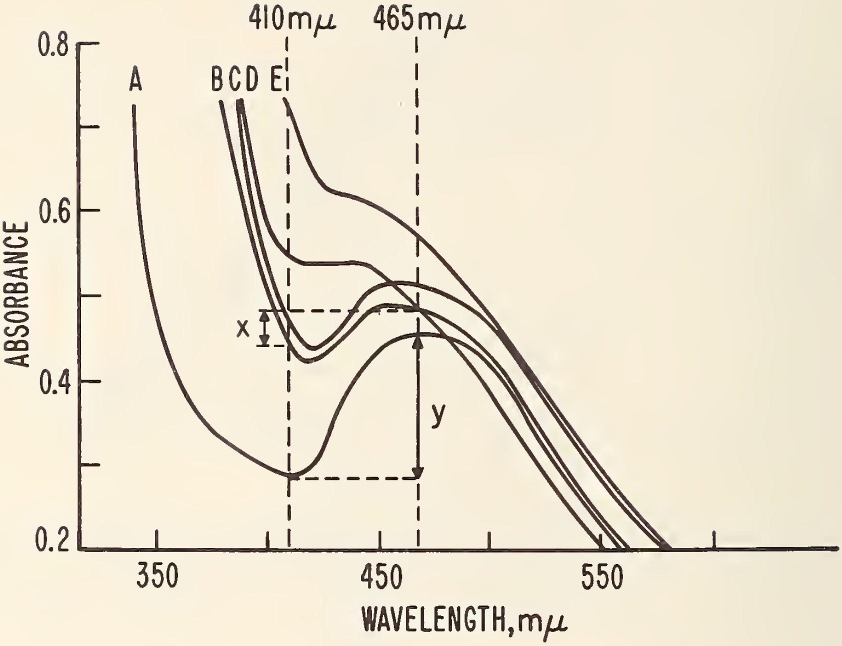

Figure 12. Spectral shift of Ni DMG complex in presence of copper and cobalt. A. 100 μg Ni; B. 100 μg Ni + 400 μg Co + 200 μg Cu (600 μg); C. 100 μg Ni + 80 μg Co + 1000 μg Cu (1080 μg); D. 100 μg Ni + 800 μg Co + 400 μg Cu (1200 μg); E. 100 μg Ni + 800 μg Co + 1000 μg Cu (1800 μg).

The extent of cobalt interference is also dependent on time. Fortunately however, as shown in figure 13, the degree of interference of this element is a linear function of time.

If copper and cobalt are present together in the sample, a modified correction factor must be applied, since the apparent interference of copper doubles in the presence of cobalt (table 15).

3. Applications of the method

This procedure has been applied to the analysis of a variety of metals and alloys. Some examples of the accuracy of the nickel determination are shown in table 16.

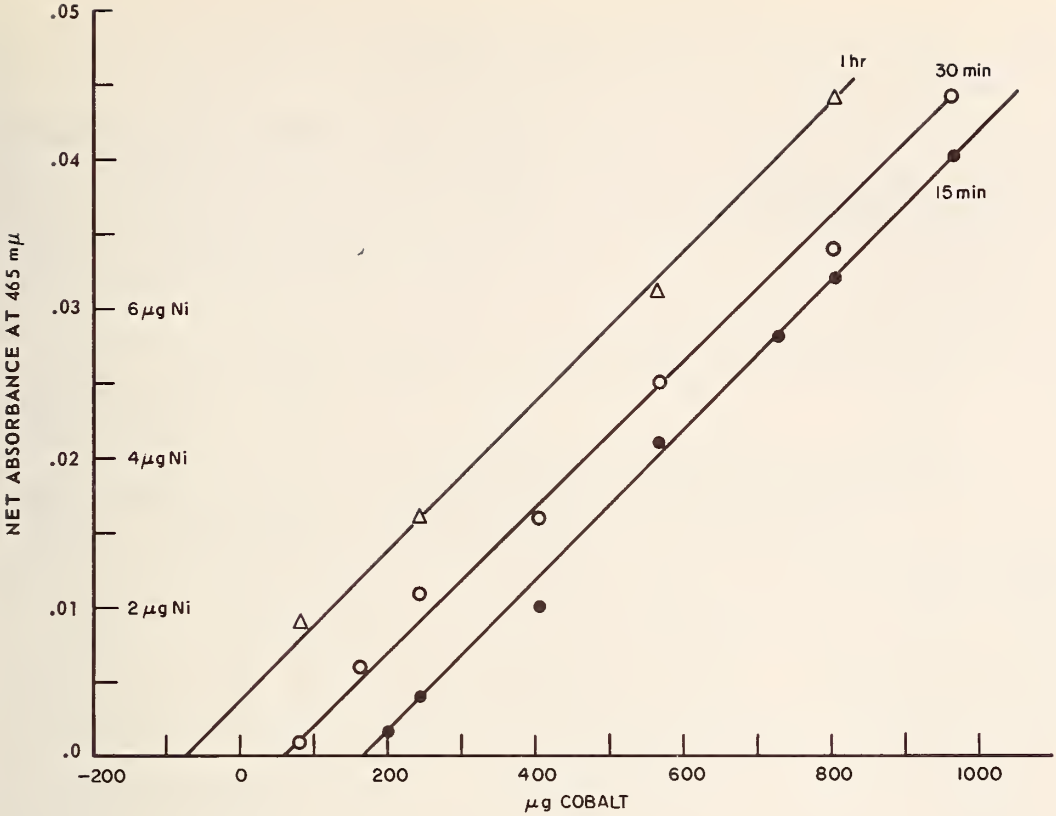

Figure 13. Effect of cobalt on Ni-DMG as a function of time.

Table 16. Determination of nickel in standard reference materials.

SRM No.	Kind	Percent					
		Co	Cu	Mn	Grav.	Spect.	Diff.
5j	Cast iron[a]		0.99	0.70	0.018	0.016	-0.002
153a	Co8-Mo9-W2-Cr4-V2 steel[a]	8.47	.094	.192	.168	.160	- .008
37e	Sheet brass		69.61		.53	.52	- .01
82b	Nickel-chromium cast iron[a]		.08	.65	1.22	1.22	.00
346	Valve steel(Cr22-Ni4-Mn9)[a]		.12	9.14	3.94	3.94	.00
167	Cobalt-base alloy Co43-Mo4-Nb3-W4	42.90	.03	1.64	20.65	20.57	- .08

Table 16. (Continued)

SRM No.		Co	Cu	Mn	Grav.	Spect.	Diff.
1193	High temperature alloy W 545		.10	.68	28.38	28.33	- .05
	Permalloy				79.62	79.75	+ .13

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[a] Hexone extraction of iron.

4. High precision spectrophotometry

a. *Differential determination of high nickel concentrations.* A closer examination of the persulfate-dimethylglyoxime procedure has permitted a two-fold improvement in the precision with which nickel can be determined in high temperature alloys. In an earlier report [1], the standard deviation for the determination of nickel at the 28 percent level was found to be 0.09 percent. A recent application of Latin Square analysis to new data indicates that the ultimate precision of the method is about 0.04 percent at this level. The arrangement of data used in this statistical treatment is shown in table 17. By means of a Latin square arrangement one can statistically evaluate the interaction and the importance of each variable. In this instance, the three variables studie were the four samples A, B, C, and D, the absorbance difference between the standards and the samples, ranging from 0.001 to 0.6, and finally the day to day variation. The analysis of these results indicate that the overall standard deviation is less than 0.04 percent while the relative standard deviation is 0.15 percent. This is a factor of 2 better than reported previously. Further analysis of this data also indicates that sample C, based on the Students "t" test, is a poor sample (exhibits the lowest result) and is significantly outside the general error limits. The next variable which shows a deviation at the 95 percent significance level is the day to day variation. However, taking all these factors into consideratio the overall relative deviation is still 0.15 percent. Thus this type of analysis of errors provides us with an objective evaluation of the expected reliability of the method when all the important sources of random error are included. Additional background information on this treatment of data may be obtained from the book by Natrella [47].

Table 17. Latin Square arrangement, percent Ni.

Differential absorbance:	0.4	0.2	0.6	0.001	Mean
Days					
1	A 28.346	B 28.324	C 28.188	D 28.283	28.285
2	B 28.324	C 28.233	D 28.214	A 28.251	28.256
3	C 28.210	D 28.263	A 28.303	B 28.335	28.278
4	D 28.443	A 28.493	B 28.346	C 28.255	28.384
Mean	28.331	28.328	28.263	28.281	

Standard deviation = 0.044

Relative standard deviation = 0.15%

5. Simultaneous determination of (a) nickel and copper, (b) nickel and cobalt or (c) nickel, copper and cobalt

From an examination of the spectra of nickel alone and those obtained in the presence of copper and cobalt (figures 10, 11 and 12) it became evident that it should be possible to determine the three elements simultaneously by measurement of the absorbance at several wavelengths. The differences in the nickel spectra are apparently caused by a formation of mixed complexes which, with higher concentrations of copper or cobalt, are finally decomposed.

Several multicomponent systems were tested to evaluate the precision and accuracy of simultaneous measurement. The measurements were taken at 465 and 410 mμ. As can be noted from the curves, the difference between the maximum and minimum absorption is a function of both the concentration of nickel and the other two ions. When dealing with an unknown, one can calculate first the apparent concentration of nickel from the absorbance measurement at 465 mμ. From that value one can calculate the theoretical absorbance at 410 mμ if it were nickel alone (value Y in figure 12). The difference between this value and the measured value (X in figure 12) provides a first estimate of the concentration of the other element. Using next the conversion factor a new corrected value of nicke can be obtained. These steps can be repeated until, by the method of successive approximations, the final nickel result does not change by a significant amount. This calculation can be performed manually or with the aid of a computer. In most instances three stages are sufficient. The results obtained by this type of calculation are presented in table 18.

Table 18. Simultaneous determination of nickel, copper and cobalt by peak-valley analysis.

Standard reference material No.	Type	μg present	μg found	No. of approximatic
37e	Sheet brass			4
	nickel	16.3	16.3	
	copper	2143	2010	
167	Cobalt-base alloy (Co43-Mo4-Nb3-W4)			2
	nickel	126.7	129	
	cobalt	263.3	300	
37e and 167	As indicated above			2
	nickel	134.9	128	
	cobalt and copper	1335	1320	

As indicated by these initial results the value for nickel at the fourth stage of approximation is in very good agreement with the certified value. The relative error for the estimation of the other ions, however, is high. It is apparent that other factors must be considered and that additional data are needed. One such consideration is based on the observation that the minimum shifts to longer wavelengths in the presence of copper or cobalt and the measurement at these minima rather than at 410 mμ may improve the estimation of the other elements. Another factor which contributed to the relative poor precision for copper in a sheet brass, SRM 37e, was that the concentration of that ion was outside the tolerance limit of 2000 μg as recommended for this method.

6. General Procedures

A detailed procedure is presented for the several types of samples for which this method is applicable.

a. Calibration, 0-200 mg of nickel. Pipet into 50-ml beakers 0, 1, 3, 5, 10, 15 and 20 ml aliquots of a standard nickel solution containing 10.0 μg of nickel per ml. Add 10 ml of dibasic ammonium citrate (400 g/liter) and 1 ml of potassium persulfate (50 g/liter). Adjust the pH of these solutions to 13 with 50 percent sodium hydroxide and transfer to 50-ml volumetric flasks. Add 2 ml of 1 percent alcoholic dimethylglyoxime and dilute to the marks with distilled water. Omit dimethylglyoxime in the blank. Measure the absorbance in 1-cm cells at 465 mμ against a water reference within 15 to 30 minutes. Subtract the blank and plot the absorbance readings against micrograms of nickel per 50 ml of solution or, alternatively, calculate the corresponding calibration factor.

b. Differential nickel determination, 200-1000 μg of nickel. The same procedure as outlined above, with slight modification, is used for the differential determination of larger amounts of nickel. The main differences are the wide variation possible in the nickel content of the reference solution (0-800 μg) and the corresponding larger amounts of potassium persulfate required (1 ml for each 200 μg of nickel present).

For example add a reference solution of 200 μg of nickel, to each of seven 50-ml beakers. Pipet 0, 1, 3, 5, 10, 15 and

20 ml aliquots of a standard nickel solution containing 10.00 μg of nickel per ml. Add 10 ml of dibasic ammonium citrate and 2 ml of potassium persulfate. Adjust the pH to 13 and transfer to 50-ml volumetric flasks. Add 2 ml of 1 percent alcoholic dimethylglyoxime and dilute to the marks with distilled water. Measure the absorbance in 1-cm cells at 465 mμ against the reference solution. Calculate the calibration factor.

For a sample analysis, take an aliquot, develop the color as directed above and measure the absorbance against the reference solution. Run a duplicate aliquot through the procedure, omitting dimethylglyoxime, and measure the background absorbance against a water reference.

c. Sample preparation. Adjust the sample weight and volume so that a 20 ml aliquot or less will fall within the tolerance limits and nickel ranges listed in table 15. Dissolve the sample in 25 ml of HCl (1:1) in a 150-ml beaker and oxidize with HNO_3. Cool, add 10 ml of $HClO_4$, and evaporate to dense fumes. Dilute to volume and add an appropriate aliquot to a 50-ml beaker. Develop the color as described in the preparation of the calibration curve, using 10 ml of potassium persulfate (50 g/liter). Determine an appropriate background by taking a duplicate aliquot and repeating all steps except the addition of dimethylglyoxime.

d. Extraction of iron with methyl isobutyl ketone (hexone). If an aliquot is expected to contain more than 1 mg of iron an extraction of the original sample is necessary. Dissolve the sample in 25 ml of HCl (1:1) in a 150-ml beaker and oxidize with HNO_3. Evaporate the solution to dryness and dissolve the salts in 25 ml of HCl (1:1). Transfer to a 125-ml separatory funnel and add 25 ml of hexone. Extract by gently shaking the solutions for two minutes at the rate of approximately 30 inversions of the funnel per minute. Siphon off the upper layer, add 25 ml of hexone and extract again. Repeat this operation until the final hexone layer remains colorless. Return the acid solution to the original sample beaker and evaporate on the steam bath to 4-5 ml. Add 10 ml of HNO_3 followed by 10 ml of $HClO_4$ and evaporate to dense fumes. Dilute to volume with water, remove a suitable aliquot for spectrophotometric measurement and proceed as under calibration curve.

e. Procedure for simultaneous determinations. The sample is prepared and the color is developed as directed previously. Absorbance readings are taken at 465 mμ and 410 mμ. When cobalt is present, the two wavelength readings are taken after 15 minutes for the nickel calculation and again at one hour when the cobalt constitutes serious interference.

f. Calculations in the simultaneous determination of nickel and copper. Using the net absorbance measurements (sample absorbance minus background absorbance) at two wavelengths and known conversion factors, nickel and copper can be determined relatively easily.

An example of such a calculation for a sample that contains 160 μg of nickel and 1000 μg of copper is as follows:

$A_s(410)$ = sample absorbance at 410 mμ vs blank

$A_s(465)$ = sample absorbance at 465 mμ vs blank

F_c = calibration factor for nickel at 465 mμ
= 217.2 μg/A_s

F_d = reciprocal calibration factor for nickel complex based on the difference of absorbances $[A_s(465)-A_s(410)]$
= 0.0018 A_s/μg

F_e = reciprocal calibration factor for copper correction from the difference in absorbances Y-X
= 0.00008 A_s/μg

Y = $A_s(465) \times F_c \times F_d$ = the calculated "apparent" nickel complex absorbance difference $[A_s(465)-A_s(410)]$

X = the observed sample absorbance difference $[A_s(465)-A_s(410)]$ (Note X may be a negative value

F_f = conversion factor for copper correction at 465 mμ

= 0.0065 μg Ni/μg Cu

$C_{1(Ni)}, C_{2(Ni)} \cdots C_{n(Ni)}$ = initial and successive values for nickel concentration

$C_{1(Cu)}, C_{2(Cu)} \cdots C_{n(Cu)}$ = initial and successive values for copper concentration

<u>Calculation for sample containing 160 μg nickel and 1000 μg copper:</u>

$$C_{1(Ni)} = A_s(465) \times F_c = 0.767 \times 217.2 = 166.6\ \mu g$$
$$Y = C_{1(Ni)} \times F_d = 166.6\ \mu g \times 0.0018 = 0.300$$
$$X = A_s(465) - A_s(410) = 0.767 - 0.563 = 0.204$$

$$C_{1(Cu)} = \frac{Y-X}{F_e} = \frac{0.300 - 0.204}{0.00008} = 1200$$

1st Ni correction: $C_{1(Cu)} \times F_f = 1200\ \mu g \times 0.0065$

$= 7.8\ \mu g$ Ni

$$C_{2(Ni)} = 166.6 - 7.8 = 158.8\ \mu g$$

Second approximation:

$$Y_2 = 158.8 \times 0.0018 = 0.286$$
$$Y_2 - X + 0.286 - 0.204 = 0.082$$
$$C_{2(Cu)} = \frac{0.082}{0.0000800} = \underline{1025\ \mu g\ Cu}$$

2nd nickel correction:

$1025 \times 0.0065 = 6.7\ \mu g$ Ni

$$C_{3(Ni)} = 166.6 - 6.7 = 159.9\ \mu g\ Ni$$

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D. Zirconium in Maraging Steel

The basic method as developed by Young and White [48] and more recently modified by Wood and Jones [49] has been applied with good success to the determination of zirconium in NBS-1156, a maraging steel. Briefly, the procedure involves the extraction of Zr^{+4} from a 7 M nitric acid medium with a 0.1 M solution of trioxtylphosphine oxide (TOPO) dissolved in cyclohexane. Any iron or titanium that might accompany zirconium is removed by backwashing the extract with a fresh portion of 7 M HNO_3. For color development, an aliquot is taken from the TOPO layer, pyrocatechol violet is added, and then pyridine to neutralize any acid which may have co-extracted. Finally, absorbance measurements are made on the resulting green complex at 655 mμ.

1. Procedure

a. Calibration. To 5, 10, 20, 30 and 40 μg Zr^{+4} contained in 60-ml separatory funnels, add sufficient nitric acid to give a resulting solution (25 ml) that is 7 M in HNO_3. Add 5.00 ml of 0.1 M TOPO in cyclohexane and extract for 15 minutes on a mechanical shaker. Drain off the acid layer and add a second 25-ml portion of 7 M HNO_3. Again equilibrate the two phases for 15 minutes. Pipet 2.00-ml aliquots from each of the TOPO extracts and deliver the same into dry 25-ml volumetric flasks. Add 10 ml of absolute ethanol and 1.5 ml of pyrocatechol violet (0.5 mg/ml absolute ethanol). Neutralize any acid in the extracts with 5 ml of pyridine and dilute the resulting solutions to the mark with absolute ethanol. After 15 minutes, measure the absorbance in a 2-cm cell at 655 mμ against an appropriate reference.

b. Analysis of maraging steel. Dissolve a suitable sample size in a minimum amount of 1:4 H_2SO_4. Add 10 ml of 7 M HNO_3 and gently bring to a boil. Cool and dilute to volume with H_2O-HNO_3 in such a manner that the final nitric acid concentration is 7 M. Take a 25.0 ml aliquot and proceed as under calibration curve.

2. Results

Table 19 shows the results that were obtained on five samples of NBS-1156.

Table 19. Zirconium in maraging steel.

Sample No.	Percent found
1	0.0043
2	0.0045
3	0.0044
4	0.0044
5	0.0045
Average	0.0044
Relative standard deviation	2%

R. W. Burke

E. Determination of Calcium as the Glyoxal-bis-(2-Hydroxyanil) Complex

Since calcium could not be titrated with EDTA after extraction as the glyoxal-bis-(2-hydroxyanil) complex (see Titrimetry section), an attempt was made to determine this complex spectrophotometrically. Subsequent studies on synthetic samples indicated that this system was capable of yielding reproducible results for calcium in the range of 1-10 µg. When this approach was applied to the analysis of NBS-1156, however, consideraable interference was encountered, especially from the relatively high manganese content of this sample. Since reliable results were obtained subsequently by atomic absorption measurements, the spectrophotometric approach was abandoned.

K. M. Sappenfield

F. Analysis of High-Purity Zinc

An investigation is currently under way to ascertain the feasibility of determining certain trace impurities in high purity zinc at the submicrogram level. A brief summary of the methods being used and our estimated detection limits are given in table 20. These sensitivities are based upon preconcentration

Table 20. Detection limits for elements in high-purity zinc.

Element	size,g	limit, ppm	Reagent	References
Sb	1	0.05	Brilliant Green	[44, 50]
Au+Tl	1	0.1	Brilliant Green	[44, 51]
Ni	1	0.005	diphenylglyoxime	[52]
Cu	5	0.005	zinc dibenzyldithiocarbamate	

of the desired element into 1-5 ml volumes, followed by absorbance measurements in either 1-cm micro cells or in the 10-cm Teflon cells previously described [1].

A limiting factor in the determination of copper is the purity of the dissolving acid. At the present time, the copper content of the best hydrochloric acid available is in the range of 5-10 ppb. Obviously, the detection limit given in table 20 cannot be obtained with acid of this quality. In hopes of remedying this situation, three purification procedures were tested--isothermal distillation, preparation from HCl gas and pre-extraction followed by subsequent re-concentration. Relatively good success was achieved by preparing the hydrochloric acid from a commercial tank source. The gas was scrubbed in a bubble tower with concentrated sulfuric acid, filtered through a column of packed glass wool, scrubbed again in a bubble tower with "copper-free water" which was saturated with the gas and finally dissolved in "copper-free water" at 0°C to give an acid concentration up to 12 $\underline{N}$. In both instances the "copper-free water" was a 0.1 $\underline{N}$ HCl solution from which copper had previously been removed by exhaustively washing with a carbon tetrachloride solution of zinc dibenzyldithiocarbamate. The copper concentration of the final product (11.7 $\underline{N}$ acid) was $\leqq$ 1 ppb. Currently, the responsibility for the preparation of high-purity reagents is part of the functions of section 9 of the Analytical

Chemistry Division. Using the acid thus prepared, however, 40 ppb copper was found in several samples of high-purity zinc (sample designation A7).

R. W. Burke

G. Modified Curcumin Procedure for Boron

The Hayes and Metcalfe modification [53] of the familiar curcumin procedure has been successfully applied to the determination of boron in maraging steel. Following separation as the methyl borate ester the spectrophotometric measurement is both rapid and simple. An aliquot of the distillate is evaporated to dryness in the presence of sodium hydroxide and the residue is treated successively with a curcumin-acetic acid solution and an acetic-sulfuric acid mixture. After allowing 15 minutes for color development, the sample is adjusted to volume with ethanol and the absorbance is measured at 555 mμ. In the absence of fluoride, the method is applicable to the determination of boron at the 10 nanogram level.

E. R. Deardorff

5. GASES IN METALS

A. Introduction

As a culmination of several years' work involved in securing, characterizing and testing ferrous materials, new Standard Reference Materials 1090, 1091 and 1092 have been certified for their oxygen content. As the oxygen content of these standards cannot be controlled synthetically the basis for establishing the accuracy of the certified values depends on the evaluation of the accuracy of independent methods, which were utilized in the measurements, and on the assurance of the homogeneity of the sample. In addition to the summary of this study in the following section, a complete report [54] dealing with the study and certification of these reference materials is available.

Work is presently in progress on the determination of oxygen in two titanium standard reference materials, and on the study of vacuum fusion methods for the determination of nitrogen. A current review [55] points up the problem that the values for nitrogen, based on vacuum methods, are lower than those reported from the chemical Kjeldahl procedure. To further evaluate this problem, a new type of furnace was installed with a sample holder which can be emptied by centrifugal action after each determination. The previous sample thus does not influence the subsequent results. In this study, the various fluxes and various types of nitrogen containing compounds or alloys will be determined and compared with other methods such as Kjeldahl, or alkali fusions under H_2 gas. Since NBS-260-14 report is available, only the abstract is quoted and a brief summary is included.

"A description is presented of methods used for the determination of homogeneity and the establishment of the oxygen values certified by NBS for three ferrous standard reference materials. These standards are represented by two low alloy materials, ingot and vacuum melted iron containing 484 and 28 ppm of oxygen respectively, and a high alloy steel containing 131 ppm of oxygen. The analyses of these materials are based on two vacuum fusion procedures. The poor results for the high alloy steel obtained by the first of these methods are explained. The first method is based on manometric measurements and depends on the conversion of CO to CO_2 by copper oxide and on a differential freezing of gases. In the second method a system is used which provides a highly efficient degassing of sample and a direct measurement of CO by infrared absorbancy. Additional data from an analysis by inert gas fusion method also indicate that the homogeneity of a single rod of ingot iron, over a wide range of sample size, has a relative standard deviation of less than two percent. From control data and homogeneity studies it was ascertained that the uncertainty limits stated in the NBS certificate include the error due to the relative inhomogeneity between rods Finally, data from eighteen laboratories cooperating in this program are presented." As indicated in this abstract, the certification was based on the evaluation of vacuum and inert gas fusion and the reports from cooperating laboratories. It should be pointed out that the study of vacuum techniques has been well covered in the literature [56,57,58], and the basis for confidence in the values by this technique is dependent upon the attainment of the degree of control of the variables essential for a reliable oxygen analysis. Some of these essentials are the selection of an appropriate flux, the attainment of a very efficient and rapid outgassing of sample to eliminate gettering problems and a reliable method of measurement of the evolved gas. As described in more detail in the report, these criteria have been met. Nickel bath and platinum bath methods have been compared, the efficiency of outgassing has been tested in a system in which 10^{-6} torr and an outgassing rate of over 100 liters per second is easily attained. This latter condition, proved in a variety of systems, avoids the errors caused by gettering of the evolved CO. Furthermore, the evolved CO is measured directly by its infrared absorbance.

B. Sample Criteria

Since the accuracy of the certified value depends both on the accuracy of the method and the relative homogeneity of the material, the latter was determined under carefully controlled conditions. In the analysis of large numbers of samples from the different materials an effort was made to check the reproducibility of the method over a long period of time and to evaluate the error arising from samples taken from different rods. In the case of SRM 1091 and 1092 consecutive samples from the same rod were taken and analyzed over a period of 15 and 10 days, respectively. In the case of SRM 1090 duplicates of adjacent samples were also taken from the center of the rods. These can be compared with all the analyses recorded and used to obtain the certified value. As shown in figures 14, 15, and 16 and also summarized in table 21, there is no significant difference in the precision for the control and SRM samples for SRM 1091 Stainless Steel and 1090 Ingot Iron. In the latter case duplicate samples B and B', as shown in figure 14, also reflect homogeneity in that the determinations from duplicate samples taken from adjacent position yield the greatest precision. The data from the SRM 1092 vacuum melted material also indicate a higher precision, the error being less from samples taken from consecutive positions. One can conclude therefore that the relative homogeneity of the rods are the dominant factors which set the limit of accuracy. The precision in the determination of oxygen from a portion of a typical 4-inch SRM sample should be better than the overall uncertainty in accuracy which is stated in the certificate (see appendix).

In addition, a limited study was carried out using an inert gas fusion apparatus in combination with a gas chromatographic measuring unit. Unfortunately, because of the

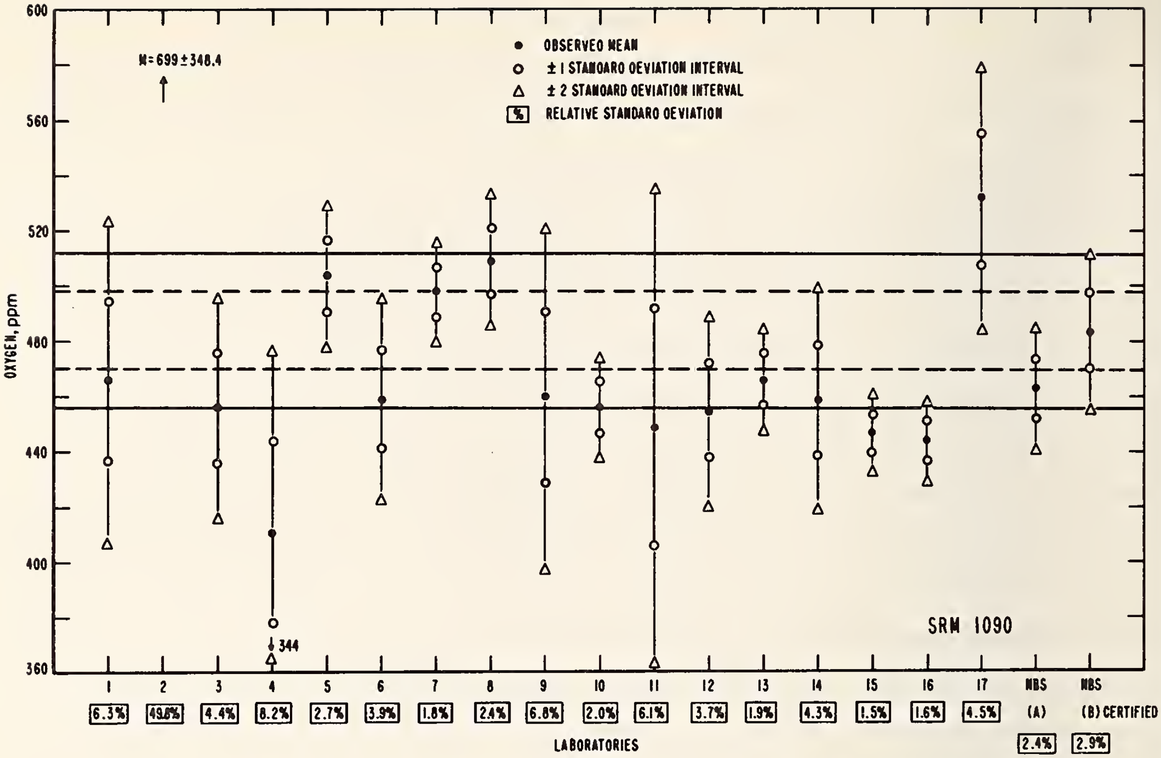

Figure 14. Control data and homogeneity study of NBS-SRM 1090 ingot iron.

Table 21. Comparison of control and SRM data.

	Control Data[a]				SRM Data[a]			
	Oxygen, ppm				Oxygen, ppm			
SRM	Mean	Std. Dev.	Relative Std. Dev. %	Number of Determ.	Mean	Std. Dev.	Relative Std. Dev. %	Number of Determ.
1092	26.4	1.2	4.4	21	28	2	7.1	105
1091	132.5	7.4	5.6	41	131	8	6.1	286
1090	494.9 494.7	15.1 8.7	3.1 1.8	68 34[b]	484.1	14	2.9	216

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[a] Taken over a period of 10 to 15 days.

[b] Based on duplicate determination from adjacent positions on a rod.

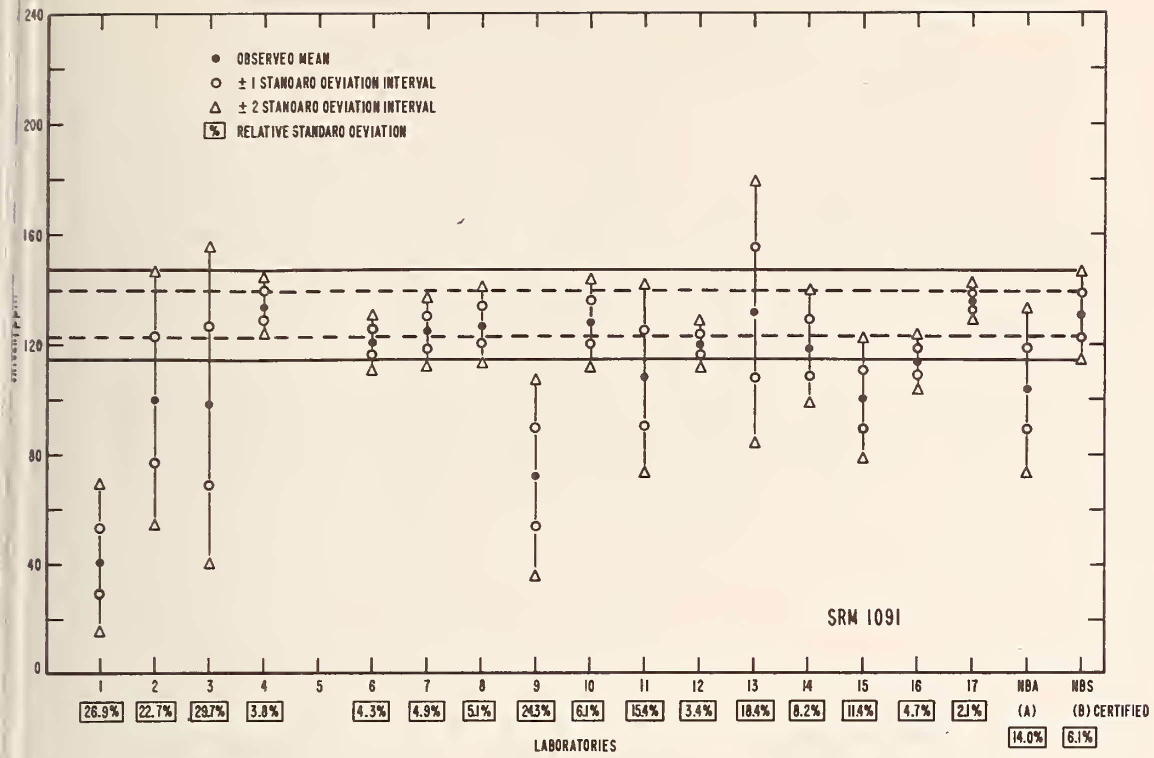

Figure 15. Control chart of a single rod of NBS-SRM 1091 high alloy steel.

initial difficulties with the integrator clock used as the readout device, the study is limited. The data were obtained from the measurement of the thermal conductivity output from the chromatograph with a recorder. Data are presented in figure 17 for consecutive samples of ingot iron which varied in weight from 0.2 g to 2 g. The relative standard deviation of the slope of the line was less than 2%. Since this value is based on data taken over a wide range of sample weights it also indicates a relative high degree of homogeneity of the oxygen content within a given rod.

C. Conclusion

While significant progress has been made in ascertaining an accurate value for oxygen in a series of ferrous material standards, more work is needed to provide a variety of matrix materials which may introduce special problems or require

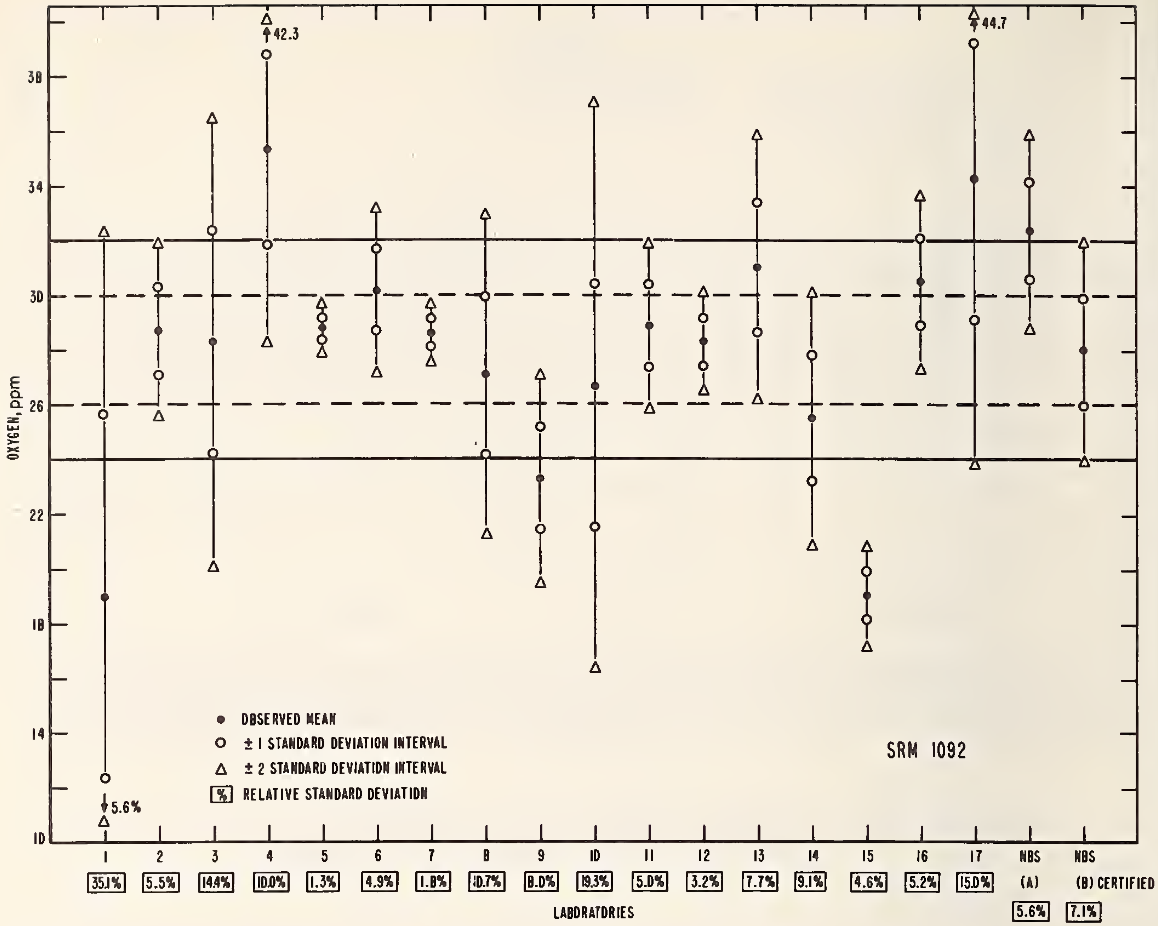

Figure 16. Control chart of a single rod of NBS-SRM 1092 vacuum melted steel.

special techniques for their analysis by vacuum fusion or any other method. For this purpose materials containing homogeneous dispersion of interstitial oxygen compounds are essential. Finally, since nitrogen and hydrogen are also of interest as a class of interstitial components, the determination of these two elements need further evaluation and study to provide more accurate data through the medium of vacuum or inert gas fusion methods.

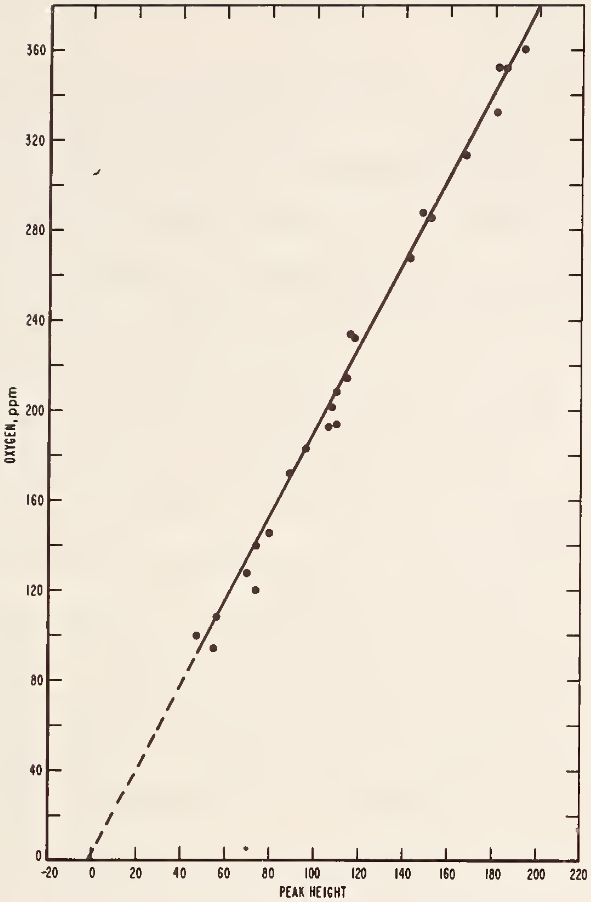

Figure 17. Homogeneity study - determination from a single rod for sample weight 0.2 to 2 grams.

J. T. Sterling and O. Menis

6. URANIUM AND PLUTONIUM ISOTOPIC STANDARDS

A. Uranium Assay

The program of re-evaluating sixteen uranium isotopic standards was continued to meet the need of accurate isotopic uranium standards for industry and science in the atomic energy field. To assist the Mass Spectrometry Section in this study mixtures of uranium isotopes were previously prepared for mass spectrometer calibration by dissolving U_3O_8 sample in nitric acid solution. In order to blend the uranium isotopes, it is necessary to know accurately 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. The following ignition procedure was previously developed to give reproducible oxides: one hour at 900 °C in air (to correlate with previous work), overnight at 1050 °C in air, followed by 1 hour in oxygen at 850 °C. To determine if this ignition procedure will give the same stoichiometry for uranium oxide prepared by different procedures, work was begun last year to assay several uranium oxides from different sources after ignition by this procedure: The ignition of the samples and solution preparation were done by Analytical Coordination Chemistry Section (310.04) and the coulometric analysis by Microchemical Analysis Section (310.05).

After ignition, the samples were dissolved in HNO_3(1+1) and diluted with water. Sulfuric acid was then added and the nitric acid was fumed off. A two gram sample and a one gram sample of each material were taken. The two gram sample was aliquoted by weight to give two samples of approximately one gram each. The coulometric assay was then carried out by Section 310.05.

The results given in Table 22 show good agreement for the various samples except for Dingot metal. The 950a was obtained through the nitrate process, the Depleted Secondary by hydrogen peroxide precipitation, and the Dingot by oxidation of the metal. Spectrographic analysis for impurities and previous assay of the metal indicate a correction of +.023% should be made on the assay figures for Dingot given in Table 22. The impurities in the other samples are less than 100 ppm.

The results of determinations of the 1g aliquots vs the 1-g samples indicate that the agreement for aliquots is not significantly better than that for the independent 1-g samples. This is taken as evidence that the ignition and dissolution procedure is not a major contributor to the variation found in the assay data. The conclusion can therefore be drawn that the adopted ignition procedure gives essentially the same U/U_3O_8 ratio independent of the origin or the isotopic composition of these oxides.

Table 22. Results of analysis of uranium solution.

Sample	Sample No.		Assay % U_3O_8	
950a	1a[a]		99.903_5	
	1b		99.946_5	
	2[b]		99.918_2	
		Average	99.923	Std. Dev. = 0.023
Depleted Secondary	1a		99.917_1	
	1b		99.910_7	
	2		99.960_0	
		Average	99.929	Std. Dev. = 0.027

Results of analysis of uranium solution (continued)

Sample	Sample No.		Assay % U_3O_8	
Depleted	1a		99.913_3	
Primary	1b		99.931_7	
	2		99.918_7	
		Average	99.921	Std. Dev. = 0.009
Enriched	1a		99.927_8	
Primary	1b		99.918_4	
	2		99.920_8	
		Average	99.922	Std. Dev. = 0.006
Dingot	1a		99.905_5	
	1b		99.900_2	
	2		99.911_1	
		Average	99.906	Std. Dev. = 0.006

[a] One gram aliquots are numbered 1a and 1b.
[b] One gram samples are numbered 2.

B. <u>Uranium Isotopic Solution</u>

Eight accurately known mixtures of uranium isotopic standards were also prepared to evaluate results of mass spectrometer laboratories. Mixtures of uranium isotopic standards U-005 and U-750, and U-010 and U-900 were used. These samples were prepared by the ignition procedure developed to give reproducible oxides. The platinum boat and uranium oxide sample were carefully transferred to teflon bottles. The samples were dissolved in HNO_3 (1+1) by heating on a steam bath. After dissolving, the samples were diluted with water. The cap of the U-750 bottle was replaced with a similar cap containing a piece of polyethylene tubing shaped for use as a wash bottle. The U-750 solution was then added in varying amounts to the U-005 samples. By weighing the U-750 bottle before and after addition, the amount of U-750 and the uranium isotopic composition of the mixture can be calculated. The U-900 solution was added to the U-010 sample in the same manner.

C. Plutonium Chemical Standard

This new standard is being prepared by the Los Alamos Laboratory. A member of Section 310.04 is helping in the analysis and sample preparation at Los Alamos Laboratory. The selection and certification of the new standard material will depend on the verification of the purity of the metal, and amperometric titrations.

D. Plutonium Isotopic Standard

Americium was separated from plutonium by an ion-exchange procedure on three samples of plutonium isotopic standard 948. This is part of a continuing program to evaluate the isotopic composition and to ensure that the actual values do not disagree with the certificate values because of uncertainties in half life.

L. A. Machlan

7. SERVICE SAMPLE ANALYSES

The work involving non-routine analyses for other groups is summarized in table 22. Over 350 hours of effort by this Section, utilizing the various competences, were required to obtain optimum values of minimum cost. The quality of this information was highly accurate. As indicated by one research group, it lead to reinterpretation of their results.

Table 23. Summary of Service Sample Analyses

Method	Matrix	Element	Conc. range	No. of samples	Time hrs.
			Per cent		
Titrimetry	Nickel alloy	V	1 - 6.5	4	8
	Monotype cavity	Pb Sb Sn	75.4 16.1 7.8	1	8
	Residue	B	0.022-3.87	8	16
	Steel	Mn S	.488 .033	1	3
Gravimetry	$KCaPO_4$	Ca K P	11.8 30.3 17.6	1	24
	$Cu_{10}(PO_4)_6(OH)_2$	Ca P	39.5 17.2	1	20
	Nickel alloy	Al	1.1-6.1	24	16
DTA & TGA	$Nb_2O_5:B_2O_3$	H_2O	Two types 1.4-1.7%	2	24
Spectrophotometry	$Nb_2O_5:B_2O_3$	Nb_2O_5	14.8-95.4	8	30
	$Nb_2O_5:GeO_2$		5.5-97.6	4	8
	$Nb_2O_5.P_2O_5$		53.8-94.1	9	58
	Pb alloy	Sb	8.7	1	4
	Al	Fe	0.003	1	4
	Non ferrous metal	Ni	1.98-3.27	2	4

continued

Table 23. Summary of Service Sample Analyses (continued)

Method	Matrix	Element	Conc. range	No. of samples	Time hrs.
			ppm		
Flame emission	Ferrous metals	Cu	6.4	1	28
	Si-Cd Metal	Li	5.88-7.49	3	2
	AgBr & AgCl	Li	0.2	3	4
		Na	.5		
		K	.5		
	Na	Ca	253-786	12	5
	NaCl	Li	1-1.6	2	2
	Metal residue	Na	0.2-2.6	4	13
		Ca	2.1		
		Sr	.02		
	$CaCO_3$	Na	18.1-18.8	4	2
	$KHC_8H_4O_4$		10-14	6	2
	KH_2PO_4		4.5-4.9		
Atomic absorption	$CaCO_3$	Na	11.9-15.9	6	6
	$Ce_2Mg_3(NO_3)_{12}:24H_2O$	R.E	1.3 separation		
	HF	Ag	0.02-0.16	3	6
		Ca	.02-.29		
		Cu	4.2-5.3		
		Ni	6.0-10		
	HCl	Mg	0.006-0.12	3	8
		Ca	.004-.035		
		Fe	.15		
			Per cent		
Gases in metals	Standard steel	O_2	0.011-0.012	8	20
		N_2	.025-.051	8	
		CO_2	.152-.153	8	
		H_2	.0002-.0006	8	
	Ag-Sn alloy	O_2	.0003-.0009	4	8
	Stainless steel	O_2	.015-.056	3	
		N_2	.056-.049		
		H	.0003-.0005		

continued

Table 23. Summary of Service Sample Analyses (continued)

Method	Matrix	Element	Conc. range	No. of samples	Time hrs.
			Per cent		
Gases in metals	Stainless steel	O_2	0.010-0.013	3	12
		N_2	.0005-.0006		
		H_2	.032-.049		
	Stainless steel	O_2	.010-.023		
		N_2	.015-.043		
		H	.0003-.0005		

O. Menis

8. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Oscar Menis, Section Chief

Mary B. Pantazis, Section Secretary

R. K. Bell	T. A. Rush
B. B. Bendigo	K. M. Sapenfield
R. W. Burke	J. T. Sterling
E. R. Deardorff	S. A. Wicks
L. A. Machlan	

B. Publications

1. Menis, O., Sterling, J. T., Determination of Oxygen in Ferrous Materials, SRM 1090, 1091 and 1092, NBS Misc. Publ. 240-14, 1966.

2. Nelson, D. J., Rains, T. C., Noris, J. A., High Purity Calcium Carbonate in Freshwater Clam Shell, Science 152, 3727, 1968 (1966).

3. Rains, T. C., Flame Photometry. A chapter in "Reagent Chemicals and Standards" by Joseph Rosen, 5th edition, D. Van Nostrand, New York, 1966.

C. Talks

1. Sterling, J. T., "A Study of Three Methods for Determination of Oxygen in Ferrous Materials", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy - Feb. 21-25, 1966.

2. Rains, T. C., "Determination of the Alkaline Earth Metals in Phosphate Rock, Limestone, Feldspar, Clay and Burnt Refraction of Flame Emission and Atomic Absorption Spectrophotometry", Pittsburgh Conference on Analytical Chemistry

and Applied Spectroscopy - Feb. 21-25, 1966.

3. Menis, O., "High Precision Spectrophotometric Determination of Macro and Micro Quantities of Nickel", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy - Feb. 21-25, 1966.

4. Burke, R. W., "Extraction-Spectrophotometric Determination of Antimony as an Ion-Pair Complex", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy - Feb. 21-25, 1966.

5. Deardorff, E. R., "Spectrophotometric Determination of Nickel in the Presence of Cobalt and Copper", ACS Meeting in Miniature at the University of Maryland - May 6, 1966.

6. Menis, O., "Flame Photometric Determination of Barium", ACS Meeting in Miniature at the University of Maryland - May 6, 1966.

7. Rains, T. C., "Role of Atomic Absorption and Flame Emission Spectrophotometry in Modern Laboratory", Department of Chemistry, Georgetown University, Washington, D. C., April 6 1966.

D. Committee Activities

Oscar Menis

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

J. T. Sterling

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

R. K. Bell

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

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