

NBS

TECHNICAL NOTE

424

**Analytical Coordination Chemistry:
Titrimetry, Gravimetry, Flame Photometry,
Spectrophotometry, and Gas Evolution,
July 1966 to June 1967**



**U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards**

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UNITED STATES DEPARTMENT OF COMMERCE
Alexander B. Trowbridge, Secretary
NATIONAL BUREAU OF STANDARDS • A. V. Astin, Director



TECHNICAL NOTE 424

ISSUED JANUARY 1968

**Analytical Coordination Chemistry:
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July 1966 to June 1967**

Edited by Oscar Menis

Analytical Coordination Chemistry Section
Analytical Chemistry Division
Institute for Materials Research

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

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

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

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1967 we plan to issue these summaries for all of our sections. The following is the third annual report on progress of the Analytical Coordination Chemistry Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

During the past year the research efforts of the Analytical Coordination Chemistry Section led to significant contributions to higher precision and accuracy of values reported on standard reference materials. The first four parts of this report, gravimetry, titrimetry, flame emission and atomic absorption, spectrophotometry and spectrofluorimetry, reveal the efforts centered around analytical coordination chemistry. The fifth section, gases in metals, covers mainly high vacuum techniques for oxygen and nitrogen in metals. This third successive annual report of this Section, while still concerned predominantly with analysis of certified standard reference material, also aims to point out the research plans and goals of next year which are expected to be considerably enlarged. To eliminate the diverging of effort, certain areas dealing with isotope preparation and nuclear materials have been transferred to another Section (310.06).

Progress on several of the new methods reported only in part here will be published shortly in scientific journals. In order to describe experimental procedures adequately, it has occasionally been necessary to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Oscar Menis, Chief
Analytical Coordination Chemistry
Analytical Chemistry Division

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ANALYTICAL COORDINATION CHEMISTRY:
TITRIMETRY, GRAVIMETRY, FLAME PHOTOMETRY,
SPECTROPHOTOMETRY, and GAS EVOLUTION,
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Edited by Oscar Menis

ABSTRACT

In the related areas of gravimetry, titrimetry, flame emission and atomic absorption spectroscopy, absorption and fluorescence spectrophotometry, and gases in metals, the versatile aspects of coordination chemistry have, in several instances, been uniquely exploited to yield either more precise and accurate results or lower detection limits. Fivefold improvement in the gravimetric analysis for beryllium has been obtained by means of an incomplete homogeneous precipitation followed by a selective spectrophotometric examination of the filtrate. In the field of thermal analysis a survey of fifteen compounds has revealed several promising, future standards for DTA studies covering the range of 75 to 900°C. In the section on titrimetry highly precise procedures are described for the determination of boron and beryllium. Various instrumental parameters have been investigated in flame emission and atomic absorption spectroscopy in order to optimize such variables as nebulizer-burner and oxidant-fuel systems, elimination of interferences, and source difficulties. The use of chelate extraction systems has led to the extension of detection limits to the submicrogram level for impurities in zinc and selenium, while modified electronics has permitted the precise determination of 10 percent Li_2O in glass with a relative standard deviation of better than 0.2 percent. In absorption and fluorescence spectrophotometry the research aspect of ternary complexes or mixed chelates

are described together with their potential use at the nanogram-picogram level. In the same area improvement in accuracy has been obtained by controlled dissolution of samples in closed systems with particular attention being given to the determination of arsenic in cast iron. Also described in this section is the differential spectrophotometric determination of dysprosium in a glass to be used as a neutron flux monitor, in which case the relative error was reduced to less than 0.25 percent. Finally, in the area of high vacuum fusion a new standard was certified for oxygen in titanium and in two titanium alloys. In addition, research in the use of the same technique for the determination of nitrogen has apparently eliminated the problem of low values that have in the past so frequently plagued the analyst.

Key words: absorption and fluorescence spectrophotometry, arsenic, atomic absorption, beryllium, DTA studies, dysprosium in a glass, flame emission, gases in metals, gravimetry, homogeneous precipitation, impurities in zinc and selenium, Li_2O in glass, nitrogen, oxygen in titanium, titrimetry.

1. GRAVIMETRY

A. Introduction

Our main objectives in the field of gravimetry have been the attainment of high accuracy for the determination of beryllium and the development of suitable standards for differential thermal analysis. A new approach to the gravimetric determination of beryllium is based on an incomplete homogeneous precipitation of this element combined with a selective spectrophotometric determination of residual beryllium in the filtrate. In this manner the accuracy of this analysis was significantly increased over reported methods which suffer from serious systematic errors [1,2]. The greater accuracy of the determination of the element in Be-Cu alloys contributed to the fulfillment of a need for a new standard reference material. These types of alloys are presently much in demand in space, oceanographic, and aviation systems and the SRMs will serve to calibrate instruments used to check quality control in their production.

In the other area, differential thermal analysis (DTA), efforts were concentrated on a search for suitable standard materials for the calibration of instruments. In cooperation with the International Committee on Thermal Analysis twelve compounds were evaluated. In addition, an organic compound and a previously studied tricalcium silicate were further tested. The new data should aid in attaining the goal of selecting and providing much needed standards in this rapidly growing science. Finally, the results of other analyses of SRMs by gravimetric procedures are summarized.

B. Accurate Determination of Beryllium by Incomplete Homogeneous Precipitation and Spectrophotometric Addition

1. Introduction

A current review [1] and a symposium report [2] have demonstrated the need for a more accurate determination of beryllium. In the analytical areas of titrimetry, gravimetry, spectrophotometry, as well as in other instrumental methods, the problem of accuracy in parts per thousand has not been completely solved up to now. In beryllium analysis the current gravimetric methods based on ammonia or phosphate precipitation in conjunction with EDTA masking still do not fulfill that need and have been the subject of considerable dispute. Unfortunately, because of the very small ionic radius and resulting high charge density of the beryllium ion, this separation is difficult and subject to compensating errors. The latter has often obscured the issues. Recently, while our study was in progress, two other homogeneous precipitation procedures have been reported [3,4]. The first paper offers only limited information about the results of the quantitative separation, and for the second paper, involving the hydrolysis of acetylacetone, only a brief abstract is available. In our studies it became evident that in the process of complexing interfering elements, solubility losses become very serious and, based on spectrographic data (Spectrochemical Analysis, Section 310.02), coprecipitation was still significant. In our approach this problem was solved by a procedure of incomplete precipitation in which approximately 98 percent of the beryllium is precipitated homogeneously as the hydroxide and the residual beryllium in the filtrate is determined

spectrophotometrically. Since the latter represents only a small correction, its somewhat poorer precision (1 - 2%) does not contribute to a large error in the final value.

Willard and Sheldon [5] first showed that they could separate iron in a two-stage homogeneous precipitation procedure prior to quantitative determination of trace constituents in the filtrate. Our findings with beryllium further point out the fact that under conditions of incomplete precipitation the bulk of the impurities remain in the filtrate. In this study it has been necessary to establish optimum precipitation conditions, especially the effects of various complexing media, impurities in the reagents and glassware, and the choice of final ignition temperature for attaining a stoichiometric BeO product. Finally, a general procedure was developed for the determination of beryllium in a complex alloy.

2. Experimental

a. The homogeneous generation of ammonia. Several reagents were investigated regarding their rates of hydrolysis, the effects of diverse salts, and the influence of various complexing agents on the final pH.

Initial tests of two reagents suitable for generation of ammonia, urea and hexamethylenetetramine, revealed that a higher pH was more readily attained with the former. The hydrolysis process with four grams of urea was complete in 30 minutes. The rate of hydrolysis at the boiling point as a function of time is shown in table 1. A final pH of 7.3 or greater was found essential for an approximately 98 percent precipitation of the beryllium hydroxide. With 20 to 40 mg of beryllium in the sample four grams of urea were

sufficient to attain this pH. However, for samples containing 60 or more milligrams of Be, the amount of urea was increased to 16 grams.

Table 1. Rate of hydrolysis of urea in homogeneous precipitation of beryllium.

Fixed conditions: 15.0 mg of Be as BeCl_2 , 4 g of urea, volume 400 ml.

<u>Boiling (minutes)</u>	<u>pH</u>	<u>Filtrate ^a (absorbance)</u>
0	4.1	0.774
5	4.8	.727
10	5.5	.674 ^b
15	6.0	.337
20	6.5	.195
25	6.7	.147
30	6.8	.024
35	6.9	.013
40	6.9	.012
45	6.9	.001
Room temp.	7.3	.016

^aUnprecipitated Be.

^bFiltrate was turbid.

b. Role of complexing agents. In gravimetric procedures for beryllium, complexation of other elements is generally attempted in order to avoid errors caused by coprecipitation. In recent years the use of salts of ethylenediaminetetraacetic acid has come to the forefront when a hydroxide [6,7] or phosphate [8] is involved. It is claimed that the stability constant of beryllium EDTA is low and its complexation does not prevent the precipitation of beryllium. The data in tables 2 and 2a indicate, on the contrary, that solubility losses increase with the EDTA concentration.

A further survey of the other complexing media, shown in table 3, did not point up any unique systems from the standpoint of purity and completeness of precipitation. While trien was quite effective in complexing cobalt, it was not as effective with other ions. For that reason a relatively small fixed concentration of EDTA was chosen.

Table 2. Effect of EDTA on the recovery of beryllium in a homogeneous precipitation.

Conditions: Be 60 mg, urea 16 g, final volume 400 ml, colorimetric determination of beryllium in filtrate, EDTA added as the disodium salt.

<u>EDTA, mg</u>	<u>Final pH</u>	<u>Filtrate Be, mg</u>
none	7.6	0.758
none	7.6	.691
100	7.5	.956
100	7.5	1.453
100 ^a	7.5	1.532
100 ^a	7.6	1.267
150	7.5	1.788
150	7.5	1.813
200	7.4	2.575
200	7.4	2.625

^aEDTA added as the ammonium salt.

Table 2a. Effect of EDTA on the recovery of beryllium in an ammonium phosphate precipitation.

<u>Beryllium, mg</u>		
<u>Taken</u>	<u>Found</u>	<u>Difference</u>
20.042	19.899	-0.143
20.815	20.540	- .275
20.160	19.983	- .177
19.328	19.077	- .251

^aSee reference [8].

Table 3. Effect of complexing media on the recovery of $\text{Be}(\text{OH})_2$.

	<u>Millimoles</u>	<u>Be recovered gravimetrically</u> %
Disodium ethylenediaminetetraacetate (Na_2EDTA)	0.27	97-98
Ethylenediaminetetraacetic acid (EDTA)	.68	94
Disodium nitriloacetate (NTA)	.68	-
N-hydroxyethylethylenediamine triacetic acid (Versenol)	.67	-
Hexamethylenetetramine (Hexamine)	.72	98
1,2-Diaminocyclohexanetetraacetic acid (DCTA)	29	0
Disodiumpyrocatechol-3,5-disulfonate (Tiron)	0.32	89
Triethylenetetramine (Trien)	1.4	87

c. Combined homogeneous precipitation and spectrophotometric determination of beryllium. To eliminate the problem of coprecipitation, the incomplete homogeneous precipitation procedure was combined with a selective spectrophotometric [9] analysis of the filtrate. The results of this procedure are presented in table 4. From these data, it is evident that the accuracy based on synthetic samples prepared from high-purity beryllium is high. In most cases the agreement is better than one part in ten thousand.

Table 4. Combined homogeneous precipitation and spectrophotometric determination of beryllium.

Beryllium Gravimetric	Found (mg)		Taken	Difference
	Spectropho- tometric	Total		
20.200	0.677	20.877	20.869	+0.008
19.510	0.750	20.260	20.260	0.0
58.53	1.715	60.245	60.250	-0.005
58.46	1.865	60.325	60.34	-0.015
58.55	1.861	60.411	60.43	-0.019
60.36 ^a	0.803	61.163	61.17	-0.007
60.75 ^a	0.732	61.483	61.48	+0.003
61.60	1.013	62.613	62.63	-0.017
58.83	1.540	60.370	60.37	0.0
60.25	1.623	61.873	61.84	+0.033
60.73	1.343	62.073	62.07	+0.003
98.13	2.555	100.685	100.69	-0.005
98.00	2.144	100.144	100.16	-0.016
98.11	2.307	100.417	100.43	-0.013

^aNo EDTA added.

d. The role of impurities. Tests were also carried out to evaluate the effectiveness of the new method in eliminating the interference of several ions. The basis for choosing these elements was their presence in the SRM alloys. In table 5 are presented data indicating that on the average the relative difference was 0.2 percent. Additional problems were caused by impurities in the reagents and glassware. Teflon beakers were used in an effort to eliminate the pick up from glassware. Spectrographic data indicated that traces of silicon of the order of 10 to 100 ppm were still present in the precipitate. The other source of impurities was the presence of sulfate in the urea reagent. Thermogravimetric data shown in figures 1 and 2 indicate that in the absence of sulfate a

Table 5. The effect of impurities^a on the beryllium determination.

<u>Beryllium, mg</u>			
<u>Added</u>	<u>Found</u>	<u>Difference</u>	<u>Rel. Diff.</u> (%)
20.870	20.868	- .002	.01
20.276	20.198	- .058	0.3
19.278	19.311	+ .033	0.2
20.871	20.902	- .031	0.1
20.220	20.230	+0.010	0.1
20.165	20.171	+0.006	0.1
10.005	10.012	+ .007	0.1
10.908	10.946	+0.04	0.4

^aImpurities, mg: Al-1.7; Ni-0.12; Mn-.04; Cr-0.02.

constant weight can be obtained at 700°C. However, our results with the synthetic samples show that an ignition temperature of 1100°C was required to obtain a stoichiometric BeO. This higher value suggested the presence of sulfate. Subsequent analysis of several preparations of urea (table 6) confirmed this. In the present investi-

Table 6. Presence of sulfates in urea; sulfate determined turbidimetrically.

<u>Source</u>	<u>Wt of reagent (g)</u>	<u>SO₄ mg/gram</u>
Mallinckrodt, AR	8	4.4
Merck's Ultrapure	8	12.5
NBS Zone Refined ^a		
1 pass	8	9.3
NBS Ion Exchange ^a		
10% Sol	2.5	non-detected

^aPrepared by Section 310.09.

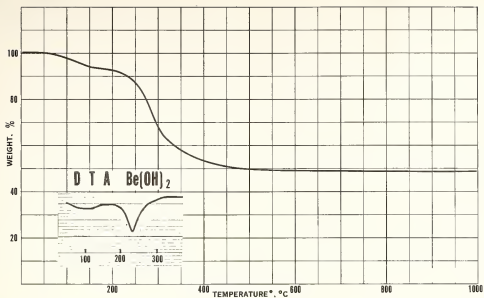


Figure 1. Homogeneous precipitation of Be(OH)₂ plus EDTA (heating rate 15°C min., dry air).

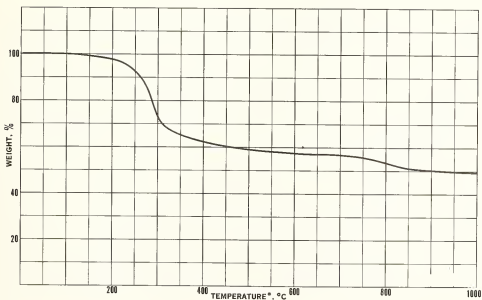


Figure 2. Homogeneous precipitation of Be(OH)₂ plus sulfate (heating rate 15°C min., dry air).

gation, Mallinckrodt AR grade was used almost exclusively and the final precipitate was ignited at 1100°C to eliminate any possible sulfate interference.

e. Scheme of analysis of Be-Cu alloys. As shown in the flow chart in figure 3 the steps of the analysis involved the electrogravimetric determination of copper, removal of silica and separation of cobalt by anion exchange prior to its electrogravimetric determination. Beryllium was then determined in the eluate by the new procedure. Results of

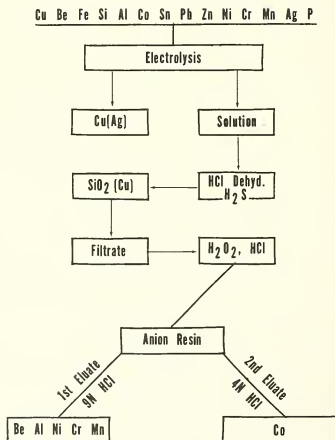


Figure 3. Flow chart of separations in the analysis of beryllium-copper alloy.

these analyses are presented in table 7. Statistical evaluation of these data indicate that based on six degrees of freedom the standard deviation of a single determination is 0.004. This is a five-fold improvement over the precision stated in the last annual report.

R. K. Bell and Oscar Menis

Table 7. Precision of the beryllium determination in a copper alloy.

<u>Alloy, SRM</u>	<u>Duplicates</u>		<u>Difference, d</u>
1121 Cast	1.936	1.943	0.007
1121 Wrought	1.914	1.918	0.004
1122 Cast	1.769	1.771	0.002
1122 Wrought	1.765	1.776	0.011
1123 Cast	0.466	0.468	0.002
1123 Wrought	0.461	0.466	0.005

$$s = \left[\frac{1}{2n} \sum d^2 \right]^{-\frac{1}{2}} = \left[\frac{0.000219}{12} \right]^{-\frac{1}{2}} = 0.0043$$

C. Differential Thermal Analysis

1. Introduction

Along the lines of reasoning presented in the last progress report [10], a survey was undertaken of suitable materials as standards for differential thermal analyses. In this initial review the round-robin arrangement of the International Conference on Thermal Analysis, Sub-Committee on Standardization, served as the focal point. At the last meeting of the committee held in London, September 1966, it was proposed that the members test twelve preparations. These were selected to cover a range of temperatures from 100-900°C representing thermodynamic enthalpy changes

reported in the literature. The materials were supplied by members of the committee. Depending on the evaluation of the results from the participating members, future recommendations are contemplated by the committee.

In addition to examining these compounds, preparations of an organic compound, stearic acid, were tested. Finally, new data with a more sensitive instrument were obtained on tricalcium silicate, a compound described in the last annual report.

2. Experimental

Two commercial instruments were used in these studies. With instrument I, weighed samples (1 to 4 mg) and an aluminum oxide reference material were spread in separate 1/4-inch platinum dishes which were placed on the ring of a platinum differential thermocouple. The thermocouple bead touched the bottom of the dishes. The sample and reference were then heated at a linear rate in a flowing helium atmosphere.

With instrument II, the sample and an aluminum oxide reference were placed in separate 2mm capillary tubes, and chromel-alumel differential thermocouples were inserted into the sample and reference materials. The sample compartment was evacuated, purged with nitrogen, and then heated at a linear rate in a flowing nitrogen atmosphere.

3. Data and Discussion

Typical DTA curves as recorded by these two instruments are presented in figures 4 through 16. The upper curves are from instrument I and the lower from instrument II. The results for replicate runs are summarized in table 8.

Table 8. Differential thermal analysis data.

		<u>Transition and fusion temperatures, °C^a</u>					
ICTA Sample		Instrument I			Instrument II ^b (850° maximum)		
<u>Lit. Temp.^c</u>	<u>Rate^d</u>	<u>A</u>	<u>B</u>	<u>D</u>	<u>A</u>	<u>B</u>	<u>D</u>
KNO ₃ 128, <u>337</u>	3				128	130	130
					327	328	328
	10	126	126	131	130	130	136
		318	318	331	328	328	330
	10	121	123	129	130	130	133
		328	322	329	328	328	330
	10	124	128	133	127	128	130
		311	317	323	327	329	328
	20	126	126	131			
		323	323	327			
	20	132	132	140			
		333	333	336			
KHSO ₄ 164, 181, <u>219</u>	3				192	192	192
					205	206	209
	10	162	180	205	181	181	183
		217	217	234	198	201	211
	10				181	181	184
					198	203	210
	10				174	174	184
					195	203	209
	10				189	189	188
					194	198	210
10				199	199	200	
				203	203	209	
	20	132	182	203			
		221	226	234			
	50				185	186	191
					202	205	215
K ₂ CO ₃ 250, 428 622, <u>896</u>	10	ND					
		ND					
		ND					
		805	876	887			
	20	ND			214	217	244

Transition and fusion temperatures, °C^a

ICTA Sample <u>Lit. Temp.^c</u>	Rate ^d	Instrument I			Instrument II ^b (850° maximum)		
		<u>A</u>	<u>B</u>	<u>D</u>	<u>A</u>	<u>B</u>	<u>D</u>
K ₂ CO ₃ (cont)		ND			ND		
		ND			ND		
	20	821	877	897	ND		
		ND					
		ND					
		ND					
	20	-	-	890			
		ND					
		ND					
		796	880	891			
KClO ₄ 300, <u>525</u>	3				300	300	300
					ND		
	10	298	298	305	301	301	302
		578	597	610	ND		
	10				301	301	302
					ND		
	10				301	301	302
					ND		
	10				300	300	301
					ND		
	10				299	300	301
					ND		
	10				298	299	300
					ND		
	10				300	300	303
				ND			
	20	293	295	300			
		583	592	605			
	20	297	297	300			
		580	597	609			
Ag ₂ SO ₄ 412, <u>660</u>	10	420	422	431	425	425	431
		621	636	647	658	658	661
	10				421	425	430
					650	657	662

Transition and fusion temperatures, °C^a

ICTA Sample	Rate ^d	Instrument I			Instrument II ^b (850° maximum)		
		A	B	D	A	B	D
Ag ₂ SO ₄ (cont)	10				425 651	427 658	432 (659)
	20	418 632	420 647	428 653			
	20	420 628	422 648	435 658			
	20	298 ND ND 774	303 ND ND 816	(304) ND ND 837			
Na ₂ CO ₃ 356, 486 618, 854	20	298 ND ND 774	303 ND ND 816	(304) ND ND 837			
	20	ND ND ND 778	805	843			
	20	ND ND ND 778	805	843			
Na ₂ CO ₃	20	ND ND ND					
	50	-	-	811	301 ND ND ND	315	349
SiO ₂ 573	3				(?)	(?)	571
	10	-	-	567	569	569	572
	10	555	562	564	560	567	570
	10				(537)	571	573
	10				571	571	573
	20	547	566	569			
K ₂ SO ₄ <u>583</u>	10	572	580	582	582	584	584
	10	559	578	581	508	583	584
	10				541	565	584
	20	556	578	582			

Transition and fusion temperatures, °C^a

ICTA Sample Lit. Temp. ^c	Rate ^d	Instrument I			Instrument II ^b (850° maximum)		
		A	B	D	A	B	D
K ₂ CrO ₄ ^e <u>665</u> (Reagent grade)	10	658	660	665	670	670	672
	10	-	-	670	629	666	671
	10				631	665	674
	20	662	667	670			
BaCO ₃ <u>810</u>	3				804	806	813
	10	777	791	803	-	-	809
	20	791	798	806			817
SrCO ₃ <u>925</u>	10	900	905	930			
	20	928	929	931			
Na ₂ SO ₄ ^e 240, <u>890</u> (Ultra pure)	10				243	246	(254)
					ND		
	10				240	249	(254)
					ND		
	10				237	243	243
					ND		
	20	241	244	254	238	241	249
20	866	874	883	-			
	241	242	254	238	239	246	
	ND						
	246	246	259				
20	865	865	883				

^aDefinition of temperatures: A = temperature of initial change from base line value. B = temperature of intercept of base line with extrapolated line for rapid change of temperature. D = temperature of peak maxima.

^bInstrument used with a low temperature furnace.

^cNBS Circular 500 and American Institute of Physics Handbook.

^dRate = °C/min.

^eSample not supplied by ICTA.

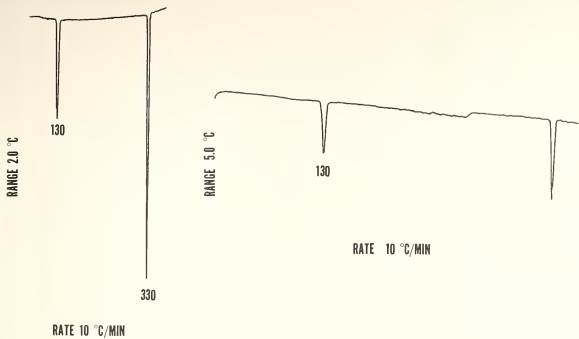


Figure 4. Typical DTA curve for potassium nitrate.

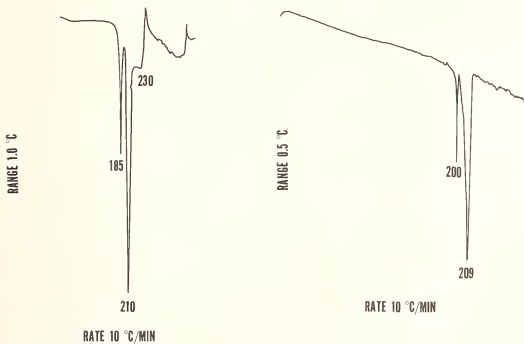


Figure 5. Typical DTA curve for hydrogen sulphate.

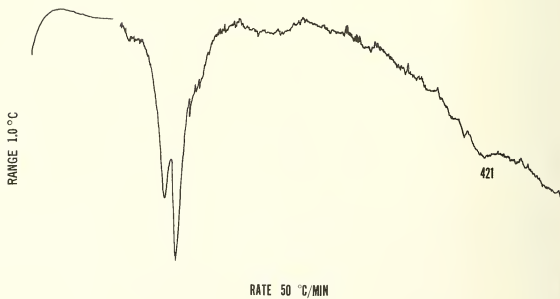
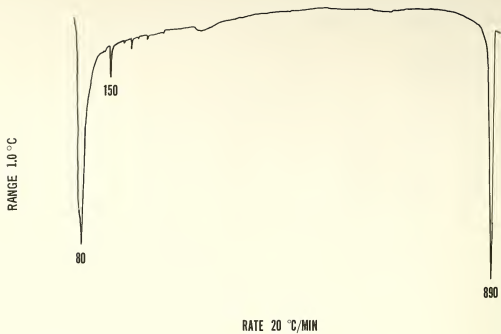


Figure 6. Typical DTA curve for potassium carbonate.

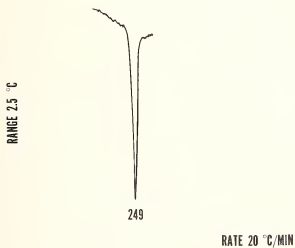
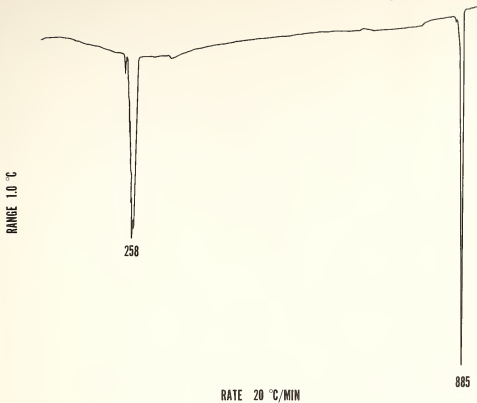


Figure 7. Typical DTA curve for sodium sulphate.

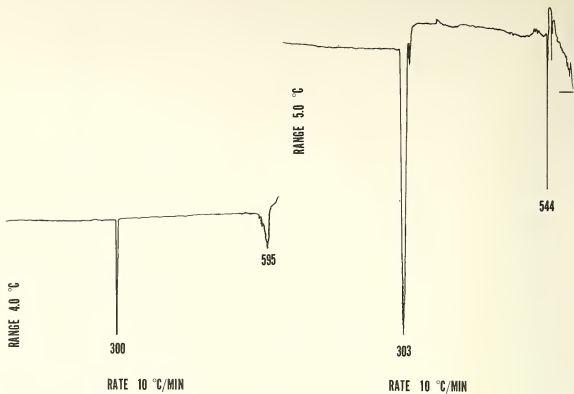


Figure 8. Typical DTA curve for potassium perchlorate.

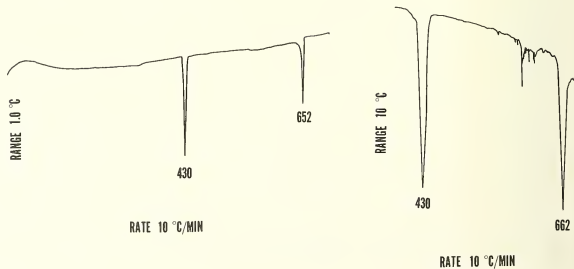


Figure 9. Typical DTA curve for silver sulphate.

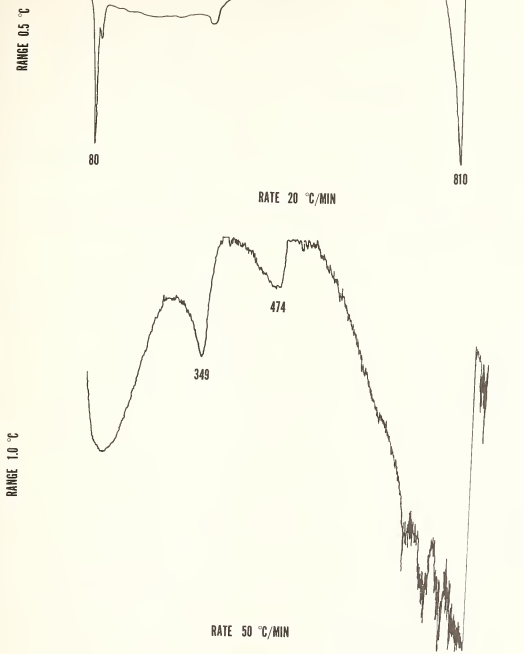


Figure 10. Typical DTA curve for sodium carbonate.

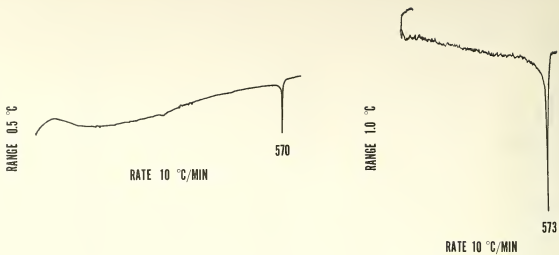


Figure 11. Typical DTA curve for silicon dioxide.

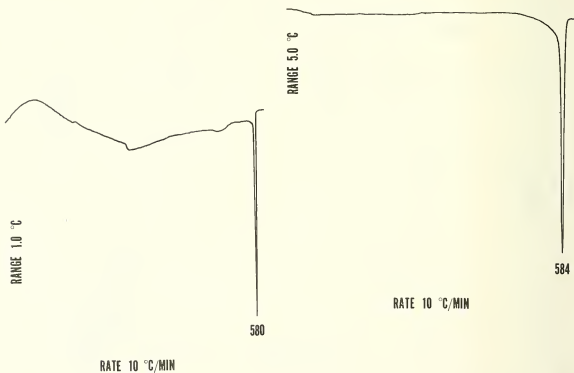


Figure 12. Typical DTA curve for potassium sulphate.

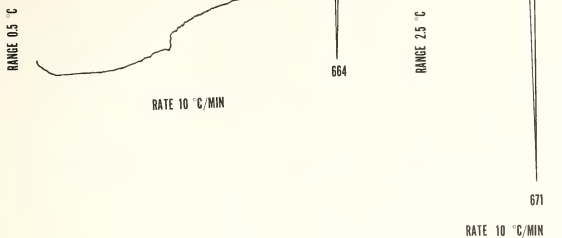


Figure 13. Typical DTA curve for potassium chromate.

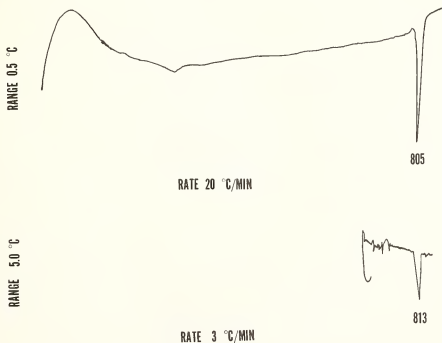


Figure 14. Typical DTA curve for barium carbonate.



Figure 15. Typical DTA curve for strontium carbonate.

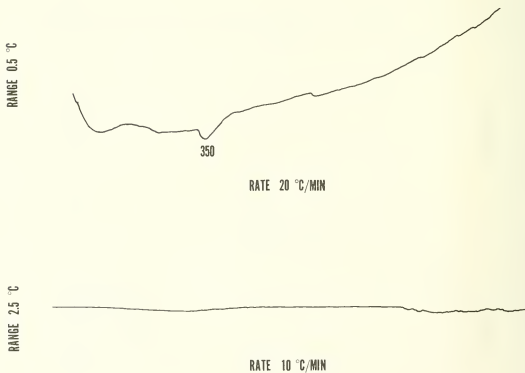


Figure 16. Typical DTA curve for aluminum oxide.

On examining the data, certain problems and tentative conclusions become apparent. First, several of the compounds yielded poor or meaningless DTA curves. The carbonates, in general, were representative of this group. On the other hand, a number of the compounds looked promising as potential standards from the standpoint of accuracy and good DTA curves. These included SiO_2 , KNO_3 , KClO_4 , (except for its uncertain decomposition), Ag_2SO_4 , K_2SO_4 , and SrCO_3 . The precision and accuracy of the data, with few exceptions, were better using instrument II. This may be due to better contact of the thermocouples with the sample. In this instrument the sample was packed in a capillary, while in the other instrument, the contact between the pan holding the sample and the thermocouple may have been poor. It was also much more difficult to measure and interpolate the temperature from the non-linear scale of the latter instrument. Nevertheless, based on this brief survey, potentially good prospects for standard reference materials are apparent. Because of concomitant interest in several of these compounds in other SRM programs as indicated by J. L. Hague, Coordinator of Inorganic Standards, Office of Standard Reference Materials, efforts will be made to obtain pure starting material for further study. These include KNO_3 , KClO_4 , Ag_2SO_4 , SiO_2 , K_2SO_4 , and SrCO_3 . These also encompass the temperature range of interest to ICTA.

From the standpoint of purity it is apparent that chemical characterization of these materials will be an important factor. The results obtained on two grades of Na_2SO_4 (see table 8) readily point out the effect of common impurities. Similarly, in the case of stearic acid (see figure 17) the

high purity of the preparation has an important bearing on the accuracy of the data. The upper curve represents a purer preparation.

In the continuation of last year's studies involving tricalcium silicate (table 9) the detection of endothermic peaks was accomplished by the use of instrument I. In this case the effect of the better geometry of the sample material in the dish is more favorable for the detection of transition temperatures than the capillary arrangement. The final small peak was now detectable. Mazieres [11] discovered this transition with his micro equipment.

Table 9. Endotherm transition temperatures for tricalcium silicate.

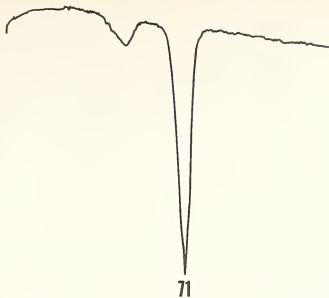
<u>Cycle</u>	<u>Temperature °C</u>			
Heating (a)	600	915	980	990
(b)	650	906	965	990 ^a
Cooling (a)	560	905	970	985 ^b
(b)	570	885	950	985

^aMazieres.

^bNBS.

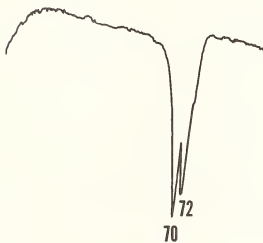
It is expected that progress in precision and accuracy can be made through better understanding and control of the instrumental variables and well characterized high-purity preparations. It is hoped that this evaluation should lead to the production of suitable standards much needed for the calibration of instruments which are now being used in biochemical, organic, and inorganic areas of science and technology.

RANGE 20 °C



RATE 0.5 °C/MIN

RANGE 20 °C



RATE 0.5 °C/MIN

Figure 17. Typical DTA curve for stearic acid.

D. Analyses of Samples

A variety of samples, mostly standard reference materials, have been analyzed by the gravimetric procedures. The tentative results of these analyses together with the relative precision are presented in table 10. No additional bibliographical references are given since they were covered in the previous reports of this section.

T. A. Rush and Oscar Menis

Table 10. Summary of gravimetric determinations.

<u>Element or Compound</u>	<u>SRM</u>	<u>Kind</u>	<u>No. Det.</u>	<u>Percent</u>	<u>Rel. std. dev., %</u>
Cu	1121	Be-Cu alloy cast	3	97.441	0.02
Cu	1121	Be-Cu alloy wrought	3	97.467	0.01
Cu	1122	Be-Cu alloy cast	3	97.426	0.002
Cu	1122	Be-Cu alloy wrought	3	97.434	0.002
Cu	1123	Be-Cu alloy cast	3	97.116	0.002
Cu	1123	Be-Cu alloy wrought	3	97.115	0.01
Cu	1080	bis(1-phenyl-1,3-butanediono)copper(II)	12	10.47	0.5
Co	1121	Be-Cu alloy cast and wrought	2	0.293	1.0
Co	1122	Be-Cu alloy cast and wrought	3	0.217	2.0
Co	1123	Be-Cu alloy cast and wrought	2	2.306	0.3
Fe	1079a	tris(1-phenyl-1,3-butanediono)iron(III)	4	10.29	0.2
SiO ₂ ^a	88a	Dolomite limestone	3	1.20	0.9
CaF ₂ ^b	79b	Fluorspar	3	98.14	0.06

^aReported as the compound.

^bBased on solubility studies as in NBS Certificate 79.

2. TITRIMETRY

A. Introduction

Studies were continued along the plans presented in the last report [10]. This included the continuation of studies of spectrophotometric and potentiometric titrations and the investigation of pyrohydrolytic separation of nitrides and fluorides. Only a relatively limited effort, however, could be carried out along these lines during this period. The current investigation involved the potentiometric titrations of boron, spectrophotometric titration of beryllium and fluoride and pyrohydrolytic separations of nitrides and fluorides.

B. Alkalimetric Titration of Boric Acid

1. Introduction

A boric acid standard reference material is needed for use in the measurement of a standard neutron cross section. For that purpose it is also desirable to know very exactly its stoichiometric composition. One approach which was studied for the latter purpose was the evaluation of a pH titration with a standard sodium hydroxide solution. It is obvious that the modified potentiometric method [2] is capable of a precision of 0.1 percent relative standard deviation. The present investigation involved refinement of the procedure to improve the precision to two parts in ten thousand.

2. Refined Procedure and Results

High purity boric acid was accurately weighed and dissolved in water. The solution was then acidified with hydrochloric acid and boiled under a reflux condenser to insure the removal of carbon dioxide without any loss of boron. It was cooled and transferred to a quartz beaker under a blanket of carbon dioxide-free air. The solution was adjusted to pH 6.9, and 0.5 M manitol was added. It was

then titrated with standard sodium hydroxide. Base was added from a weight burette until a final pH of 6.9 was attained.

The results presented in table 11 indicate a precision of 0.02 percent relative standard deviation for a single determination based on six degrees of freedom. Thus, the desired precision can be readily obtained by this procedure. However, the method is highly empirical in that a predetermined pH is selected for the endpoint. The method can be used to advantage in preparing a precise ratio in boron isotope mixtures. It is evident that it cannot, at present, be used to establish absolute values.

Table 11. Potentiometric titration of boric acid.

<u>Sample No.</u>	<u>Wt. of H_3BO_3</u>	<u>Wt. of NaOH</u>	<u>gNaOH/gH_3BO_3</u>
1	0.25207	49.3807	195.898
2	0.25010	48.9869	195.867
3	0.25026	49.0278	195.908
4	0.24953	48.8908	195.930
5	0.25241	49.4700	195.990
6	0.25124	49.2301	195.952
7	0.25338	49.6471	<u>195.935</u>
	Average:		195.925
	Standard deviation:		0.040
	Relative standard deviation (percent):		0.02

C. Spectrophotometric Titration of Beryllium

1. Introduction

In conjunction with studies on the gravimetric determination of beryllium in a copper-beryllium alloy, an alternate method for its determination was sought. The

most promising method found in the literature [13] involves the back titration of excess sodium sulfosalicylate with standard beryllium solution.

2. Results and Discussion

In initial studies with a standard solution of beryllium, the precision of the endpoint determination, based on a plot of a "S" shape titration curve, was only 0.65 percent relative standard deviation. This value was improved in six subsequent titrations to 0.25 percent, calculated by means of a computer program.

Further tests were carried out with SRM copper-beryllium alloys. The results are presented in table 12 and compared with gravimetric values. Based on this limited study the method offers a potentially rapid and reliable method for the determination of beryllium. Its main limitation is that it requires an accurate primary standard of beryllium.

K. M. Sappenfield

Table 12. Spectrophotometric titration of beryllium in Be-Cu alloys.

<u>Sample</u>	Set:	<u>Beryllium, Percent</u>		
		<u>Titration</u>		<u>Gravimetric^c</u>
		<u>I^a</u>	<u>II^b</u>	
1		1.78	1.91	1.94
2		-	1.89	1.92
3		1.75	1.76	1.77
4		1.72	1.72	1.77
5		0.42	0.41	.47
6		0.43	-	.47

^aTitration in HCl media.

^bTitration in H₂SO₄ media.

^cProcedure described in section 1 of this report.

D. Spectrophotometric Titration of Fluoride and Pyrohydrolytic Separation

1. Introduction

The continuation of efforts for the separation and determination of fluoride in fluorspar centered around the spectrophotometric titration of fluoride and test of several flux materials for the pyrohydrolytic separation [10].

2. Studies of Separation Procedures

Several pyrohydrolytic procedures were tested in search of optimum conditions for the separation of fluoride from CaF_2 . In an attempt to increase the recovery of fluoride at a temperature of 850°C the following three fluxes were used in addition to the sodium tungstate flux used earlier: (1) sodium tungstate flux plus NaOH , (2) sodium tungstate flux plus SiO_2 , and (3) sodium bismuthate. In all cases the recovery of fluoride from CaF_2 was low; with the NaOH addition about 21 percent, with SiO_2 addition about 24 percent, and with the sodium bismuthate about 15 percent. The reduction of sample weight from 200 mg to 100 or 25 mg resulted in a recovery of only about 16 percent in each case.

Another approach, involving the use of higher temperature is underway. For that purpose a heavy-duty furnace with a nickel ignition tube, as shown in figure 18, has been assembled. Tests with other fluxes at temperatures above 1000°C will be undertaken to assure the complete release of fluoride.

3. Titration Studies

A brief study of the spectrophotometric titration of fluoride by the thorium-Alizarin Red S reaction revealed a precision of 0.6 percent. The relative error is too high for the needed accuracy of this analysis. In addition, tests of possible interference from tungsten which may be a

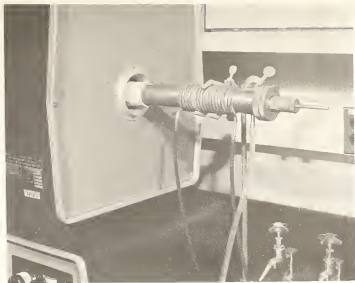


Figure 18. Pyrohydrolysis apparatus.

byproduct of the pyrohydrolysis revealed an anomolous effect. As shown in figure 19, a negative error occurs when less than 8 mg of tungsten is present in the distillate solution, while a positive error is noted with higher concentrations. For these reasons this approach was abandoned.

Recently an ion-specific fluoride indicator electrode was acquired. It is planned to continue this work by potentiometric titrations involving this indicator electrode.

E. Separation of Nitrogen From Refractory Nitrides

Further studies of fusion pyrohydrolysis of refractory nitrides centered around the design of a modified apparatus. The design of the apparatus, shown in figure 18, includes a new high temperature furnace with automatic control of temperature and a modified ignition tube. The tube is equipped with a Wilson valve which enables one to insert the sample slowly into the hot section of the furnace while the main section of the ignition tube is sealed at the entrance. A nickel guard tube is also included to prevent the molten flux from attacking the ignition tube.

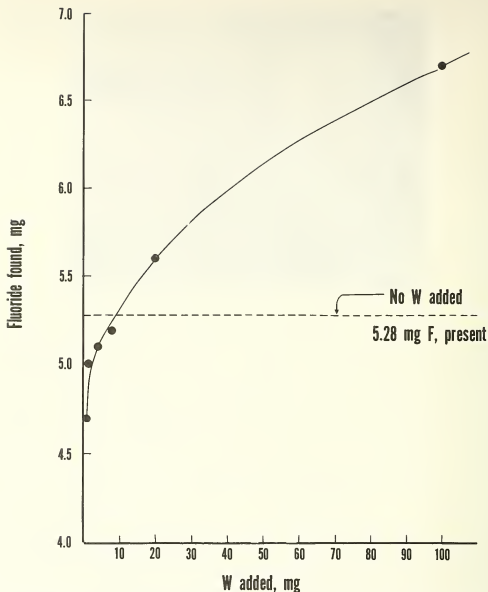


Figure 19. Interferences of tungsten in the determination of fluorine by thorium titration.

A modified procedure which would permit the determination of both NH_3 and N_2 is contemplated. It provides the elimination of the use of hydrogen and substitution of helium as the purge gas. Under those conditions the ammonia and the nitrogen which may form during the reaction could be collected separately. The first could be collected in an aqueous scrubber and the latter in a molecular sieve.

The two components could then be determined independently by spectrophotometric and gas chromatographic procedures.

B. B. Bendigo

F. Analyses of Samples

A variety of samples, mostly standard reference materials, have been analyzed by the titrimetric procedures. The tentative results of these analyses together with their relative precisions are presented in table 13. No additional bibliographical references are given since they were covered in the previous reports of this section.

S. A. Wicks

Table 13. Summary of titrimetric determinations.

<u>Element</u>	<u>SRM</u>	<u>Kind</u>	<u>No.</u>		<u>Rel. std.</u>
			<u>Det.</u>	<u>Percent</u>	<u>dev., %</u>
Cr	4j	Cast iron	6	0.0938	0.4
Cr	163	Steel	8	0.982	0.1
Cr	30f	Cr-V steel	9	0.939	0.2
Cr	3b	White iron	2	0.0525	-
Cr	3c	White iron	2	0.0465	-
Cr	196	Ferrochromium (Low C)	5	70.89	0.05
Fe	1b	Argillaceous Limestone	3	0.772	0.3
Fe	1121	Cast Be-Cu alloy	2	0.088	-
Fe	1121	Wrought Be-Cu alloy	2	0.089	-
Fe	1122	Cast Be-Cu alloy	2	0.158	-
Fe	1122	Wrought	2	0.153	-
Fe	1123	Cast	2	0.043	-
Fe	1123	Wrought	2	0.041	-
Fe	1079a	tris (1 phenyl-1,3-butanediono)iron(III)	6	10.30	0.2
N	3b	White iron	4	0.106	3
N	3c	White iron	3	0.0057	4
N	4j	Cast iron	7	0.0037	7
N	30f	Cr-V steel	8	0.0089	6
N	163	Steel	8	0.0091	5
V	4j	Cast iron	4	0.0298	0.4
V	30f	Cr-V steel	5	0.182	0.5
V	3b	White iron	2	0.0055	-
V	3c	White iron	2	0.0063	-

3. FLAME EMISSION AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

A. Introduction

The emphasis in the fields of atomic absorption (AAS) and flame emission spectrophotometry (FES) during the past year has been on ways to improve the precision and accuracy of these methods. To accomplish this goal an evaluation of various parameters which included nebulizer-burner, oxidant-fuel systems, interferences, slit widths, sources of monochromatic light, digital readout and electronics was undertaken. During this period, some of the accomplishments include the determination of impurities at the submicrogram level in high-purity zinc and selenium, and a differential technique for high-precision flame emission spectrophotometry. Methods were developed for separation of trace quantities of copper and arsenic by solvent extraction as well as for the separation of macroquantities of iron without loss of trace constituents. The copper was extracted with 2-thenoyltrifluoroacetone, while the arsenic was extracted with diethylammonium diethyldithiocarbamate from an acid medium. The precision of flame emission spectrophotometry was increased to less than 0.2 percent by a new differential technique. This increase in precision was accomplished with the aid of a phase shifter and attenuator on our ac synchronous detector. Also, the limit of detection of arsenic by atomic absorption spectrophotometry was extended to 0.5 ppm with the aid of a new gas mixture of argon-hydrogen.

The basic instrumentation remained the same as described in the last report [10]. However, a digital readout was acquired which was found to speed the acquisition of data with increased precision.

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

1. Introduction

In the previous report [10] the determination of trace impurities in a high-purity zinc (99.999) was briefly discussed. During the past year, copper, cadmium, gallium, and potassium were determined in the material by AAS or FES at the submicrogram level. The cadmium, gallium and potassium were determined without any preconcentration which minimized trace contamination; however, a separation and preconcentration of copper was necessary. The instrumental conditions were also modified which increased the precision and sensitivity of the method.

2. A Study of Nebulizers and Burners

A study was conducted using four different burner systems to obtain the lowest detection limits by AAS of several elements of interest in high-purity zinc. Table 14 gives a comparison of the detection limits of the four different burner systems. Burner B yielded the lowest detection limit; however, this burner has a definite memory effect with samples containing more than 5 mg of solids per ml. The same was true for burner A, but to a lesser extent. The Fuwa-Vallee tube arrangement can only be used when the total solids are less than 1 mg/ml. The total consumption burner C was slightly less sensitive but free of any memory effect with concentration of solids as high as 50 mg/ml. Also, this type of burner can be used for organic solvents while caution must be exercised with the premix burners.

Table 14. Comparison of detection for various burners by atomic absorption (aqueous solutions).

Element	Detection limits = $\mu\text{g/ml}/\%$ absorption				
	Burner ^a :	A	B	C	D
Ag		0.01	0.006	0.01	-
Cd		0.04	0.001	0.01	-
Cu		0.02	0.01	0.04 ^b	0.01 ^b
Mg		0.005	0.003	0.01	-
Pb		0.2	0.06	0.5	-

^aA, premix burner; B, premix burner in hot mode; C, total consumption; D, Fuwa-Vallee tube arrangement [14].

^bOrganic solution.

3. Separation and Preconcentration

It was found in the initial studies with AAS that the aspiration of a high concentration of zinc leads to high results especially when the atomic line of interest is in the ultraviolet region of the spectrum. For example, by measuring the absorption of the element in a solution containing 50 mg of zinc per ml at the resonance line of cadmium (2288A), the absorption value indicated a concentration of cadmium of one ppm. As a check for scattered light the cadmium ionic line at 2265A was tested with a standard solution of cadmium and found not to produce any absorption. However, when a solution containing 50 mg of zinc per ml was nebulized, the same absorption was observed as found at the resonance line.

It was concluded that the observed absorption at 2288A was due to scattered light and not cadmium. For this reason, a pre-separation and concentration step was adapted for the determination of copper in the high-purity zinc. After investigating several separational procedures including

anion exchange resin and chelating agents, 2-thenoyltrifluoroacetone and ammonium pyrrolidine dithiocarbonate, as well as high-molecular-weight amines, a method was developed for the separation of submicrogram quantities of copper from zinc with 0.2 M 2-thenoyltrifluoroacetone in methy isobutyl ketone (hexone). The results for the copper, cadmium, gallium, and potassium are given in table 15. The accuracy of the procedure was checked by the standard addition technique [15].

Table 15. Values for trace elements in high-purity zinc.

NBS SRM No.	Method	Element, $\mu\text{g/g}$			
		Cd	Cu	Ga	K
High-purity zinc	AAS	<0.1	$0.044^{+0.005}$	-	-
	FES	-	-	<0.1	<0.02
631 ^a	AAS	$0.8^{+0.1}$	$6.3^{+0.4}$	-	-
	FES	-	-	20^{+1}	-

^aControl sample.

C. Effect of Calcium and Phosphate on the Atomic Absorption Determination of Barium

An evaluation of the effect of calcium and phosphate on the AAS determination of barium has been carried out. An experiment was performed to test the effect of calcium and phosphate using the Beckman laminar flow burner with an air-acetylene flame. The results of this experiment are given in table 16. It has been reported by Koirtyohann [16]

that the intense oxide and hydroxide bands of calcium and strontium observed in emission are also observed in atomic absorption. In our study calcium was observed to have two distinct effects on the absorption of barium. First, calcium suppressed the absorption of barium and, secondly, when the calcium concentration exceeds 1 mg per ml, a relative strong absorption was observed by calcium at the resonance line of barium at 5536A. This absorption by calcium must be due to the strong CaO-CaOH band which has a maximum at 5540A. To overcome the interference of calcium on barium when the ratio of calcium to barium is greater than 10, a separation of barium was effected using $PbCrO_4$. This procedure is described in a previous publication by this author [17].

The absorption of barium was found to be severely suppressed by the phosphate even with concentration as low as 0.001 M or 0.1 mg per ml. However, the phosphate interference was eliminated by the addition of glycerol and perchloric acid as releasing agents.

D. High-Precision Flame Emission Spectrophotometry

1. Introduction

A new technique of differential flame emission spectrophotometry was developed whereby a precision of one part in a thousand was obtained over a concentration gradient of a few ppm to several percent. While our efforts in this field in the past several years have been to increase the limits of detection of the various elements, little effort has been spent on techniques to improve precision and accuracy of the method. The limits of detection which were reported in our previous report [10] were obtained with a sacrifice

Table 16. Effect of calcium and phosphate on the absorption of barium.

Barium present, μg/ml	Interfering ion, mg/ml	Barium found, μg/ml	Recovery ^a , %
10	Ca-0.01	10	100
-	0.01	0	
10	0.1	9.8	94
-	0.1	0.4	
10	1.0	13.0	57
-	1.0	7.3	
10	5.0	13.2	12
-	5.0	12.0	
10	10.0	18.5	0
-	10.0	18.5	
10	H ₃ PO ₄ - 0.1	9.0	90
-	0.1	0	
10	1.0	8.8	88
-	1.0	0	
10	10	3.0	30
-	10	0	
10	100	0	0
-	100	0	

^aRecovery after correcting for calcium.

of precision. Therefore, our present aim was to ascertain those parameters under which the precision of the measurement for FES for various elements could be optimized, and to test our theory in the determination of lithium in standard reference material.

As flame emission and atomic absorption spectrophotometry become more and more widely used in science and industry, the relative precision of the method is reported to be from 2 to 5 percent [15]. However, with the instrumentation that is available, a precision of less than two percent relative error could be maintained for most elements. The precision of the method which is normally quoted for

trace or milligram quantities is \pm 5 percent [18]. Ingamells [19] modified the Horstman method for the determination of lithium, sodium and potassium in silicates, and obtained a precision of one percent. This was accomplished by placing a sensitivity indicating ammeter in the circuit of the spectrophotometer and applying the principle of differential measurement.

2. Experimental Variables

In our investigation various parameters were optimized such as slit width, regulation of oxidant and fuel, and measuring the signal. The effect of the slit width in the FES determination of lithium is given in table 17. The current data are insufficient to statistically evaluate any effect of varying the exit or entrance slit width while keeping the other constant.

Table 17. Effect of slit width on the flame emission spectrophotometric determination of lithium.

<u>Slit Width, μ</u>		<u>Scale reading</u> ^a	<u>Std. dev.</u>	<u>Rel. std.</u>
<u>Entrance</u>	<u>Exit</u>			<u>dev. %</u>
25	25	74.53	0.18	0.25
25	50	85.31	0.26	0.31
25	100	78.43	0.23	0.29
50	25	84.69	0.16	0.18
50	50	89.13	0.20	0.22
50	100	83.18	0.29	0.35
100	25	75.88	0.17	0.22
100	50	84.11	0.14	0.16
100	100	94.36	0.17	0.18

^aAverage of 6 readings.

The regulation of the flow of oxidant and fuel became a critical factor in our study. It was found that flow of gases could not be controlled precisely by the pressure reducing valves. However, by using precision rotometers in conjunction with the reducing valves, a constant flow of oxidant and fuel could be maintained.

Generally, in the measurement and calibration of flame emission, a calibration curve of 0 to 80 percent emissivity is prepared for an element over a concentration range such as 0 to 5 or 0 to 10 ppm as shown in figure 20. By this method the inability to read the data from the graph to better than one percent becomes a limiting factor. However, by expanding a small portion of the curve as shown in figure 21, the precision can be increased to 0.1 percent. To achieve scale expansion a phase shifter and attenuator was designed and built for our ac synchronous detector as shown in figure 22. This modification in the electric circuit permits the setting of any desired concentration at zero percent transmission and then a finite concentration above this value expanded to give full scale deflection. In addition, the recorder was replaced with a digital readout which circumvented the inherent drag of the pen on the recorder and eliminated the error of trying to measure the peak height on the chart paper.

3. Results for Lithium

To evaluate this new approach to FES, a synthetic sample of Dy_2O_3 glass for neutron flux measurement was prepared which contained 350 mg of SiO_2 , 200 mg of Dy_2O_3 , 50 mg of Al_2O_3 , 300 mg of B_2O_3 , and 124.8 mg of Li_2CO_3 . The synthetic sample was dissolved with HF and $HClO_4$ and then the lithium content was determined using a typical

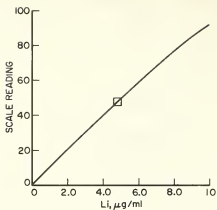


Figure 20. Typical lithium calibration curve.

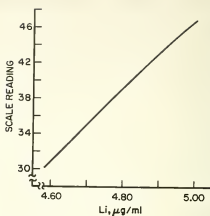


Figure 21. Lithium calibration curve - scale expanded.

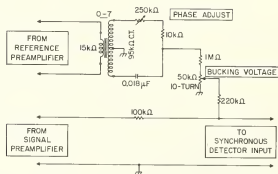


Figure 22. AC buck-out adaptor for synchronous detector.

calibration curve and by the expanded scale technique. The results are shown in table 18. The data shows that the expanded scale gave an improvement by a factor of three in the precision, relative standard deviation, over the conventional calibration curve.

Table 18. Lithium in synthetic Dy_2O_3 glass.

(Li added as Li_2CO_3 - 124.80 mg)

	Li_2CO_3		Average	Std. dev.	Rel. std. dev., %	Rel. std. error, %
	Found, mg					
Calibration curve, 2-10 $\mu\text{g/ml}$	124.6	127.2				
	125.4	127.2				
	124.2	123.8	124.9	1.3	1.1	0.9
	124.2	123.8				
	123.8	124.7				
Expanded scale	125.11	124.48				
	124.74	124.16	124.63	0.45	0.37	0.5
	124.48	124.85				

This technique was applied to the determination of lithium in three different glass beads which are to be used for neutron flux measurements. To obtain a realistic value of the precision of the method, the analysis of the samples was performed over a period of two weeks by two operators. The results are listed in table 19. From these data and subsequent work the major limiting factor of the method was the reproducibility in the preparation of standards.

The successful analysis with a precision and accuracy of better than 0.2 percent met the requirements for a neutron flux monitor. In addition, this technique helped to conserve precious sample needed for the analysis of other constituents.

Table 19. Determination of lithium in glass beads for neutron flux measurement.

Material	No. of determinations	Li ₂ O, %	Std. dev.	Rel. std. dev., %	Rel. std. error, %	
Dy ₂ O ₃ Glass-A	6	10.177	.013	.13		
	6	10.147	.025	.25		
	-B 6	10.065	.024	.24		
	-C 6	10.123	.033	.33		
	3	10.067	.022	.22		
	-D 6	10.181	.014	.14		
	6	10.146	.018	.17		
	5	10.181	.10	1.0		
	<u>44</u>					
	Av. of \bar{X} :		10.139	.052	.51	.16
CoO Glass	-A 6	10.020	.023	.23		
	-B 6	10.060	.085	.85		
	6	9.989	.085	.85		
	4	9.995	.010	.10		
	-C 6	10.058	.044	.44		
	<u>7</u>	10.018	.023	.23		
	<u>35</u>					
	Av. of \bar{X} :		10.040	.058	.57	.20
	In ₂ O ₃ Glass-A	5	10.008	.022	.22	
		-B 6	10.075	.028	.28	
-C 4		10.174	.035	.35		
4		10.070	.019	.19		
<u>4</u>		10.131	.035	.35		
<u>23</u>						
Av. of \bar{X} :			10.087	.064	.64	.28

E. Determination of Arsenic by Atomic Absorption

Spectrophotometry

1. Introduction

A new method was developed for the determination of arsenic in standard reference material of high-purity selenium and cast iron by AAS. It involved the establishing of

new parameters for the AAS measurement and a new approach to the separation and preconcentration of arsenic. This investigation led to a significant improvement in accuracy of the arsenic value.

Since the resonance lines of arsenic are below 2000Å, very little information was available on the AAS determination of arsenic [20]. Arsenic has three resonance lines which are located at 1890, 1937, and 1972Å. A preliminary survey of these lines was made and the sensitivities were found to be in a ratio of 1:1:2, respectively. The line at 1890Å was greatly affected by the aspirating media and the presence of other cations. For this reason the line at the longer wavelength (1937Å) was chosen for further investigation. The variables studied were sources of monochromatic light, effect of multiple pass system, burners, oxidant-fuel system, dissolution of sample, and ways of separating and preconcentration of the arsenic.

2. New Source of Monochromatic Light

Since the resonance line of interest is in the far ultraviolet region of the spectrum, a line source of high intensity is required. The hollow cathode for arsenic is very difficult to produce and has relative low intensity. The high frequency electrodeless discharge tube described by Meggers and Westfall [21] was investigated as a line source. This source was found to be stable and extremely intense for arsenic. This type of source should prove useful in future work for many elements.

3. Effect of Oxidant Fuel

Various oxidant-fuel systems and nebulizer burners were tested and the most satisfactory system was an argon-hydrogen flame with a Zeiss burner. A limit of detection of less

than 0.5 ppm of arsenic was obtained in this system. All systems using oxygen or acetylene were found to have strong absorption in this region of the spectrum. With the argon-hydrogen flame the light from the radiating source could be passed three times through the flame without serious loss of radiation. Of the interferences investigated, carbon radicals in the flame from the acetylene or organic solvents and high concentrations of solids produced a high absorption blank. This difficulty was overcome by the use of hydrogen as the fuel and the removal of organic material and high solids from the nebulized solution.

4. Determination of Arsenic in High-Purity Selenium

Another phase of this study was the investigation of preconcentration methods. In the determination of arsenic in high-purity selenium several procedures were investigated for its separation. It was found that selenium could be precipitated with sulfurous acid from a 2N HCl medium without loss of arsenic. Since losses of As^{+3} may occur during evaporation from an HCl medium, the arsenic was concentrated by an extraction with diethylammonium diethyldithiocarbamate (DEDC) in chloroform from 2N HCl. This extraction step was found to give excellent recoveries at a ratio of aqueous to organic of 20 to 1. To make the extraction of arsenic quantitative, the arsenic was reduced to As^{+3} with KI and $Na_2S_2O_5$ in a hot water bath ($55^{\circ}C$). Since the organic constituents were found to interfere in the final determination, the arsenic was stripped with copper from the DEDC in chloroform by an exchange reaction. The resulting solution was analyzed for arsenic by AAS.

By this method the arsenic content for a 4-5 gram sample of high-purity selenium was found to be less than

one $\mu\text{g/g}$. All the separations were followed with ^{77}As and by the standard addition technique.

5. Determination of Arsenic in Cast Iron

In the determination of arsenic in cast iron several additional problems were encountered. It was found with the aid of ^{77}As that losses of arsenic do occur during the dissolution of the cast iron with HNO_3 or HNO_3 plus HCl when the operation is carried out in a covered beaker. However, no loss was observed if the dissolution is performed in a conical flask. Several procedures were investigated for the removal of the major component, iron. Of the methods surveyed, 2-thenoyltrifluoroacetone in CCl_4 was found to be an excellent extractant of iron without a loss of arsenic. This general approach is described in the literature [22]. By this method as much as 0.5 g of iron was removed within 30 minutes. The arsenic in the aqueous solution was then extracted with DEDC as described previously. This procedure is being used to determine arsenic in several SRM cast iron samples.

F. Analysis of SRM by Atomic Absorption and Flame Emission Spectrophotometry

During the past year considerable effort has been spent in the analysis of SRM by atomic absorption as well as flame emission spectrophotometry. A summary of SRM work is given in tables 20 and 21. The copper in white iron was determined by AAS without any preconcentration or separation using a total consumption burner. In each case recoveries were checked by the standard addition method [15].

T. C. Rains

Table 20. Summary of analysis performed by flame emission spectrophotometry of standard reference material.

NBS SRM No.	Material	Element	No. of determinations	Conc., %	Std. dev.	Rel. std. dev., %
1a*	Limestone	Na ₂ O	8	0.316	.008	3
1b			16	0.040	.003	7
88*	Dolomite	Na ₂ O	6	0.024	.002	7
88a			12	0.0088	.0006	7
97*	Flint clay	Li ₂ O	6	0.226	.003	1.5
97a			17	0.120	.001	1
97*	Flint clay	Na ₂ O	3	0.065	.002	3
97a			11	0.034	.001	3
97*	Flint clay	K ₂ O	6	0.532	.011	2
97a			18	0.528	.008	1
98*	Plastic clay	Li ₂ O	5	0.0256	.0001	0.5
98a			17	0.0749	.0011	1
98*	Plastic clay	Na ₂ O	4	0.268	.001	4
98a			12	0.080	.002	2
98*	Plastic clay	K ₂ O	4	3.18	.04	1
98a			48	1.06	.01	1
<u>µg/g</u>						
727	RbCl	Li	4	<0.2	-	-
		Na	4	2.3	.3	11
		K	4	420	9	2
		Cs	6	24	3	14
1121	Cu-Be alloy	Ag	8	50	2	4
1122			8	54	3	5
1123			8	87	3	4

* Control sample.

Table 21. Summary of analysis performed for copper by atomic absorption spectrophotometry of standard reference material.

<u>SRM No.</u>	<u>Material</u>	<u>No. of determi- nations</u>	<u>Conc.,%</u>	<u>Std. dev.</u>	<u>Rel. std. dev., %</u>
3b*	White iron	7	0.051	.001	2
3c	White iron	10	0.055	.001	2
4i*	White iron	8	0.256	.008	3
4j	White iron	56	0.238	.008	3
30f	White iron	13	0.076	.002	2
13e*	Steel	6	0.110	.002	2
163	Steel	8	.0921	.0011	1

* Control sample.

4. SPECTROPHOTOMETRY AND SPECTROFLUORIMETRY

A. Introduction

Described in the following section are the philosophy, some of the approaches being tried, and the pertinent results obtained during the past year in the twin areas of spectrophotometry and spectrofluorimetry. While greater sensitivity and selectivity have again been the principal goals, precision and accuracy have also been given considerable attention. The evolution of improved methods based on the formation of ternary complexes and on the controlled dissolution of samples in closed systems has been especially encouraging. Likewise, the speed and simplicity with which high-accuracy results have been obtained by differential spectrophotometry suggests the need for even more extensive studies in this area. While some experience has been gained in the use of variable path-length cells and scale expansion, the added advantages of digital readouts have thus far not been exploited. Although the studies in fluorimetry are still very much in the planning stage, considerable effort has been spent in evaluating several of the currently available instruments. An objective summary of this study is given in the text.

B. Study of Ternary Systems

Although a tremendous amount of effort has gone into the development of more sensitive and selective chelating agents, the net result has not been overly rewarding. Most of the complex or chelate systems that are presently used in inorganic absorption spectrophotometry are binary ones, i.e., one or more metal ions are combined with one or more ligand molecules of the same type. Unfortunately,

especially from the standpoint of trace analysis, such systems are generally not very selective and may prove unsuitable in practical applications unless adequate separation procedures can be developed. While one of the more successful approaches to selectivity in the past has been the introduction of steric hindrance into reagent molecules near their chelating center, one should be cautioned that such improvement is closely related to the manner in which they are later used. Thus, although a reagent is specific within the context of spectrophotometry the same may not be true when it is utilized in an extraction system.

In recent years a more promising approach to selectivity has been through the use of ternary complexes. In these systems not one but two different ligands react with the central ion. As a result the selectivity of such systems can be considerably improved since an additional variable has been introduced which may eliminate many potential interferences. An added dividend in that sensitivity may also be higher because it is often possible for a much more complex absorbing organic molecule to be placed around the metal ion.

There are two principal ways in which ternary complexes can be formed [23]. In the first, the situation must arise that one ligand does not fully satisfy all the coordinative requirements of the ion and therefore a second ligand species may still react, i.e., neither ligand alone must form a coordination-saturated complex with the ion. The other alternative is that the first ligand, on entering the coordination sphere of the cation, satisfies it only in a dative fashion so that the primary complex still bears

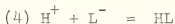
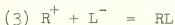
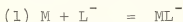
an overall positive or negative charge which may then ion-associate with an appropriate dyestuff or other similar molecule.

As illustrative of our experience with the first type was the determination of zirconium in a variety of white cast irons through utilization of the Zr-EDTA-Pyrocatechol Violet complex. This reaction was first described by Flaschka and Sadek [24], and more recently has been studied in detail by Raber [25]. It exploits the unique property of zirconium (and hafnium) of being able to present 8 coordination positions for bonding. Since EDTA is capable of utilizing only 6 of these, 2 positions remain for additional complexation. In this instance these latter 2 positions are occupied by a Pyrocatechol Violet (PCV) molecule and the overall stoichiometry is Zr-EDTA-PCV. More recently, we have made numerous unsuccessful attempts to incorporate the Zr-EDTA complex into a solvent extractable 4-membered ion-association system of the type $R^+[Zr-EDTA-R']^-$. Intorre and Martell [26], however, have studied a number of mixed complexes of the type Zr-EDTA-R in which the R ligand contained one or more sulfonic acid groups. Combining their results with the recent discovery [27] that some chelating agents containing a single sulfonic acid group can be extracted may eventually prove useful. Furthermore, it may be possible to extract the Zr-EDTA-PCV complex directly in this manner.

The second type of ternary complex, the ion-association system, has commanded most of our attention to date. During the past year we have described [28] a highly reliable method for antimony in various materials, especially cast irons. In this method an Sb-complex of the type $R^+SbCl_6^-$

is extracted from a strongly acidic solution leaving the excess dye, R^+ , in the aqueous phase. West and co-workers have described similar procedures [29,30] for a number of metals that are initially complexed with 1,10-phenanthroline and subsequently with Bromopyrogallol Red or Rose Bengal Extra.

During the course of studying the [Brilliant Green]⁺ $SbCl_6^-$ reaction, it became apparent that for such systems to have general applicability detailed information must be obtained regarding the direct interaction of such dyes with the intermediate ligand and also the effect of acidity on such interactions. The principal reactions that must be considered in such systems are as follows:

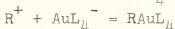
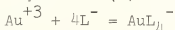


Where: M = metal ion.

L^- = simple intermediate ligand such as F^- , Cl^- , Br^- , CNS^- , etc.

R^+ = large dye cation such as derived from Crystal Violet, Brilliant Green, Methylene Blue, etc.

In the study to be described Au^{+3} was selected as the pilot cation in preference to Sb^{+5} because it does not form non-extractable hydroxy complexes. The desired sequence of reactions as given by equations (1) and (2) then becomes:



Reactions (3) and (4) represent competing reactions and must be eliminated or at least minimized in order for such systems to be applicable. To do so an extensive investigation of several R^+ cations was carried out with various L^- ligands at three concentrations and at three acidities. The extent to which reactions (3) and (4) occurred was studied by making absorbance measurements on benzene extracts. The analytical conditions were as follows:

$$L^- \text{ conc.} = 10^{-3}, 10^{-2}, \text{ and } 10^{-1}M$$

$$H^+ \text{ conc.} = 10^{-2}, 1 \text{ and } 6M H_2SO_4$$

$$R^+ = 0.01\% \text{ w/v}$$

Aqueous Vol.= 25 ml

Organic Vol.= 5 ml

Table 22 gives detailed results for the extraction of Crystal Violet and Brilliant Green as simple binary complexes.

Table 22. Extraction of Crystal Violet and Brilliant Green as binary complexes.

Ligand	Ligand Conc. Added, M	H^+ Conc., M	Absorbance, 1-cm cell	
			Crystal Violet 590 μ	Brilliant Green 625 μ
Cl^-	10^{-3}	10^{-2}	0.010	0.040
	10^{-2}	10^{-2}	0.007	0.056
	10^{-1}	10^{-2}	0.017	-
Cl^-	10^{-3}	1	0.005	0.010
	10^{-2}	1	0.002	0.019
	10^{-1}	1	0.001	-
Cl^-	10^{-3}	6	0.005	0.000
	10^{-2}	6	0.003	0.000
	10^{-1}	6	0.000	0.000

(continued)

Table 22. Extraction of Crystal Violet and Brilliant Green as binary complexes (continued).

Ligand	Ligand Conc. Added, M	H ⁺ Conc., M	Absorbance, 1-cm cell	
			Crystal Violet 590 m μ	Brilliant Green 625 m μ
Br ⁻	10 ⁻³	10 ⁻²	0.022	-
	10 ⁻²	10 ⁻²	0.094	-
	10 ⁻¹	10 ⁻²	0.990	-
Br ⁻	10 ⁻³	1	0.007	-
	10 ⁻²	1	0.009	-
	10 ⁻¹	1	0.008	-
Br ⁻	10 ⁻³	6	0.000	-
	10 ⁻²	6	0.000	-
	10 ⁻¹	6	0.000	-
CNS ⁻	10 ⁻³	10 ⁻²	inf.	inf.
	10 ⁻²	10 ⁻²	inf.	inf.
	10 ⁻¹	10	inf.	inf.
CNS ⁻	10 ⁻³	1	0.010	0.052
	10 ⁻²	1	0.039	0.680
	10 ⁻¹	1	inf.	inf.
CNS ⁻	10 ⁻³	6	0.000	0.000
	10 ⁻²	6	0.005	0.008
	10 ⁻¹	6	0.010	0.039
I ⁻	10 ⁻³	10 ⁻²	0.395 ^a	-
	10 ⁻²	10 ⁻²	inf. ^a	-
	10 ⁻¹	10 ⁻²	inf. ^a	-
I ⁻	10 ⁻³	1	0.071 ^a	-
	10 ⁻²	1	0.775 ^a	-
	10 ⁻¹	1	inf. ^a	-
I ⁻	10 ⁻³	6	0.018 ^a	-
	10 ⁻²	6	0.053 ^a	-
	10 ⁻¹	6	-	-

(continued)

Table 22. Extraction of Crystal Violet and Brilliant Green as binary complexes (continued).

Ligand	Ligand Conc. Added, M	H ⁺ Conc., M	Absorbance, 1-cm cell	
			Crystal Violet 590 m μ	Brilliant Green 625 m μ
CCl ₃ COO ⁻	10 ⁻³	10 ⁻²	1.42	2.0
	10 ⁻²	10 ⁻²	inf.	inf.
	10 ⁻¹	10	inf.	inf.
CCl ₃ COO ⁻	10 ⁻³	1	0.015	0.046
	10 ⁻²	1	-	inf.
	10 ⁻¹	1	inf.	inf.
CCl ₃ COO ⁻	10 ⁻³	6	0.010	0.010
	10 ⁻²	6	0.025	0.080
	10 ⁻¹	6	0.039	0.142
F ⁻	10 ⁻³	10 ⁻²	0.000	0.003
	10 ⁻²	10 ⁻²	0.000	0.002
	10 ⁻¹	10 ⁻²	0.000	0.005
F ⁻	10 ⁻³	1	0.000	0.000
	10 ⁻²	1	0.001	0.001
	10 ⁻¹	1	0.004	0.001
F ⁻	10 ⁻³	6	0.000	0.000
	10 ⁻²	6	0.000	0.000
	10 ⁻¹	6	0.002	0.001
None	-	10 ⁻²	0.015	-
	-	1	0.014	-
	-	6	0.017	-
C ₇ H ₅ O ₂ ⁻	10 ⁻³	10 ⁻²	-	0.030
	10 ⁻¹	10 ⁻²	-	1.75
C ₇ H ₅ O ₂ ⁻	10 ⁻³	1	-	pptd.
	10 ⁻²	1	-	pptd.
	10 ⁻¹	1	-	pptd.
CH ₃ COO ⁻	10 ⁻¹	10 ⁻²	-	0.055
	10 ⁻¹	1	-	0.037
	10 ⁻¹	6	-	0.001

^aAbsorbance due primarily to air oxidation of I⁻.

From the results given it is apparent that reaction (3) becomes a serious problem in those extraction-spectrophotometric systems when the intermediate ligand concentration and acidity reach certain designated values. Not only are the reagent "blanks" quite high in such instances but also their stability is much less than the corresponding ternary complexes. As seen in table 22, CNS^- and CCl_3COO^- extract considerably at low acidities but their effects become much less pronounced at high acid concentrations. Bromide ion is somewhat intermediate in behavior whereas the smaller Cl^- and F^- ions exhibit negligible extraction over the concentration and acidity ranges investigated.

In comparing the extraction ability of the two dyes it is seen that, under essentially the same conditions of acidity and ligand concentration, the absorbances obtained with Brilliant Green are generally higher than those obtained with Crystal Violet. Undoubtedly these differences are attributable to the lower solubility of the reaction products of the former dye. While Crystal Violet contains only methyl-substituted amino groups, Brilliant Green has two diethyl-substituted ones which, by means of their greater inductive effect would be expected to more effectively stabilize their respective dye cation.

The availability of data of this nature should allow one to more readily select the optimum conditions for the selective formation of a particular ternary complex. The only additional question is whether, under the conditions selected, there is sufficient intermediate ligand available to complex the metal ion.

C. Spectrofluorimetry

1. Introduction

The sensitivity of absorbance measurements is limited by two factors, both of which suggest that the lower limit of detection is about 10^{-8} M for any complex in solution. The first factor is the inability of most spectrophotometers to measure less than 0.001 absorbance units while the second is that all molecules have a limited capacity to absorb light. Braude [31] has discussed this point extensively and has shown that the maximum extinction coefficient for any organic molecule is about 100,000. Scaling down of solution volume has permitted some increase in absolute sensitivity but the problems associated with reproducible cell positioning has frequently masked any marked improvement. As a result of these limitations we have recently initiated studies into the closely related field of fluorescence. In these systems greater selectivity is achieved because of the added characteristic excitation variable whereas sensitivity is also generally improved because one is no longer concerned with measuring a ratio of light intensities. While instrumental amplification in absorption spectrophotometry only permits the use of narrower slits, amplification of a fluorescence signal leads to a smaller detection limit whose ultimate value is governed by signal-to-noise considerations. Furthermore, measurements on small volumes contained in capillaries are also much simpler in the case of fluorescence. No longer does one need to carefully mount such cells in an end-on position, but, when mounted vertically, the effect of scattered light may become a limiting factor.

2. Discussion and Results

As the first step in our investigations of fluorescence we have made an effort to evaluate several commercial instruments. The compound studied was Rhodamine 6G, the butyl derivative of Rhodamine B. Structurally, both of these materials are quite similar to the triphenylmethane dyes previously employed in spectrophotometric studies and can readily be incorporated into ternary systems. They are especially well suited for evaluation purposes since they have closely overlapping excitation and emission spectra and consequently any problems associated with instrumental light scatter should be readily discernable. In addition, their excitation spectra, as typified in figure 23, exhibit considerable structure. For the purposes of comparison, the absorption spectrum of Rhodamine 6G is given in figure 24. Its expected similarity to the excitation spectrum is quite apparent. An important difference, however, is the fact that in the former case the solution is essentially 500 times more dilute (100×5) than the solution on which the absorption measurements were taken.

3. Instrument Evaluation

Three instruments have recently been under study. For the purpose of evaluation they are identified only as instruments A, B, and C. All yield essentially non-corrected spectra, although C is capable of operating in a ratio mode insofar as the source is concerned. A brief summary of their design and capabilities are given in table 23.

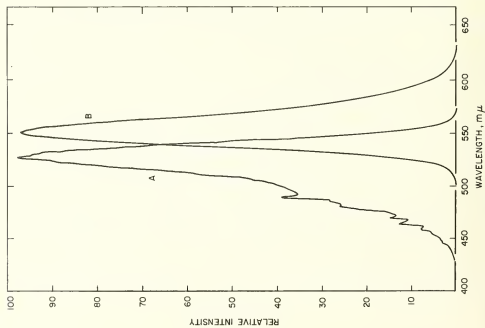


Figure 23. Uncorrected excitation (A) and emission (B) spectra of Rhodamine 6G in ethanol, concentration = 40 ppb.

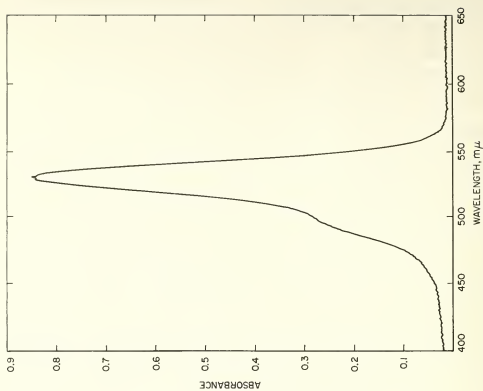


Figure 24. Absorption spectrum of 4 ppm Rhodamine 6G in ethanol, 5-cm light path.

Table 23. Comparison of three spectrofluorimeters.

<u>Instrument Ident.</u>	<u>A</u>	<u>B</u>	<u>C</u>
Monochromators	Two single gratings	Four single gratings	Two single gratings
Filter facilities	Yes	Yes	Yes
Range, $m\mu$	220-700	220-700	220-650; 220-800
Slits	Fixed, 1-20 $m\mu$	Fixed, 2-32 $m\mu$	Variable, 1-40 $m\mu$
Source	150-Watt xenon	150-Watt xenon	150-Watt xenon
Wavelength drive	Mechanical	Electrical	Electrical
Resolution, $m\mu$	2	2	0.5
No. scanning speeds	8	2	3
Standard sample volumes	3 ml-2 μ l	3 ml-4 μ l	3 ml-200 μ l
Scatter	Moderate	Low	Low
Approx. cost including recorder	\$6,000	\$7,000	\$8,500

4. Application to Micro Samples

Both spectrophotometric and spectrofluorimetric techniques have been considered for the analysis of micro samples. While not as broadly applicable at the moment, the fluorescence approach appears more promising not only because of the inherently higher sensitivity (100-10,000-fold) but, as previously mentioned, cell positioning is much less a problem. Recently, while attempting to extend sensitivity to a maximum, we have been able to obtain

meaningful measurements on solutions containing approximately 5 picograms of Rhodamine 6G with a signal-to-noise ratio of better than 3:1.

D. Spectrophotometric Determination of Arsenic in Cast Iron

1. Introduction

The procedure that is generally used for the wet-chemical determination of arsenic in ferrous materials is dissolution in an oxidizing acid, reduction of As(V) to As(III) and separation of the arsenic by distillation of the trihalide. This practice, however, is subject to systematic errors that lead to poor accuracy. Not only do dissolution problems compound the uncertainty of the results, but also it has recently been shown [32] that high combined carbon contents can lead to low results when a halogen acid (HX) is present. Presumably, this loss is due to the reduction of arsenic by the carbon and its subsequent volatilization as AsX_3 . Even when the carbon content is relatively small it is our opinion that low results are obtained when only a few micrograms of arsenic are present.

When the need recently arose for the accurate determination of arsenic in SRM 4j, a cast iron, we applied to advantage the procedure outlined below:

- (1) Dissolve sample in sealed tube with HCl and a small amount of $SnCl_2$.
- (2) Extract arsenic as $AsCl_3$ with chloroform.
- (3) Back extract with water and oxidize As(III) to As(V) with Br_2 .
- (4) Determine arsenic as the heteropoly molybdate, following reduction with hydrazine sulfate.

The novel features of this method are that the sample can be dissolved with no danger of losses by volatilization and, by carrying out the dissolution in hydrochloric acid, the arsenic is obtained only in the $+3$ state which is necessary for the quantitative extraction. The SnCl_2 prevents any possible oxidation of As(III) by the residual air entrapped in the sealed tube. Although in most cases the iron matrix would no doubt serve the same function, the fact that one obtains no ferric color during dissolution also verifies that the system was air-tight. If by chance any colored solutions are obtained, they are discarded.

2. Procedure

A 0.1-gram sample is added to a dissolution vial followed by 10 ml concentrated HCl and 4 mg Sn(II). The mixture is immediately frozen in a 1:1 carbon tetrachloride and chloroform-dry ice slush and the tip sealed off. The vial is placed in a steel shell, dry ice is added to compensate for pressure that will develop upon dissolution and the whole is heated overnight at 250°C . Upon removing from the furnace and cooling, the sample is taken from the shell, frozen, and the tip opened by means of a torch. It is quickly thawed under tap water and transferred to a 60-ml separatory funnel. The vial is rinsed with 5 ml concentrated HCl and then 5 ml of concentrated H_2SO_4 is cautiously added to the funnel. Before adding the H_2SO_4 prior cooling of the sample in ice water is advisable to minimize the heat of mixing and the evolution of HCl gas. The sample is then extracted twice with 20-ml portions of chloroform by shaking vigorously for 2 minutes. The combined extracts are backwashed with two 10-ml portions of H_2O (1 minute shaking time) and the aqueous layers transferred to a

25-ml volumetric. Three-tenths ml of H_2SO_4 is added followed by 1 drop of saturated Br_2 water. Upon dilution to volume an appropriate aliquot is taken and analyzed by the molybdenum blue procedure [33].

3. Results and Discussion

Table 24 lists the results obtained on SRM 4j when the above procedure was employed.

Table 24. Arsenic in SRM 4j.

<u>Can number</u>	<u>Wt % Arsenic</u>
3	0.0270
9	0.0282
13	0.0285
16	0.0272
Average and standard deviation:	0.0277 \pm 0.0006
Recommended value and estimated uncertainty:	0.028 \pm 0.001

The accuracy of the above values was ascertained from tracer studies, from spike additions and from analysis of control sample 41. The average value obtained for the latter sample was 0.0202 percent as compared with the certificate value of 0.018 percent. The certificate result was based on the average of those obtained by four cooperating laboratories, i.e., 0.018, 0.016, 0.020, and 0.017. Such variations clearly demonstrate the need for a more reliable method of determining arsenic in these types of materials.

During the course of developing the proposed procedure, tracer experiments with As^{77} showed that considerable arsenic was retained in the insoluble residue, especially

when relatively large samples were analyzed. At the 0.5 gram level approximately 35 percent of the tracer was found in the residue while at the 0.1 gram level less than 5 percent was retained. Consequently, as pointed out in the procedure, a maximum sample size of about 0.1 gram is recommended. It is possible that a closer examination of the dissolution temperature on the percentage of arsenic retained will permit the use of larger samples. While dissolutions in this study were carried out at temperatures near 250°C it is conceivable that some lower temperature may be just as effective insofar as dissolution is concerned, but that absorption on the SiO₂ (a probable mechanism) may be somewhat less.

E. Arsenic in High-Purity Selenium

Arsenic has recently been determined in high-purity selenium by the heteropoly molybdenum blue procedure. It was quantitatively separated from the matrix (>99% from tracer results) by reduction of the latter to the metal with SO₂. The procedure used was essentially the one recommended by Reed [34].

The major drawback encountered in this study was the variability of the reagent blanks. This difficulty was ultimately attributed to impurities in the plant steam which was initially employed in the evaporation steps. By changing to a small electrically-heated water bath this variability was reduced approximately tenfold. However, when this procedure was applied to the analysis of 1-gram samples the residual variation still limited the matrix sensitivity to about 2 ppm. As a result, we have only been able to report the arsenic content of SRM 726 (99.9% selenium) to be \leq 2 ppm.

F. High Precision Differential Spectrophotometry

1. Introduction

Differential techniques are now being employed to extend spectrophotometric methods into the domain of macro-analysis. While such determinations have been carried out in the past primarily by gravimetry and titrimetry, the differential spectrophotometric approach today frequently presents itself as a simple and rapid alternative. Although the precision presently obtainable is only about one part in a thousand, the use of digital readouts and averaging circuits and the closer control of experimental parameters should ultimately yield values at least 10-fold better than this.

2. Differential Spectrophotometric Determination of Dysprosium in Glass Beads

A high precision method has been investigated for the determination of dysprosium in small glass beads which are ultimately to be used as monitors of neutron flux. The nominal composition of these beads was:

B_2O_3	(92% B^{10})	35%
SiO_2		30%
Dy_2O_3		20%
Li_2O		10%
Al_2O_3		5%

For the results to be useful a minimum value of ± 0.25 percent of the amount present was established as the cut-off point. Since the sample was limited and additional analyses would be required by other techniques, it was further advised that as much sample as possible be conserved.

As is well known, the absorption spectra of the rare-earth ions are characterized by a number of exceedingly sharp peaks. For good quantitative analysis a high resolution monochromator is both desirable and necessary. Because these ions have relatively low molar absorptivity indexes and require no additional complexing agent, they are especially well suited for differential analysis.

a. Development of method. Perchloric acid solutions of Dy_2O_3 exhibit three major absorption peaks, at 350, 807, and 909 $m\mu$. While all are of nearly equal sensitivity, measurements at the latter two wavelengths are complicated by OH absorption and require that the water content be closely controlled. In actual sample analysis, however, it was found that sufficient control of $HClO_4$ content (and therefore H_2O) was not possible because of the vigorous fuming associated with the dissolution step. These two wavelengths were subsequently abandoned in favor of the 350 $m\mu$ peak.

By use of scale expansion (full scale = 0.100 A_g), absorbances could be measured to the nearest 0.0002 A_g unit. This variation represented an uncertainty in the dysprosium concentration of ± 0.005 mg/ml. Thus, by making differential measurements on samples containing approximately 2 mg Dy/ml (the reference solution contained 1.75 mg Dy/ml), it was possible to reduce the relative error to the prescribed 0.25 percent.

b. Procedure. Half-gram samples of the crushed glass were taken for analysis, treated with 4 ml $HClO_4$ and heated to strong fumes with several additions of HF. A clear solution was normally obtained after 3-4 evaporations. Upon dilution to 50 ml, spectrophotometric measurements

were then carried out at 350 $m\mu$ in 10-cm cells. To facilitate the establishment of the baseline and to obtain more meaningful sample measurements, the following procedure is recommended:

- (1) Record differential sample absorbance at 350 $m\mu$ while keeping wavelength fixed.
- (2) Record differential sample absorbance at 400 $m\mu$, again keeping wavelength fixed.
- (3) Scan from 400 to 325 $m\mu$.
- (4) Record differential sample absorbance at 350 $m\mu$.
- (5) Subtract the best estimate of (2) from the average of (1), (3), and (4) to obtain the net absorbance and convert to dysprosium by means of a calibration curve.

c. Results and conclusions. The results obtained for the dysprosium content of several samples of glass beads are listed in table 25. The slope of the calibration curve was 0.129 $A_s/mg/ml$.

Table 25. Dysprosium content of glass beads.

<u>Sample</u>	<u>Dy₂O₃, %</u>
1	19.93
2	19.88
3	19.93

While slightly greater instrument noise was observed at the 350 $m\mu$ setting than at either 807 or 909 $m\mu$, the uncertainty was still considerably less than that caused by OH absorption and variable H₂O content at the longer wavelengths. The accuracy of the results was established by comparison with standard solutions (w/w) prepared from spec-pure Dy₂O₃.

3. Other Studies

In addition to dysprosium, other systems that are currently under investigation are those of cobalt and of chromium. The results of these studies will be published in a subsequent report.

G. Miscellaneous Spectrophotometric Results Obtained on Various Standard Reference Materials

Summarized in table 26 are the results obtained for six elements of interest in a variety of SRM samples. The methods used for Mn and P are standard ASTM procedures, while that for nickel has been fully described in an earlier report [10].

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Table 26. Miscellaneous spectrophotometric results.

<u>Element</u>	<u>SRM No.</u>	<u>Kind</u>	<u>No. of determinations</u>	<u>Percent found</u>	<u>Rel. std. dev.,%</u>	<u>Reference</u>
Mo	3b	White iron	4	0.0020	14	35
	3c	White iron	5	0.0019	7	
	4j	Cast iron	8	0.080	2	
	163	52100 steel	8	0.0296	0.9	
Ti	4j	Cast iron	8	0.0514	0.7	36
Mn	3b	White iron	2	0.351	0.3	37
	3c	White iron	2	0.301	0.3	
	4j	Cast iron	4	0.781	0.4	
	30f	Cr-V(SAE 6150) steel	4	0.790	0.1	
	163	52100 steel	4	0.894	0.4	

(continued)

Table 26. Miscellaneous spectrophotometric results
(continued).

<u>Element</u>	<u>SRM No.</u>	<u>Kind</u>	<u>No. of determinations</u>	<u>Percent found</u>	<u>Rel. std. dev., %</u>	<u>Reference</u>
Ni	3b	White iron	2	0.013	1.5	10
	3c	White iron	2	0.014	1.5	
	4j	Cast iron	4	0.068	2	
	30f	Cr-V(SAE 6150) steel	4	0.071	1	
	163	52100 steel	4	0.083	2.5	10
	1121	Be-Cu alloy	4	0.013	4	
	1122	Be-Cu alloy	4	0.012	4	
	1123	Be-Cu alloy	4	0.012	4	
P	3b	White iron	3	0.087	2	38
	3c	White iron	2	0.100	2	
	30f	Cr-V(SAE 6150) steel	5	0.010	2	
	1121	Be-Cu alloy	4	0.0048	2.5	39
	1122	Be-Cu alloy	4	0.0045	2.5	
	1123	Be-Cu alloy	4	0.0020	2.5	
Cu	4j	Cast iron	11	0.235	2.5	40

5. GASES IN METALS

A. Introduction

The determination of gases in metals has been, and will continue to be in the future, of vital importance in all sectors of the metal industry, both to the producers and the fabricators. This stems from the correlation between the interstitial content (gas components) of metals and their physical and mechanical properties. This has led to recent developments of vacuum steel-making practices on a commercial scale as well as other controlled atmosphere processes for heat treatment and fabrication in order to produce cleaner metals.

The need for oxygen standards in titanium has grown rapidly over the past few years. This is due to the increase in the applications of titanium and its alloys especially in aircraft and other aeronautic applications, as well as in general usage requiring materials of high resistance to corrosion. It has been demonstrated that the gas content of the titanium base metals has a marked effect on the hardness and other physical properties and especially on the fabricability of these materials. Most often these effects are deleterious. The ultimate answer for production and fabrication of these "cleaner metals" of all types must lie in the development of metal processing techniques which would prevent the initial introduction as well as subsequent accumulation of gas in deleterious amounts. Accurate analytical methods are, therefore, essential in control of these processes.

We have at NBS tried to supply standards by means of which these analytical procedures can be kept under control. Two new Standard Reference Materials Nos. 355 and 356,

which were issued this year, are of this nature. These samples are an unalloyed titanium and a 6 percent aluminum-4 percent vanadium titanium base alloy, which are representative of many of the titanium base materials which are now in general commercial use. These samples were certified for their oxygen content.

The problem of the determination of nitrogen in metals has also plagued the analytical chemist for many years; the determination of nitrogen by the vacuum fusion method has fallen into disrepute. There has been a general consensus of opinion that nitrogen values obtained by the chemical dissolution of the metal and the subsequent determination of the ammonia formed by titration or spectrophotometric methods were more reliable. There is reason to believe, however, that the determination of nitrogen by the vacuum fusion method is potentially as sensitive and often more accurate than any of the chemical methods now in use for the determination of nitrogen in metals.

We have, therefore, been investigating variations of the vacuum fusion method. Mainly, a crucible arrangement is employed by means of which it is possible to empty the crucible between each analysis without breaking the vacuum and thus analyze each sample in an effectively clean out-gassed crucible. Also, the role of nodulizing alloys as additions which will increase the fluidity of the melt have been studied.

It is possible to show that with certain materials such as ferrous metals containing high-silicon additions, the results obtained by the usual chemical methods are indeed low; and other methods such as alkaline fusion or

possibly sealed-tube dissolution methods must be employed in order to effect complete recovery of the nitrogen.

B. Production of Oxygen Standards for Titanium Base Metals

1. Introduction

The issuance of two Standard Reference Materials Nos. 355 and 356 for oxygen content in unalloyed titanium and in 6 percent aluminum-4 percent vanadium titanium alloy is the first certification of a non-ferrous material for oxygen content, thus bringing to completion: (1) the lengthy process of developing suitable test methods, (2) selecting and procuring adequate materials, and (3) the testing necessary for proving homogeneity and certifying oxygen content of the material.

2. Sampling and Method of Analysis

The Standard Reference Materials 355 and 356 are in the form of 1/2" and .245" diameter rods respectively, and are 2 inches long. The samples were analyzed at NBS using the following conditions:

- (1) Method - Vacuum Fusion.
- (2) Furnace Temperature - 1950°C.
- (3) Initial Furnace Pressure - $<10^{-5}$ Torr.
- (4) Collection Time - 4 minutes.
- (5) Bath Material - Platinum (2 to 3 grams).
- (6) Flux Material - Platinum (Pt:Sample = 10:1).
- (7) Carbon Monoxide Determination - Infrared Absorption.

The material received was in the form of four-inch bars, centerless ground, that has been cut from the original rods and marked in such a manner as to retain the positional relationship of each piece with respect to all the others. In the case of the unalloyed titanium (355) there were 18

original long bars, and in the case of the 6 percent Al-4 percent V alloy (356) there were seven original long bars. Samples were taken from both ends of each bar as well as a sample from the center. These samples were retained for homogeneity testing and analysis.

It was found that a slice with a thickness of approximately 0.1 inch, cut from the original bar stock that was then quartered through the center with a jeweler's hacksaw, produced a sample that was representative of the total cross section of the bar and of the proper size for analysis. The surfaces of these specimens were then cleaned by careful filing with a clean, oil-free fine mill file. The cleaned sample was then wrapped in platinum wire that had been specially prepared to have a low oxygen content. The ratio of the weight of platinum to sample was maintained at 10 to 1. The sample with platinum flux was then dropped into a previously outgassed ($>2100^{\circ}\text{C}$) graphite crucible containing 2 to 3 grams of platinum as a bath material.

When the sample is dropped into the hot crucible at 1950°C a reaction takes place which is very strongly exothermic, as indicated by a sudden flash when the sample and platinum melt. This exothermic reaction aids in the quantitative recovery of the oxygen from the titanium. It was observed that when this reaction is not evident low recovery of oxygen always occurs.

The gases evolved are then pumped into the gas measurement system by means of a high-speed oil diffusion pump (150 liters/sec.), and the oxygen is determined as carbon monoxide by an infrared absorption measurement.

Blanks were determined after every fourth sample. The value of the mean of these blanks was six micrograms per

minute. In this case, four-minute collection periods were used for both the blank and the sample. Whenever unusual variations in the blank were noted, experimental conditions were checked and tests were repeated until a normal blank was attained.

3. Discussion of Results

The values obtained on the two titanium base materials are shown in tables 27 and 28. In order to obtain information on the homogeneity of the material as well as the oxygen content of the material, the original rods were sampled at each end and the center, and a single rod was also analyzed at all three positions throughout the course of the investigation.

Table 27. Unalloyed titanium.

<u>Material</u>	<u>No. of det.</u>	<u>Oxygen mean, ppm</u>	<u>Std. dev. ppm</u>	<u>Rel. std. dev., %</u>
18 rods sampled, both ends & center	54	3031	57	1.9
Single rod sampled, both ends & center	27	3067	48	1.6

Table 28. 6% Al - 4% V Titanium alloy.

<u>Material</u>	<u>No. of det.</u>	<u>Oxygen mean, ppm</u>	<u>Std. dev. ppm</u>	<u>Rel. std. dev., %</u>
7 rods sampled, both ends & center	63	1332	77	5.8
Single rod sampled, both ends & center	12	1322	50	3.8

These results indicate that the variation observed in both materials reflects at least partially the inhomogeneity present in the metal. We would expect that samples taken from a single rod of unalloyed titanium and a 6 percent

Al-4 percent V titanium alloy to show a relative standard deviation of only 1.5 percent and 4.0 percent respectively.

4. Results from Cooperating Laboratories

These same samples were also analyzed for oxygen content by several cooperating laboratories. The results are shown graphically in figures 25 and 26. From an inspection of these results it can be seen that of the twelve laboratories reporting on the unalloyed titanium, by one or more methods, seven laboratories reported mean values that were within

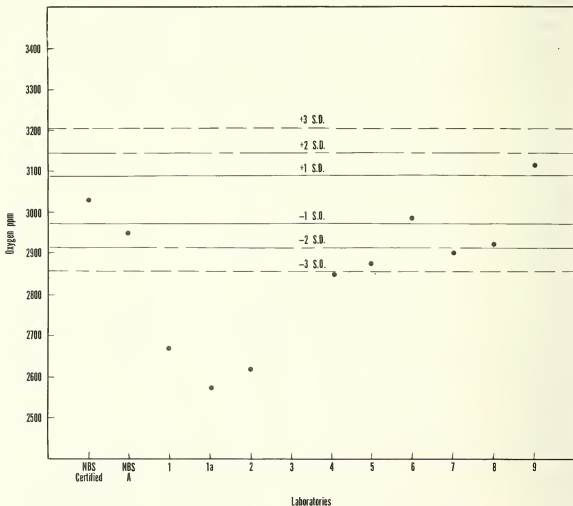


Figure 25. Unalloyed titanium.

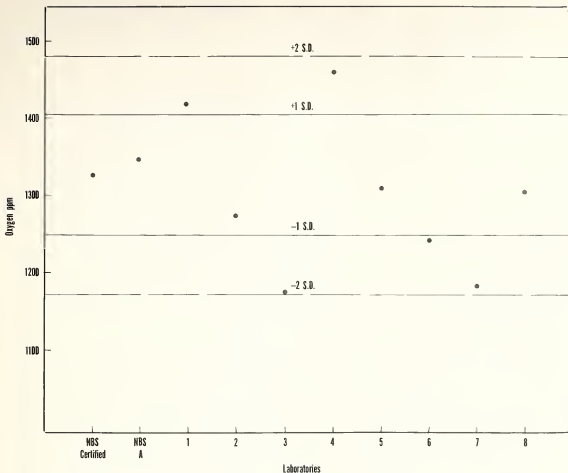


Figure 26. 6% Al 4% V - titanium alloy.

three standard deviations of the certified value. Four laboratories were within two standard deviations. In the case of the laboratories falling outside the three standard deviation limits, four of these laboratories reported mean values on the low side which is the usual bias shown when the method or equipment is not under complete control.

For the 6 percent Al-4 percent V titanium alloy, all ten laboratories reporting results were within two standard deviation units of the certified value, and five laboratories were within one standard deviation.

C. Studies of the Determination of Nitrogen in Metals by the Vacuum Fusion Method

1. Introduction

Jordan and Eckman [41] reported as early as 1929 that the total nitrogen content of steels could be quantitatively determined by the vacuum fusion method. There has developed over the years, however, a feeling of distrust with regard to nitrogen contents as determined by the typical vacuum fusion procedures. In a review article, Goward [42] discusses this question quite thoroughly and points out that the vacuum fusion procedure is potentially as sensitive as, or more sensitive than, any other method currently in use for the determination of nitrogen.

Traditionally, wet chemical methods have been in the forefront for the analysis of metals for nitrogen content. These methods date back to Boussingault [43], Kjeldahl [44], and Allen [45]. Essentially these methods consist of dissolution and digestion of the sample in excess acid, distillation of the ammonia from this solution in the presence of excess alkali, and determination of the ammonia by titration or use of color reactions. In recent years these chemical methods have been generally accepted as more reliable, as mentioned above, than the vacuum fusion procedures. However, Karp, Lewis, and Melnick [46], among others, have shown that with certain metals such as heat-treated ferrous materials containing silicon, the chemical procedures must be drastically modified in order to obtain accurate results. They employed an alkali fusion in the presence of hydrogen in order to obtain accurate results on this type of alloy.

Recently, Evens and Fassel [47], Dallmann and Fassel [48], Masson and Pearce [49], and Gerhardt, Kraus, and Froberg [50] have, by several modifications in conditions for analysis, made reliable nitrogen determinations by the vacuum fusion or inert gas fusion methods.

The basic apparatus of Gerhardt et al. [50] has been procured at NBS. Studies are being made on the determination of nitrogen in ferrous materials and the results compared with those obtained by the chemical methods.

2. Materials and Methods

For the most part, the materials studied in this program are SRM samples in chipped form which have been analyzed in the past by chemical methods or are in the process of being analyzed. Presently both methods (i.e., vacuum fusion and chemical) are being used concurrently.

The sample size used in most of the studies by vacuum fusion was approximately 0.5 grams. The chipped material was, if possible, compressed into 1/4-inch diameter pellet by means of a steel die and hydraulic pressure. This permitted a coherent sample to be obtained which may be dropped into the hot crucible without disintegration. However, with some chips, such as the cast iron, which will not form coherent compacts by cold pressing, the samples were contained in nickel capsules prepared from type 205 nickel tubing.

The samples were dropped into a previously outgassed graphite crucible ($>2100^{\circ}\text{C}$) and reacted at 1650°C along with a piece of nickel-cerium alloy that has been saturated with carbon. The weight of the Ni-Ce flux is such that the resulting melt (sample + Ni-Ce alloy) contains approximately 0.5 percent cerium.

By means of a high-speed oil diffusion pump, the gases were then transferred from the furnace section of the apparatus to the measuring chamber containing a thermal conductivity detector. This operation was completed in approximately two minutes. The gas collected consists of carbon monoxide, nitrogen, and hydrogen. The amounts present are measured by physical methods. The thermal conductivities of carbon monoxide and nitrogen are identical, but that of hydrogen is about eight times greater. It is possible to obtain the sum of the nitrogen and carbon monoxide by means of a conductivity measurement of the gas at a given total pressure. In order to obtain this constant total pressure before each measurement, pure hydrogen is admitted to the measuring chamber. The carbon monoxide fraction of the gas obtained from the sample is found by the use of an infrared analyzer. The amount of nitrogen is then found as the difference between the two results.

The blanks were determined after every sample and subtracted from it. During the period of these tests, the average blank was 2.8 micrograms per minute.

The calibration of the apparatus is achieved by means of a valving system which allows known amounts of pure gases, carbon monoxide and nitrogen, to be added to the furnace chamber from a supply vessel. These gases are added in increments of 10mm^3 and, taking into account the temperature and volume of the calibration system which are held constant, and the atmospheric pressure, the actual amounts of the gases added may be derived by computation. This calibration system is also used to recheck the analysis of the unknown sample by adding known amounts of the pure

gases through the calibration system equivalent to that obtained from the sample measurement.

One of the principal differences between this apparatus and most vacuum fusion systems is that the furnace is designed in such a manner that the crucible, which is cone shaped (figure 27), may be rotated by means of a high-speed motor and emptied of its contents by centrifugal force. This method of emptying of the crucible after every analysis provides an essentially clean melting container for every analysis. This procedure, of course, then prevents the accumulation of "Kish" or dross from previous melts as well

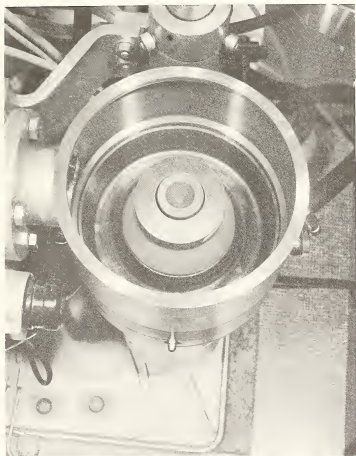


Figure 27. Spinning crucible.

as the buildup of insoluble graphite in the melt. The latter condition has been observed to give unreliable results for nitrogen. The use of the Ni-Ce alloy additive prevents the precipitation of flake graphite in the melt during the outgassing of the sample. This flake form of graphite markedly increases the viscosity of the melt. However, the addition of the Ni-Ce alloy causes the graphite to form in a spheroidal form which contributes to lower viscosity and the melt can be, under these conditions, degassed more quickly and easily. A quantitative recovery of the nitrogen in the sample can, under the above conditions, be attained.

3. Results

Table 29 shows the results obtained on SRM materials, as well as some samples for Bundesanstalt für Materialprüfung (BAM) in Berlin, by both chemical and the spinning-crucible vacuum-fusion method. Table 30 contains the reported results of Dallmann and Fassel [48] which were obtained at Iowa State University by the platinum bath-platinum flux method in both helium fusion equipment and by vacuum fusion. As can be seen from both tables, the results show good agreement with the chemical method and methods of Dallmann and Fassel. For the most part, the new results are higher in contrast to the previous low values expected from vacuum fusion techniques. This is especially noticeable in several of the cast irons and the SRM 125a steel which contain appreciable amounts of silicon. As was noted earlier, Karp, Lewis, and Melnick [46] demonstrated that materials containing appreciable amounts of silicon are very difficult to decompose by ordinary chemical procedures, and require an alkali fusion in the presence of hydrogen gas for complete recovery of the nitrogen. This

has been vividly demonstrated by sample SRM 125a on which results of 20 ppm nitrogen were obtained by regular Kjeldahl procedures, but when treated by the alkali fusion method yielded results twice as high or about 42 ppm. These higher values were also obtained by the vacuum-fusion spinning-crucible method. In the cases of SRM 30f and SRM 163, on which slightly lower results were obtained, there is some indication that the chromium content of sample 30f may be interfering. We have not as yet resolved the deficiencies observed in the analysis of sample SRM 163. Both of these problems will be studied at much greater length by both the vacuum fusion and inert gas fusion methods, and also by chemical methods as mentioned elsewhere in this report.

Table 29. Nitrogen values in standard reference material(ppm).

<u>Material</u>	<u>No. of det.</u>	<u>Chemical Kjeldahl^a method</u>	<u>No. of det.</u>	<u>Vacuum fusion spinning crucible method^a</u>
SRM 3a				
White iron Si - 1.12%	4	86 ± 4	17	147 ± 13
SRM 3b				
White iron	3	84 ± 5	23	92 ± 4
SRM 3c				
White iron	3	46 ± 4	21	52 ± 1
SRM 4i				
Cast iron Si - 1.45%	2	70	9	85 ± 5
SRM 4j				
Cast iron	7	37 ± 2	20	46 ± 3
SRM 30f				
Cr-V steel (SAE 6150)	6	75 ± 5	27	79 ± 5
SRM 163 (SAE 52100)	8	91 ± 4 80 ^b	30	73 ± 5

(continued)

Table 29. Nitrogen values in standard reference material(ppm).
(continued)

SRM 5k			
Cast iron			
S1 - 2.08%		5	161 \pm 16
SRM 5l			
Cast iron		19	58 \pm 5
SRM 6f			
Cast iron			
S1 - 1.85%		3	74 \pm 3
SRM 6g			
Cast iron		15	66 \pm 4
BAM			
Cr Mo Ni #5	118 \pm 4 ^c	10	117 \pm 2
BAM			
Steel #9	43 \pm 5 ^c	6	48 \pm 2
BAM			
Cr Ni Mn #1	682 \pm 17 ^c	4	667 \pm 6

^aStandard deviation of a single determination.

^bCooperating laboratory.

^cSamples obtained from and values attested by Bundesanstalt für Materialprüfung (BAM) in Berlin-Dahlem. These samples are presumably certified on basis of chemical solution methods for determining nitrogen.

Table 30. Comparison of nitrogen values by several methods.
(nitrogen, percent)

<u>Material</u>	<u>He- fusion^a</u>	<u>Chemical Kjeldahl method^a</u>	<u>Vacuum fusion^a</u>	<u>Vacuum fusion spinning crucible</u>	<u>Remarks</u>
125a - 3.3% High silicon	.0045		.0039	.0043 ⁺ .0004	(1)
101d, Cr 18N19 (SAE 304)	.023	0.024	0.024	.0222 ⁺ .0008	(2)
129b High sulfur (SAE x112)	0.014		.014	.0143 ⁺ .0006	(3)

Remarks: (1) 0.002 % NBS certified value.
.0042% N obtained by alkaline-fusion method.
(2) 0.024 % NBS certified value.
(3) 0.014 % NBS certified value.

^aValues of Dallmann and Fassel, Anal. Chem. 39, 133R (1967).

J. T. Sterling

6. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Oscar Menis, Section Chief

Leona M. Puffenberger, Section Secretary

R. K. Bell

T. A. Rush

B. B. Bendigo

K. M. Sappenfield

R. W. Burke

(From Jan. 1967 -
Section 310.06)

E. R. Deardorff

J. T. Sterling

T. C. Rains

S. A. Wicks

B. Publications

1. R. W. Burke and Oscar Menis, "Extraction-Spectrophotometric Determination of Antimony as a Ternary Complex", Anal. Chem. 38, 1719, November 1966.

C. Talks

1. Oscar Menis, "Differential Thermal Analysis Standards", International Conference on Thermal Analysis, Sub-Committee on Standards, Hopatcong, New Jersey, June 26, 1967.

2. J. T. Sterling, "The Determination of Nitrogen in Steels by Vacuum Fusion, Kjeldahl and Caustic Fusion", Annual Meeting, Division I, Committee E-3, A.S.T.M., San Diego, California, April 4-6, 1967.

3. J. T. Sterling, "Task Force on Oxygen in Nickel", Annual Meeting, Division I, Committee E-3, A.S.T.M., San Diego, California, April 4-6, 1967.

4. Oscar Menis and R. K. Bell, "Homogeneous Precipitation of Beryllium in a Cu-Be Alloy--A Comparison of Methods Study", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 6-10, 1967.

5. T. C. Rains and Oscar Menis, "High Precision Atomic Absorption and Flame Emission Spectrophotometry", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 6-10, 1967.

6. J. T. Sterling, B. B. Bendigo, and Oscar Menis, "The Determination of Nitrogen Ferrous Materials by the Vacuum Fusion Method", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 6-10, 1967.

7. Oscar Menis, "Chemical Spectrophotometry", Rapporteur Report, 1st Materials Research Symposium held at NBS - October 3-7, 1966.

8. T. C. Rains, "Determination of Trace Elements in High Purity Zinc by Atomic Absorption and Flame Emission Spectrophotometry", American Chemical Society, New York, N.Y., September 15, 1966.

D. Committee Activities

Oscar Menis

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

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

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

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

J. T. Sterling

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

R. K. Bell

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

T. C. Rains

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

E. Acknowledgements

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