ANL-80-41

177
8/1/80
T.S.

Dr. 1580

ANL-80-41

MAS ER

METHODS OF CHEMICAL ANALYSIS USED TO CHARACTERIZE BATTERY MATERIALS

by

Kenneth J. Jensen and W. Elane Streets

ARGONNE
NATIONAL
LABORATORY

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Prepared for the U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38

DISCLAIMER

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) among the U. S. Department of Energy, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
The University of Iowa
Iowa State University
The University of Kansas
Kansas State University
Loyola University of Chicago
Marquette University
The University of Michigan
Michigan State University
University of Minnesota
University of Missouri
Northwestern University
University of Notre Dame
The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
The University of Texas at Austin
Washington University
Wayne State University
The University of Wisconsin-Madison

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government or any agency thereof, nor any of their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A04
Microfiche copy: A01

Distribution Category:
Chemistry (~~UC-4~~) uc-94c

ANL-80-41

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

METHODS OF CHEMICAL ANALYSIS USED TO CHARACTERIZE BATTERY MATERIALS

by

Kenneth J. Jensen and W. Elane Streets

Analytical Chemistry Laboratory
Chemical Engineering Division

May 1980

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

TABLE OF CONTENTS

TABLE OF CONTENTS (contd)

TABLE OF CONTENTS (contd)

LIST OF TABLES

METHODS OF CHEMICAL ANALYSIS USED
TO CHARACTERIZE BATTERY MATERIALS

by

Kenneth J. Jensen and W. Elane Streets

ABSTRACT

Procedures are given for the chemical analysis of a variety of materials of interest in battery development and research. These materials include LiCl-KCl eutectic, Li-Al alloys, lithium sulfide, lithium aluminum chloride, calcium sulfide, titanium sulfide and various sulfides of iron, nickel, copper, and cobalt.

I. INTRODUCTION

Energy research at Argonne National Laboratory has created a need for the chemical characterization of materials used in various programs. This report details methods that have been developed and found to be useful for the chemical analysis of materials of interest in research leading to the development of advanced-design batteries. These materials include LiCl-KCl eutectic, the battery electrolyte; lithium sulfide, a discharge product in the battery cycle which is also used to assemble experimental batteries in the discharged state; lithium aluminum chloride, used to dust unstabilized boron nitride felt separators to allow good wettability of the felt by LiCl-KCl eutectic; Li-Al alloy, a negative electrode material; and a variety of sulfide compounds including FeS, FeS_2, Cu_2S, $CuFeS_2$, Co_2S_3, NiS, TiS_2, and CaS which are used either as positive electrodes or as additives to study battery performance.

Details are given for the preferred method of analysis of these compounds along with a discussion of sampling techniques, possible interferences, and reliability of the analysis. In some cases our experiences with alternative methods of analysis are presented.

These analytical methods are subject to continual revision and improvement. This report summarizes work to date and is expected to serve as a source of information to interested analysts, cooperating industrial laboratories, and others who have requested such information. It should also be of value in quality assurance efforts.

II. ANALYSIS OF LiCl-KCl EUTECTIC SALT

A. Principle of the Method

Chloride is determined by titration with standardized $AgNO_3$ using an adsorption indicator, dichlorofluorescein. Potassium is determined gravimetrically as $KClO_4$ after conversion of the sample salts to perchlorates and extraction with ethyl acetate.[1] Lithium is determined by atomic absorption spectrophotometry.

B. Reagents and Standards

(1) Dichlorofluorescein indicator (∿0.1% wt/vol[*]). Dissolve 0.1 g 2',7'-dichlorofluorescein in 70 mL ethyl alcohol plus 30 mL distilled water.

(2) Standardized silver nitrate solution (∿0.1M). Dissolve 34 g reagent grade $AgNO_3$ in 2 L water. Standardize as follows:

(a) Accurately weigh ∿150 mg reagent grade NaCl (dried at 105°C) into a 250-mL Erlenmeyer flask.

(b) Dilute to 100 mL with H_2O. Swirl until the NaCl is dissolved.

(c) Add five drops dichlorofluorescein indicator.

(d) Titrate in diffuse light with 0.1M $AgNO_3$ until a sharp, pink tinge is observed. Use magnetic stirring.

(e) Calculate the molarity of the $AgNO_3$ solution:

$$\underline{M}_{AgNO_3} = \frac{(A)}{58.44\ (B)}$$

where A = weight NaCl, mg

B = volume $AgNO_3$ used in the titration, mL.

Alternatively, the solution may be prepared from commercially available standardized $AgNO_3$ solutions. Typically, when diluted according to directions, these standards yield a 0.1000 ± 0.0005M $AgNO_3$ standard solution.

(3) Sodium chloride, NaCl - reagent grade.

(4) Ethyl acetate - reagent grade.

(5) Potassium chloride solution, 50 mg KCl/mL. Dissolve 50 g KCl in H_2O and dilute to 1 L.

(6) Lithium standards for the atomic absorption spectrophotometric determination of lithium. Prepare from reagent grade lithium chloride, LiCl. Since LiCl is very hygroscopic, weighed amounts of the salt are not used to prepare solutions of known Li^+ concentration. Rather, solutions of approximately 1 mg Li^+/mL are prepared and standardized gravimetrically by conversion to Li_2SO_4 at 600°C according to a modification of the procedure of Farquhar.[2] More dilute standards containing 1.00, 2.00, and 3.00 μg Li^+/mL are prepared from the concentrated, standardized LiCl solution. All of the lithium atomic absorption standard solutions are made up to contain 2.0 mg KCl/mL in addition to the stated lithium concentrations.

(7) Nitric acid, HNO_3 - conc. reagent grade.

(8) Perchloric acid, $HClO_4$ - conc. reagent grade.

---

[*] This expression of concentration indicates (g solute/mL solvent) x 100.

C. Preparation of Samples for Analysis

Dissolve a weighed sample in deionized water and dilute to a volume such that the final solution contains 10 mg sample/mL or more. (See Note 1, p. 9.)

D. Chloride Determination

(1) Transfer an aliquot of the sample solution containing ∿2.5 meq Cl^- into a 250-mL Erlenmeyer flask.

(2) Dilute to 100 mL with H_2O. Add five drops dichlorofluorescein indicator solution.

(3) Titrate with standardized 0.1M $AgNO_3$ solution to a definite permanent pink tinge.

(4) Calculate the concentration of chloride:

$$\text{wt \% } Cl^- = \frac{(A)(B)(3.5453)}{(C)(D)}$$

where A = mL $AgNO_3$ solution used in the titration

B = molarity of the $AgNO_3$ solution

C = aliquot fraction, $\dfrac{\text{aliquot taken for analysis, mL}}{\text{total sample volume, mL}}$

D = sample weight, g

E. Potassium Determination

(1) Transfer an aliquot of the sample solution containing 0.2-0.5 g K^+ to a 150-mL beaker.

(2) Add 5 mL conc. HNO_3 and 3 mL conc. $HClO_4$.

(3) Evaporate to dryness.

(4) Rinse down the sides of the beaker with a minimum amount of water, add 1 mL conc. $HClO_4$, and heat to copious fumes of $HClO_4$. Perform this operation with the beaker uncovered and using a heat lamp in addition to a hot plate so that after the sample has fumed, no droplets of water condense and remain on the side of the beaker.

(5) Allow the moist residue to cool for a few minutes and then add 30 mL ethyl acetate. Warm with stirring to dissolve $LiClO_4$. Allow to cool.

(6) Filter through a dry, 9-cm Whatman 42 (or equivalent) paper, keeping the bulk of the $KClO_4$ precipitate in the beaker using ethyl acetate as the wash solution. Save the filtrate.

(7) When all of the ethyl acetate has drained from the funnel stem, place the sample beaker containing the bulk of the $KClO_4$ under the filter.

(8) Wash the paper with increments of boiling H_2O. Use 140 mL of H_2O.

(9) Add five drops $HClO_4$ to the solution and evaporate to dryness.

(10) Repeat steps II-E-(4) and II-E-(5) above.

(11) Transfer the $KClO_4$ precipitate into a weighed, medium porosity, 30-mL sintered glass filtering crucible using ethyl acetate to effect the transfer. Combine this filtrate with that from II-E-(6) above if (a) lithium is determined gravimetrically after potassium separation or if (b) the filtrate is to be checked for K^+.

(12) Dry the crucible and precipitate at 170°C, cool, and weigh. Obtain the weight of the $KClO_4$ precipitate by subtracting the empty crucible weight from the weight of crucible plus $KClO_4$ precipitate.

(13) Calculate the wt % potassium:

$$\text{wt \% } K^+ = \frac{(A)(28.22)}{(B)(C)}$$

where A = weight $KClO_4$, g

B = aliquot fraction, $\frac{\text{aliquot taken for analysis, mL}}{\text{total sample volume, mL}}$

C = sample weight, g.

F. Lithium Determination

(1) Pipette an appropriately sized aliquot of the sample solution into a small (25-, 50- or 100-mL) volumetric flask such that the final Li^+ concentration will be 1-3 μg Li^+/mL. If the sample solution is too concentrated to allow such dilution in one step, make further dilutions as necessary.

(2) Add sufficient KCl solution (50 mg KCl/mL) and dilute to volume with H_2O so that the final solution contains 2.0 mg KCl/mL as well as Li^+ in the concentration range stated in II-F-(1) above.

(3) Set up the atomic absorption instrument for the determination of Li^+ at 670 nm according to the manufacturer's recommendations. (See Note 2, p. 9.)

(4) Aspirate and record the absorbances of the standards, the diluted sample solutions, and then the standards again. Measure the absorbance of the blank (2 mg KCl/mL solution) before and after each absorbance measurement and correct each measurement for this blank.

(5) Determine the concentration of Li^+ (μg Li^+/mL) in the diluted sample solution by comparison of net sample absorbance with the average net absorbance per microgram of lithium per mL as determined from the standards.

(6) Calculate the wt % lithium:

$$\text{wt \% Li}^+ = \frac{(A)(B)}{(C)(D)10^4}$$

where A = µg Li^+/mL in the aspirated sample solution as determined by comparison with the standards

B = volume, mL, of the diluted sample solution

C = aliquot fraction, $\frac{\text{sample aliquot, mL}}{\text{total sample volume, mL}}$

D = sample weight, g

G. Discussion

The salts presented for analysis to date have been quite pure, consisting of a mixture of fused LiCl-KCl with traces of barium present in some samples, as revealed by emission spectroscopy. Most of the samples analyzed contained very little water. The purpose of the analysis has usually been to determine or verify the composition of purchased salt.

Originally these samples were analyzed for Cl^- and Li^+ by gravimetric methods--Cl^- by precipitation as AgCl, and Li^+ in the combined filtrates from the K^+ determination by conversion to and weighing as Li_2SO_4 after ignition at 600°C of the carefully dried residue. Small amounts of Ba^{2+}, if present, were corrected for by dissolving the Li_2SO_4 ($BaSO_4$) residue in H_2O and then filtering and weighing the insoluble $BaSO_4$. Chloride has also been determined by the volumetric Volhard method and, in cases where sample was limited, we have employed the gravimetric determination of K^+ as potassium tetraphenylboron, $K\phi_4B$, using the procedure of Cluley.[3] Ten-milligram amounts of K^+ can be accurately determined by this method.

Table I shows the results obtained when a series of salt samples were analyzed by the recommended and alternative procedures. Comparison of the Li^+ determinations on the same five samples by atomic absorption and by weighing as Li_2SO_4 using the t-test for correlated data shows no significant difference ($t_{dep} = 1.909$).

The dependent t-test applied to the Cl^- data shows a significant difference ($t_{dep} = 5.084$) between the two methods. The Volhard data show a high bias of about 0.5% relative deviation when compared with the data obtained on the same samples titrated directly with standardized silver nitrate using an adsorption indicator (Fajan's titration).

For these materials this difference has not been of concern. In general, the Fajan's titration is used since it is simple and direct. For samples containing acid, the Volhard titration is used.

Finally it should be noted that the ratio of the total moles of cations to moles of anion is, within experimental error, 1.000 as would be expected for this material. The mass-balance data are consistent for a total ion analysis of an essentially moisture-free salt mixture.

Table I. Analysis of LiCl-KCl Eutectic Salt by Different Methods. [Lithium was determined directly by atomic absorption spectrophotometry (AAS) or gravimetrically (Grav) as Li_2SO_4 after separation and determination of potassium as $KClO_4$. Chloride was determined volumetrically with standardized silver nitrate using either an adsorption indicator (Ads) or the Volhard method (Volh). Barium was determined as $BaSO_4$ in the Li_2SO_4 residue.]

Sample Designation	wt % Li^+		wt % K^+	wt % Cl^-		wt % Ba^{2+}	Mass[a] Balance wt %	mol/g x 100			Molar Ratio $(Li^+ + K^+)/Cl^-$
	AAS	Grav	Grav	Ads	Volh	Grav		Li^+	K^+	Cl^-	
LITHCOA #3 78-0300-01	7.33	7.43	28.66	63.50	63.85	0.01	99.72	1.0636	0.7330	1.7962	1.0002
LITHCOA #7 78-0300-02	7.35	7.44	28.58	63.43	63.79	0.012	99.59	1.0664	0.7309	1.7942	1.0017
LITHCOA #10 78-0300-03	7.38	7.38	28.78	63.43	63.74	0.011	99.74	1.0636	0.7360	1.7934	1.0035
GOULD #A 78-0300-04	7.54	7.56	28.21	63.94	64.12	0.003	99.79	1.0881	0.7214	1.8061	1.0019
GOULD #B 78-0300-05	7.95	7.95	27.02	64.70	65.32	0.001	99.98	1.1457	0.6910	1.8337	1.0016

[a] The average wt % Li^+ and wt % Cl^- by the two methods were used to determine mass balance and molar ratio.

Since the salts analyzed have contained, for all practical purposes, only Li^+, K^+, and Cl^-, interferences have not presented a problem.

The chloride determination is subject to interference if halides such as Br^- and I^- are present. Other possible interferences include SCN^- and $S^=$.

The determination of Li^+ by atomic absorption is almost specific and much faster than the gravimetric determination described above. The use of a radiation buffer eliminates any reduction in absorption due to ionization of lithium in the flame; and background effects are not common at 670 nm, the wavelength used to measure the absorption of lithium. The precision of the Li^+ determination by atomic absorption has been estimated over a period of time to be ±2% relative deviation from the stated value of the standards.

Ions which could interfere in the K^+ determination include NH_4^+, Rb^+, and Cs^+. Lithium presents no interference since K^+ is cleanly separated in the procedure as evidenced by the fact that $KClO_4$ residues from some analyses have been analyzed for Li^+ by atomic absorption spectrophotometry and found to contain remarkably low concentrations of Li^+--20 ppm at most and typically much less than 10 ppm.

Attention should be drawn to the fact that, given a pure sample containing only Li^+, K^+, and Cl^-, once one of the elements has been determined the concentration of the other elements is defined. For example, with the above assumption, having determined wt % Cl^-, one can calculate wt % K^+ and wt % Li^+ from:

$$\text{wt \% Li}^+ = 0.4538\ (\text{wt \% Cl}^-) - 21.58$$

and

$$\text{wt \% K}^+ = 121.58 - 1.4538\ (\text{wt \% Cl}^-)$$

Similar equations can be derived when the Li^+ or K^+ percentage has been determined. These equations are based on the concept of mass balance and electrical neutrality:

$$\text{wt \% Cl}^- + \text{wt \% K}^+ + \text{wt \% Li}^+ = 100$$

$$\text{mol Cl}^- = \text{mol K}^+ + \text{mol Li}^+$$

and can be used to make quick estimates of the composition of pure eutectic materials utilizing the results of the determination of only one constituent. These estimates are also useful in allowing the analyst to make the proper dilutions for the Li^+ determination by atomic absorption spectrophotometry after having determined chloride by titration. Some data comparing predicted values for Li^+ and K^+ percentages with experimentally determined values are given in Table II.

Table II. Comparison of Predicted K^+ and Li^+ Percentages with Experimentally Determined Values

		Experimental Values				Predicted Values from Wt % Cl^-	
				Wt % Li^+			
Sample Number	Wt Sample Analyzed, g	Wt % Cl^-	Wt % K^+	Grav	AAS	Wt % K^+	Wt % Li^+
78-0829-01	3.8578	63.23	29.06	7.25	7.03	29.66	7.11
78-0829-02	2.7305	63.22	28.87	7.30	7.14	29.66	7.11
78-0829-03	2.6300	62.98	29.67	7.08	6.83	30.02	7.00
78-0829-04	3.7970	64.47	27.50	7.72	7.55	27.85	7.68
78-0829-05	3.4926	64.51	27.33	7.82	7.65	27.80	7.69
78-0829-06	2.6402	62.80	29.88	7.04	6.92	30.28	6.92
78-0829-07	0.3110	65.08	26.51[a]	--	8.07	26.97	7.95
78-0829-08	0.4192	65.02	26.42[a]	--	7.88	27.05	7.93

[a] Wt % K^+ determined gravimetrically as $K\phi_4B$.

H. Notes

Note 1. Typically, samples were submitted for analysis as chunks of fused material weighing up to 50 g. The eutectic material is hygroscopic. The samples were normally protected from the atmosphere prior to analysis by being placed in sealed containers, which in turn were stored in sealed Mason jars, usually in a dry helium atmosphere. With fused specimens, the samples could be weighed quickly in the laboratory with no appreciable moisture pickup. Smaller, powdered samples were stored and weighed in a helium-atmosphere dry box prior to analysis. The conditions under which the sample is to be weighed depend on a number of factors including sample form and size, humidity conditions and accuracy of analysis desired.

Note 2. The use of an R456 photomultiplier tube has been found to improve the signal-to-noise ratio for the lithium determination.

III. ASSAY OF LITHIUM SULFIDE

A. Principle of the Method

Sulfur is determined by two methods. (1) For total S, the samples are oxidized with Br_2 to convert $S^=$ to $SO_4^=$. The $SO_4^=$ is then determined gravimetrically as $BaSO_4$ on an aliquot of the oxidized sample. (2) To determine $S^=$, a weighed sample is reacted with a known volume of standarized $AgNO_3$ in excess of the volume required to precipitate $S^=$ as Ag_2S. After reaction the Ag_2S is filtered and the excess Ag^+ is determined in the filtrate by a Volhard titration. The amount of Ag^+ reacting to form Ag_2S is calculated by subtracting the milliequivalents of Ag^+ found after formation of Ag_2S from the total milliequivalents of Ag^+ added to the sample.

Lithium is determined by atomic absorption spectrophotometry on an aliquot of the oxidized sample.

B. Reagents and Standards

(1) Carbon tetrachloride.

(2) Bromine in CCl_4. Pour the contents of a 1-lb bottle of reagent grade Br_2 into a clean, dry 1-L volumetric flask. Dilute to volume with CCL_4. Wear protective gear, and perform this operation in a hood.

(3) Conc. HNO_3 - reagent grade.

(4) Conc. HCl - reagent grade.

(5) Barium chloride solution, 10% (wt/vol). Dissolve 100 g $BaCl_2 \cdot 2H_2O$ in 1 L water. Allow to stand overnight. Filter through a fine-porosity filter (Whatman 42) prior to use.

(6) Primary standard silver nitrate solution, 0.1$\underline{M}$ $AgNO_3$. Prepare by dissolving ∿10.8 g pure silver metal (accurately weighed) in an excess of HNO_3 in a large, covered beaker. After dissolution, carefully evaporate to dryness. Dilute to 1000.0 mL with distilled water. Calculate the molarity

of the solution, $\underline{M} = \frac{\text{wt AgNO}_3\text{, g}}{107.87}$. Use this solution to standardize the 0.05$\underline{M}$ KSCN solution as described below.

(7) Ferric ammonium sulfate indicator solution, ∿40% (wt/vol) $FeNH_4(SO_4)_2 \cdot 12\ H_2O$. Prepare a saturated solution of $Fe(NH_4)(SO_4)_2 \cdot 12\ H_2O$ by adding ∿80 g of the salt to 200 mL of H_2O and magnetically stirring overnight. Add 10 mL conc. HNO_3 to partially bleach the solution.

(8) Standardized potassium thiocyanate solution, ∿0.05$\underline{M}$. Dissolve ∿5 g reagent grade KSCN in H_2O and dilute to 1 L. Standardize as follows:

(a) Transfer 20.00 mL of primary standard 0.1$\underline{M}$ $AgNO_3$ solution to a 600-mL beaker.

(b) Add 3 mL of ferric ammonium sulfate indicator solution.

(c) Add 5 mL concentrated nitric acid.

(d) Dilute to ∿300 mL with H_2O.

(e) Titrate with 0.05$\underline{M}$ KSCN solution to the permanent appearance of a reddish-brown color that persists for 30 s while the solution is vigorously stirred.

(f) Determine the indicator blank and subtract this blank from the volume of titrant measured III-B-8-(e) above.

(g) Calculate molarity of KSCN solution:

$$\underline{M}_{KSCN} = \frac{20(A)}{B}$$

where A = molarity of primary standard $AgNO_3$

B = net volume of KSCN used in titration

(9) Standardized silver nitrate solution, 0.1$\underline{M}$. Dissolve 17 g reagent grade $AgNO_3$ in 1 L H_2O. Standardize against the standardized 0.05$\underline{M}$ KSCN as described in III-B-8 above.

(10) Filter pulp tablets.

(11) Sodium chloride, NaCl - reagent grade.

(12) Potassium chloride solution, 50 mg KCl/mL. Dissolve 50 g KCl in H_2O and dilute to 1 L.

C. Preparation of Samples for Analysis

Lithium sulfide, Li_2S, is readily hydrolyzed with loss of H_2S:

$$Li_2S + 2H_2O \rightarrow 2LiOH + H_2S$$

Therefore, the weighed sample must be protected from the atmosphere prior to analysis.

Samples were accurately weighed in a helium atmosphere dry box. For the total sulfur determination, samples weighing about 200 to 300 mg were transferred into a clean, dry 125-mL Erlenmeyer flask and stoppered immediately. Parafilm was wrapped around the top of the flask to insure an air-tight seal until the sample was analyzed. For the sulfide sulfur assay, samples weighing about 100 mg were transferred into stoppered weighing bottles, sealed in Mason jars, and transferred to the analyst in these containers.

D. Total Sulfur Determination

(1) Add 30 mL of Br_2 in CCl_4 to the sample flask containing the weighed sample.

(2) Carry a blank along with the samples through the entire procedure.

(3) Stopper the flask and allow to stand ∿30 min.

(4) Add 3 drops conc. HNO_3, swirl, and allow to stand, loosely stoppered, for a few minutes.

(5) Repeat step D-(4), above, a number of times until the Li_2S residue on the bottom of the flask is dissolved. (See Note 1, p. 14.)

(6) Add a microspatula (∿100 mg) of NaCl to each flask. (See Note 2, p. 14.)

(7) Add a total of 15 mL conc. HNO_3, let stand, loosely stoppered, about 30 min, and then evaporate to dryness.

(8) Add 5 mL conc. HCl, rinse down the sides of the flask with water and again take to dryness.

(9) Add 1.5 mL conc. HCl and 50 mL H_2O. Heat until salts are in solution.

(10) Cool and dilute to 100.0 mL.

(11) Transfer a 75.0-mL aliquot into a 400-mL beaker. Dilute to ∿300 mL.

(12) Heat to boiling.

(13) Slowly add 15 mL 10% (wt/vol) $BaCl_2 \cdot 2H_2O$ solution with stirring.

(14) Remove the beaker from the hot plate, cover, and allow to stand overnight.

(15) Add 1/4 tablet of Whatman filter pulp. Stir until the pulp disintegrates into fine particles and is homogeneously distributed in the solution. Allow to settle.

(16) Test the solution for completeness of precipitation of $BaSO_4$ by adding a few drops of $BaCl_2$ solution. No $BaSO_4$ precipitate should appear.

(17) Filter through an 11-cm Whatman 42 (or equivalent) paper.

(18) Transfer all of the $BaSO_4$ precipitate to the paper with wash H_2O.

(19) Wash the paper and precipitate. Wash by spraying a stream of water around the top of the paper until the filter is full. Allow to drain and repeat four times.

(20) Remove traces of $BaSO_4$ from the beaker wall and stirring rod by wiping with a portion of 11-cm Whatman 42 paper. Transfer the paper and $BaSO_4$ precipitate to a weighed platinum crucible.

(21) Place the crucible on a raised silica triangle in a muffle furnace at room temperature.

(22) Allow the temperature to rise to 850°C with the furnace door slightly ajar and ignite the crucible at 850°C for an hour or overnight, if convenient.

(23) Place the crucible in a dessicator.

(24) Cool for 1/2 hour and weigh.

(25) Calculate the percentage of total sulfur.

$$\text{wt \% S} = \frac{(A - B)(13.736)}{(C)(D)}$$

where A = weight $BaSO_4$, g

B = blank weight, g

C = aliquot fraction, $\frac{\text{sample aliquot, mL}}{\text{total sample volume, mL}}$

D = sample weight, g

E. Sulfide Sulfur Determination

(1) Estimate the amount of $S^=$ in the weighed sample (∿100 mg Li_2S). Transfer to a 400-mL beaker an accurately measured aliquot of standardized 0.1M $AgNO_3$ about 1 meq in excess of that required to form silver sulfide, Ag_2S:

$$Li_2S + 2AgNO_3 \rightarrow Ag_2S\downarrow + 2LiNO_3$$

(2) Dilute to ∿200 mL with H_2O.

(3) Remove the weighing bottle containing the weighed sample from the sealed Mason jar. Open quickly and immerse the weighing bottle in the $AgNO_3$ solution.

(4) Stir the solution to promote contact of the Li_2S with the $AgNO_3$ solution.

(5) After about 5 minutes heat the solution to boiling.

(6) Cover the solution and allow to stand overnight or at least until cool.

(7) Lift the weighing bottle out of the solution using a stirring rod. Rinse the bottle, inside and outside, with water, catching the rinse in the beaker. Set the bottle aside.

(8) Filter the solution using an 11-cm Whatman #40 (or equivalent) paper. Wash the beaker, precipitate, and paper several times with H_2O. Adjust volume to 300 mL with H_2O.

(9) Add 5 mL conc. HNO_3 and 3 mL ferric ammonium sulfate indicator to the filtrate.

(10) Determine the meq of excess Ag^+ in the filtrate by titration with standardized 0.05$\underline{M}$ KSCN to a definite, reddish-orange tinge. Correct the volume of KSCN for blank.

(11) Calculate the wt % sulfide sulfur.

$$\text{wt \% } S^{=} = \frac{(A - B)(1.603)}{C}$$

where A = meq Ag^+ added: volume $AgNO_3$ x molarity $AgNO_3$

B = net meq of Ag^+ found in the filtrate after reaction of Li_2S with $AgNO_3$: volume KSCN x molarity KSCN

C = sample weight in grams

F. Lithium Determination

(1) Transfer an aliquot (containing 50-150 μg Li^+) of the sample solution from the total S determination, III-D-(10), above, to a 50-mL volumetric flask.

(2) Add 2 mL of 50 mg KCL/mL solution to sample aliquots and blank.

(3) Dilute to 50.0 mL with H_2O.

(4) Determine lithium by atomic absorption spectrophotometry as described for Analysis of LiCl-KCl Eutectic, II-F.

G. Discussion

Samples of Li_2S from various manufacturers have been analyzed by the above procedures in order to verify stated compositions. Some typical results are given in Tables III and IV. The data indicate that these materials are essentially pure Li_2S as evidenced by the mass-balance data and the Li/S molar ratio which is close to 2.000.

Table III. Results Obtained on Repeated Analysis of One Batch of Li_2S for Total Sulfur and Lithium

Sample Designation	Wt % Total S (grav. as $BaSO_4$)	Wt % Li^+ (AAS)	Wt % Li^+ + Wt % S	Molar Ratio, Li^+/S
FM-1	69.1_9	29.9_6	99.2	2.000
FM-2	69.2_8	29.6_6	98.9	1.978
FM-3	69.1_3	29.7_6	98.9	1.989
FM-4	69.0_1	29.6_9	98.7	1.987
FM-5	69.0_6	30.0_5	99.1	2.010
Average	69.1_2	29.8_2	99.0_6	1.993
Standard Deviation	±0.082	±0.172	±0.19	±0.012
Rel. % Std. Dev.	±0.12	±0.58	±0.20	±0.62

Forms of sulfur other than sulfide would be revealed by a difference between the total sulfur and sulfide sulfur values. The presence of significant amounts of impurities such as H_2O or CO_2 (as Li_2CO_3, a starting material for the synthesis of Li_2S) would result in a molar ratio (Li/S) significantly greater than 2.000.

Regarding interferences with the recommended methods, the Li^+ determination, as mentioned above, is essentially specific, as is the determination of total sulfur. The determination of sulfide sulfur is subject to interference from anions such as Cl^-, Br^-, and I^- which are precipitated by silver. In the unlikely case that metallic lithium were present, Ag^+ would be reduced to metal yielding high $S^=$ values. The sensitivity of the compound to water has been mentioned earlier.

H. Notes

Note 1. The purpose of steps III-D-(4) and III-D-(5) is to dissolve and oxidize Li_2S to Li_2SO_4 without loss of sulfur. Nitric acid floats on the CCl_4. Swirling is necessary to allow contact of HNO_3 with the Li_2S residue. Small increments of HNO_3 are added to avoid too vigorous a reaction with Li_2S.

Note 2. If the compound being analyzed contains excess sulfur, then H_2SO_4, in addition to Li_2SO_4, could be formed and volatilized when the sample is evaporated to dryness. Addition of NaCl results in the formation of nonvolatile Na_2SO_4 rather than H_2SO_4 under these conditions.

Table IV. Results Obtained on Repeated Analysis of One Batch of Li_2S for Total Sulfur, Sulfide Sulfur, and Lithium

Sample Designation (wt)	Wt % Total S (grav. as $BaSO_4$)	Wt % S as $S^=$ (Ag^+ Titration)	Wt % Li^+ (AAS)	Wt % Li^+ + Wt % S	Molar Ratio, Li^+/S
EP-1 (0.3257 g)	69.4_2	--	30.2_6	99.7	2.014
EP-2 (0.5561 g)	68.3_5	--	29.5_7	97.9	1.999
EP-3 (0.8390 g)	68.9_3	--	30.4_7	99.4	2.042
EP-4 (0.8274 g)	68.7_8	--	30.2_9	99.0	2.036
Average	68.8_7	--	30.1_5	99.0	2.023
Standard Deviation	±0.44	--	±0.40	±0.79	±0.020
Rel. % Std. Dev.	±0.64	--	±1.31	±0.80	±0.98
EP-5 (0.3340 g)	--	68.9_1	--	--	--
EP-6 (0.1359 g)	--	68.9_0	--	--	--
EP-7 (0.1463 g)	--	69.0_2	--	--	--
EP-8 (0.2286 g)	--	68.9_4	--	--	--
Average	--	68.9_4	--	--	--
Standard Deviation	--	±0.054	--	--	--
Rel. % Std. Dev.	--	±0.08	--	--	--

IV. ANALYSIS OF ALUMINUM-LITHIUM ALLOY

A. Principle of the Method

A weighed sample is dissolved in excess alcohol, acidified with HCL, evaporated to dryness to volatilize the alcohol solvent, and the resulting chloride residue is taken up in dilute HCl and diluted to volume. Aluminum is determined gravimetrically by precipitation with 8-hydroxyquinoline after separation from other elements, if required. Lithium is determined by atomic absorption spectrophotometry.

B. Reagents

(1) Alcohol solvent - reagent grade propanol.

(2) Hydrochloric acid (1) concentrated reagent ∿12<u>M</u>, (2) 6<u>M</u> HCl by dilution of 50 mL conc. HCl to 100 mL with H_2O (3) 2<u>M</u> HCl by dilution of 16 mL of conc. HCl to 100 mL with H_2O.

(3) Ammonium hydroxide, 2<u>M</u>. Dilute 13 mL of conc. reagent grade NH_4OH to 100 mL with H_2O.

(4) 8-Hydroxyquinoline, 2.5% (wt/vol). Dissolve 25 g reagent grade 8-hydroxyquinoline (oxine) in 29 mL of 6<u>M</u> HCl and dilute to 1 L with H_2O. Filter if necessary.

(5) Ammonium acetate, 20% (wt/vol). Dissolve 200 g reagent grade CH_3COONH_4 in 600 mL H_2O. Filter and dilute to 1 L with H_2O.

(6) Bromocresol purple indicator solution, 0.1% (wt/vol). Dissolve 0.1 g bromocresol purple (5',5"-dibromo-o-cresolsulfonephthalein) in 20 mL ethyl alcohol and dilute to 100 mL with H_2O.

(7) Wash liquid. Dilute 8 mL of 2.5% (wt/vol) 8-hydroxyquinoline solution with H_2O to about 500 mL. Add 3 drops of 0.1% bromocresol purple indicator solution and add 2<u>M</u> NH_4OH drop by drop until the indicator changes to purple (pH 6) and dilute to 1 L with H_2O.

(8) Ferric nitrate solution, 3.6% (wt/vol), (∿5 mg Fe(III)/mL). Dissolve 3.6 g ferric nitrate $[Fe(NO_3)_3 \cdot 9H_2O]$ in 100 mL 0.1<u>M</u> HNO_3. (Prepare 0.1<u>M</u> HNO_3 by diluting 1 mL conc. HNO_3 to 150 mL with H_2O.)

(9) Sodium hydroxide, 4<u>M</u> NaOH. Dissolve 16 g NaOH in water and stir until dissolved. Dilute to 100 mL with water. Store in a tightly sealed, plastic container.

(10) Sodium hydroxide wash solution, ∿0.01<u>M</u> NaOH. Dilute 0.5 mL of 4<u>M</u> NaOH to 200 mL with H_2O.

(11) Methyl red indicator solution, 0.1% (wt/vol) in ethyl alcohol. Dissolve 0.1 g methyl red in 100 mL ethyl alcohol.

C. Preparation of Samples for Analysis

(1) Transfer a weighed sample (0.1-3 g) into a clean, dry 600-mL Teflon beaker (see Notes 1 and 2, p. 19).

(2) Add 100 mL of propanol (see Note 3, p. 19).

(3) Allow the sample to react in the alcohol. Add water in small increments if the reaction is too slow (see Note 4, p. 20).

(4) When the dissolution rate of the sample has slowed or stopped, add 6M HCl in small increments until the solution is acidic.

(5) Heat until the sample is dissolved. Evaporate to dryness to volatilize the alcohol, being careful not to splatter.

(6) Cover the residue with ∿50 mL H_2O + ∿1 mL conc. HCl. Heat, if necessary to dissolve the residue. Use sufficient HCL, finally, to yield an HCL concentration about 0.5M.

(7) Dilute to volume. (For small samples, dilute to 100 mL; for larger samples, dilute to 500 mL or 1 L, depending on sample size.)

D. Aluminum Determination

(1) Transfer an aliquot of the sample solution from IV-C-(7) above containing 20-30 mg Al^{3+} into a 250-mL beaker.

(2) Add 1 mL of 3.6% (wt/vol) ferric nitrate solution.

(3) Dilute to 75 mL with H_2O and heat to boiling.

(4) Add 10 mL of 4M NaOH solution.

(5) Allow the hydrated ferric oxide precipitate to settle and filter through a 9-cm Whatman #42 (or equivalent) paper into a 600-mL beaker.

(6) Filter and transfer the precipitate onto the paper. Wash the beaker and paper five times with 0.01M NaOH wash solution. Discard the filter paper and precipitate.

(7) Add three drops of methyl red indicator solution.

(8) Add conc. HCl drop by drop, with stirring, until the indicator turns red.

(9) Add 2M HCl drop by drop with stirring between additions of acid, until any $Al(OH)_3$ precipitate that may have formed dissolves.

(10) Add 0.7 mL of 2.5% (wt/vol) solution of 8-hydroxyquinoline for each mg of aluminum present plus 10 mL in excess and sufficient H_2O to bring the volume to about 350 mL.

(11) Slowly introduce 20 mL of 20% (wt/vol) CH_3COONH_4 with stirring (see Note 5, p. 20).

(12) Heat to boiling, digest on a steam bath for 30 minutes, and cool to 50°C. If necessary, the solution can stand overnight at room temperature.

(13) Filter through a weighed, medium porosity, sintered glass filtering crucible.

(14) Wash the precipitate with no more than 100 mL of warm (50-60°C) 8-hydroxyquinoline wash solution. Finally wash with two 5-mL portions of cold H_2O.

(15) Dry the crucible and precipitate at 150°C for at least 3 h or overnight, if convenient.

(16) Cool the crucible and precipitate in a dessicator for 45 minutes, allow to cool another 15 minutes in ambient air, and weigh.

(17) Calculate the wt % aluminum.

$$\text{wt \% Al}^{3+} = \frac{(A)(5.873)}{(B)(C)}$$

where A = weight of aluminum-8-hydroxyquinolate, g

B = aliquot fraction $- \dfrac{\text{Sample aliquot, mL}}{\text{Total sample volume, mL}}$

C = sample weight, g

E. Lithium Determination

Lithium is determined by atomic absorption spectrophotometry as described in Analysis of LiCl-KCL Eutectic Salt, II-F.

F. Discussion

The oxinate method for the determination of Al^{3+} is subject to interference, since most other metals (except alkalies and alkaline earths) are also precipitated by 8-hydroxyquinoline under the conditions described herein. The alloys submitted for analysis have usually been reasonably pure, containing only small amounts (<1%) of impurities such as Cu, Fe, SiO_2, etc. The simple separation used here, wherein a small (5 mg) amount of Fe(III) is precipitated as the hydrated ferric oxide to coprecipitate and adsorb other insoluble metal hydroxides and silica, is useful to separate Al^{3+} from commonly encountered impurities found in aluminum-lithium alloys.

Aluminum-8-hydroxyquinolate is a bright yellow precipitate. Traces of coprecipitated metal impurities are revealed when the oxine precipitate is discolored, usually gray-green to brown.

An attempt has been made to use anion-exchange columns to separate Al^{3+} from a number of elements as oxalato complexes, based on the data of Strelow *et al.*[4] The sample aliquot was taken to dryness, dissolved in 0.25M oxalic acid-0.05M HCl solution, and passed through a 25 x 2 cm column of AG1-X-8 anion-exchange resin. After washing the column with 0.25M oxalic acid-0.05M HCl, Al^{3+} was eluted with 7M HCl effecting a separation of a large number of elements as reported by Strelow. This separation was tried with some success but was not practical since, when Al^{3+} was eluted from the column with 7M HCl, oxalic acid precipitated and tended to clog the column, necessitating the use of large volumes of 7M HCl eluant. Also, excess HCl and oxalic acid had to be removed by evaporation and oxidation before the aluminum determination could be made.

Other classical separation procedures can be used to separate many metals from Al^{3+} including electrodeposition of heavy metals into a mercury cathode[5] and precipitation with hydrogen sulfide.[6]

The use of complexing agents to allow the determination of Al^{3+} in the presence of certain interferences is reported by Tikhonov.[7]

The effect of Al^{3+} on the determination of Li^+ by atomic absorption spectrophotometry was tested. No interference was found when Al^{3+} was present in the concentration expected after dilution of the sample for the determination of Li^+.

Data obtained using this procedure for the analysis of two lots of Al-Li alloy are given in Table V. Spectrographic analysis indicated the presence of 1-2% of cation impurity in each lot. The samples were submitted as chunks rather than ground material. The observed relative percent standard deviation may, in part, reflect an inhomogeneity of these samples.

The accuracy and precision of the Al^{3+} determination is currently being monitored by analyzing Al^{3+} standards whenever the determination of Al^{3+} using oxine is required. Accumulated data indicate an average recovery of 99.6% with a precision of ±0.4% relative standard deviation.

The precision of the Li determination by atomic absorption is discussed in II-G.

G. Notes

Note 1. Aluminum-lithium alloy reacts with moisture and must be protected from the atmosphere prior to analysis. The samples were usually weighed in a dry box and placed in a sealed container (usually plastic) which was stored in a sealed Mason jar in a helium atmosphere.

Note 2. The sample solution after dissolution in alcohol is very basic and could react with an ordinary borosilicate glass beaker to introduce unwanted impurities. The use of Teflon beakers avoids this problem.

Note 3. A number of other alcohols including methyl, ethyl, and isopropyl can and have been used to dissolve the alloys. Propanol has the advantages of being less reactive and having a relatively high flash point.

Table V. Analysis of Al-Li Alloy

Sample Designation	Sample Aliquot Wt, g	Wt % Li	Wt % Al	Total Wt %	Molar Ratio, Li/Al
Lot #14 79-0283-01	1.46400	17.4_2	80.3_2	97.7_4	0.843
	3.00736	17.2_5	79.8_6	97.7_1	0.840
	Average	17.3_4	80.0_9	97.4_3	0.842
	Rel. % Dev.	1.0	0.6		
Lot #17 79-0283-02	1.28930	17.0_6	80.1_1	97.1_7	0.828
	1.37373	17.5_6	79.5_9	97.1_5	0.858
	1.25465	18.5_5	79.9_1	98.4_6	0.903
	1.25878	18.2_7	80.2_0	98.4_7	0.886
	2.84814	17.7_3	79.7_3	97.4_6	0.865
	Average	17.8_3	79.9_1	97.7_4	0.868
	S. D.	±0.59	±0.25		
	Rel. % S. D.	3.3	0.32		

When necessary, the reaction can be speeded up with the addition of small increments of H_2O. See, however, Note 4.

Note 4. Reaction of the alloy should occur under controlled conditions. If too much water is added, the reaction can become violent, and the solution can overheat, splatter, and possibly froth out of the beaker. In addition, the possibility that so much heat is generated that the alcohol or alloy ignites must be considered. It is recommended that a large (600-mL or larger) beaker be used in order to avoid loss of sample if frothing should occur. It is also recommended that the beaker not be covered during dissolution to avoid possible accumulation of an easily ignited concentration of hydrogen in the beaker above the sample.

Note 5. The pH of the solution after the precipitation should be 5.2 to 5.8.

V. ANALYSIS OF LITHIUM ALUMINUM CHLORIDE, $LiAlCl_4$

A. Principle of the Method

A weighed sample is dissolved in H_2O, diluted to volume and separate aliquots are taken for the Li^+, Al^{3+}, and Cl^- determinations. Lithium is determined by atomic absorption spectrophotometry, Al^{3+} is determined gravimetrically with 8-hydroxyquinoline, and Cl^- is determined by titration with standardized $AgNO_3$ using an adsorption indicator.

B. Reagents and Standards

(1) Chloride determination - see II-B-(1 to 3).

(2) Lithium determination - see II-B-(5 to 6).

(3) Aluminum determination - see IV-B-(2 to 11).

C. Preparation of Samples for Analysis

Since the compound absorbs water, samples to be analyzed should be stored in a dry box prior to analysis.

The materials analyzed to date have been solid chunks and could be weighed rapidly in the air with no appreciable pick up of moisture. Finely divided samples might have to be weighed in a dry box.

$LiAlCl_4$ is water soluble and presents no dissolution problem.

D. Chloride Determination

Determine Cl^- as described in II-D.

E. Lithium Determination

Determine Li^+ as described in II-F.

F. Aluminum Determination

Determine Al^{3+} as described in IV-D.

G. Discussion

Interferences with the procedures used have been discussed above and do not present a problem for a pure $LiAlCl_4$ compound dissolved in water where only Li^+, Cl^-, and Al^{3+} ions are present.

Our experience with the analysis of this compound has been limited to only a few samples. The analytical results obtained on one sample at first appeared to be inconsistent since the mass balance was only 98.1%, and the ratio $\frac{\text{mol } Cl^-}{(\text{mol } Li^+ + 3 \text{ mol } Al^{3+})}$ was 0.963.

Hydrogen was subsequently determined on a separate sample by ignition at 900°C in oxygen and measurement of evolved H_2O. A value of 0.082% H was found. This corresponded to 1.40% OH^- and yielded a mass balance of 99.5% with a ratio $\frac{(\text{mol } Cl^- + \text{mol } OH^-)}{(\text{mol } Li^+ + 3 \text{ mol } Al^{3+})} = 0.998$ compared with the expected 1.000.

This result can be explained as the result of partial hydrolysis of the compound prior to analysis according to equation (1)

$$LiAlCl_4 + X\ H_2O \rightarrow LiAl(OH)_XCl_{4-X} + X\ HCl\uparrow \qquad (1)$$

with some loss of HCl. The result could of course also be due to an improperly synthesized compound.

In either case, with compounds of this type, the presence of reacted or absorbed H_2O must be considered when interpreting the analytical results obtained.

VI. ANALYSIS OF IRON, NICKEL, COPPER, AND COBALT SULFIDES

A. Principle of the Method

A weighed sample is reacted with bromine and HNO_3 to dissolve the metal sulfides and oxidize sulfide sulfur to sulfate. After dissolution and oxidation, HCL is added and the solution is taken to dryness to remove nitrate. Insoluble silicate material (if present) is filtered off and the solution is diluted to volume. Sulfate is determined gravimetrically as $BaSO_4$ on an aliquot of the sample solution after separation from cations by ion-exchange. The metal cations are determined on separate aliquots. Iron and cobalt are determined colorimetrically, nickel gravimetrically with dimethylglyoxime, and copper by electrodeposition of the metal.

B. Preparation of Samples for Analysis

Materials analyzed include various sulfides of iron, nickel, cobalt, copper, and chalcopyrite, $CuFeS_2$.

These materials are stable in air and usually do not require any special handling prior to analysis to protect from traces of moisture in air. However, Hillebrand, *et al.*[8] note that pyrite, FeS_2, can be oxidized with loss of sulfur as sulfur dioxide and formation of sulfate, when finely ground. They also note that care should be taken to avoid oxidation of sulfide minerals during sample preparation. They recommend that samples be crushed by concussion to 60-80 mesh, if necessary, and that grinding be avoided.

C. Apparatus

(1) Cation-exchange column, 2.5 x 32 cm, fitted with a coarse fritted disk, and a Teflon 2-mm-bore stopcock. To prepare the column for use, fill with water, open the stopcock, and pour in a slurry of Bio-Rad AG50WX-8 100-200 mesh cation-exchange resin in the H^+ form until a 12- to 14-cm column of resin has been transferred. Wash with 100 mL $6\underline{M}$ HCl, 100 mL $3\underline{M}$ HCl, and then with water until the eluate is free of acid.

(2) Spectrophotometer. Any commercial spectrophotometer suitable for photometric measurements in the visible region is satisfactory. The Cary Model 16 spectrophotometer, capable of measuring 0.5 absorbance to ±0.0007 has been used in this work.

(3) Sintered glass filtering crucibles, 30 mL, medium porosity, low form.

(4) Electrodeposition apparatus. Eberbach Electroanalyzer, Fischer Scientific Co. #9-260-200 or equivalent.

(5) Platinum gauze electrode, stationary, 4-cm-dia gauze cylinder, Fisher Scientific Co. #9-309 or equivalent.

(6) Platinum stirring electrode; Fisher Scientific Co. #9-306 or equivalent.

D. Reagents and Standards

(1) Sodium chloride, reagent grade NaCl.

(2) Carbon tetrachloride, reagent grade CCl_4.

(3) Bromine in carbon tetrachloride. See III-B-(2).

(4) Nitric acid 15$\underline{M}$, concentrated reagent grade HNO_3.

(5) Hydrochloric acid, 12$\underline{M}$, concentrated reagent grade HCl.

(6) Iron Standard Solutions, 1.000 mg Fe/mL and 10.00 µg Fe/mL.

(a) Preparation of stock iron standard solution, 1.000 mg Fe/mL. Weigh an amount of assayed electrolytic iron wire which, when corrected for the assay, will yield 1.000 g of Fe. Transfer to a 400-mL beaker and add 50 mL conc. HCl. Cover and heat until the wire is dissolved. Cool and dilute to 1000 mL with H_2O. The concentration of this stock solution will be 1.000 mg Fe/mL.

(b) Preparation of dilute iron standard solution, 10.00 µg Fe/mL. Transfer 10.00 mL of the stock iron standard solution (1.000 mg Fe/mL) into a 1-L volumetric flask. Add 10 mL conc. HCl and dilute to volume to yield a solution containing 10.00 µg Fe/mL.

(7) Hydroxylamine hydrochloride, 10% (wt/vol). Dissolve 10 g reagent grade $NH_2OH \cdot HCl$ in 100 mL H_2O. Filter before use. Prepare fresh each week.

(8) 1,10-Phenanthroline saturated solution, ∿0.016$\underline{M}$. Magnetically stir 0.5 g 1,10-phenanthroline in 100 mL H_2O for 10 minutes. Filter before use. Prepare fresh each week.

(9) Ammonium hydroxide, conc. reagent grade NH_4OH.

(10) Glacial acetic acid, reagent grade.

(11) Cobalt Standard Solutions, 1.000 mg Co/mL and 5.00 µg Co/mL.

(a) Preparation of stock cobalt solution, 1.000 mg Co/mL. Weigh an amount of pure, assayed cobalt metal which, when corrected for assay, will yield 1.000 g of Co. Transfer to a 400-mL beaker, and add 30 mL conc. HCl, 20 mL conc. HNO_3, and 25 mL H_2O. Cover and heat until the metal is dissolved. Cool and dilute to 1000 mL with H_2O to yield a solution containing 1.000 mg Co/mL.

(b) Preparation of dilute cobalt standard solution, 5.00 µg Co/mL. Transfer 5.00 mL of the stock cobalt solution (1.000 mg Co/mL) into a 1-L volumetric flask. Add 10 mL conc. HCl and dilute to volume with H_2O to yield a solution containing 5.00 µg Co/mL.

(12) Perchloric acid, conc. reagent grade $HClO_4$.

(13) Sodium citrate solution, 45% (wt/vol). Dissolve 113 g reagent grade sodium citrate, $C_6H_5O_7Na_3 \cdot 2H_2O$, in 250 mL H_2O. Filter through a Whatman #41 (or equivalent) paper.

(14) Bromocresol purple indicator solution, 0.04% (wt/vol). Dissolve 100 mg 5',5"-dibromo-o-cresolsulfonephthalein in 18.5 mL 0.01<u>M</u> NaOH and dilute to 250 mL.

(15) Sodium hydroxide, 11<u>M</u>. Cautiously dissolve 44 g reagent grade NaOH in 100 mL H_2O with stirring. Cool and store in a screw-cap plastic bottle.

(16) Sulfuric acid, conc. reagent grade H_2SO_4.

(17) Nitroso-R salt solution, 0.2% (wt/vol). Dissolve 200 mg Nitroso-R salt (1-nitroso-2-naphthol-3,6-disulfonic acid disodium salt) in 100 mL H_2O. Filter before use. Prepare fresh each day.

(18) Sulfuric acid, 9<u>N</u>. Slowly and cautiously add 25 mL conc. reagent grade H_2SO_4 to 75 mL H_2O with stirring. Cool before use.

(19) Tartaric acid, 25% (wt/vol). Dissolve 63 g reagent grade tartaric acid, in 250 mL H_2O. Filter thru a Whatman #41 (or equivalent) paper.

(20) Dimethylglyoxime solution, 1% (wt/vol). Dissolve 2.5 g dimethylglyoxime in 250 mL ethyl alcohol.

(21) Copper Standard Solutions, 0.1000 mg Cu/mL and 0.1, 0.3, and 0.5 µg Cu/mL. Weigh 0.1000 g copper metal (assay >99.9%) into a 400-mL beaker. Add 25 mL conc. HNO_3 and 25 mL H_2O. Cover and heat until the metal is dissolved. Cool and dilute to 1 L with H_2O to yield a solution containing 0.1000 mg Cu/mL. Dilute 1.00, 3.00, and 5.00 mL aliquots of this solution each to 1 L with 0.05<u>M</u> HNO_3 to make atomic absorption working standards containing 0.100, 0.300, and 0.500 µg Cu/mL.

(22) Barium Chloride Solution, 10% (wt/vol), see III-B-(5).

(23) Nitric Acid, 6<u>M</u>. Dilute 40 mL conc. HNO_3 to 100 mL with H_2O.

(24) Ethyl alcohol, reagent grade C_2H_5OH.

(25) ∿6<u>M</u> HCl. Dilute conc. HCl with an equal volume of water.

(26) ∿7<u>M</u> NH_4OH. Dilute conc. NH_4OH with an equal volume of water.

(27) Wash solution 1M NH_4OH - 1M NH_4Cl. Mix equal volumes of 2M NH_4OH and 2M NH_4Cl. (2M NH_4OH - dilute 12 mL of conc. NH_4OH to 100 mL with H_2O. 2M NH_4Cl - dissolve 10.6 g NH Cl in 100 mL H_2O.)

E. Determination of Total Sulfur

(1) Accurately weigh 0.5-1 g of sample into a clean, dry, 250-mL stoppered Erlenmeyer flask (see Note 1, p. 31).

(2) Add ∿0.25 g reagent grade NaCl (see Note 2, p. 31).

(3) Carry a blank of 0.25 g NaCl along with the samples through the procedure.

(4) Add 20 mL of Br_2 in CCl_4.

(5) Allow to stand, loosely stoppered, for at least 30 min.

(6) Add 1-2 mL of conc. HNO_3. Swirl to allow the acid to react with the sample while the flask is loosely stoppered.

(7) Continue to add acid in 1-2 mL increments, with swirling after each addition. Allow the acid to react with the sample before addition of more acid.

(8) Continue with the addition of increments of conc. HNO_3 until a total of 15 mL of acid has been added.

(9) Add 5 mL conc. HCl. Allow to stand, loosely stoppered, for about 1 h or until the sample has reacted with the acid mixture.

(10) Evaporate to gentle dryness.

(11) Rinse down the inside of the flask with water, add 5 mL conc. HCl, and take just to dryness.

(12) Add 4 mL conc. HCl and warm to dissolve the metal salt residue.

(13) Add about 50 mL H_2O and, if necessary, filter off any insoluble silicate material using a 9-cm Whatman #40 (or equivalent) filter paper. Catch the filtrate in a 100-mL volumetric flask.

(14) Wash the paper and residue seven times with 0.025M HCl.

(15) Dilute the filtrate to 100 mL.

(16) If of interest, dry and ignite at 850°C, and weigh the insoluble residue.

(17) Calculate weight percent of insoluble residue:

$$\text{wt \% insoluble residue} = \frac{(A)(100)}{\text{sample weight, g}}$$

where A = weight of insoluble residue, g.

(18) Transfer an aliquot of the sample solution VI-E-(15) containing about 100 mg S into a 150-mL beaker and dilute to 100 mL with H_2O.

(19) Pass the solution through the cation-exchange column catching the eluate in a 400-mL beaker.

(20) Wash the column with 150 mL H_2O, in increments. Dilute the eluate to 300 mL with H_2O.

(21) Precipitate and determine sulfur as $BaSO_4$ as described in III-D-(12 to 25).

F. Determination of Iron

(1) Transfer an accurately measured aliquot of the oxidized sample solution [VI-E-(15)] containing about 100 μg of iron into a 50-mL volumetric flask.

(2) Carry a reagent blank and three iron standards containing 50, 100, and 150 μg of iron through the iron determination procedure exactly as the sample.

(3) Add 2-3 drops conc. HCl and 4.00 mL of 10% hydroxylamine hydrochloride solution and dilute to about 25 mL with H_2O.

(4) Heat to almost boiling temperature.

(5) Cool to room temperature and add 2.00 mL 10% hydroxylamine hydrochloride and 2.00 mL saturated (∿0.016M) 1,10-phenanthroline solution.

(6) Add conc. NH_4OH drop by drop, until the solution is just basic as evidenced by the formation of the red Fe(II) 1,10-phenanthroline complex. Add 2 drops of NH_4OH in excess.

(7) Add 5 drops glacial acetic acid. The pH of the solution will now be in the range 5 to 7.

(8) Dilute to volume with H_2O.

(9) Measure the absorbance of the solution at 507 nm *vs.* water using 1-cm light path cells.

(10) Similarly measure the absorbances of the reagent blank and the iron standards concurrently carried through the color development steps.

(11) Subtract the absorbance of the reagent blank from the absorbances of the samples and standards.

(12) Determine the micrograms of iron in the sample aliquot from the net absorbance of the sample and the average net absorbance per microgram of iron as determined from the standards.

(13) Calculation:

$$\text{wt \% Fe} = \frac{A}{(B)(C)(10^4)}$$

where A = micrograms of iron found in the sample aliquot

B = aliquot fraction, $\frac{\text{volume sample aliquot, mL}}{\text{total sample volume, mL}}$

C = sample weight, g

G. Determination of Cobalt

(1) Transfer an accurately measured aliquot of the oxidized sample solution [VI-E-(15)], containing about 50 µg of cobalt into a 100-mL beaker.

(2) Carry a reagent blank and three cobalt standards containing 25, 50, and 75 µg cobalt through the procedure exactly as the sample.

(3) Add 5 drops conc. $HClO_4$ and evaporate to near dryness.

(4) Dilute to about 25 mL with H_2O, add 4.00 mL of 45% (wt/vol) sodium citrate solution and 5 drops 0.04% (wt/vol) bromocresol purple indicator solution.

(5) Add 11<u>M</u> NaOH, drop by drop, until the indicator changes to purple.

(6) Add conc. H_2SO_4 dropwise until the solution turns yellow. The pH will now be 5.5.

(7) Dilute to about 75 mL with water and add 4.00 mL 0.2% (wt/vol) nitroso-R salt solution.

(8) Heat to near boiling and maintain at this temperature for about 5 min.

(9) Cool to room temperature, transfer to a 100-mL volumetric flask, add 4.00 mL of 9<u>N</u> H_2SO_4, and dilute to volume.

(10) Measure the absorbance of the sample at 545 nm *vs.* water using 5-cm light path cells.

(11) Similarly measure the absorbances of the reagent blank and cobalt standards concurrently carried through the procedure.

(12) Subtract the absorbance of the reagent blank from the absorbances of the sample and standards.

(13) Determine the micrograms of cobalt in the sample aliquot from the net absorbance of the sample and the average absorbance per microgram of cobalt as determined from the standards.

(14) Calculation:

$$\text{wt \% Co} = \frac{A}{(B)(C)(10^4)}$$

where A = micrograms of cobalt found in the sample aliquot

B = aliquot fraction, $\frac{\text{volume sample aliquot, mL}}{\text{total sample volume, mL}}$

C = sample weight, g

H. Determination of Nickel

(1) Transfer an aliquot of the sample solution [VI-E-(15)] containing about 30 mg Ni into a 400-mL beaker.

(2) Add 5 mL 25% (wt/vol) tartaric acid solution and dilute to about 200 mL.

(3) Heat to nearly boiling.

(4) Add conc. NH_4OH until basic. Add 1-2 mL in excess (see Note 3, p. 32).

(5) Add ∿6M HCl until the solution is acidic.

(6) Add 20 mL of 1% (wt/vol) of dimethylglyoxime in ethyl alcohol.

(7) Dilute to about 300 mL with H_2O and heat to 80°C.

(8) Add ∿7M NH_4OH until basic. Add 2 mL in excess.

(9) Digest at 60°C for 30 min.

(10) Allow to stand for 1 h or more at room temperature.

(11) Filter through a weighed, low-form, 30-mL, medium-porosity, sintered glass filtering crucible.

(12) Transfer all of the precipitate onto the filter using a rubber policeman and water as wash solution.

(13) Wash the beaker and precipitate five times with water.

(14) Dry the crucible and precipitate at 150°C for 2 h or overnight, if convenient.

(15) Cool for 45 minutes in a dessicator and 15 min in the ambient air.

(16) Weigh the crucible and precipitate. Determine the weight of the nickel dimethylglyoxime precipitate.

(17) Calculate the percentage of nickel in the sample:

$$\text{wt \% Ni} = \frac{(A)(20.31)}{(B)(C)}$$

where A = weight of nickel dimethylglyoxime, g

B = aliquot fraction, $\frac{\text{volume sample aliquot, mL}}{\text{total sample volume, mL}}$

C = sample weight, g

I. Determination of Copper

(1) Transfer an aliquot of the sample solution [VI-E-(15)] containing 0.3-0.5 g Cu into a 300-mL electrolytic beaker.

(2) Add 5 mL conc. H_2SO_4 and evaporate to fumes of H_2SO_4 to remove chloride.

(3) Dilute to 200 mL with H_2O.

(4) Add 3 mL boiled, 6M HNO_3 (free of oxides of nitrogen).

(5) Connect a weighed platinum gauze electrode (cathode) to the negative terminal of the electrodeposition apparatus and the platinum stirrer (anode) to the positive terminal.

(6) Place the electrolytic beaker containing the sample solution into position so that most of each electrode is covered by the solution.

(7) Cover the beaker with split watch glasses.

(8) Turn on the current (and stirrer) and adjust the applied potential to about 2.2 V. Allow 0.5 to 1 A current to flow through the cell.

(9) Electrodeposit copper (with stirring) until the solution is colorless.

(10) Add 25 mL more H_2O, reduce the current to about 0.5 A, and electrodeposit for another 15 min.

(11) If no more copper has been deposited on the newly exposed platinum surface, turn off the stirrer.

(12) With the current still flowing, quickly lower the electrolytic beaker below the electrodes and immediately replace with another 300-mL electrolytic beaker containing 250 mL H_2O.

(13) Repeat step VI-I-(12) with a second electrolytic beaker containing 250 mL H_2O.

(14) Remove the second rinse beaker while washing the electrode with a fine stream of wash water as the beaker is lowered.

(15) Turn off the current, remove the cathode from the electrodeposition apparatus, and immerse once more in H_2O.

(16) Rinse the electrode twice in ethyl alcohol, allow to drain, and dry for 5 min. at 110°C.

(17) Cool in ambient air for about 15 min and weigh the electrode plus deposited copper.

(18) Determine the weight of copper deposited by subtracting the weight of the electrode before deposition from the weight of the electrode plus deposited copper.

(19) Combine the solution remaining after electrodeposition with the water used to rinse the electrodes and dilute to 1 L. Use this solution to determine copper which was either not deposited or which dissolved while rinsing the electrode.

(20) Determine μg Cu/mL in solution VI-I-(19) by atomic absorption.

(a) Set up the atomic absorption instrument for the determination of Cu at 324.7 nm according to the instrument manufacturer's recommendations.

(b) Measure the absorbances of the standards, the sample, and then the standards again.

(c) Determine the concentration of copper (μg Cu/mL) in the solution by comparison of the sample absorbance with the average absorbance per microgram of copper per mL as determined from the standards.

(21) Calculate the total grams Cu undeposited by dividing the μg Cu/mL found in solution VI-I-(19) by 1000. Add this number to the grams of deposited copper and calculate the percentage of copper in the sample (see Note 4, p. 32).

$$\text{wt \% Cu} = \frac{(A + a)(100)}{(B)(C)}$$

where A = weight of deposited copper, g

a = weight undeposited copper, g

B = aliquot fraction, $\frac{\text{volume of aliquot analyzed, mL}}{\text{total sample volume, mL}}$

C = sample weight, g

J. Discussion

Materials assayed have included relatively pure commercial sulfide minerals and specially prepared sulfide compounds used to fabricate test batteries. In these cases sulfur and the metal(s) are the major constituents and can be analyzed by the methods reported above without modification.

In other cases, specimens presented for analysis have included sections of sacrificed cells containing LiCl-KCl eutectic, LiAl alloys, and separator materials, and sometimes other materials, in addition to the metal sulfide phase(s). Possible interferences must be considered in these cases.

The determination of sulfur after oxidation to sulfate and subsequent separation from metal cations is quite specific.

The colorimetric iron determination is subject to very few interferences. Silver and bismuth form precipitates with the reagent as does perchlorate. Zinc, cadmium, and mercury form colorless complexes which consume 1,10-phenanthroline yielding low results if excess reagent is not used. Some other elements, as discussed by Sandell,[9] interfere under certain conditions. These elements are usually not present in sufficient quantity, relative to iron, to interfere with its determination.

The colorimetric Co procedure assures that the red Co-nitroso-R salt complex is formed at the required pH of 5.5. Other metal complexes also formed at this pH are later decomposed by addition of sulfuric acid. The cobalt complex, once formed at pH 5.5, is stable in the final acid medium. The addition of citrate, prior to pH adjustment, prevents formation of insoluble hydroxides, especially Mn(II) and Cr(III), which can occlude cobalt and render it unavailable for color development. Limited tests have shown that the procedure as described allows for the determination of 50 micrograms of Co in the presence of at least 11 mg Fe(III), 0.9 mg Ni(II), 0.5 mg Al(III), 0.8 mg Cr(VI), 10 mg Mg(II), and 0.25 mg Mn(II). Many other elements are known not to affect the formation of the Co-nitroso-R salt complex. Sandell[10] and Young[11] discuss, in detail, the determination of Co with nitroso-R salt in the presence of a variety of elements.

The procedure given for the determination of nickel tolerates reasonable amounts of most metals. Palladium and gold would be precipitated by dimethylglyoxime in the unlikely event that they would be present. Hillebrand and Lundell[12] recommend precipitation of nickel from a solution containing acetic acid and sodium acetate when considerable cobalt, manganese, or zinc is present and also discuss, generally, the determination of nickel with dimethylglyoxime.

The determination of copper by electrodeposition requires the absence of elements more readily reduced than copper including As, Sb, Sn, Mo, Au, Ag, Hg, Bi, Se(IV), Te, and platinum metals. Chloride and oxides of nitrogen also interfere. Examination for undeposited copper by atomic absorption spectrophotometry enables the analyst to verify completeness of deposition or to correct for undeposited copper, if necessary.

K. Notes

Note 1. For copper sulfide materials, use a larger sample, 1 to 2 g.

Note 2. Compounds such as FeS_2, after oxidation, yield $Fe_2(SO_4)_3$ + H_2SO_4. Upon evaporation to dryness, H_2SO_4 could be lost by volatilization if heated too hot. Addition of NaCl yields a final product of $Fe_2(SO_4)_3$ and Na_2SO_4 minimizing possible loss of sulfur as H_2SO_4 when the solution is heated to dryness to remove nitrate.

Note 3. The solution should be clear. If a precipitate has formed, remove it by filtration through a 9-cm Whatman #40 (or equivalent) paper. Wash the paper with a hot, dilute 1M ammonium chloride-1M ammonium hydroxide solution. Combine filtrate and washings in 400-mL beaker. Proceed to step VI-H-(5).

Note 4. If the amount of undeposited copper is found to be less than 0.3 mg, the correction can be ignored since the error in the analysis from this source would be less than 0.1% if the amount of deposited copper is 0.3 g or more as recommended in the procedure.

VII. ANALYSIS OF TITANIUM SULFIDE MATERIALS

A. Principle of the Method

A weighed sample is reacted with bromine and HNO_3 to dissolve the titanium sulfide and oxidize sulfur to sulfate. After dissolution and oxidation, the solution is taken to dryness, treated with HCl, and again evaporated to dryness to remove nitrate. The residue is dissolved in HF and diluted to volume. Titanium and sulfate are determined in separate aliquots of the solution. Titanium is determined colorimetrically as the peroxide complex after vigorous fuming with H_2SO_4 to remove F^-. Sulfate is determined gravimetrically as $BaSO_4$ after addition of boric acid to complex excess HF.

B. Reagents, Standards, and Apparatus

(1) NaCl, reagent grade.

(2) Conc. HNO_3, reagent grade.

(3) Conc. HCl, reagent grade.

(4) Conc. HF, reagent grade.

(5) Carbon tetrachloride, reagent grade.

(6) Bromine in CCl_4. See III-B-(2).

(7) Conc. H_2SO_4, reagent grade.

(8) $BaCl_2$, 10% wt/vol. See III-B-(5).

(9) Standardized sulfate solution, $\sim 0.18M$ H_2SO_4. Cautiously add 10 mL conc. H_2SO_4 to about 500 mL H_2O, cool and dilute to 1.000 L. Determine the sulfur concentration of the solution by gravimetric determination of sulfate as $BaSO_4$.

(a) Transfer two 10.00-mL aliquots into 400-mL beakers.

(b) Add 1 mL conc. HCl to each aliquot and to a third beaker, a blank.

(c) Precipitate and determine the weights of $BaSO_4$ in the standards and blank as described in III-D-(12 to 24).

(d) Calculate the mg S/mL in the standard sulfate solution.

$$\text{mg S/mL} \doteq \frac{(A - B)(137.36)}{10}$$

where A = wt $BaSO_4$, g

B = wt blank, g

(10) Ti metal standard, assayed wire.

(11) Hydrogen peroxide, 30% H_2O_2 reagent grade.

(12) Spectrophotometer - see VI-C-(2).

(13) Titanium standard solution, 1.000 mg Ti/mL and 100 μg Ti/mL.

(a) Preparation of stock Ti solution, 1.000 mg Ti/mL. Weigh an amount of Ti metal standard which, when corrected for the assay, will yield 1.000 g Ti. Transfer to a 600-mL beaker, add 100 mL conc. H_2SO_4, and heat until the Ti is dissolved. Cool, cautiously dilute with ∿400 mL H_2O, cool again, and finally dilute to 1.000 L. The concentration of this stock solution will be 1.000 mg Ti/mL.

(b) Preparation of dilute Ti standard, 100 μg Ti/mL. Transfer 20.00 mL of the 1.000 mg Ti/mL stock solution into a 200-mL volumetric flask. Cautiously add 18 mL conc. H_2SO_4 plus about 100 mL H_2O. Cool and then dilute to volume to yield a solution containing 100 μg Ti/mL.

(14) Boric acid solution, saturated solution, about 0.85<u>M</u>.

(15) Filter paper, Whatman #42, 11-cm, or equivalent.

(16) Filter pulp tablets.

(17) Platinum crucibles, 30 mL.

(18) Muffle furnace, capable of attaining a temperature of 850°C.

(19) Sulfuric acid solution, 1.8<u>M</u>. Cautiously add 100 mL conc. H_2SO_4 to approximately 800 mL H_2O. Cool and dilute to 1000 mL with H_2O.

C. Preparation of Samples for Analysis

(1) Weighing the sample. Materials analyzed to date have been supposedly pure materials of nominal composition TiS_2. These materials are somewhat unstable in air so care must be taken in handling and weighing the samples. Samples (∿0.1 g) are transferred to stoppered glass vials in a small, dry, N_2-atmosphere glove bag. Immediately before weighing, the sample vial is uncapped for about 5 seconds to allow the vial to fill with air. The vial is then restoppered and weighed. The sample is then transferred to a

250-mL Teflon beaker containing 30 mL of Br_2 in CCl_4. The empty vial is recapped and reweighed to obtain the net sample weight.

(2) Oxidation and dissolution of sample.

(a) Seal the Teflon beaker containing the sample in 30 mL Br_2-CCl_4 with parafilm.

(b) Swirl to promote contact of the sample with Br_2 in CCl_4. Allow to stand overnight.

(c) Carry a blank of ∿0.5 g NaCl through the entire procedure along with the samples.

(d) Remove the parafilm cover and replace with a watch glass.

(e) Add 15 mL conc. HNO_3 dropwise, swirling after each addition to control the reaction rate.

(f) When dissolution is complete, add 0.5 g NaCl to the sample beaker and evaporate to dryness.

(g) Rinse down the sides of the beaker with H_2O, add 10 mL conc. HCl, and evaporate to dryness. Repeat the addition of HCl and evaporation to dryness.

(h) Add 5 mL conc. HF and 1 mL conc. HCl.

(i) Heat until the residue is in solution.

(j) Cool, transfer to a 100-mL plastic volumetric flask, and dilute to volume.

(k) Carry a synthetic sample along with the sample and blank.

Preparation of synthetic sample: Accurately weigh about 40 mg of Ti metal standard into a 250-mL Teflon beaker. Add 10.00 mL of standardized sulfate solution into the beaker and 0.5 g NaCl and 5 mL conc. HF. Heat at low heat until the Ti metal is dissolved and then take to dryness.

Continue with steps VII-C-(2)-(h) through (j) and carry the synthetic sample along with the samples and blank.

D. Determination of Titanium.

(1) Transfer an aliquot of the solution to be analyzed, containing about 2 mg of Ti, into a 100-mL quartz beaker.

(2) Add 5 mL conc. H_2SO_4 and heat to dryness.

(3) Repeat VII-D-(2), above, twice.

(4) Add 10 mL conc. H_2SO_4 and heat until the residue dissolves.

(5) Cool and carefully add ∿50 mL H_2O.

(6) Transfer to a 100-mL volumetric flask.

(7) Cool, add 2 mL 30% H_2O_2, and dilute to volume with H_2O.

(8) Transfer 10-, 20-, and 30-mL aliquots of the 100 µg Ti/mL standard solution into 100-mL flasks.

(9) Add 2 mL of 30% H_2O_2 to each and to a blank.

(10) Dilute each to volume with 1.8<u>M</u> H_2SO_4.

(11) Measure the absorbances of the samples, sample blank, standards, and standard blank at 407 nm in 1-cm cells *vs.* distilled water as a reference.

(12) Subtract the absorbance of the appropriate blank from the absorbance of each sample and standard to obtain the net absorbance of each.

(13) Determine the micrograms of Ti in the sample aliquot from the net absorbance of the sample and the average net absorbance per microgram of Ti as determined from the standards.

(14) Calculate the percentage of Ti in the sample.

$$\text{wt \% Ti} = \frac{A}{(B)(C)10^4}$$

where A = micrograms of Ti found in the sample aliquot

B = aliquot fraction, $\frac{\text{volume sample aliquot, mL}}{\text{total sample volume, mL}}$

C = sample weight, g

E. Determination of Sulfur

(1) Transfer 20.0 mL of the H_3BO_3 solution into a 600-mL beaker.

(2) Transfer an aliquot of the sample solution containing about 50 mg S into the boric acid solution.

(3) Carry along a blank and an aliquot of the synthetic sample solution.

(4) Dilute the solutions to 300 mL with H_2O.

(5) Heat to boiling and slowly add 5 mL 10% $BaCl_2$ solution.

(6) Add 1/4 tablet filter pulp and stir to disintegrate the tablet.

(7) Cover with a watch glass and allow the solution to digest overnight on the steam bath.

(8) Test the solution for completeness of precipitation of $BaSO_4$ by adding a few drops of 10% $BaCl_2$ solution. No $BaSO_4$ precipitate should appear.

(9) Filter and determine sulfur as described in steps III-D-(17 to 25).

F. Discussion

Experience with the analysis of Ti-S materials has been limited. The main problem we have encountered has been in dissolving the titanium sulfate residue remaining after oxidation with Br_2-HNO_3 in dilute HCl, prior to precipitation as $BaSO_4$. It was found that HF was necessary to keep Ti in solution. The use of HF presents two problems: (1) fluoride ion interferes with the colorimetric Ti determination and (2) fluoride ion will precipitate as BaF_2 and interfere in the sulfate determination. The F^- interference in the Ti determination can be avoided by intensive fuming with H_2SO_4 to volatilize HF. Boric acid was used to complex F^- as HBF_4, thus avoiding interference in the gravimetric sulfate determination.

The results obtained on duplicate determinations of the limited number of samples we have had submitted for analysis are given in Table VI. These data indicate a relative precision of better than ±1% for each determination. Preparation and analysis of synthetic standards, as described above, will allow an estimate of the accuracy of the individual determinations.

Table VI. Summary of TiS_2 Data

Sample Identification	Sample Wt, g	Wt % S	Wt % Ti	Total % S + % Ti	Molar Ratio, S/Ti
77-0406-01,	0.20648	56.92	41.97	98.89	2.03
Great Western	0.20304	56.36	41.84	98.20	2.01
Average		56.64	41.90	98.54	2.02
		1.0% rel.	0.3% rel.		
77-0581-01,	0.10942	50.69	38.39	89.08	1.97
Cerac	0.11648	50.55	38.62	89.17	1.96
Average		50.62	38.50	89.12	1.96
		0.3% rel.	0.6% rel.		
77-0624-01,	0.09574	51.94	45.82	97.76	1.69
Ventron	0.12985	51.81	45.78	97.59	1.69
Average		51.88	45.80	97.68	1.69
		0.3% rel.	0.08% rel.		

VIII. ANALYSIS OF CALCIUM SULFIDE

A. Principle of the Method

Calcium sulfide is assayed by determining calcium, sulfide sulfur, and total sulfur. To determine sulfide sulfur, a weighed sample is reacted with a known volume of standardized $AgNO_3$ in excess of the volume required to precipitate sulfide as Ag_2S. After reaction the Ag_2S is filtered, and the excess Ag^+ is determined in the filtrate by a Volhard titration. The amount of Ag^+ reacting to form Ag_2S is calculated by subtracting the meq of Ag^+ found after formation of Ag_2S from the total milliequivalents of Ag^+ added to the sample.

Calcium and total sulfur are determined on a separately weighed sample. After oxidation of all forms of sulfur to sulfate with bromine the sample is dissolved in dilute HCl, diluted to volume, and separate aliquots are taken for the total S and Ca determinations. Sulfate is determined gravimetrically as $BaSO_4$ after separation of calcium by adsorption onto a cation-exchange column. Calcium is determined by titration with standardized EDTA at pH 12.5 using Acid Alizarin Black SN indicator.

B. Apparatus and Reagents

(1) Cation-exchange column - see VI-C-(1).

(2) Platinum crucibles - 30-mL size.

(3) Muffle furnace, capable of attaining a temperature of 850°C.

(4) Primary standardized silver nitrate solution, 0.1$\underline{M}$ $AgNO_3$. See III-B-(6).

(5) Standardized potassium thiocyanate solution ∿0.05$\underline{M}$. See III-B-(8).

(6) Standardized silver nitrate solution, 0.1$\underline{M}$. See III-B-(9).

(7) Ferric ammonium sulfate indicator solution, ∿40% (wt/vol) $FeNH_4(SO_4)_2 \cdot 12H_2O$. See III-B-(7)

(8) Concentrated nitric acid, reagent grade HNO_3.

(9) Carbon tetrachloride, reagent grade CCl_4.

(10) Bromine in carbon tetrachloride. See III-B-(2).

(11) Concentrated hydrochloric acid, reagent grade HCl.

(12) Barium chloride solution, 10% (wt/vol). See III-B-(5).

(13) Filter pulp tablets.

(14) Calcium standard solution, ∿0.025$\underline{M}$.

(a) Transfer ∿2.5 g primary standard grade $CaCO_3$ to a weighing bottle and dry for 1 h at 285°C.

(b) Cool for 1 h in a dessicator and weigh.

(c) Quantitatively transfer the $CaCO_3$ to a 1-L volumetric flask.

(d) Reweigh the weighing bottle to obtain the weight of $CaCO_3$.

(e) Add ∿100 mL H_2O + 15 mL conc. HCl.

(f) Swirl until $CaCO_3$ is dissolved and dilute to 1 L with H_2O.

(g) Calculate the molarity of the calcium standard solution using:

$$\underline{M} = \frac{\text{wt } CaCO_3\text{, g}}{100.089}$$

(15) Diethylamine, reagent grade.

(16) Acid Alizarin Black SN, 1.0% (wt/vol) aqueous solution. Indicator for titration of calcium with EDTA.

(17) Standardized EDTA solution, 0.01$\underline{M}$. Prepare by dissolving 3.7 g of reagent grade disodium ethylenediaminetetraacetic acid ($Na_2H_2EDTA \cdot 2H_2O$) in H_2O and dilute to 1.000 L. Standardize by the following procedure:

(a) Pipette 10.00 mL of 0.025$\underline{M}$ standard Ca solution into a 150-mL beaker.

(b) Gently evaporate to dryness to remove excess acid.

(c) Add 10 mL H_2O, 1 drop conc. HCl, swirl until the salts are in solution, add 5 mL diethylamine, and dilute to 50 mL with H_2O.

(d) Add 10 drops Acid Alizarin Black SN indicator and titrate with 0.01$\underline{M}$ EDTA until the indicator changes from purple to greenish blue.

(e) Calculate the molarity of the EDTA solution

$$\underline{M}_{EDTA} = \frac{(10)(A)}{B}$$

where A = molarity of Ca standard solution

B = volume, mL, of EDTA used in the titration

C. Preparation of the Sample for Analysis

(1) Weighing the Sample. Calcium sulfide does not appear to be rapidly hydrolyzed by moisture in the air. In one test, a sample, labelled reagent grade CaS, was first assayed for sulfide and found to contain 40.58 wt % $S^=$. The material was then exposed to the atmosphere (in a humid time of the year) for three days and again analyzed for sulfide and found to contain 40.36 wt % $S^=$.

Samples are stored and weighed in a dry box. Subsequent analytical operations are carried out in the laboratory atmosphere. Duplicate aliquots (∿0.1 g) for the $S^=$ determinations and (∿0.4 g) for Ca and total S determinations are accurately weighed into small glass vials fitted with plastic snap tops. The vials are then sealed in a wide mouth, screw-cap jar and removed from the dry box prior to analysis.

(2) Dissolution and Oxidation of Sample for Ca and Total S Determinations

(a) Open the vial containing a weighed sample (∿0.4 g) and transfer it into a glass-stoppered 250-mL Erlenmeyer flask containing 30 mL Br_2 in CCl_4.

(b) Carry a blank through the procedure along with the samples.

(c) Stopper the flask and allow to stand 30 min.

(d) Add 15 mL conc. HNO_3, in increments, swirling after each addition until the reaction has subsided.

(e) Let stand, loosely stoppered, about 30 min and then evaporate to dryness.

(f) Rinse the sides of the flask with H_2O, add 10 mL conc. HCl, and evaporate to dryness.

(g) Repeat VIII-C-(2)-(f).

(h) Add 5 mL conc. HCl and 50 mL H_2O. Warm until salts are dissolved.

(i) Cool, transfer to a 250-mL volumetric flask, and dilute to volume. Use this solution to determine Ca and total S.

D. Determination of Calcium

(1) Transfer 10.00 mL of the oxidized sample solution [VIII-C-(2)-(i)] into a 150-mL beaker.

(2) Carefully evaporate to dryness.

(3) Add 1 drop conc. HCl and 10 mL H_2O. Heat until the $CaSO_4$ residue is dissolved.

(4) Add 5 mL of diethylamine and dilute to 50 mL with H_2O.

(5) Add 10 drops Acid Alizarin Black SN indicator.

(6) Titrate with standardized 0.01<u>M</u> EDTA solution to a bright, blue-green color.

(7) Calculate wt % Ca.

$$\text{wt \% Ca} = \frac{(A)(B)(4.008)}{(C)(D)}$$

where A = mL 0.01<u>M</u> EDTA used to titrate sample

B = molarity EDTA titrant

C = aliquot fraction, $\frac{\text{volume sample aliquot, mL}}{\text{total sample volume, mL}}$

D = sample weight, g

E. Determination of Total Sulfur

(1) Transfer 75.0 mL of the oxidized sample solution [VIII-C-(2)-(i)] into a 150-mL beaker.

(2) Dilute to 100 mL with water.

(3) Separate Ca^{2+} by ion-exchange and determine total S as described in VI-E-(18 to 21) and III-D-(12 to 25).

F. Determination of Sulfide Sulfur

(1) Transfer 40.00 mL of standardized 0.1<u>M</u> $AgNO_3$ into a 500-mL, plastic, wide-mouthed, screw-cap bottle.

(2) Add 0.25 mL conc. HNO_3.

(3) Uncap a vial containing the weighed sample (∿0.1 g) and drop the vial into the $AgNO_3$ solution.

(4) Screw the cap onto the bottle and shake the solution to allow the sample to contact the acidified, standardized $AgNO_3$ solution.

(5) Let stand 4 hours or preferably overnight.

(6) Transfer the $AgNO_3$ solution (and Ag_2S) to a 400-mL beaker using H_2O as rinse solution.

(7) Boil to coagulate Ag_2S.

(8) Filter through an 11-cm, Whatman #40 (or equivalent) filter paper.

(9) Wash filter paper 10 times with H_2O, allowing solution to drain completely between washings.

(10) Dilute the filtrate to 300 mL.

(11) Titrate the excess silver in the filtrate as described in III-E-(9 and 10).

(12) Calculate the percentage of sulfide sulfur.

$$\text{wt \% } S^{=} = \frac{[40(A) - (B - C)(D)](1.603)}{E}$$

where A = molarity of the standardized 0.1$\underline{M}$ $AgNO_3$ solution

B = mL of standardized 0.05$\underline{M}$ KSCN used to titrate excess Ag^+ in VIII-F-11

C = mL of standardized 0.05$\underline{M}$ KSCN to determine indicator blank

D = molarity of standardized 0.05$\underline{M}$ KSCN

E = sample weight, g

G. Discussion

The method for the determination of sulfide sulfur in calcium sulfide is essentially the same as that used for the determination of sulfide in Li_2S except that it is necessary to carry out the metathesis of CaS with $AgNO_3$ to form Ag_2S in an acid medium, 0.1$\underline{M}$ HNO_3. Only under these conditions could consistent sulfide sulfur results be obtained.

Some results obtained on one batch of CaS using the procedures described above are given in Table VII.

The duplicate values for each determination agree well and the essentially perfect agreement between the total and sulfide sulfur values indicate that all of the sulfur is present as sulfide. The molar ratio Ca/S = 0.9994 suggests that the sulfide is present as CaS even though the sum of the Ca and S determinations indicate an assay of only 97.5% CaS. Impurity analysis by emission spectroscopy revealed the presence of Al and Mg as major impurities, each at about 1%, along with ppm amounts of Ba, Fe, Si, Sr, and Ti.

The total sulfur determination is not necessary if only sulfide is to be determined. When compared with the sulfide value, it can indicate the presence of other forms of sulfur, if present.

The calcium determination as described assumes that Ca^{2+} is the only cation present in the sample that will react with EDTA at pH 12.5 and that significant amounts of elements which could precipitate at pH 12.5 and occlude Ca are not present. Otherwise a separation of calcium is necessary, or appropriate masking agents must be used to avoid serious error in the Ca determination.

Acid Alizarin Black SN indicator and its application to the determination of calcium with EDTA is discussed in numerous papers.[13-15]

Table VII. Analysis of One Batch of CaS for Sulfide Sulfur, Total Sulfur, and Calcium

Sample Designation	Wt Sample Analyzed, g	Found, Wt %		
		Ca	$S^=$	Total S
CASA-1	0.1008	--	43.1_8	--
CASA-2	0.1144	--	43.4_5	--
CASA-3	0.3828	54.1_4	--	43.2_9
CASA-4	0.3966	54.1_6	--	43.4_4
Average		54.1_5	43.3_2	43.3_6
Rel. % Dev.		0.04	0.62	0.35

Molar Ratio Ca/S = 0.9994 (using average of $S^=$ and total S values)

ACKNOWLEDGMENTS

Grateful acknowledgment is made to R. C. Crooks and R. E. Telford who tested some of the procedures and made suggestions for improvement. Acknowledgment is also made to Dr. R. J. Meyer and A. Essling for their help in the analysis of titanium sulfide materials.

REFERENCES

1. H. H. Willard and H. Diehl, *Advanced Quantitative Analysis,* D. Van Nostrand Co., Inc., New York, pp. 256-257 (1943).

2. M. C. Farquhar and J. A. Hill, Anal. Chem. *34,* 222 (1962).

3. H. J. Cluley, The Analyst *80,* 354 (1955).

4. F. W. E. Strelow, C. H. S. W. Weinert, and Cynthia Eloff, Anal. Chem. *44,* 2352 (1972).

5. J. A. Page, J. A. Maxwell, and R. P. Graham, The Analyst *87,* 245 (1962).

6. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis,* 2nd Ed., John Wiley and Sons, Inc., New York, pp. 58-66 (1953).

7. V. N. Tikhonov, *Analytical Chemistry of Aluminum,* John Wiley and Sons, Inc., New York, pp. 32-34 (1973).

8. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis,* 2nd Ed., John Wiley and Sons, Inc., New York, p. 712 (1953).

9. E. B. Sandell, *Colorimetric Determination of Trace Metals,* 3rd Ed., Interscience Publishers, Inc., New York, pp. 537-542 (1959).

10. *ibid,* pp. 415-420.

11. R. S. Young, *The Analytical Chemistry of Cobalt,* Pergamon Press, New York, pp. 71-74 (1966).

12. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis,* 2nd Ed., John Wiley and Sons, Inc., New York, pp. 410-411 (1953).

13. R. Belcher, R. A. Close, and T. S. West, Talanta *1,* 238 (1958).

14. R. A. Close and T. S. West, Anal. Chim. Acta *23,* 261 (1960).

15. G. Ross, D. A. Aikens, and C. N. Reilley, Anal. Chem. *34,* 1776 (1962).

Distribution for ANL-80-41

Internal:

M. Ader
R. W. Bane
D. L. Barney
J. E. Battles
M. Blander
M. F. Bouchard
S. Bourne
D. L. Bowers
L. Burris
F. A. Cafasso
E. L. Callis
A. A. Chilenskas
C. S. Chow
C. C. Christianson
M. Contos
G. M. Cook
E. J. Croke
P. T. Cunningham
A. Engelkemeir
A. M. Essling
D. G. Ettinger
P. R. Fields
A. K. Fischer
I. M. Fox
E. C. Gay
D. G. Graczyk
P. F. Gustafson
J. Harmon
R. R. Heinrich
M. I. Homa
F. Hornstra
E. A. Huff
K. J. Jensen (5)
A. M. Jirka
V. M. Kolba
M. Krumpelt
E. T. Kucera
R. F. Malecha (8)
R. L. Malewicki
V. A. Maroni
W. E. Massey
C. C. McPheeters
A. Melton
R. J. Meyer
W. E. Miller
F. C. Mrazek
N. C. Otto
R. J. Popek
P. Raptis
L. Redey
G. Reedy
J. J. Roberts
M. F. Roche
H. Shimotake
J. A. Smaga
M. J. Steindler
J. E. Steinquist
W. E. Streets (5)
R. K. Steunenberg
B. S. Tani
R. J. Thorn
Z. Tomczuk
D. R. Vissers
M. A. Wahlgren
D. S. Webster
F. L. Williams
J. Williams
A. B. Krisciunas
ANL Contract File
ANL Libraries (3)
TIS Files (6)

External:

DOE-TIC, for distribution per UC-4 (177)
Manager, Chicago Operations and Regional Office, DOE
Chief, Office of Patent Counsel, DOE-CORO
President, Argonne Universities Association
Chemical Engineering Division Review Committee:
  C. B. Alcock, U. Toronto
  R. C. Axtmann, Princeton U.
  J. T. Banchero, U. Notre Dame
  T. Cole, Ford Motor Co.
  P. W. Gilles, U. Kansas
  R. I. Newman, Warren, N. J.
  H. Perry, Resources for the Future, Washington
  G. M. Rosenblatt, Pennsylvania State U.
  W. L. Worrell, U. Pennsylvania
W. Adams, Dept. of National Defense, Ottawa, Canada
C. Fillmore, Gould Inc., Rolling Meadows, Ill.
L. McCoy, North American Rockwell Corp., Canoga Park, Calif.