Additional Field Methods Used in Geochemical Prospecting

By The U. S. Geological Survey

This report is preliminary and has not been edited or reviewed for conformity with Geological Survey standards or nomenclature.

Report released for public inspection 16 Sept. 53

Contents

Introduction

The field methods described in this open-file report were developed for use in geochemical prospecting and have not been published. They are being placed on open file to make them available to interested persons. The methods for niobium and vanadium are preliminary reports and as such should be used with caution. The methods for copper, zinc, and lead by nitric acid digestion, and for manganese, antimony and arsenic have been in use for more than a year and have been found reliable. The method for the determination of cobalt in water has been used successfully in one district, and the method for determining citrate-soluble heavy metals has given favorable results in several districts. The method for determining germanium in coal has been tested briefly on coals of known germanium content.

Determination of Microgram Quantities of Antimony in Soils and Rocks

by

F. N. Ward and H. W. Lakin

Introduction

A relatively simple, rapid, and moderately accurate method for the determination of traces of antimony in soils and rocks is described. The suggested procedure is applicable to samples containing from 0.5 to 50 ppm, and with modifications it can be used on samples containing larger amounts. Data obtained during the development of the method shows that four determinations on two rocks containing less than 2 ppm of antimony agree within 0.4 ppm and that four determinations on seven soils containing 2 to 10 ppm of antimony agree within 1 ppm of the mean.

The reaction of antimony (V) with rhodamine B, an anthrone dye, was announced by Eegriewe (1927), in 1927. In hydrochloric acid or in sulfuric acid containing chloride, antimony (V) reacts with rhodamine B to form a red-violet compound or complex ion of unknown composition.

The reaction of rhodamine B with antimony (V) is selective rather than specific. Therefore, antimony must be separated from as many interfering elements as possible. Extraction of antimony (V) from hydrochloric acid solution with isopropyl ether, studied in detail by Edwards and Voigt (1949), effects a reasonable separation of antimony from many elements. Specifically Maren (1947) observed that isopropyl ether extracted slightly more than 90 percent of antimony (V) from 1.5 to 2 molar hydrochloric acid, and that the antimony-rhodamine B, although not extractable by isopropyl ether, could be formed as a fine dispersion in the isopropyl ether phase by shaking an isopropyl ether solution of antimony (V), with an aqueous solution of rhodamine B.

Experiments were made which established the conditions under which the antimony-rhodamine B compound could be obtained as a stable dispersion and subsequently treated as a solution. The isopropyl ether extraction separates antimony from bismuth, chromium, cobalt, lead, and tungsten (Sandell, 1950). Conversely, the isopropyl ether extracts with antimony such elements as iron (III), arsenic, gold, tin, and thallium. Therefore, it was necessary to establish the maximum permissable amounts of these elements which could be allowed during a single determination. The suggested procedure permits the determination of 2 micrograms of antimony in the presence of iron, 30,000 micrograms; arsenic, 250 micrograms; gold and/or thallium, 300 micrograms, and tin, 1000 micrograms.

The method was found to be applicable to routine laboratory and field use. Under field conditions, the method has been used to determine traces of antimony in as many as 20 soil samples in an 8-hour day.

Reagents and Apparatus Required for Field Determinations

Flux, fused sodium bisulfate. Prior to use, heat in a porcelain casserole and fuse gently for 5 minutes. Cool and crush cake.

Hydrochloric acid, 6 M.

Hydrochloric acid, 1 M.

Standard antimony solution, 0.1 percent antimony in 6 M hydrochloric acid. Dissolve 0.274 grams of antimony potassium tartrate in 100 ml 6 M hydrochloric acid.

Standard antimony solution, 0.002 percent antimony in 6 M hydrochloric acid. Dilute 2 ml of 0.1 percent standard solution to 100 ml with 6 M hydrochloric acid.

Ceric sulfate. Dissolve 3.3 grams of anhydrous ceric sulfate in 100 ml 0.5 M sulfuric acid.

Hydroxylamine hydrochloride. Dissolve 1 gram of hydroxylamine hydrochloride in 100 ml water.

Isopropyl ether. Practical grade is suitable provided it is peroxide-free. Saturate with 1 M hydrochloric acid.

Rhodamine B reagent. Dissolve 0.02 grams of rhodamine B, (Tetraethyl rhodamine) in 100 ml 1 M hydrochloric acid.

Sodium sulfite. Dissolve 1 gram sodium sulfite in 100 ml water.

Mullite mortar and pestle, outside diameter of mortar, 75 mm.

One sieve, 80 mesh. The sieve consists of silk bolting cloth, an aluminum holder having an outside diameter of 100 mm.

One aluminum receiver, to fit the sieve holder.

One small camel's hair brush.

Borosilicate glass culture tubes, 18 x 150 mm.

Tubes, flat bottom, 1¼ x 80 mm outside dimensions.

Separatory funnels, Squibb type, 125 ml capacity.

One 100-ml borosilicate glass volumetric flask with stopper.

One test tube rack holding at least 20 tubes.

One separatory funnel rack holding 4 to 6 funnels.

Balance, torsion, with sensitivity of 0.002 gram.

Six 5-ml pipettes, calibrated in tenths of a ml.

One 0.1-ml pipette, calibrated in hundredths of a ml.

One 50-ml graduated cylinder.

Filter paper, No. 42 Whatman, 7-cm diameter.

Funnels, small, diameter of top, 40 mm.

Spatula, small porcelain.

One portable gasoline stove.

Water, purified by passing tap water through one of the several types of resin demineralizers now commercially available.

Procedure

Solution of Sample

Place 0.2 gram of soil or rock ground to pass the 80 mesh sieve and 1.5 grams of flux in a culture tube. Mix the contents by alternately rotating the tube and tapping gently against a hard surface. Heat the tube to effect a fusion of the contents. Continue the fusion until practically all of the organic matter is destroyed and the tube is full of white fumes. Remove tube from heat and while cooling, rotate to form a thin cake around the inner wall. When the tube and contents are cool, add 6 ml 6 molar hydrochloric acid; heat the tube gently and stir the contents until the salts resulting from the fusion are in solution. Do not allow the solution to boil. Add 1 ml sodium sulfite reagent and 3 ml 6 molar hydrochloric acid. Shake tube gently to mix contents. Transfer the contents of the tube to a funnel fitted with a dry, number 42, fluted filter paper and collect filtrate in a 125-ml separatory funnel. Rinse tube and the residue on the filter paper twice with 3 ml hot 6 molar hydrochloric acid and once with 2 ml hot water.

Isopropyl ether extraction of antimony

Cool filtrate in the separatory funnel to 25° C or less, add 3 ml ceric sulfate solution and shake. Add 10 drops of aqueous hydroxylamine hydrochloride, shake and allow the funnel contents to stand 1 minute or until the excess ceric sulfate is destroyed. Add 45 ml water and cool the solution to 25°C or less. Add 5 ml isopropyl ether to the funnel and shake the funnel with moderate vigor for 30 seconds. Allow the solution to stand 5 minutes and drain off all but about 0.5 ml of the aqueous phase. Add 2 ml of a 1 molar hydrochloric acid solution of hydroxylamine and shake the funnel for 1 to 2 seconds. Allow phases to separate and drain off all but about 0.5 ml of the aqueous phase. Add 2 ml of a 1 molar hydrochloric acid and shake for 1 to 2 seconds. Allow phases to separate as before and drain aqueous phase.

Estimation

Laboratory.--Add 2 ml of rhodamine B reagent to the funnel and shake the contents for 10 seconds. When the phases have separated, pour the isopropyl ether into a cuvette and measure the absorbance at 545 to 555 millimicrons. Determine the number of micrograms of antimony from a previously established standard curve.

Field.—In the field, transfer a 3-ml portion of the isopropyl ether solution of the antimony-rhodamine B compound obtained from a sample to a small flat-bottomed Nessler tube. View axially and compare with the isopropyl ether solutions of the antimony-rhodamine B compound prepared similarly from 0.5, 1, 2, 3, and 4 micrograms of antimony.

In the laboratory, if the absorbance of the isopropyl ether solution obtained from a sample is too great for accurate measurement, or in the field, if the color intensity of the ether solution is greater than that of the standard solution prepared from 4 micrograms of antimony, dilute the isopropyl ether solution obtained from a sample with isopropyl ether and shake with 2 ml of rhodamine B reagent. Repeat until the absorbance is within a measurable range. Multiply the number of micrograms of antimony present in the similar standard by a factor obtained by dividing the final volume of isopropyl ether by 4, instead of 5, because about 1 ml of isopropyl ether is not recovered from the first extraction.

Multiply the results obtained by either method of estimation by 5 to convert to parts per million, or divide by 2000 to convert to percent.

Literature Cited

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A Field method for the Determination of Traces of Arsenic in Soils

A confined Spot Procedure Using a Modified Gutzeit Apparatus.

by

Hy Almond

Introduction

Generally traces of arsenic are determined by either the Gutzeit or molybdenum blue procedure. Although reduction to the molybdenum blue complex is a very sensitive test, it is not a suitable method under field conditions because silica and phosphate interfere. In the laboratory, arsenic is separated from most interfering substances by distilling the arsenic halide or hydride, but this method is too awkward for field use. Furthermore, to determine arsenic by the reduction to molybdenum blue the reagents must be free of arsenic, phosphorus, silicon and germanium, all of which react with ammonium molybdate. The ammonium molybdate itself is reduced by the reducing agent, and, to carry out the determination properly, exactly the same amount of reducing agent must be added to the unknown as to the standard solution and both must be under identical conditions (Robinson, Dudley, and Williams, 1934).

None of the macro constituents present in ordinary soils interfere with the Gutzeit method for the determination of arsenic, and this procedure is modified for field use. Solution of the sample is carried out by fusing a wetted sample with potassium hydroxide at a relatively low temperature. Zinc is added to an acidified aliquot in the Gutzeit apparatus, and the gases are passed through lead acetate to a confined spot on mercuric chloride paper. The principle of the confined spot applied to arsenic analysis has been described by Lachele (1934) in a somewhat more complicated procedure. As employed here arsine is passed through a section of glass pipe (fig. 1) to the mercuric chloride paper. The glass pipe is commercially available, and may be acquired as a unit consisting of two sections of glass pipe, an aluminum coupling, and necessary washers and gaskets.

A suitable sensitivity is obtained by this procedure because samples containing as little as 5 ppm arsenic can be determined. This quantity is listed as the average content of arsenic in igneous rocks by Rankama and Sahama (1949).

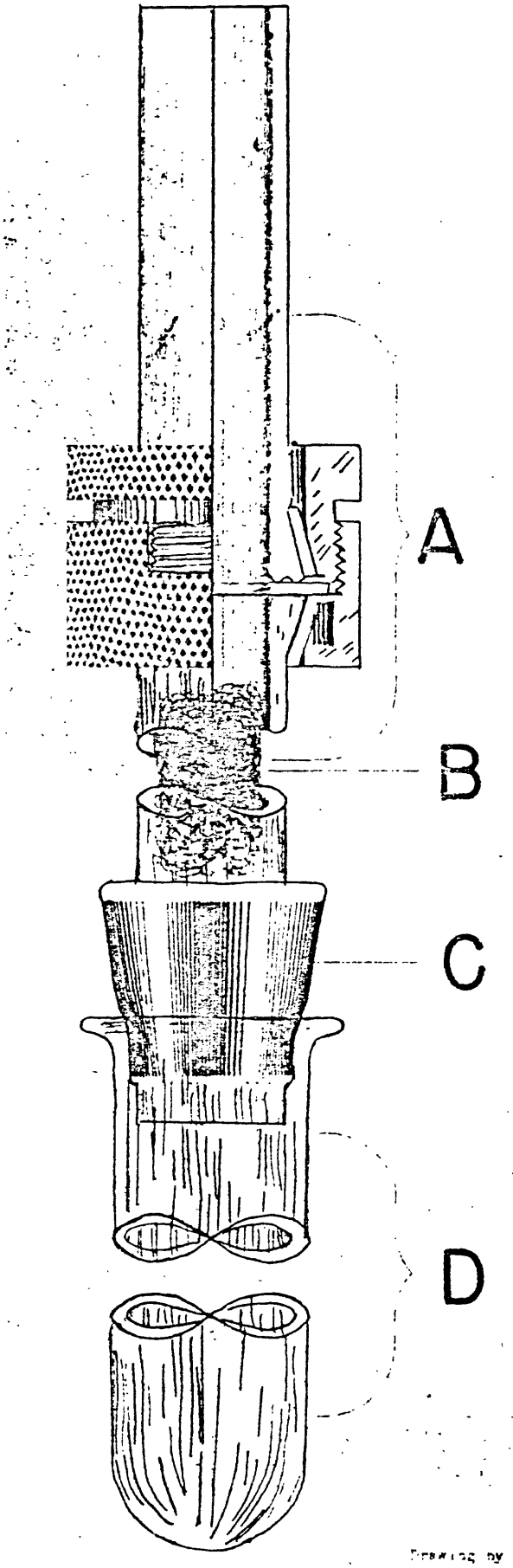
Reagents and Equipment

All reagents should be reagent-grade chemicals free of arsenic.

Potassium hydroxide, pellets.

Hydrochloric acid, concentrated.

Stannous chloride, $SnCl_2.2H_2O$, 10 percent. Dissolve 10 g of stannous chloride in 100 ml concentrated hydrochloric acid. Add about 2 to 3 g of mossy tin.



Drawing by

Fig. 1 Gutzeit Apparatus

Robert L. Tranter, U. S. G. S.

Zinc, mossy.

Standard arsenic solution. Dissolve 0.13 g of arsenic trioxide in 2 ml of 1 N sodium hydroxide, dilute with water to about 50 ml, add 4 ml 1 N hydrochloric acid and dilute to 100 ml. From this stock solution (1,000 micrograms of arsenic per ml), prepare more dilute solutions as needed.

Mercuric chloride paper. Dissolve about 25 g of mercuric chloride in 100 ml ethyl alcohol. Place S&S no. 589 black ribbon filter paper in the solution for one hour. Remove and allow to dry in the air. Cut in 1/2 in. squares and store in a box using only the inside portion of the paper. Prepare fresh batches once a week.

Comparison spots. Prepare artificial standard spots from chrome yellow and deep chrome yellow water colors for the series 1, 2, 4, 10, 20, and 40 micrograms of arsenic. Paint various shades of the chrome yellow and deep chrome yellow on filter paper, and allow to dry. Prepare four spots, each representing 1 microgram of arsenic, in the manner described below under "procedure". Compare these spots with the dry paper which has been colored with water colors and select and punch out a spot as nearly matching the average of the 1 microgram arsenic spots as is possible. Similarly, prepare artificial spots representing 2, 4, 10, 20, and 40 micrograms of arsenic.

Gutzeit apparatus (Fig. 1).

A - Sections of glass pipe with aluminum coupling. Inner diameter 1/4 in. and length 6 in.

B - Lead acetate on glass wool. Dissolve 15 g of $Pb(C_2H_3O_2)_2$ in 100 ml of water acidified with acetic acid. Saturate glass wool in this solution, then dry. Fill the lower section of glass pipe with the dry glass wool saturated with lead acetate. Store excess in a stoppered bottle.

C - No. 4 one-hole rubber stopper.

D - Test tube with rim, borosilicate, 25 x 150 mm.

Water. Pass tap water though a resin demineralizer to free it of arsenic.

Nickel crucible, capacity, 20 ml.

Stirring rod.

Pipet, 10 ml grad. in 0.1 ml.

Graduated cylinders, 5 and 10 ml.

Gasoline stove, a "G. I." pocket stove is suitable for field use.

Procedure

Place a strip of mercuric chloride paper on the washer of the glass pipes and screw the aluminum coupling together.

Transfer a 0.1-gram soil sample ground to pass an 80-mesh sieve to a nickel crucible. Add 4 pellets (about 0.3 gram) of potassium hydroxide and about 5 drops of water to wet the soil. Heat over the gasoline stove until the water evaporates and then fuse for about 2 minutes. Allow the crucible to cool, add 3 ml of water, and stir with a stirring rod until the melt dissolves. Transfer to a 10-ml graduated cylinder. Add 3 ml of hydrochloric acid to the nickel crucible, stir and combine with the original extract. Dilute to 10 ml with water, then mix the solution. Transfer a 2-ml aliquot to a test tube, add 2 ml of concentrated hydrochloric acid, then 1/2 ml of stannous chloride solution, and dilute to 10 ml with water. Add a 2 to 4 gram piece of zinc and quickly insert the rubber stopper holding the glass pipe of the Gutzeit apparatus. Allow to stand 1 hour. Remove the mercuric chloride paper and compare the spot obtained with standards. Determine the arsenic content of samples containing more than 2,000 ppm by transferring a smaller aliquot to the test tube, adding 2 ml of concentrated hydrochloric acid and preparing another spot as directed above.

Literature cited

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Determination of Cobalt in Water

by

Hy Almond

Introduction

Traces of cobalt react with 2-nitroso-1-naphthol in slightly alkaline solution to yield a pink cobalt 2-nitroso-1-naphtholate that is soluble in carbon tetrachloride (Almond, 1953). This property is the basis for a simple method for determining as little as 8 parts per billion of cobalt in water. The yellow color in the aqueous phase is due to reagent; the pink, in the carbon tetrachloride phase, to cobalt-2-nitroso-1-naphtholate. The pH of the solution is adjusted to about 8.5 by adding ammonium hydroxide. The pH of different samples can be reproduced, and subsequently the nitrosonaphtholate is extracted into carbon tetrachloride.

Although the reagent reacts with other elements, notably iron and copper (the nitrosonaphtholates of which are soluble in organic solvents (Boyland, 1946)), conditions are such that the determination is fairly specific for cobalt. Iron III reacts with the reagent optimally at pH 1-2. No iron nitrosonaphtholate is formed at pH of 8.5. As much as 10 micrograms of copper in 50 ml of water did not react with the reagent in the presence of the suggested citrate concentration, whereas 0.4 microgram of cobalt can be determined under these conditions.

Reagents and Apparatus

Sodium citrate solution. Dissolve 10 g sodium citrate in 100 ml water. Adjust to pH 7-8, with 1 N sodium hydroxide, using phenol red as an external indicator.

2-nitroso-1-naphthol, 0.01 percent. Add 2 drops 1 N sodium hydroxide to 0.01 g of the reagent in a 250-ml beaker, enough water to wet the reagent, stir, then add about 2 ml of water and stir until the reagent is in solution. Dilute to 100 ml with water.

Ammonium hydroxide, (1+12).

Thymol blue, W. S., 0.02 g in 100 ml water.

Standard cobalt solution, 0.01 percent. Dissolve 0.04 g of $CoCl_2.6H_2O$ in water, add 1 ml concentrated hydrochloric acid and dilute to 100 ml. This solution contains 100 micrograms of cobalt per ml. Prepare more dilute solutions as needed.

Graduated glass cylinder, G. S., 100 ml.

Automatic pipette, 2-ml capacity, plunger type.

Procedure

To 50 ml of stream water in a glass stoppered graduated cylinder, add 0.5 ml of sodium citrate, 1 drop of thymol blue, then ammonium hydroxide until the solution just turns blue. Add 1 ml 2-nitroso-1-naphthol reagent and 1 ml carbon tetrachloride. Shake for 90 seconds. Compare with standards prepared as follows:

Prepare a series of standard solutions containing 0, 0.4, 0.6, and 0.8 microgram of cobalt. Dilute to 50 ml and proceed as above starting with the addition of citrate. Standards are stable for about a month or more.

To convert the results to parts per million in the water sample, use the following:

$$\frac{\text{Micrograms found}}{50} = \text{parts per million}$$

Literature Cited

Almond, Hy, 1953, Determination of traces of cobalt in soils: Anal. Chem., v. 25, p. 166-167.

Boyland, E., 1946, Separation of the cobalt complex of B-nitroso-α-naphthol from other colored metallic complexes: Analyst, v. 71, p. 230-231.

Determination of Readil, Soluble Copper, Zinc, and Lead in Soils and Rocks; Nitric Acid Extraction

by

Harold Bloom and H. E. Crowe

Introduction

Procedures for the determination of copper, lead and zinc are described by Almond and Morris (1951); Lakin, Stevens and Almond (1949); and Lovering, Huff and Almond (1950). They are also summarized in U. S. Geological Survey Circular 161.

In the procedure given below, a simple attack of the sample with 1+3 nitric acid serves to effect adequate solution of the heavy metals for purposes of geochemical prospecting. Copper, lead, and zinc may be determined on a single sample solution prepared in this way. About 30 samples can be analyzed daily for these constituents.

Reagents

Note: All references to "water" refers to the metal-free type obtained by passing it through a resin demineralizer.

Reagent A. (for lead). Dissolve 25 g of ammonium citrate and 5 g of potassium cyanide and 4 g of hydroxylamine hydrochloride in about 400 ml of water. Add concentrated ammonium hydroxide until solution has a pH of 8.5, using pH test paper as an indicator. Dilute to 500 ml with water.

Purify by extracting the mixture with 15-ml portions of 0.01 percent dithizone solution or until final color of dithizone is green. Wash the aqueous solution with about three 25-ml portions of chloroform, or until the chloroform is colorless. Extract the chloroform from the aqueous solution with about three 25-ml portions of carbon tetrachloride.

Reagent B (for zinc).

(1) Weigh 125 g $Na_2S_2O_3 \cdot 5H_2O$ and bring into solution with about 400 ml water. Purify by shaking with 15-ml portions of 0.01 percent dithizone solutions until the CCl_4 layer is gree Remove dithizone by successive extractions with small portions of CCl_4.

(2) Add 60 ml of glacial acetic acid to about 400 ml water. Weigh out 306 g of sodium acetate$\cdot 3H_2O$ and dissolve in the acetic acid solution. Purify as described above.

(3) Mix 1 with 2 and dilute to 2 liters with water. This is reagent B.

Potassium cyanide, 0.1 percent. Dissolve 1 gram KCN in 1 liter of water. CAUTION: Potassium cyanide is exceedingly poisonous; a very small amount taken internally is fatal. Therefore, never transfer a potassium cyanide solution with a pipette; always wash the hands immediately after handling the reagent and its solutions.

Acidification of cyanide solutions produces a toxic gas (HCN). Never store near acids. Use meticulous care to avoid any possible contact of the salt or its solution with acids resulting from breakage in transport. Never acidify solutions containing cyanide. Always thoroughly wash vessels in which the reagent has been used.

Ammonium hydroxide, 1N. Dilute 70 ml concentrated ammonium hydroxide to 1 liter.

Dithizone, 0.01 percent. Dissolve 0.01 g dithizone in 100 ml CCl_4. Shake intermittently and allow to stand overnight before using.

Dithizone, 0.001 percent. Dilute 10 ml of 0.01-percent dithizone with CCl_4 to 100 ml. Prepare daily and keep in a bottle covered with dark paper. A common thermos bottle (see illustration IV) has been used in the field as a dispenser;2/ in the laboratory, however, an automatic burette has been found satisfactory. It is inadvisable to pipette dithizone solutions by mouth.

Thymol blue indicator, 0.04 percent. Dissolve 0.04 g of the sodium salt in 100 ml of water.

Hydroxylamine hydrochloride. Use best grade obtainable.

pH test paper. pH test paper with range of 2 to 10.

Nitric acid, 1+3. Add 1 volume of concentrated nitric acid to 3 volumes of water.

Carbon tetrachloride. Use the best grade obtainable. If the size of the job is large, it might be advisable to recover the spent organic solvent for reuse. This requires the use of an all-Pyrex distillation setup. However, the still has additional uses: technical grade carbon tetrachloride can be purchased at a cheaper price, purified, and used in place of the more expensive grade. Hydrochloric and nitric acids can be purified by the same distillation setup.

Method of purification: Accumulate the spent liquid in a carboy until it is about three-quarters full. Transfer about 2 liters to a 4-liter separatory funnel. Add about 1 liter of 0.5 N NH_4OH and shake vigorously for approximately 2 minutes. This strips the unreacted dithizone from the organic layer and neutralizes any acid present. The organic layer is transferred to another carboy to which has been added about 1/4 lb activated carbon. In a few days the CCl_4 is clear and ready for distillation. Add about 20 g of lime to a 4-liter distillation flask. Pour about 2 liters of the clear organic liquid into the flask through a large funnel containing a "fast" fluted filter. Distill at about 80°C.

2/ Suggested by Mr. L. M. Wilson of American Smelting and Refining Co.

Ammonium citrate, 10 percent. Dissolve 100 g $(NH_4)_2 HC_6H_5O_7$ in about 400 ml of water. Purify by shaking with successive portions of 0.01-percent dithizone until the carbon tetrachloride layer is green. Remove dithizone by successive extractions with small portions of CCl_4. Dilute to 1 liter.

Preparation of standard solutions

Copper, 0.01 percent (100 micrograms per ml). Dissolve 0.2 g of $CuSO_4.5H_2O$ in water; add 50 ml of 1N HCl and dilute to 500 ml with water.

Copper, 0.001 percent (10 micrograms per ml). Transfer 10 ml of the above to a 100-ml volumetric flask. Add 9 ml of 1N HCl and dilute to 100-ml volume with water.

Zinc, 0.01 percent (100 micrograms per ml). Dissolve 0.1 g reagent grade, 30 mesh, zinc in a slight excess of conc. HCl, and dilute to 1 liter with water.

Zinc, 0.001 percent (10 micrograms per ml). Transfer 10 ml of above solution to a 100-ml volumetric flask and dilute to volume with water.

Lead, 0.01 percent (100 micrograms per ml). Dissolve 0.016 g of dried $Pb(NO_3)_2$ in water containing 1 drop of conc. HNO_3, and dilute to 100-ml volume with water.

Lead, 0.001 percent (10 micrograms per ml). Add 10 ml of above solution to about 25 ml of 1N nitric acid and make up to 100-ml volume with water.

Apparatus

Hot plate. 6 in. x 6 in. with built in thermostat control. See illustration I.

1 test tube digestion rack. Fabricated from 1/4 in. metal plate, 8 1/2 in. square, supported by four legs 8 1/2 in. high. Plate has 33 holes 11/16 in. in diameter, grouped in a 5 3/8" square. See illustration I.

50 anti-bump glass tubes. A 5-ft. length of Pyrex tubing 4mm in diameter is divided up into 7 in. lengths. One inch from the bottom the tube is heated until soft and a 1/4 in. area is fused by pinching the tube with a pair of tongs. (M. Matviak, 1951) See illustration II.

100 Pyrex culture tubes. 16 x 150 mm, marked at 10 ml.

30 screw capped culture tubes. 25 x 200 mm. See illustration III.

3 screw capped culture tube holders. A block of wood 9 in. x 1 1/2 in. x 4 1/2 in. has 5 holes, 1 1/8 in. in diameter bored 3 1/2 in. deep. A hole 1 1/8 in. in diameter is put through at the base of the 3 1/2 in. bore, and perpendicular to it. See illustration III.

Water demineralizer. A resin demineralizer type producing 10 gallons of demineralized water.

Sieve. An inexpensive sieve may be made this way: Remove the center piece from the cover of a 1 pint size ice cream container. Replace the center piece with a piece of silk bolting cloth (80 mesh size) and press the band of the cover back in place. Finally, remove bottom of container.

2 separatory funnel holder.

1 separatory funnel, 2 liter (Pyrex).

1 separatory funnel, 125 ml (Pyrex).

2 test tube racks to hold 30 16x150 mm culture tubes each.

Test tube brushes.

1 spatula

1 camel's hair brush.

4 dropping bottles. 250-ml size

1 wash bottle, polyethylene, 500-ml size.

6 400 ml beakers.

4 glass stirring rods.

1 2-liter Pyrex bottle for storing reagent B.

2 500-ml Pyrex bottles.

8 1-liter Pyrex or polyethylene bottles.

1 automatic pipette. 25 ml capacity, graduated in tenths.

6 25-ml graduate cylinders with ground glass stoppers.

3 100-ml graduates.

3 0.5-ml capacity micro pipettes. Graduated in tenths.

2 each, 4-ml, 3-ml, and 1-ml transfer pipettes.

Balance. Sensitivity 2 mg.

2 serological pipettes. 1.0 ml, graduated in hundreths of a ml.

2 serological pipettes. 5.0 ml, graduated in tenths of a ml.

1 porcelain pipette holder.

Procedure

Weigh 0.1 gram sample (minus 80 mesh) and transfer to a 16x150 mm culture tube previously marked at 10 ml volume. Add 3 ml of 1+3 HNO_3 to the tube and digest for 1 hour on the hot plate. If, during the digestion, the volume gets very low, add some water to prevent dryness. If solution bumps, insert an anti-bump glass tube. Remove the tube from the heat, bring volume to the 10-ml mark with water, close with thumb and mix by inverting the culture tube. Allow the solution to settle for about 15 minutes. From this solution run zinc, lead, and copper as follows:

Zinc.--Add 8 ml of reagent B to the screw cap culture tube and 1-ml aliquot of the unknown. Maximum aliquot is 3 ml (larger amounts may not be buffered satisfactorily). Add 5 ml of 0.001 percent dithizone, tighten screw cap and shake actively for 30 seconds. Compare with standards. If zinc content of aliquot used is less than or greater than the end standards, repeat using an appropriate aliquot. Five or more unknowns can be run simultaneously.

Standards:--Add 8 ml of reagent B to each of 5 screw-cap culture tubes. Add 0, 1, 2, 3, and 4 micrograms (taken from the 10 micrograms/ml standard solution) to these tubes followed by 5 ml of 0.001 percent dithizone. Shake actively for 30 seconds. Examine blank for any sign of contamination.

Lead.--Add 10 ml of reagent A to separatory funnel, 2-ml aliquot of the unknown sample, and two drops of thymol blue. Adjust to pH 8.5 by titrating with 1N NH_4OH to a blue-green color (a mixture of the blue of the thymol blue and the yellow of the solution). Add 5 ml of 0.001 percent dithizone and shake gently for about 12 seconds. Drain the CCl_4 phase into a 25 ml glass stoppered Pyrex graduated cylinder containing 10 ml of 0.1 percent KCN. Shake gently for about 5 seconds or until the excess of green dithizone is removed. Compare the pink solutions with standards. If lead content of aliquot used is less than or greater than the end standards, repeat using an appropriate aliquot.

Standards:--Prepare standards of 0, 1, 2, and 3 micrograms as follows: Add 10 ml of reagent A to a separatory funnel, followed by 1, 2, or 3 micrograms of lead. Add 2 drops of thymol blue and titrate, if necessary, with 1N NH_4OH to first blue color (pH 8.5). Add 5 ml of 0.001 percent dithizone and shake gently for about 12 seconds. Proceed as with the unknowns from this point.

A 1-microgram lead standard is a weak pink color and corresponds to 30 ppm when the above procedure is followed. A visual estimation of a pink color containing more than 3 micrograms of lead is difficult. Either increase or decrease the aliquot depending upon the concentration of the pink layer.

These standards are easily decomposed and should be kept away from direct light as much as possible. They are good for about 4 hours at best. If the pink color of the lead dithizonate of either the standards or the unknowns is observed to fade within a few minutes after they are prepared, the cause might be due to

a deteriorated CCl_4. It has been noted that, after repeated distillations of CCl_4 under field conditions, a decomposition product accumulates, which interferes in the test. Extraction of two parts of CCl_4 with one part of 1N NH_4OH may often restore this distillate. (See reagents - carbon tetrachloride).

Copper.--Add 1 ml of 10 percent ammonium citrate to a screw-capped culture tube followed by a 2-ml aliquot of the unknown solution. Wash sides of tube down with water. Add 2 drops of thymol blue indicator and titrate to a pink tinge using 1 N HCl. It can be back-titrated with 1N NH_4OH, if necessary. Add 2 1/2 ml of 0.001 percent dithizone and shake actively for two minutes. Compare with standards. If copper content of aliquot used is less than or greater than the end standards, repeat using an appropriate aliquot. If oxidation of the dithizone (as evidenced by the appearance of yellow hues) is observed, repeat the analysis but add about 0.1 g hydroxylamine hydrochloride before adjusting the pH. About 5 samples can be handled at the same time.

Standards.--Add 1 ml of 10 percent ammonium citrate to 5 screw-capped culture tubes and 0, 1, 2, 3, 4 micrograms of copper, respectively. Add 2 drops of thymol blue and titrate to pink tinge with 1N HCl. Wash down the sides with water. Add 2 1/2 ml dithizone and shake actively for 2 minutes. One microgram of copper is equivalent to 50 ppm copper when the above procedure is followed.

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Matviak, M., 1951, On the prevention of bumping: Chemist Analyst, v. 40, p. 64-65.

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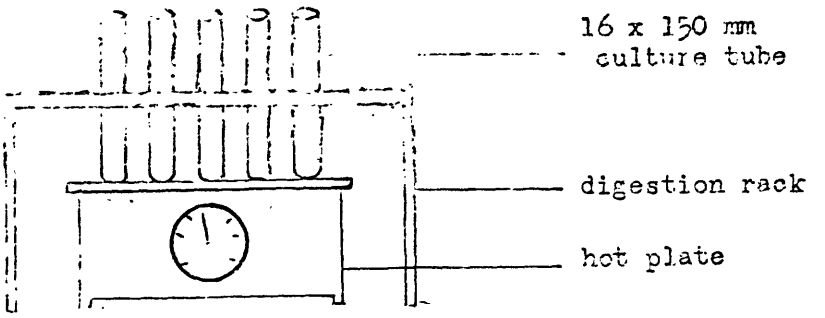
Conversion of micrograms per aliquot to parts per million in samples

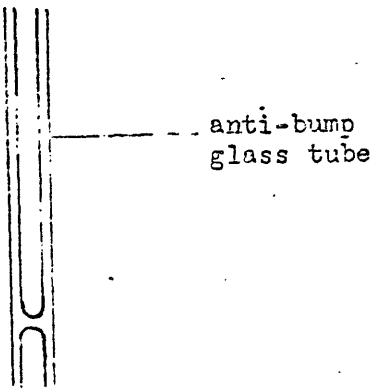
(Based on 0.1 g sample diluted to 10 ml)

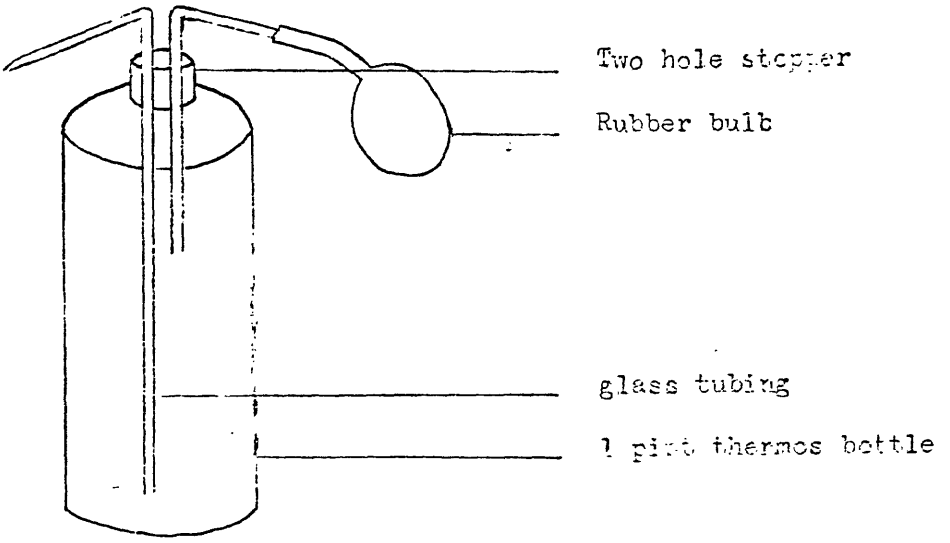
Micrograms found 0.5	1	1.5	2.0	2.5	3	3.5	4
Aliquot taken (ml)	Parts per million						
0.01	5,000	10,000	15,000	20,000	25,000	30,000	35,000	40,000
0.05	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000
0.25	200	400	600	800	1,000	1,200	1,400	1,600
0.5	100	200	300	400	500	600	700	800
1.0	50	100	150	200	250	300	350	400
2.0	20	50	70	100	130	150	180	200
3.0	20	30	50	70	80	100	120	130
4.0	10	20	40	50	60	70	90	100
5.0	10	20	30	40	50	60	70	80

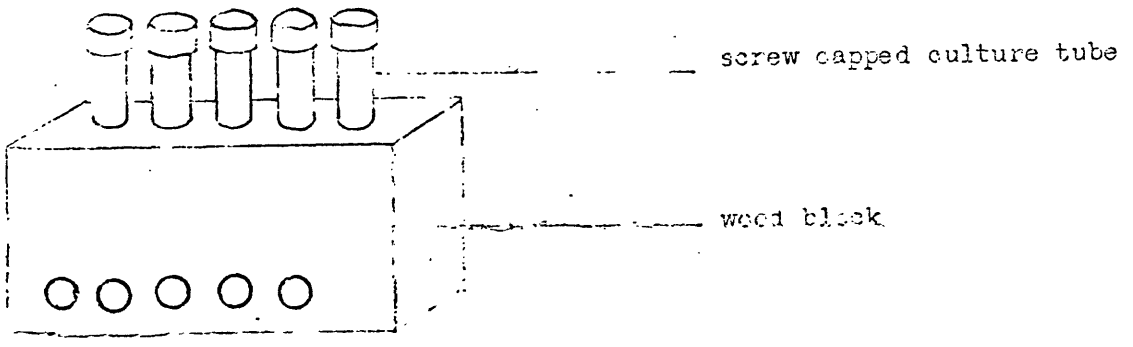
This chart is used for calculating directly in parts per million, the zinc, copper or lead values.

An example of the use of the chart: A 3.0 ml aliquot gave a zinc standard of 2.0 micrograms. Pick out the 3 in the column under "Aliquot", move horizontally until you intersect the vertical column under 2.0 micrograms, and read 70 ppm.


16 x 150 mm
culture tube
digestion rack
hot plate


anti-bump
glass tube


Two hole stopper
Rubber bulb
glass tubing
1 pint thermos bottle


screw capped culture tube
wood block

Determination of Germanium in Coal

by

Hy Almond

Introduction

As part of a geochemical study of the occurrence of minor elements in American coals, Stadnichenko, Murata, Zubovic and Hufschmidt (1953) have obtained data on the concentration of germanium in coal. The ashes of the coal sample were analyzed spectrographically. To supplement this program a rapid method for the determination of germanium in coal under field conditions was developed. With slight modification, the phenylfluorone absorptiometric method described by Cluley (1950) was found to be satisfactory. Cluley prepared a calibration graph using an Ilford No. 603 blue-green filter; however, he gave no information concerning absorption studies.

Absorptiometric studies carried out with a Beckman DU spectrophotometer indicated the reagent absorbed maximally between 450 and 460 mμ, whereas the germanium phenylfluorone complex absorbed maximally at 490 mμ. Adherence to Beer's law was good between 1 and 10 micrograms of germanium at 490 mμ.

In order to carry out the analysis in temporary laboratories in the field, the sample decomposition was modified from a fusion with sodium carbonate to one with sodium hydroxide. The distillation apparatus is an all-glass Erlenmeyer wash bottle to which a pipette is attached. A pink-orange color is developed in an aliquot of the distillate and gum arabic is added to stabilize the color.

Reagents and Apparatus

Phenylfluorone. Dissolve 0.03 g in 85 ml of ethyl alcohol and 5 ml (1+6) sulfuric acid by warming on steam bath, then dilute to 100 ml with ethyl alcohol.

Gum arabic. Add 0.05 g to 100 ml water and warm until in solution.

Potassium hydroxide, reagent grade, pellets.

Hydrochloric acid, conc., reagent grade.

Hydrochloric acid, approximately 1 N. Dilute 83 ml of concentrated acid to 1 liter with water.

Hydrochloric acid, (1+1). To 500 ml of water, add 500 ml of concentrated acid. This is essentially constant boiling acid.

Standard germanium solution, 0.01 percent. Dissolve 0.144 g of germanium dioxide in a minimum of 0.1 N sodium hydroxide and dilute to 1 liter. This solution has 100 micrograms of germanium per ml.

Glass still. Remove the capillary lower tip and the upper end at the calibrated mark of a 10-ml volumetric pipette. Connect the long stem of the pipette to the inlet end of an all-glass 125-ml Erlenmeyer wash bottle head, by sealing glass to glass. Seal off the outlet end of the Erlenmeyer head.

Test tubes, 18 x 150 mm.

Culture tubes, 16 x 150 mm.

Nickel crucibles, capacity 20 ml.

Stirring rod, Pyrex.

Beaker, 50 ml.

Pipettes, graduated, 1 ml.

Litmus paper.

Procedure

Transfer 0.1 g finely ground coal sample and about 0.5 g potassium hydroxide (4 pellets) to a nickel crucible. Moisten the mixture with water, then fuse for about 1/2 hour. Cool, add 10 ml water, and stir with a glass rod. Transfer the contents of the crucible to a graduated cylinder, add 1 N hydrochloric acid until just acid to litmus, then note the volume and transfer the contents to the Erlenmeyer still. Add a volume of concentrated hydrochloric acid equal to the previously noted volume to the still. Place the modified inlet and outlet head in the Erlenmeyer, apply a low flame to the still and collect about 10 ml of distillate in a test tube resting in a beaker of cold water.

Transfer exactly 1.0 ml to a culture tube, add 1 ml gum arabic solution, and dilute to 10 ml with water. Add exactly 0.5 ml of phenylfluorone solution. Compare with standards.

Prepare a series of standard solutions by adding 0, 0.1, 0.3, 0.6, 1.0, 2.0, 4.0, 8.0 and 15.0 micrograms of germanium from standard solutions to a series of culture tubes. Slightly acidify with N hydrochloric acid, then add exactly 1 ml of (1+1) hydrochloric acid. Add 1 ml of gum arabic solution and dilute to 10 ml with water. Add exactly 0.5 ml phenylfluorone solution. These standards are stable for about one work day. Calculate germanium concentration as follows:

$$\frac{\text{ml of the distillate} \times \text{micrograms in the unknown} \times 10}{} = \text{ppm Ge.}$$

Example. Starting with 0.1 g sample, collect 9 ml of distillate. The color developed from 1-ml aliquot corresponds to the 0.3 microgram standard. Substituting above:

$9 \times 0.3 \times 10 = 27$ ppm of Ge in the unknown coal.

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A Field Method for the Determination of Ammonium Citrate - Soluble Heavy Metals in Soils and Sediments as a Guide to Ore

by

Harold Bloom

Introduction

Procedures have been described for the rapid determination of copper by Lovering, Huff and Almond (1950), lead by Almond and Morris (1951), zinc by Lakin, Stevens and Almond (1949), and heavy metals by Huff (1951), in soil and sediment. A still more rapid and simple method was needed for reconnaisance studies in geochemical prospecting.

Agricultural scientists have long used sodium acetate extractions to determine "available" elements in soils; the methods are summarized by Lunt, Swanson and Jacobson (1950). Lovering, Sokoloff and Morris (1948) used a cold acetate extraction on crushed rock to determine heavy metals as related to alteration halos. Chisholm (1950) found distilled water adequate as an extractant of heavy metals from soils for prospecting purposes.

In the method described here, the sample is shaken with an ammoniacal solution of citrate and a solution of dithizone in xylene, and is then allowed to stand for 30 seconds to permit the phases to separate. Colors from green, to blue, and finally to red in the xylene layer reflect increasing amounts of heavy metals.

Xylene (Warren, Delavault and Irish, 1951) is used in preference to carbon tetrachloride or chloroform because it collects on the surface of the aqueous phase, free of sediment. Reagent "A", dithizone solution, and water in polyethylene wash bottles are conveniently carried in an apron. Appropriate amounts of reagents are delivered by squeezing these bottles. About a minute is required for each determination.

Reagents and Apparatus

Note: All references to "water" refers to metal-free water, which is obtained by passing it through a resin demineralizer. Frequently, stream water of low heavy metal content may be used.

Dithizone in carbon tetrachloride, 0.01 percent, (for purifying solution "A"). Dissolve 0.01 g of dithizone in 100 ml carbon tetrachloride approximately 12 hours before using.

Dithizone in xylene, 0.01 percent. Prepare stock solution by dissolving 0.01 g dithizone in 100 ml xylene approximately 12 hours before using. Prepare solution of 0.003 percent by diluting 30 ml of stock solution to 100 ml with xylene.

Solution "A". Dissolve 25 g of ammonium citrate and 4 g of hydroxylamine hydrochloride in about 300 ml of water. Add concentrated ammonium hydroxide until the solution has a pH of about 8.5 using a pH test paper and dilute to 500 ml with water. Remove heavy metals by extracting the solution with 15-ml portions of 0.01 percent dithizone or until the final color of dithizone is green. Wash the aqueous solution with 25-ml portions of chloroform, until the latter is colorless.

Xylene, C. P. grade.

Carbon tetrachloride, C. P. grade

pH test paper, range pH 2 to pH 10.

Potassium cyanide, 5 percent. Dissolve 5 g of KCN in 100 ml of water.

6 glass-stoppered cylinders, 25 ml, Pyrex

3 polyethylene wash bottles, 16 oz.

2 bottles, 1 liter, Pyrex or polyethylene

2 bottles, 500 ml, Pyrex or polyethylene.

Lucite spoon. A lucite bar with cavity, accomodating about 0.1 g of finely ground soil, drilled at one end.

2 dropping bottles. 200 ml.

2 graduate cylinders, 100 ml.

Procedure

Place one scoopful of sample (preferably fine fraction) into a 25-ml glass-stoppered cylinder. Add 5 ml of solution "A", 1 ml of 0.003 percent dithizone solution, and shake vigorously for 5 seconds. Allow about 30 seconds for the layers to separate and observe the color of the upper (xylene) layer. If the color is green, green-blue or blue, record as 0, 1/2, or 1 ml, respectively. If the color is blue-purple to red, titrate with about 1-ml increments of dithizone solution, shaking for 3 seconds after each addition, until a blue color is obtained. Record the volume of dithizone solution used, as an index of the heavy-metal content. Thus, ascending values for heavy metals would be recorded as 0, 1/2, 1, 2, 3 ml etc.

One can identify the predominating metals by the following tests:

Lead: Add 3 drops of 5 percent KCN solution to the cylinder containing sample, dithizone, and solution, and shake vigorously for 5 seconds. Should the color in the xylene layer persist, it may be attributed to lead.

Copper: Introduce an abnormal amount of sample, about a gram, and extract as described. A brown color in the xylene layer which will turn to purple upon the addition of more dithizone, indicates a predominance of copper.

Zinc: If the predominating metal is neither lead nor copper, it may be assumed to be zinc.

Discussion

Dithizone solutions should be as fresh as possible when used. Vials containing a fairly accurate weighing of 0.01 g should be prepared before leaving for the field to facilitate preparation of fresh solutions.

Ammonium citrate and hydroxylamine hydrochloride need not be accurately weighed. A container previously calibrated may be used to scoop the approximate weight of the chemical. The adjustment of the alkalinity of solution "A" should be carried out rather carefully as the rate of formation of the metal dithizonates varies with the pH.

If the dithizone colors are not clear, the dithizone solution may have deteriorated. The old dithizone solutions should be discarded and a fresh set prepared. Occasionally a manufacturer's best grade of xylene may prove to be unsatisfactory. This may be restored for use if it is distilled in the presence of lime. As xylene is inflammable, the distilling flask should be heated by means of a controlled electric heating coil.

Xylol, the commercial grade of xylene, should not be used unless distilled.

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A Field Method for the Determination of Manganese in Soils

Adapted from methods described in the literature

by

Hy Almond

Introduction

The possibility that manganese mineralization is associated with economic ore deposits such as zinc and that, by locating manganese mineralization, a prospector may find other elements of economic importance, led to the request for a method for determining manganese in soils. There are several ways of oxidizing manganese compounds in solution to the purple permanganate. All of these have suitable sensitivity for determining manganese in soils. The periodate method was selected and found to be satisfactory.

A potassium bisulfate fusion followed by acid leachings dissolves most of the manganese present in soils or rocks; field estimation of manganese is feasible from this solution. The color is developed by boiling the resulting solution to which periodate has been added. The purple color is compared with permanganate standards which are stable for at least several weeks.

Reagents and Equipment

All reagents and equipment should be free of manganese, and all reagents should be analytical reagent grade.

Standard manganese solution. Dissolve 0.2 g of pure manganese metal in (1+6) nitric acid, boil to expel nitrogen oxides, and dilute to 1 liter. This solution contains 200 micrograms per ml. Prepare more dilute solutions from this stock solution.

Potassium bisulfate, $KHSO_4$, ground to a fine powder.

Sulfuric acid, H_2SO_4, concentrated.

Sulfuric acid, 1 N. Transfer 28.5 ml of concentrated sulfuric acid to a 1-liter volumetric flask containing about 500 ml of water and dilute to 1 liter with water.

Nitric acid, 1+3. Add 100 ml of concentrated HNO_3 to 300 ml of water.

Phosphoric acid, ortho, H_3PO_4, 85 percent.

Potassium periodate, meta, KIO_4, powdered.

Culture tubes, 16 x 150 mm. Calibrate at 10 and 20 ml.

Water, free of chloride. Water passed through a resin demineralizer is adequate.

Gasoline stove. A "G. I." pocket stove is satisfactory.

Wash bottle, 250-ml capacity, polyethylene.

Pipets, 1 and 5 ml, graduated.

Automatic pipet, calibrated to deliver 2, 1, 0.5, and 0.25 ml.

Digestion and fusion rack. This piece of apparatus is used to support 8 culture tubes over a gasoline stove. The rack consists of two disks of sheet steel welded to a central supporting rack. Each disk has eight holes for test tubes; the holes in the bottom are smaller so that culture tubes cannot slip through but large enough to permit the ready flow of heat.

Balance, torsion, with a sensitivity of 2 mg.

Procedure

Mix 0.1 g of finely ground soil or rock with 0.5 g of potassium bisulfate in a culture tube and fuse for 3 minutes over a gasoline stove. Cool, add 3 ml 1 N sulfuric acid, and digest in a water bath until the lumps of flux decompose to a fine powder. Dilute to 10 ml with water. Allow to stand for 30 minutes, then transfer 0.5 ml of the supernatant solution to a clean culture tube. Using automatic pipets add 2 ml 1:3 nitric acid, 1 ml concentrated sulfuric acid and 0.5 ml phosphoric acid. Add 0.2 g potassium periodate. Boil for 1 minute, then digest in a water bath for 10 minutes, cool and dilute to 20 ml. Compare with standard solutions.

Preparation of standard solutions.--Prepare a series of standard permangate solutions as follows: Add 1, 3, 5, 8, 12, and 20 micrograms of manganese to six culture tubes. To each culture tube add 2 ml 1:3 nitric acid, 1 ml concentrated sulfuric acid, and 0.5 ml phosphoric acid, then 0.2 g KIO_4. Boil for 1 minute, then digest in a water bath for 10 minutes. Cool and dilute to 20 ml. Stopper with a cork stopper.

To calculate the percent of manganese use the following:

micrograms found ÷ 50 = percent manganese

or

micrograms found x 200 = ppm manganese

Determination of Microgram Quantities of Niobium in Rocks

by

F. N. Ward and A. P. Marranzino

Introduction

Until recently the determination of traces of niobium was impracticable except by spectrographic methods, because sufficiently sensitive chemical reactions were unknown.

In 1938, Mon' jakova and Fedorov (1938) discovered that the yellow product resulting from the reaction of niobium and thiocyanate in an acid stannous chloride medium was extractable with ethyl ether. Alimarin and Podvalnaja (1946) used this extraction in developing a colorimetric method based on the above reaction. Freund and Levitt (1951) determined the effects of a number of variables when the yellow niobium-thiocyanate was formed in an acetone-water mixture. Lauw-Zecha, Lord and Hume (1952) made a similar study using ethyl ether to extract the niobium-thiocyanate from the aqueous solution.

As niobates that are somewhat refractory are amenable to an alkali pyrosulfate fusion (Hillebrand, Lundell, Bright and Hoffman, 1953), and pyrosulfate is effective solvent-wise against a number of minerals (Axelrod, 1942-45), it seemed logical to try such a fusion to effect solution of niobium in rocks. Accordingly, the pyrosulfate fusion of the rock was extracted with tartaric acid and an aliquot of the acid was treated with stannous chloride and thiocyanate. The yellow-colored niobium-thiocyanate was extracted into ethyl ether.

The extraction step separates niobium from iron and reasonable amounts of molybdenum and tungsten. Lauw-Zecha, Lord, and Hume (1952) show that in the presence of tartaric acid, iron, uranium, and titanium do not interfere in a 100-fold excess; vanadium, molybdenum, tungsten, and platinum interfere in a 10-fold excess.

If a suitable instrument is available to measure the absorbance of the yellow-colored niobium-thiocyanate, a standard curve can be established, and then the proposed method can be applied to materials containing from 25 to 2000 ppm of niobium. However, if no instrument is available, and standards are prepared as directed in the procedure, the method can be applied to materials containing from about 250 to 2000 ppm of niobium. Although the method can be used in the field, it has been tested and found to be extremely useful in a routine laboratory for screening samples; thirty to forty samples can be run in an ordinary day.

Ethyl ether. Unless specially packaged, all dry ethers on standing tend to form explosive peroxides. Peroxides of ethyl ether are not only dangerous, but they interfere with the niobium method. To test for peroxides, shake 5 ml of ether with 5 ml of an acidified aqueous solution of potassium iodide. If the aqueous solution shows more than a faint yellow color, due to free iodine produced by the reaction of peroxides with iodide, the ether contains appreciable quantities of peroxides and should not be used. Shake peroxide-free ether with 1/10 its volume of equal amounts of stannous chloride and potassium thiocyanate reagents on the day it is to be used.

Hydrochloric acid-tartaric acid reagent. Dissolve 15 g tartaric acid in 100 ml of 9 molar hydrochloric acid.

Potassium thiocyanate. Dissolve 20 g KSCN in 100 ml water.

Sodium bisulfate, fused, reagent quality. Grind to a powder to facilitate mixing with sample.

Stannous chloride. Dissolve 15 g $SnCl_2 \cdot 2H_2O$ in 100 ml of concentrated hydrochloric acid.

Standard niobium solution, 0.02 percent. Solution A. Prepare by fusing 0.0286 g Nb_2O_5 with 1.5 g fused sodium bisulfate in a porcelain, or preferably a vitreosil crucible. Dissolve the fused mass in 1 molar tartaric acid and make up to 100 ml with 1 molar tartaric acid. This solution contains 200 micrograms of niobium per ml.

Standard niobium solution, 0.002 percent. Solution B. Prepare by diluting 10 ml of solution A to 100 ml with 1 molar tartaric acid and mixing thoroughly. This solution contains 20 micrograms of niobium per ml.

Tartaric acid, 1 molar. Dissolve 15 g tartaric acid in water and make up to 100 ml.

Water. Pass tap water through a resin demineralizer.

Balance, torsion, sensitivity 2 mg.

Borosilicate culture tubes, 18 x 150 mm.

1 borosilicate volumetric flask with stopper, 100 ml.

12 borosilicate volumetric flasks, capacity 10 ml.

1 camel's hair brush, length of brush part - 18 mm.

1 digestion and fusion rack to support 8 to 10 tubes over the gasoline stove.

Ear syringes.

Glass filtering fiber, fineness AAA.

Mullite mortar and pestle, outside diameter of mortar, 75 mm.

1 portable gasoline stove.

8 separatory funnels, Squibb type, capacity 60 mm.

1 separatory funnel rack.

2 sereological pipettes, 10-ml capacity, calibrated in tenths of a ml.

Sieve, 80 mesh. 80 mesh silk bolting cloth in an aluminum holder with outside diameter of 100 mm.

Steven's extraction sticks. These are made by constructing a glass tube, 170 mm long and 7 mm inside diameter, near one end and packing the resulting small bulb with fine borosilicate glass fiber to serve as a filtering medium. Small cork stoppers can be inserted in the opposite end, or a number 13 ground-glass joint provided with a number 13 glass stopper can be fused on that end. In the niobium method, corks are satisfactory.

1 test tube rack, capacity 20 tubes.

Procedure

Solution of sample.--Place 0.2 g of soil or rocks ground to pass an 80 mesh sieve and 4 g of sodium bisulfate in a borosilicate glass culture tube. Mix by alternately rotating the tube and tapping gently against a hard surface. Place the tube in the fusion rack over the gasoline stove and heat to effect a fusion of the contents. Continue the fusion for 15 minutes. Remove the tube from the heat and rotate while cooling in order to form a thin coating around the inside. Add 10 ml of 1 molar tartaric acid and insert a corked Steven's extraction stick, fitted with glass filtering fiber. Without heating the solution, use the extraction stick to break up the fused mass. If convenient, fuse samples in the afternoon, add the tartaric acid and allow to stand overnight. When the fused mass is broken up, place tube and contents in a boiling water bath for 2 to 3 minutes. Remove the tube from the water bath and allow to cool. As the tube cools, the tartaric acid extract filters into the extraction stick.

Development of niobium-thiocyanate complex.--Transfer a 1-ml aliquot of the clear filtrate to a separatory funnel and add 3 ml of stannous chloride. Add 9 ml of water and 7 ml of the hydrochloric acid-tartaric acid reagent. Cool contents of separatory funnel to 20 to 25°C and add 5 ml of potassium thiocyanate. Within 5 minutes add 10 ml of the ethyl ether reagent to the funnel and shake the contents for 30 seconds. Allow the phases to separate and drain off the aqueous layer. Transfer th ether phase to a volumetric flask, add a little ether to make volume up to 10 ml, and allow to stand 1 hour.

Estimation.--If the equipment is available, transfer the ether solution of the niobium-thiocyanate to a cuvette and measure the absorbance at 385 m . From a previously established standard curve, determine the number of micrograms of niobium in the 0.02 g aliquot and multiply by 50 to obtain parts per million.

Alternately determine the niobium content of the sample solution as follows: Transfer a 10-ml portion of the ether solution of the niobium-thiocyanate complex to small flat-bottomed Nessler tubes and compare with standard ether solutions of niobium-thiocyanate prepared by the foregoing procedures and containing, respectively, 10, 20, 30, and 40 micrograms of niobium. If the color intensity of the ether extract obtained from a sample solution is greater than that of the highest standard, dilute the extract obtained from the sample with ether until its intensity is similar to that of one of the standards. Multiply the number of micrograms of niobium in the comparable standard by the ratio of the final volume of ether to the original volume (10 ml). Multiply the results by 50 to convert to parts per million.

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The Field Determination of Small Amounts of Vanadium in Rocks

by

F. N. Ward and A. P. Marranzino

Introduction

During the course of another investigation (Ward and Marranzino, 1953) it was observed that vanadium (III) reacted with thiocyanate in an acid medium to produce a yellow-colored complex ion or compound. Moreover, the complex ion was extracted from the acid phase with ethyl ether. Vanadium (V) did not react with thiocyanate, but the higher valence was readily reduced by stannous chloride to vanadium (III) (Latimer and Hildebrand, 1940)

It occurred to the authors that a method for determining vanadium in certain types of rocks could be based on the reaction with thiocyanate, if the other elements reacting with thiocyanate could be eliminated or if the conditions could be adjusted to minimize the interference caused by them.

Molybdenum, rhenium, tungsten, niobium, and uranium are likely interferences because they react with thiocyanate to form colored compounds extractable with ether.

Under the conditions stipulated below, the amber color of the molybdenum-thiocyanate faded within half an hour. Rhenium occurs in extremely small quantities in the earth's crust (Goldschmidt, 1937), and as an interference it can be ignored. In the presence of citrate tungsten is sufficiently complexed to prevent any interference. Niobium would probably interfere if it were present in large amounts. Although uranium (VI) reacts with thiocyanate to form a yellow-colored complex similar to that of vanadium (III), uranium is not considered to be a serious interference because the reaction is not sensitive.

In order to test the method, 90 rock samples from three different areas were analyzed by the proposed method. The results agreed favorably with those obtained by a recognized laboratory method. With the standards suggested below 72 out of 90 determinations were within one standard of the accepted value. Moreover, the suggested procedure is extremely rapid as shown by the fact that 66 determinations can be made in 4 1/2 hours.

Reagents and Apparatus

Ethyl ether. Reagent quality. Prior to use shake with a mixture of 5 ml of stannous chloride in 4 molar hydrochloric acid and 5 ml of 20-percent potassium thiocyanate.

Ethylenediaminetetraacetic acid, disodium salt. Dissolve 2 g of reagent in 100 ml water.

Potassium thiocyanate. Dissolve 20 g of KSCN in 100 ml water.

Sodium citrate. Dissolve 10 g sodium citrate in 100 ml water.

Standard vanadium solution, 0.1 percent. Solution A: Dissolve 1.785 g pure vanadium pentoxide previously ignited at 500°C in a slight excess of sodium hydroxide. Neutralize with 1:1 sulfuric acid, add 28 ml concentrated sulfuric acid, and dilute to 1 liter with water. This solution contains 1000 micrograms of vanadium per ml.

Standard vanadium solution, 0.01 percent. Solution B: Dilute 10 ml of solution A with water to 100 ml. This solution contains 100 micrograms of vanadium per ml.

Stannous chloride. Dissolve 15 g $SnCl_2.2H_2O$ in 100 ml concentrated hydrochloric acid.

Sulfuric acid, 9 molar. Add concentrated sulfuric acid to an equal volume of water.

Alcohol lamp.

Borosilicate glass culture tubes 16 x 150 mm.

Lucite spoon. A lucite bar with a cavity, 5mm in diameter, 5.5 mm deep, drilled near one end.

Mullite mortar and pestle, outside diameter of mortar, 75 mm.

Pipettes automatic, rubber bulb and plunger type.

2 2-ml capacity

2 5-ml capacity

1 10-ml pipette, graduated in tenths of a ml.

1 1-ml pipette, graduated in tenths of a ml.

Test tube rack, capacity at least 20 tubes.

Procedure

Place one lucite spoonful (0.1 g) of rock sample ground to pass an 80-mesh sieve in a borosilicate glass culture tube. Add 1 ml of 9 molar sulfuric acid to the tube and heat until the mixture begins to boil. Remove the tube from the heat and allow the contents to cool to room temperature. Add successively 4 ml of sodium citrate, 2 ml of disodium ethylenediaminetetraacetic acid solution, and 3 ml of stannous chloride. Place cork in the tube and shake to mix the reagents. Allow the contents to cool, remove the cork and add 2 ml of potassium thiocyanate. Again place a cork in the tube and shake. Remove cork and add 2 ml of ethyl ether. Again stopper the tube and shake for 15 seconds. Allow the phases to separate and compare the intensity of the yellow color of the ether layer over a sample solution with that obtained from standard solutions prepared as follows:

volume of water

Pipet the required amounts of the appropriate standard solutions into separate culture tubes each containing 1 ml of 9 molar sulfuric acid.

Standard	Vol. of Solution B ml=	Vol. of Solution A ml	Vanadium Content micrograms
a	none	none	0
b	0.3	--	30
c	0.6	--	60
d	1.5	--	150
e	--	0.3	300
f	--	0.5	500
g	--	1.0	1000
h	--	2.0	2000

To each tube add 4 ml of sodium citrate and proceed with the addition of the versene, stannous chloride as directed above.

To obtain the vanadium content of the sample in parts per million multiply the vanadium content of the standard whose color intensity matches the color intensity of the sample by 10.

Literature cited

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