Analytical Methods Used in Geochemical Exploration by the U.S. Geological Survey

By F. N. WARD, H. W. LAKIN, F. C. CANNEY, *and others*

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A compilation of trace and semimicro-analytical methods yielding semiquantitative data on geologic materials useful in geochemical prospecting for ore deposits

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ANALYTICAL METHODS USED IN GEOCHEMICAL EXPLORATION BY THE U.S. GEOLOGICAL SURVEY

By F. N. Ward, H. W. Lakin, F. C. Canney, and others

ABSTRACT

Chemical methods for 24 elements are described in sufficient detail to permit use by relatively nontechnical persons. These elements are as follows: antimony, arsenic, barium, bismuth, chromium, cobalt, copper, germanium, iron, lead, manganese, mercury, molybdenum, nickel, niobium, phosphorus, selenium, sulfur, tin, titanium, tungsten, uranium, vanadium, and zinc. Some of these methods are modifications of methods developed in laboratories abroad; others were developed originally in U.S. Geological Survey laboratories. A few are modifications of well-known analytical procedures.

After sample dissolution by acid digestion or fusion with different fluxes, the methods are similar in that the element being determined is obtained as a colored compound whose intensity or shade of color is proportional to the amount of the element present. The methods differ in the operations employed to separate the element from interferences and to concentrate enough of the element to form the colored compound. Solvent extraction, confined spot tests, and paper chromatography comprise the major chemical operations to achieve the necessary separations and optimum concentrations.

A field-applicable semiquantitative spectrographic procedure permits the determination of elements in addition to those given above as follows: beryllium, boron, cadmium, gallium, indium, lanthanum, magnesium, scandium, silicon, silver, strontium, tantalum, thallium, yttrium, and zirconium.

INTRODUCTION

The purpose of this compilation is to make available in a single publication detailed descriptions of analytical methods for 24 elements currently used in the development of geochemical prospecting techniques by the U.S. Geological Survey. A few of these methods—the paper chromatographic procedures—were developed in other laboratories; a few are long-established well-known chemical methods that are, with little or no modification, suitable for geochemical prospecting; and the remainder were developed by the U.S. Geological Survey. Of the Geological Survey methods, some have been described in other publications in greater detail than is given here, and some have not previously been published. Revised descriptions are presented for procedures that have been modified, and descriptions from earlier publications are reprinted without major change for those techniques still in use virtually as previously published. They vary in their suitability to prospecting needs, and not all have been thoroughly tested. Research is continuing in U.S. Geological Survey laboratories for improvement of existing procedures and development of new ones.

Three types of colorimetric procedures are included. In the first type—used for the determination of copper, lead, molybdenum, tungsten, and other elements—the desired metal is extracted from an aqueous solution into an immiscible solvent, so that a separate layer colored by a complex of the element is obtained. The intensity or shade of the color is proportional to the quantity of the element present. The second type of colorimetric procedure—used for the determination of arsenic—is a confined-spot test in which a colored precipitate is obtained in a fixed area, the intensity of this color, too, being a function of the quantity of the metal present. In the third type, a paper-chromatographic separation of the desired element is followed by reaction of this constituent with a suitable compound to produce on the paper colored bands whose width and intensity of color are proportional to the amount of the constituent present. A paper so prepared is called a chromatogram. The methods for the determination of uranium and one method for the determination of cobalt, copper, and nickel are of this type.

In addition, a field-applicable semiquantitative spectrographic method is included in this compilation to complement the colorimetric methods. The latter methods, with few exceptions, require a sample for each determination, whereas the spectrograph permits the simultaneous determination of 34 elements on a single sample. Obviously the spectrographic procedure lends itself to preliminary and diagnostic appraisals.

Most of these methods are designed for field use and are characterized by brevity and simplicity compatible with producing large amounts of moderately precise analytical data. Each permits 25 to 30 or more determinations in an ordinary day. Separations and other chemical operations have been held to a minimum, and so far as possible the required apparatus has been restricted to common laboratory equipment. Most of the methods yield positive tests on natural materials containing background amounts of the element sought. Results are commonly within 30 to 50 percent of the correct value for natural materials containing abnormal amounts of the elements. The minimum content of elements detectable by each of the methods described here is given

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TABLE 1.—A
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Cadmium
Chromium
Cobalt

Copper

Gallium
Germanium
Indium
Iron

Lanthanum
Lead
Magnesium
Manganese
Mercury
Molybdenum
Nickel

Niobium
Phosphorus
Scandium
Selenium
Silicon
Silver
Strontium
Tantalum
Thallium
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Titanium
Tungsten
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in table 1, together with the average content of the same elements in soils.

The useful range of each method for a given element depends on (a) the minimum concentration of the element in the sample

TABLE 1.—*Average content of the elements in soils and minimum concentrations detectable by methods described in this compilation*

[In parts per million. Average content in soils, from Vinogradov (1948)]

Element	Average content in soils	Sensitivity of method	
		Colorimetric and others	Spectrographic field equipment
Antimony	[1] 0.2	1	200
Arsenic	5	10	500
Barium	500	1,000	10
Beryllium	6	-------------	1
Bismuth	[1] .2	10	10
Boron	10	-------------	10
Cadmium	.5	-------------	20
Chromium	200	100	10
Cobalt	8	10 [2] 50	10
Copper	20	10 [2] 50	5
Gallium	30	-------------	5
Germanium	(3)	4	20
Indium	[1] .1	-------------	10
Iron	38,000	[4] 50 [5] 200	100
Lanthanum	40	-------------	50
Lead	30	25	10
Magnesium	6,300	-------------	20
Manganese	850	50	10
Mercury	.01	2	-------------
Molybdenum	2	4	5
Nickel	40	25 [2] 50	5
Niobium	[1] 24	100	20
Phosphorus	800	50	-------------
Scandium	7	-------------	10
Selenium	.01	10	-------------
Silicon	330,000	-------------	100
Silver	.1	-------------	1
Strontium	300	-------------	20
Tantalum	[1] 2	-------------	50
Thallium	[1] 1	-------------	100
Tin	10	10	10
Titanium	4,600	100	10
Tungsten	[1] 1	20	100
Uranium	1	[2] 4	200
Vanadium	100	50	10
Yttrium	50	-------------	10
Zinc	50	25	200
Zirconium	300	-------------	10

[1] No values available for soils. The value given is crustal abundance (Mason, 1958).
[2] By paper chromatography.
[3] An unknown figure between 1 and 9.
[4] By *o*-phenanthroline.
[5] By dichromate.

solution for which a positive result can be achieved by the method (hereafter designated sensitivity), and (b) the concentration that produces a color beyond which color differences are not perceptible. These concentrations can be determined experimentally and are conveniently expressed in micrograms per milliliter. Because the quantity of a constituent present in the solution to be tested is proportional to the size of the sample used, the weight of the sample can be increased by trial and error until the concentration in the test solution of the constituent being determined is sufficient to give a positive test. The extent to which the sample size can be increased while the volume of the sample solution is held constant, however, is limited. The concentration of the element producing a maximum color governs the largest concentration of the given element that can be determined by these methods unless one takes smaller aliquots. The reliability of results obtained by the latter technique is largely dependent on the accuracy with which smaller aliquots can be measured.

Generally, the production figures given for these methods take into account the time required to prepare reagents and clean the equipment, but not the time required to prepare the sample for analysis. Also, these production rates are more easily attained in the laboratory than in the field.

Our plan is to furnish direct instructions that can be followed by a relatively untrained operator and to present only as much information as is necessary for proper performance of the determinations. For every method, a brief introduction, a list of reagents and apparatus, and a concise statement of the procedure are given, with an occasional warning for critical operations. Those interested in the reactions involved, the interfering elements, and the comparative accuracy should refer to the original papers from which these methods were taken. A more complete discussion of the reagents used in these methods will be found in the comprehensive treatises of Feigl (1954), Sandell (1959), Boltz (1958), and Snell and Snell (1959).

Laboratory and field methods for preparation of vegetation samples for analysis are given herein in some detail. No procedures are given for preparing the rocks, soil, or sediment for analysis. The fine material in soil that passes through an 80-mesh sieve is usually taken for analysis. Rocks may be ground to pass an 80-mesh or a 200-mesh sieve; the latter is preferable. Detailed information on sampling procedures and sample preparation for these materials is available in a discussion of the principles of geochemical prospecting by Hawkes (1957).

The following members of the U.S. Geological Survey helped to assemble the material in this report: C. E. Thompson, Uteana Oda, J. Howard McCarthy, Jr., A. P. Marranzino, and Ellen L. Markward.

GENERAL PROCEDURES

WARNING ABOUT THE USE OF SOME REAGENTS

Most reagents used in analytical chemistry are poisonous. When the analyst is cautioned here about a reagent, however, it is because one of its specific properties, such as volatility, makes handling the reagent especially dangerous. Some volatile substances may be dangerous because they are very poisonous. Hydrofluoric acid either as vapor or as liquid causes serious and very painful burns on the skin. The vapor is extremely irritating to the respiratory tract, causing congestion of the lungs. As little as 50 ppm of the vapor in air may be fatal in an exposure of 30 to 60 minutes (Sax, 1951). Other volatile substances are dangerous because chronic poisoning results from continued exposure to relatively low concentrations. Liver damage has been produced by continued exposure to the vapors of carbon tetrachloride in concentrations of about 100 ppm (Elkins, 1950). Some reagents are hazardous because they are flammable. The thoughtless lighting of a match near an open container of ethyl ether may result in serious injury.

Special precautions must be exercised with potassium and sodium cyanide solution because of their toxicity. *Do not measure a cyanide solution with a pipet operated by mouth. Do not add acid to cyanides or their solutions.*

Unless specially packaged, all dry ethers (ethyl, isopropyl) on standing tend to form explosive peroxides, which not only are dangerous but also may interfere with the determination, as in the method for antimony. To test for peroxides, shake 5 ml of the ether with 5 ml of an acidified aqueous solution of potassium iodide. If the aqueous solution shows more than a faint tinge of the yellow color due to free iodine produced by the reaction of peroxides with iodide, the ether contains appreciable quantities of peroxides and is unsatisfactory for use. Preferably a new supply should be obtained; otherwise the peroxides can be removed by shaking the ether with a reducing agent such as ferrous sulfate, separating the ferrous sulfate, and then distilling the ether in dry equipment. Most of the peroxides are removed by this treatment.

How much caution must be observed in handling the more hazardous chemicals used in the tests described in this compilation may be determined by studying the data in table 2. The boiling point, noted in degrees centigrade (°C), gives a measure of the volatility of the compound; the flash point, also noted in degrees centigrade, gives a measure of the fire hazard involved in the use of the compound; and the maximum allowable concentration in the air (MAC) in parts per million (volume per volume) gives a measure of the toxicity of the compound. The MAC indicates the worst condition that can be tolerated continuously. Concentrations greater than the MAC values must be avoided by proper ventilation. The last column of table 2 gives the number of milliliters of the liquid that will produce a vapor equal to the maximum allowable concentration in a closed room 20 by 10 by 8 feet (1,600 cu ft).

TABLE 2.—*Boiling point, flash point, and maximum allowable concentration in air (MAC) of some dangerous reagents*

[Data compiled from Merck and Company, Inc. (1952), Sax (1951), and Elkins (1950)]

Compound	Boiling point (°C)	Flash point (closed cup) (°C)	Maximum allowable concentration (vol. per vol.) (ppm)	Volume of liquid producing the MAC in closed room 20×10×8 ft [1] (ml)
Amyl alcohol	138	43	100–200	22
Benzene	80	−11	100	18
Bromine	59		.15–1.0	.5
Carbon tetrachloride	76		100	20
Chloroform	61		100	16
Cyclohexanone	157	64	100	20
o–Dichlorobenzene	180	66	50	11
Ethyl acetate	77	−4	400	80
Ethyl ether	35	−40		
Hydrocyanic acid (anhydrous)	26	−18	10–20	.08
Hydrofluoric acid (anhydrous)	19		3	.1
Isoamyl acetate	143	33	200–400	60
Isoamyl alcohol	132	46	50	11
Isopropyl ether	67	−8	400	110
Xylene	138–144	17	200	48

[1] Calculated from minimum MAC values in column 4.

PREPARATION AND PURIFICATION OF REAGENTS

The use of metal-free water is imperative for successful application of the methods of trace analysis presented in this compilation. For example, the ratio of water to sample used in the method for zinc is 500 to 1. Tap water of city water supplies may contain 1 ppm zinc. If used in the zinc test without purification, a blank would be obtained equivalent to 500 ppm in the sample.

Many small demineralizers for preparing metal-free water are available commercially. They are usually mixed-bed ion-exchange columns with an excess of the cation exchanger. Water passed through such columns is usually slightly acid, but satisfactory for use in these tests. Nonionized materials such as colloids and bacteria are not removed by demineralizers; therefore, it is best to use relatively pure water from public water supply or clear streams. In some instances natural stream water is sufficiently free of dissolved ions to be used without treatment.

Reagent chemicals used in trace analyses must be checked for traces of the element determined. Dithizone methods are particularly susceptible to error due to high reagent blanks. Solutions prepared from solid reagents are conveniently purified by extraction with a carbon tetrachloride solution of dithizone. The procedure for this type of purification is to be found in the instructions for preparing specific reagents.

The salts used in fusions (potassium bisulfate, sodium carbonate, sodium chloride, and potassium nitrate) are usually sufficiently pure to give satisfactory results; nevertheless, each batch should be checked by running blanks on the reagent. Fluxes giving a high reagent blank should be rejected, as purification is tedious.

Hydrochloric and nitric acids usually have a very low heavy-metal content and frequently can be used without purification. If necessary, they can be purified by distillation from a Pyrex still.

Pure ammonium hydroxide is easily obtained by dissolving ammonia (NH_3) in cool metal-free water. The change in weight of the solution indicates its concentration.

Carbon tetrachloride of reagent quality is usually satisfactory. Distillation in a Pyrex still in the presence of calcium oxide will give a product free of heavy metals.

A procedure for the purification of ethyl and isopropyl ethers is given on page 5.

Table 3 gives the usual specific gravity and composition of concentrated reagent acids, together with the directions for preparation of 1-molar (1*M*) solutions of the acids.

CALCULATION OF TRACE-ELEMENT CONCENTRATION

Most of the natural materials analyzed in geochemical exploration contain only trace amounts of the elements sought. The colorimetric methods described can conveniently be used for samples containing less than 0.5 percent of the given element; the optimum range of applicability is frequently less than 0.1 percent, and the minimum detectable amount may be as small as 0.0001 percent. To express the trace-element content of soils, rocks, and vegetation in small whole numbers, parts per million (ppm) is used throughout the text.

TABLE 3.—*Composition of concentrated reagent acids with dilution directions to 1-molar (1M) solution*

	HCl	HBr	HNO_3	H_2SO_4
Molecular weight	36.465	80.92	63.016	98.082
Approximate specific gravity concentrated reagent	1.19	1.5	1.42	1.84
Approximate content present in concentrated reagent...percent	37.0	48	69.5	96.0
Molarity of concentrated reagent	12.1	8.1	15.7	18.0
Approximate content of reagent per liter for 1M solution...ml	83.0	124	64.0	56.0

The formula to calculate trace-element concentration for all methods where specific instructions are not given is:

$$\text{ppm} = \frac{\text{volume of sample solution, in milliliters (ml)}}{\text{sample weight taken for analysis, in grams (g)}} \times \frac{\text{micrograms } (\mu g) \text{ of trace element found}}{\text{aliquot of sample solution, in milliliters}}$$

One microgram $= 1 \times 10^{-6}$ gram. All standard solutions are expressed in micrograms per milliliter (μg per ml), and all standard series in micrograms (μg).

In the method for determining uranium in water, the uranium content is calculated in parts per billion (ppb). In the United States, 1 billion is equal to 1,000 million, thus 1 ppb = 0.001 ppm.

Conversion factors

1 microgram per gram = 1 ppm
1 milligram per liter = 1 ppm
1 microgram per kilogram = 1 ppb
100 ppm = 0.01 percent

APPARATUS

The required number of items of apparatus, and their size, depends upon the magnitude of the operation. Although the methods as written describe the procedure in terms of a single sample, batch operation is normal. Basic equipment that must be available for field operation includes stoves, water baths, test-tube racks, and fusion rack, or test-tube holders. Provision for measuring the sample must be made either with a balance or a calibrated scoop.

The following discussion may help in determining equipment needed for a specific job. All glassware, including reagent bottles, should be of borosilicate glass. It has been observed that some soft-glass bottles yield a continuing contamination to reagents from their surface. Culture tubes (rimless test tubes) are often specified simply because packaging is easier and breakage lower than with test tubes. Ignition tubes are listed when a thick-walled tube is required for a fusion. These tubes (culture, test, or ignition) may be calibrated for volumes designated in the individual methods (as, 5 and 10 ml) by filling each tube to the required volume with water from a buret and circling the tube at the miniscus with a stylus. A metal sleeve forms a convenient guide for the stylus.

Polyethylene ware may be used for storing aqueous solutions and as wash and dropping bottles. Its light weight and durability are obvious advantages for field use. Concentrated sulfuric and nitric acid and most organic solvents attack polyethylene to some extent.

It is frequently desirable to sieve soil samples in order to obtain fine material for analysis. (See Hawkes, 1957.) A suitable sieve can be made as follows: Remove the center piece from the cover of a round ice-cream carton of 1-pint capacity. Cover the carton with a piece of 80-mesh silk bolting cloth and press the band of the cover in place. Remove the bottom of the container.

Two methods of measuring the sample are used. The more accurate, but slower, method is to weigh the sample on a torsion balance, 120-g capacity and 2-mg sensitivity. In the method for determining molybdenum in vegetation, a microtorsion balance, Roller Smith type, of 75-mg capacity is desirable. A fast procedure that yields satisfactory results is based on the use of a measured volume of the sample powder; scoops are used for the measurement. The volume of the scoops is based on the assumption that the volume density of the powder is 1.0; thus, the volume in milliliters is equivalent to grams of packed powder. Bars of plastic, hardwood, or aluminum about 2 inches long, ½ inch wide, and ⅜ inch thick are suitable blanks from which the scoops are made. To make a scoop of 0.1-g capacity, drill a hole about ⅛ inch deep and ¼ inch in diameter near one end of the bar; for a scoop of 0.5-g capacity, make the hole about ¼ inch deep and ⅜ inch in diameter. Calibrate the weight of the measured powder with a balance. With a little practice, one can obtain reproducible packing of the scoop with powder. The volume density used here is applicable for powdered soils and rocks; it is not applicable for heavy minerals.

Supports (racks) are required for the various sizes of culture, test, and ignition tubes that are used. Aluminum test-tube racks made to fit in a water bath are convenient for those methods that call for digestion of the sample in a water bath. A suitable capac-

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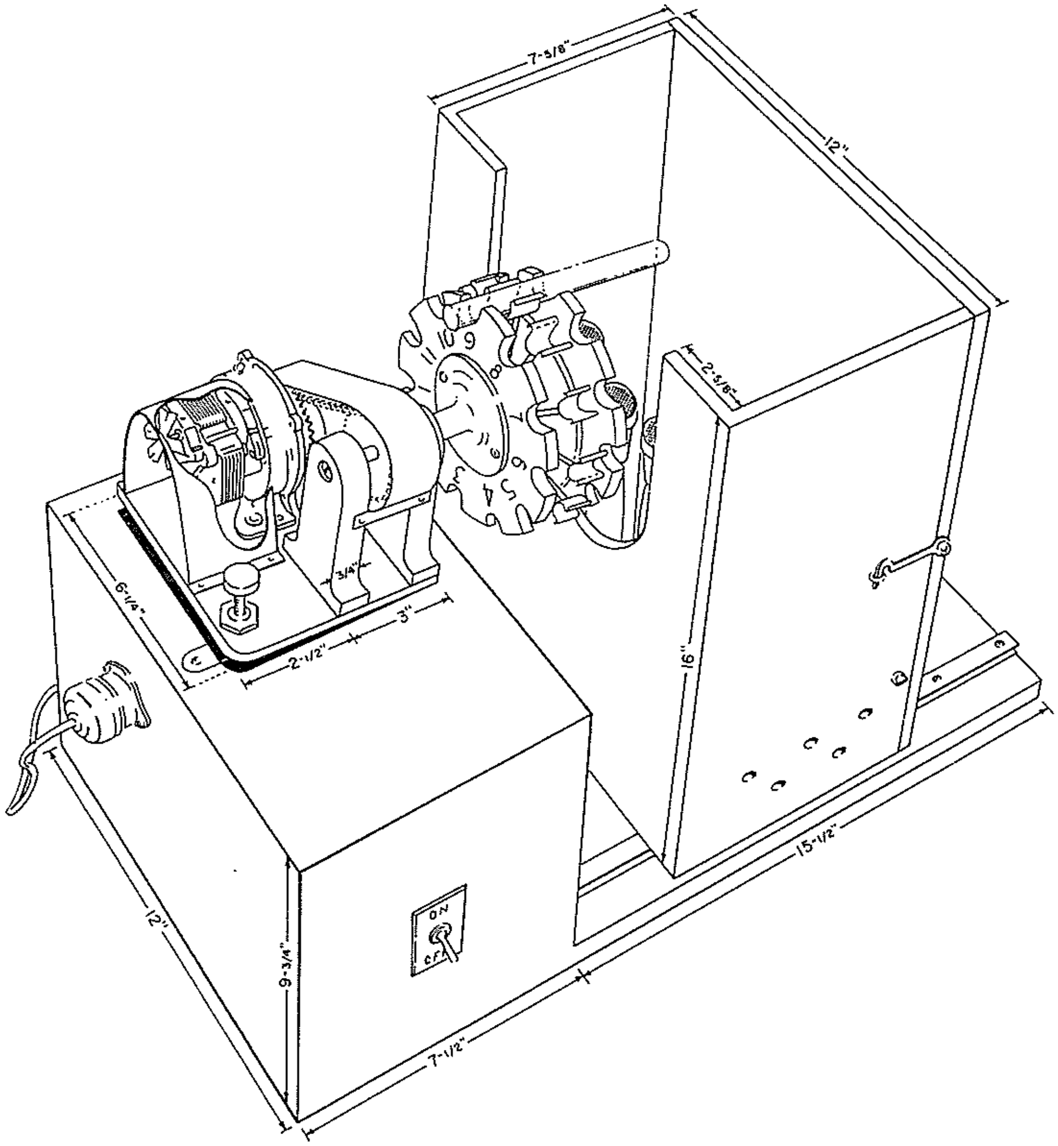

FIGURE 1.—Multiple-fusion rack, drive mechanism. (Diagram courtesy of "Analytical Chemistry.")

ity for the racks and water baths is 50 tubes because, for most methods, batches of 50 to 100 can be completed in 1 workday.

Fusion racks must be varied to fit the heat source and the tubes used in the test. Supports with a readily replaced wire-gauze bottom allow maximum heat to reach the bottom of the test tube. A multiple-unit fusion rack developed by Marranzino and Wood (1956) is designed to meet the requirements of the methods given herein if gas and electricity are available. This apparatus heats each tube uniformly by passing the tube, rotating on the axis of the unit, over a series of burners. The rotation assures mixing of the sample with the flux, and continued rotation during cooling causes the melt to coat the wall of the tube with a thin layer, which may be easily dissolved in the next step

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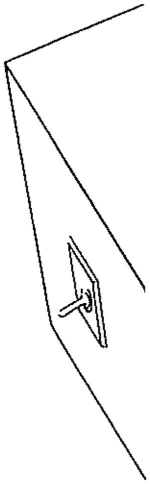

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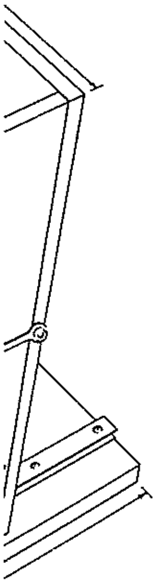

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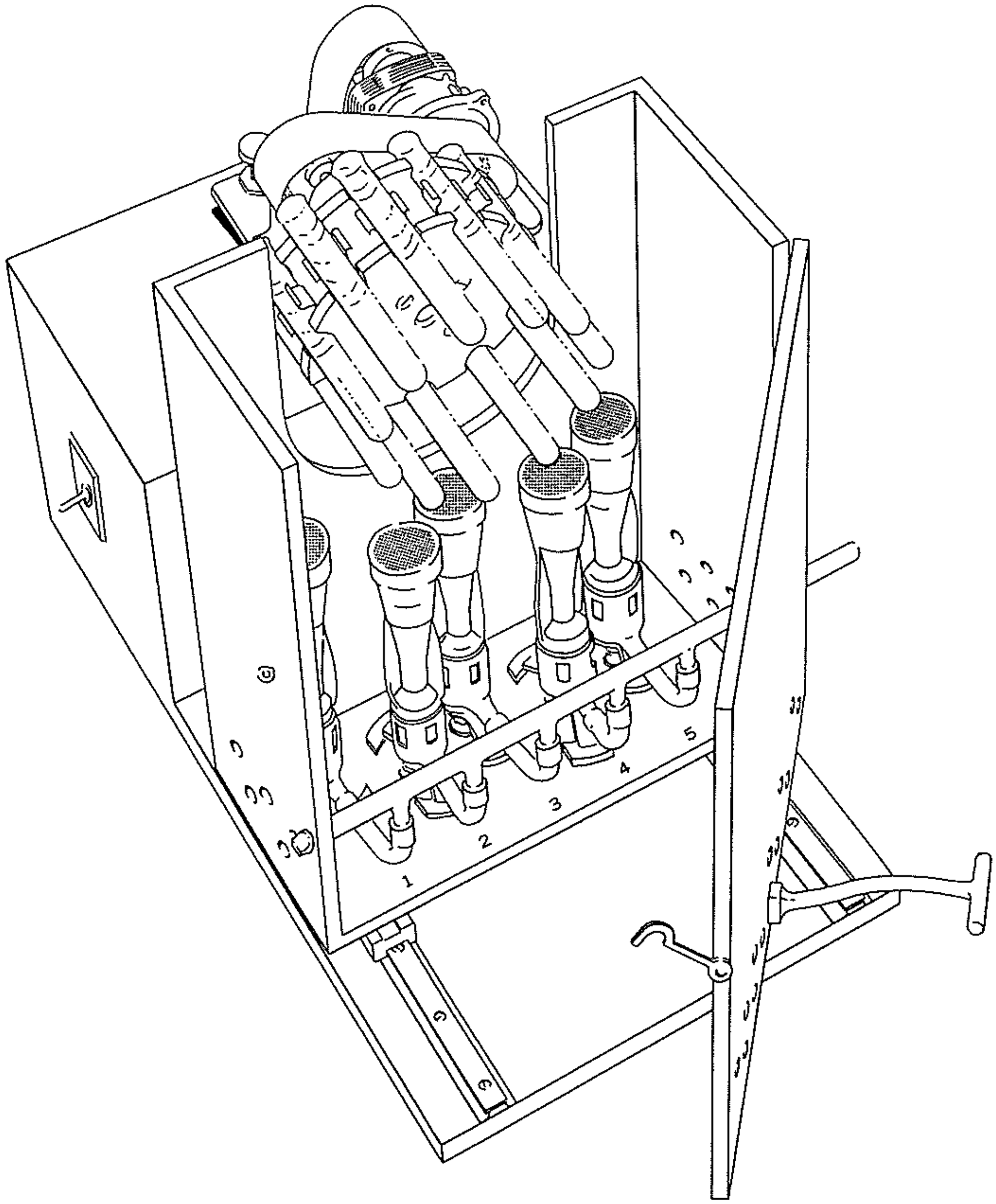

FIGURE 2.—Multiple-fusion rack, burner assembly. (Diagram courtesy of "Analytical Chemistry.")

of the procedure. Marranzino and Wood (1956) described the construction and operation of the multiple-fusion rack (see fig. 1) as follows:

> A perspective dimensional drawing is shown in figure 1. The entire unit is 23 inches long, 12 inches wide, and 16 inches high, and weighs approximately 45 pounds.
>
> The carriage assembly for holding the test tubes is rotated at 15 r.p.m. by a $\frac{1}{75}$-h.p., 115-volt, alternating current, continuous-action, gear-reducing motor connected to the drive shaft of the carriage by a chain drive (a No. 1A steel ladder chain having a yield point of 37 pounds). A sprocket (20-teeth, 1.18-inch pitch diameter with a $\frac{7}{8}$-inch hub that has a $\frac{5}{16}$-inch hole) is mounted on the drive shaft of the same size between the aluminum bearing

posts of the carriage. This arrangement gives the drive unit a 1 to 1 ratio; other ratios may be obtained by a suitable selection of sprockets and chains.

A fan is mounted on the motor and serves both to cool the motor and to drive any corrosive fumes away from the unit. Safety covers are mounted over both the fan and the chain drive.

The carriage shaft is carried by two roller bearings. The carriage assembly is fastened to the end of the drive shaft by a brass flange and is made of two ⅜-inch asbestos cement disks, 5⅞ inches in diameter, which are separated by a 1½ inch brass insert 1 inch in diameter. Eleven steel posts (⅛ × 1¾ inches) are fastened with silver solder on the brass insert in a line with the 11 semicircular sectors. A curved test tube clamp, ⅝ inch wide, fashioned from 1/32-inch sheet stainless steel is fastened to the end of the 11 posts with silver solder.

The motor, gears, and carriage are mounted on an aluminum plate (see fig. 1) that is fastened to the chassis by a piano-type hinge placed under the chain-drive assembly. A thumb-screw at the opposite end of the plate allows the entire unit to be rotated about the hinge to 20 degrees from the horizontal and thus permits the closed end of the test tube to be depressed into the furnace unit.

Two flat brass ways, ⅛ × 1½ inches, on the underside of the furnace are fitted to two T-shaped aluminum ways fastened to the chassis, providing tracks on which the furnace moves.

The furnace is constructed from 0.5-inch asbestos cement board and is assembled with machine screws. Figure 2 illustrates interior design and figure 1 gives dimensions. A curved slot is cut in the back wall of the furnace to permit the entry of the carriage when the furnace is moved toward the motor and gear assembly. Twenty holes, ½ inch in diameter, are drilled along the lower edges of the sides and front of the furnace to furnish sufficient ventilation for the gas burners. Five high-temperature natural gas-type burners, whose bases have been cut to permit close assemblage, are connected to a copper manifold by short lengths of rubber tubing. The burners can be regulated in the normal manner and can be removed easily for occasional cleaning. The front of the furnace is a door held by two piano-type hinges 1.5 inches in length and fastened by a hook and eye. A projecting handle is placed on the door to facilitate moving the furnace. The chassis is made of hard pine painted with heat-resistant metal paint.

The fusion is accomplished in the multiple-unit fusion rack as follows:

The position of the furnace and the carriage at the beginning of the fusion is shown in figure 2. Eleven 16 × 150-mm borosilicate glass test tubes containing the samples of soil or rock mixed with an appropriate flux are placed around the periphery of the carriage. The carriage is adjusted by the thumb-screw to lower the bottom end of the test tubes, and the motor is started. The burners are then lighted and the furnace is pushed under the revolving test tubes. After the fusion is completed, the furnace is withdrawn from the carriage, which is then adjusted to support the test tubes in a horizontal position. The unit is allowed to rotate until the melt has solidified on the sides of the test tubes in a thin layer.

While the fusion process is taking place, the operator is free to utilize his time on another operation, thus cutting down greatly the number of man-hours spent in making a large number of test tube fusions.

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In the field, the source of heat used may vary, depending on the volume of work to be done, from a simple alcohol lamp to large gasoline or propane stoves. Small pocket-sized gasoline stoves have been used in many field operations. Trucks have been equipped with bottled gas and Bunsen burners. Generators attached to the truck motor have been used to power electric hotplates for water baths. It is preferable to select the equipment for the heat source first and build the test-tube racks, fusion racks, and water bath to fit the capacity of the heating units.

PREPARATION OF PLASTIC STANDARDS FOR PROSPECTING

Hawkins, Canney, and Ward (1959) have published a method for the preparation of plastic standards, by adding small amounts of suitable dyes and pigments to a transparent thermosetting polyester resin, known commercially as Castolite. The plastic is colored and molded into appropriate shapes to form standards that are less bulky and more stable than the standards conventionally used in rapid field methods. The plastic standards should be cast and hardened in tubes of the same dimensions as those containing the liquid standards, so that color comparisons with sample solutions are made under similar geometrical conditions. For most procedures, all the standards are incorporated into a single rod, where they appear as a stack of colored discs separated by layers of clear plastic.

Advantages of plastic standards over liquid standards include (a) the elimination of the frequent and time-consuming preparation of a standard series in those procedures that produce relatively unstable liquid standards; (b) the elimination of six or more bulky and fragile glass tubes to contain the standards, a particular advantage when analyses are performed at the sample site; and (c) the resistance of the hardened plastic to rough handling.

GENERAL PROCEDURE

1. Prepare a set of the liquid standards that are to be matched in plastic.
2. a. For standards that are of the same color but differ in intensity throughout the range of values covered by the method, pour about 3 tablespoonfuls clear Castolite into a paper cup and add small amounts of dye until the color matches that of the liquid standard having the most intense shade. Prepare the remaining plastic standards by dilution of this colored resin with appropriate amounts of clear resin to produce a series of the proper intensities.
   b. For standards that differ in color with different concentrations of metal, each standard must be prepared separately.
3. Take a glass tube of the same dimensions as those containing the standard solutions to be used as color guides. Clamp it in a vertical position and

pour in about 1 teaspoonful clear resin mixed with the hardener and cold-setting promoter. Allow the mixture to gel for about 10 min.

4. Mix the hardener and cold-setting promoter with the colored resin corresponding to the lowest standard and pour this mixture into the tube until the volume of the layer is approximately equal to the volume of the organic layer in the liquid standard. Allow to gel.
5. After the colored layer has gelled, add a layer of clear resin and allow to gel.
6. Continue process of pouring alternating clear and colored layers until the whole series of standard colors have been matched; then pour a clear layer about three-fourths of an inch thick on top of the last colored layer.
7. Allow the gelled plastic to cool to room temperature, then cure the plastic rod by heating the tube for 30 mins. in a water bath at 70°C. (Some heat is liberated by the plastic as it gels. Unless the plastic is cooled to room temperature prior to curing, the casting will crack while it is being cured.)
8. Take tube from water bath and add about 5 ml acetone. Remove casting from the glass tube by inverting the tube and tapping its mouth sharply against a solid surface. Wipe rod with tissue to remove a thin adhering layer of syrupy resin.

COPPER BIQUINOLINE STANDARDS

The field method used by the U.S. Geological Survey for the determination of copper in soils and rocks is based on the reaction between 2,2′-biquinoline and copper (I) to form a pink compound. It was developed by Almond (1955), whose paper contains directions for preparing the liquid standards which do not differ in hue but vary only in intensity of color. (See page 23.) A rod containing colored discs matching the liquid standards can be prepared easily by the general procedure given above. However, no commercially available dye satisfactorily duplicates in plastic the color of the copper-biquinoline complex. The authors found that a complex formed by the reaction of tin (IV) with 4,5-dihydroxyfluorescein (Gallein) gives the resin a red color closely resembling that of the copper complex. This red complex is prepared by allowing stannic ion to react with 4,5-dihydroxyfluorescein in an acetate-buffered aqueous medium at a pH of 2–2.5. The complex is extracted by a binary mixture of *o*-dichlorobenzene and cyclohexanone.

A difficulty experienced with the use of this compound as a dye is that the color tends to fade slightly in the curing. To correct this, the resin should be made slightly deeper in color than the standard it is to match; the necessary correction must be determined experimentally. Once the plastic has been cured, however, the color is resistant to fading.

ZINC DITHIZONATE STANDARDS

The field method of analysis for zinc is based on the reaction of zinc with dithizone to form a zinc dithizonate, which in the presence of an excess of dithizone exhibits a color varying from green to red, depending on the amount of dithizone present. A discussion of the procedure and directions for the preparation of the zinc dithizone standards are given by McCarthy and Lakin (1956). (See p. 23.) The dyes that are commercially available for coloring Castolite can be used in preparing the plastic standards for zinc. The best results are obtained by using dilute alcohol or acetone solutions of these dyes to color the resin. The dyes are diluted in the following manner:

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Dilution of dyes for coloring resin

Green ...... 50 mg green dye dissolved in 10 ml acetone.
Blue .... 4 drops concentrated blue dye in 19 ml acetone.
Violet . 4 drops concentrated violet dye in 10 ml acetone.
Red .... 4 drops concentrated red dye in 10 ml acetone.

The following shows the dye mixtures required to obtain a fair approximation of the colors of the zinc standards:

Metal content of standard	*Amount of dye to be added to 1 tablespoonful clear resin*	
Micrograms	*Number of drops*	*Color of dye*
0	2	Green.
1	1	Green.
	4	Blue.
	2	Violet.
2	2	Blue.
	5	Green.
	2	Red.
3	7	Violet.
	1	Blue.
	4	Red.
4	1	Blue.
	7	Violet.
	6	Red.

The standard rod is prepared according to the general procedure.

MERCURY-DITHIZONATE STANDARDS

Mercury reacts with dithizone to form an orange-colored dithizonate, and in the rapid method devised by Ward (1958), 10 solutions ranging in color from pale gold to deep orange constitute a useful standard series. (See p. 59).

To prepare plastic standards for mercury, use a saturated ethyl alcohol solution of Orange II to dye the resin. About 7 drops of Orange II dye in 1 tablespoonful clear resin are required to match the standard with the highest metal content. Dilute portions of this preparation with sufficient amounts of clear resin to match the other members of the standard series. Cast each standard separately in a pointed 15-ml centrifuge tube to conform as nearly as possible to the dimensions of the liquid standards, which are prepared and used in 60-ml separatory funnels.

TIN STANDARDS

The tin procedure described by Marranzino and Ward (1958) utilizes the reaction of 4,5-dihydroxyfluorescein with tin (IV) to form a colored complex. (See p. 74.) To prepare a plastic rod of standards for tin the same general procedure is used as for the preparation of a plastic rod of copper standards; the calibration is made, of course, by means of comparison with liquid standards for tin.

DISCUSSION

Plastic standards do not compensate, as do real standards, for variations in color intensity caused by small changes in reagent strength and operating conditions. Consequently, when using plastic standards it is often advisable to include a standard sample with the routine samples as a check on reagent strength and operating conditions.

The preparation of a plastic rod takes about 5 hours. However, because the preparation of such rods is something of an art rather than an exact procedure, an inexperienced person should not expect his first attempts to yield a perfect product.

Castolite as obtained from the manufacturer is a water-clear syrupy liquid that pours easily and sets to a crystal-clear solid that is extremely durable and resistant to heat and chemicals. The syrupy resin is caused to solidify by addition of a hardener and cold-setting promoter. The hardener must be added in a definite ratio to the resin; the amount of cold-setting promoter, however, can be varied depending upon the time desired for hardening and the size of the casting being made. The proper amounts of hardener and cold-setting promoter needed should be determined from the manufacture's directions.

PREPARATION OF VEGETATION FOR ANALYSIS

Organic constituents of plant material must be destroyed before its metal content can be determined. The term "ashing" is applied to all procedures used to decompose—and, so far as possible, to eliminate— the organic matter of plant samples, though not all produce a true ash. In "dry ashing," samples are ignited and organic material is burned away leaving ash as a residue; in "wet ashing," samples are decomposed by means of an acid digestion in which organic material is oxidized by action of reagents. Although a more complete ashing with less probability of error can be accomplished in the laboratory than in the field, field ashing may sometimes be preferred because of expediency.

Three methods of ashing are described here. Two of these, one dry and one wet, can be used only in the laboratory; the third, a dry method, is designed for field use. Included with the description of each method is a statement of the element or elements for whose determination the method either has been tried or is considered best suited.

LABORATORY METHODS

PELLETIZING—A MEANS OF HASTENING DRY ASHING

Compressing plant material into pellets before ignition is a relatively short, easy process that greatly increases the number of samples that can be dry ashed at one time. An advantage, in addition to saving time, is that pellets give uniform ash. This method has been successfully used for ashing of vegetation samples before determination of copper, lead, and zinc.

Contamination from soil on the surface of the plant material must be avoided; therefore, plants should be washed with metal-free water as the first step in their preparation for ashing. The plants are dried at 60°C and then ground in a Wiley mill. A suitable amount (either 5 or 10 g) of the dried, ground plant material is weighed and transferred to a 1⅛-inch stainless-steel test cylinder of the type manufactured by Carver. The cylinder is placed in a press of the type manufactured by Loomis, and the pressure is increased to 13 or 14 tons. By keeping the sample under this pressure for about 15 seconds, a pellet is formed. A 10-g pellet is about 1⅛ inches in diameter and ⅝ inch thick. Each pellet is placed in a flat bottom porcelain dish, size 0. It is possible to accommodate 3 of these dishes in the space required for 1 porcelain dish of the size necessary for a plant sample of the same weight that has not been compressed into a pellet.

Ashing is accomplished by placing dishes containing pellets in a cold muffle furnace. The temperature of the muffle is increased 50°C every hour up to 550°C; then it is left at 550°C for about 10 hours and allowed to cool. The dishes are then removed and the ash weighed.

RAPID WET ASHING

Rapid wet ashing is useful in preparing plant samples for determining readily volatilized elements such as antimony, arsenic, germanium, mercury, and selenium.

The dried vegetation is pulverized in a blender or pulverizer, and a weighed portion is put into a hydraulic press. (See above.) The pellet is digested in a gently boiling mixture of sulfuric and nitric acids contained in an Erlenmeyer flask fitted with a 12-inch air condenser. Small amounts of concentrated nitric acid are added at short intervals to the boiling mixture until the liquid is pale yellow, and finally a few milliliters of hydrogen peroxide is added to remove the last traces of organic matter and the lower valent oxides of nitrogen.

REAGENTS AND APPARATUS

Hydrogen peroxide, 30-percent.
Nitric acid, A.C.S. grade, concentrated.
Sulfuric acid, A.C.S. grade, concentrated.
Flask, 500-ml Erlenmeyer, having ground-glass joint that fits a 12-inch air condenser.

PROCEDURE

1. Prepare a sample pellet as described above and transfer pellet to flask containing 25 ml conc. H_2SO_4 and 20 ml conc. HNO_3.
2. Fit flask with 12-inch air condenser and boil mixture gently.

3. Continue gentle boil, adding small amounts of conc. HNO_3 at frequent intervals until liquid is yellow.
4. Cautiously add H_2O_2 dropwise until all color is removed.
5. Cool; dilute the colorless solution to 100 ml with 0.5*M* H_2SO_4.

DISCUSSION

Early in the research it was found that 3 to 5 grams of pulverized vegetation could be ashed in about 20 minutes, if the vegetation was added in small increments to the boiling acid mixture. Devising a technique of thus adding the sample without removing the air condenser was the next problem. To add the sample bit by bit through the air condenser not only seemed impracticable and messy, but it would allow portions to stick to the sides of the condenser and thereby escape oxidation. It was found that a tightly pressed pellet would release small amounts of the sample to the acid mixture at a rate sufficient to permit rapid ashing yet slow enough to prevent the frothing that often occurs when finely ground vegetation is added all at once to a mixture of hot oxidizing acids.

Under the conditions described above, the time of ashing is about 20 minutes; after the addition of the few drops of peroxide to finish the oxidation, the sample solution is practically colorless and free of any lignin residue.

FIELD METHOD

A modified charcoal brazier has been found satisfactory for field ashing of vegetation, producing an ash comparable in quality to that obtain by use of a muffle furnace in the laboratory. (A. P. Marranzino, written communication, 1959.) To date, this method has been used on vegetation only for determination of uranium; it has proved successful for that element.

The bottom of a charcoal brazier is covered with aluminum foil. (See fig. 3.) A 1- to 4-inch layer of coarse gravel is placed in the bottom of the brazier. A covered aluminum can 3 inches in

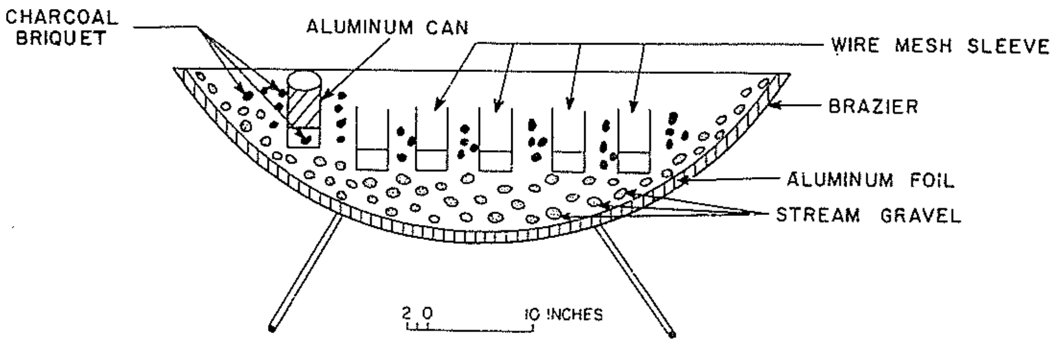

FIGURE 3.—Cross section of brazier.

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diameter and 4 inches in depth, with a ½-inch hole cut in the center of the cover, is used as container for each sample. In order to keep the aluminum cans from melting from the intense heat of burning charcoal, each is held in the brazier by a 14-gage wire sleeve of 4- by 4-mesh, fashioned 3⅛ inches in diameter by 6 inches in depth, and with a 14-gage cross-wire insert 2⅗ inches from one end. Twelve or more such sleeves are placed, one for each sample can, in the charcoal brazier, utilizing the space to the fullest advantage. Commercial charcoal briquets supply the fuel. One briquet is placed in the bottom of each sleeve, and each sleeve is then surrounded by briquets.

PROCEDURE

1. With pruning shears, cut the samples of vegetation into small pieces so that 50–75 g of each sample will fit into its aluminum container.
2. Place the covers on the containers, place the containers into the sleeves in the brazier, and ignite the charcoal.
3. When the excess smoke has ceased pouring from the hole in the cover of each container, remove the cover and stir the sample with a glass rod.
4. Let containers stand open until the organic material has oxidized; remove the containers from the sleeves.

NOTE.—The entire procedure takes about 2 hours. Since the coals around the sleeves are already burning, a new batch of samples may be placed in the unit and the operation repeated.

DISCUSSION

The best ash obtainable in the laboratory is considered a "white ash," although traces of iron oxide may color the ash. It is not possible, however, to oxidize all vegetation to that condition. In the field a white ash is even more difficult to obtain, since a constant heat cannot be maintained around the sample for a long period of time.

DETERMINATION OF THE CONSTITUENTS

COPPER, LEAD, AND ZINC IN SOILS AND ROCKS

Several rapid methods have been used for the determination of copper, lead, and zinc in soils and rocks. They differ principally in the manner in which the sample solution is prepared. The proportion of the total copper, lead, and zinc extracted from a sample of either rock or soil depends upon the vigor of the digestion used and upon how refractory the sample is. It is not always necessary to determine the total amount of these metals in a sample; values obtained by the determination of only the readily soluble copper, lead, and zinc sometimes demonstrate greater contrasts among the samples than total or near-total values. The best method for use in a particular study will be the quickest and cheapest method that gives satisfactory results.

In a study of the East Tintic district in Utah, Almond and Morris (1951) determined the amount of copper, lead, and zinc dissolved by dilute sulfuric acid from samples of hard rock. Successful results on samples from the same area have also been achieved by determining the amount of these metals soluble in hydrochloric acid. Huff (1951) determined the amount of heavy metals (combined copper, lead, and zinc) in soils and sediments that was soluble in dilute nitric acid, and Bloom and Crowe (1953) also determined the copper, lead, and zinc extracted from soils by dilute nitric acid. Lakin and others (1949) and Fulton (1950) used a simple pyrosulfate-fusion technique in the analysis of soils for zinc. All these methods and others have been used successfully in geochemical prospecting, but different ones apply to samples of different types encountered in exploration.

The pyrosulfate-fusion technique, given in the procedure which follows, is one that gives near-total solution of the copper, lead, and zinc in most soils and rocks. Dithizone is used for determining zinc by the mixed-color method. When a solution of dithizone in carbon tetrachloride is shaken with a buffered solution containing zinc, red zinc dithizonate is formed. The resulting color of the solution—a mixture of red zinc dithizonate and unreacted dithizone—ranges from blue through purple to red, depending on the amount of zinc extracted. Dithizone is used, in the presence of cyanide, to determine lead as the lead dithizonate by means of the monocolor method, in which different shades of pink indicate the amount of lead present. The reaction between 2,2′-biquinoline and copper (I) to form a pink compound is used to determine copper (Almond, 1955).

REAGENTS AND APPARATUS

General reagents

Dithizone stock solution (0.01 percent): Dissolve 0.005 g dithizone (diphenylthiocarbazone) in 500 ml carbon tetrachloride (CCl_4). Shake the mixture intermittently over a period of about 1 hr. to effect solution.

Dithizone test solution (0.001 percent): Dilute 50 ml dithizone stock solution (0.01 percent) to 500 ml with CCl_4.

Hydrochloric acid, $6M$: Add 100 ml metal-free water to 100 ml conc. reagent-grade HCl.

Potassium pyrosulfate ($K_2S_2O_7$) fused powder, reagent grade.

Lead reagents

Lead buffer solution: Transfer 50 g ammonium citrate ($(NH_4)_2\ HC_6\ H_5O_7$) 10 g potassium cyanide (KCN) (see p. 5) and 8 g hydroxylamine hydrochloride ($NH_2\ OH \cdot HCl$) into a large separatory funnel; add 800 ml metal-free water and shake the funnel until the reagents are dissolved. Add 2 ml thymol blue indicator and then conc. NH_4OH until the pH of the solution is

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8.5 (color is blue). Remove any contaminating heavy metals by the following procedure:

Transfer 50 ml dithizone solution (0.01-percent) to the separatory funnel, shake, allow the CCl_4 phase to collect in the bottom of the funnel and discard. Continue this process with additional 50-ml increments until the discarded organic phase is green.

Some dithizone is dissolved in the buffer solution, imparting to it a yellow color. This is removed by successive extractions with 50-ml portions of chloroform ($CHCl_3$).

Chloroform dissolved in the buffer solution is removed by shaking the buffer solution with 100 ml CCl_4 and discarding the organic phase.

Dilute the aqueous buffer solution to 1 liter with metal-free water.

Potassium cyanide solution (0.1 percent aqueous). *CAUTION* (see p. —): Dissolve 1 g potassium cyanide (KCN) in 1 liter metal-free water.

Standard lead solution (100 μg per ml). Dissolve 0.016 g lead nitrate ($Pb(NO_3)_2$), dried for 1 hr at 110°C, in 100 ml metal-free water containing 1 ml conc. HNO_3.

Standard lead solution, 10 μg per ml: Add 10 ml standard lead solution (100 μg per ml) to a 100-ml volumetric flask containing 1 ml conc. HNO_3 and about 10 ml metal-free water. Dilute to 100-ml volume with metal-free water.

Thymol blue, 0.2-percent aqueous. Dissolve 0.2 g sodium salt of thymol blue in 100 ml metal-free water.

Copper reagents

2,2′-biquinoline solution, 0.02-percent: Add 0.2 g 2,2′-biquinoline to about 900 ml isoamyl alcohol in a beaker. Warm on a steam bath in a well-ventilated room away from open flame until the biquinoline is dissolved. Allow the solution to cool, and dilute to 1 liter with isoamyl alcohol. The solution should be colorless; if it is yellow, the reagent is impure and should not be used.

Copper buffer solution: Dissolve 400 g sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$), 100 g sodium tartrate ($Na_2C_2H_4O_6 \cdot 2H_2O$), and 20 g hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 1 liter metal-free water. If necessary, adjust the pH of this solution with HCl or NaOH solution to between 6 and 7, using pH test paper. To check for copper contamination, place 10 ml of buffer in a culture tube, add 1 ml of the biquinoline reagent, cap, and shake for 2 min. Absence of a pink color in the organic layer indicates that the solution is satisfactory for use. If found to be contaminated, the buffer solution may be cleaned by the procedure given for the lead buffer solution above.

Hydrochloric acid, 6*M:* Add 500 ml conc. reagent-grade HCl to 500 ml metal-free water.

Standard copper solution, 100 μg per ml: Dissolve 0.200 g copper sulfate ($CuSO_4 \cdot 5H_2O$) in 500 ml 0.1*M* HCl.

Standard copper solution, 10 μg per ml: Transfer 10 ml standard copper solution (100 μg per ml) to a 100-ml volumetric flask, and dilute to 100 ml with 0.1*M* HCl.

Zinc reagents

Zinc buffer solution:

A. Dissolve 125 g sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in about 400 ml metal-free water in a large separatory funnel. Remove heavy metals by extracting them from the solution with dithizone solution (0.01 percent) in one or more 50-ml portions, as follows: after the addition, the funnel is shaken and the CCl_4 layer allowed to settle to the bottom. If this layer shows any color except the characteristic clear green of dithizone, heavy metals are present and are reacting with the dithizone to form colored dithizonates. In that case, the layer should be drained away and another 50-ml portion dithizone (0.01 percent) added. When the lower layer is green and remains green, the excess dithizone must be removed from the buffer solution by extracting it with successive 50-ml portions CCl_4. The process is the same as that described above, except that now the portions are added, shaken, then discarded until the lower layer is colorless.

B. Dissolve 300 g sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$) in 400 ml of metal-free water, then add 60 ml of glacial acetic acid. Remove heavy metals by the procedure used for solution A, above.

C. Combine solutions A and B and dilute to 2 liters with metal-free water.

Standard zinc solution, 100 μg per ml: Dissolve 0.100 g of reagent-grade 30-mesh zinc metal in 10 ml conc. HCl and dilute to 1 liter with metal-free water.

Standard zinc solution, 10 μg per ml: Transfer 10 ml standard zinc solution (100 μg per ml) to a 100-ml volumetric flask and dilute to volume with metal-free water.

Apparatus

Culture tubes, 16- by 150-mm.
 22- by 175-mm.
Caps, polyethylene, size S–3, to fit 22- by 175-mm tubes.
Scoop, 0.1-g and 0.5-g.
Spatula.
Pipets, volumetric, 1-ml and 2-ml.
 1-ml, graduated in tenths.
Separatory funnels, 125-ml.
Separatory-funnel rack.
Graduated cylinders, 25-ml, glass-stoppered.
Ear syringe, rubber. Used to provide suction for pipetting poisonous solutions such as potassium cyanide.

PROCEDURE

Preparation of sample solution

1. Weigh or scoop a 0.1-g sample and transfer it to a 16- by 150-mm culture tube. Scoop 0.5 g $K_2S_2O_7$ flux into the culture tube and shake the tube to mix the sample and flux. Fuse the mixture for about 2 min. after the flux melts. Remove the tube from the flame and rotate the tube so that the melt cools in a thin film on the side of the tube.
2. When the tube is cool, add 3 ml 6*M* HCl to the tube, and place it in a hot water bath until the melt has disintegrated. To hasten disintegration of the melt, shake the tube intermittently or crush the melt with a glass rod.
3. Remove the tube from the water bath and dilute the sample solution to 10 ml with metal-free water. Shake the tube vigorously to mix the sample solution.
4. Take suitable aliquots from this single sample solution for copper, lead, and zinc estimation.

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Estimation of lead

1. Transfer of 2-ml aliquot of the sample solution to a 125-ml separatory funnel containing 10 ml lead buffer solution.
2. Add 2 drops thymol blue indicator solution to the funnel, then add conc. NH_4OH dropwise until the pH of the solution is 8.5 to 9, as indicated by a change from yellow to blue.
3. Add 5 ml dithizone solution (0.001 percent) and shake the separatory funnel gently for about 15 sec.
4. Drain the CCl_4 layer into a 25-ml glass-stoppered graduated cylinder containing 10 ml KCN solution (0.1 percent).
5. Shake the cylinder gently for 5 sec. Compare the color of the CCl_4 layer with the similarly prepared standard solutions. If sample color is above the highest standard, repeat, using a smaller aliquot.
6. Calculate the lead concentrations in the sample according to instructions on p. 8.

Lead standard solution

Prepare lead standards of 0, 1, 2, and 3 μg by pipetting suitable aliquots from a standard lead solution (10 μg per ml) into 125-ml separatory funnels containing 10 ml lead buffer. Then proceed from step 2 above. As these liquid standards for lead usually begin to fade after approximately one-half day, they should be prepared fresh twice daily.

Estimation of zinc

1. Transfer a 2-ml aliquot of the sample solution to a 22- by 175-mm culture tube containing about 8 ml zinc buffer solution.
2. Add 5 ml dithizone solution (0.001 percent) and tightly cap the culture tube. Shake the tube vigorously for 30 sec. Compare the color in the CCl_4 layer with similarly prepared standard zinc solutions. If the sample solution color is above the highest standard, repeat, using a smaller aliquot.
3. Calculate the zinc concentration in the sample according to instructions on p. 8.

Zinc standard solutions

Prepare zinc standards of 0, 1, 2, 3, and 4 μg by pipetting into each of five 22- by 175-mm culture tubes respectively, suitable aliquots from a standard zinc solution (10 μg per ml). Add 8 ml zinc buffer solution to each of the tubes and proceed from step 1 above. These standards are usually stable for at least 2 days.

Estimation of copper

1. Transfer a 2-ml aliquot of the sample solution to a 22- by 175-mm culture tube containing 10 ml copper buffer solution.
2. Add 2 ml 2,2′-biquinoline solution to the tube. Tightly cap the tube and shake vigorously for 45 sec.
3. Allow the layers to separate, and compare the color of the isoamyl alcohol layer with similarly prepared standards of known copper content. Repeat, if necessary, using a smaller aliquot.
4. Calculate the copper concentration in the sample according to instructions on p. 8.

Copper standard solution

Prepare copper standards of 0, 0.2, 0.4, 0.8, 1.5, 3, and 6 μg by pipetting into seven 25- by 200-mm culture tubes respectively, suitable aliquots from a standard copper solution (10 μg per ml). Add 10 ml copper buffer solution and proceed from step 1 above. If kept tightly stoppered to prevent evaporation of the isoamyl alcohol, these standards are usually stable for several months.

DISCUSSION

Because of the sensitivity of dithizone reactions, a constant source of difficulty with these methods is contamination. It is therefore necessary to use metal-free water and to purify the reagents to be used. Dithizone solutions are oxidized by light and heat, and by oxidizing agents in the sample. The oxidation product is yellow and may be detected in the carbon tetrachloride by shaking a small amount of dithizone solution with pure $1M$ amonium hydroxide. The more dilute the solution, the more readily it is oxidized. For practical work, a strong solution is prepared for the stock solution, which is diluted as needed. This stock solution usually remains stable for several weeks if kept in a covered bottle and in a cool place. The dilute solution, if kept in a covered bottle in a cool place, may remain stable for a week or two.

Lead reacts with dithizone most easily at a pH of about 8.5. Copper, zinc, and several other elements, however, also react at this pH. Copper and zinc will not interfere with the determination of lead if potassium cyanide is added, because the cyanide forms a complex with copper and zinc, preventing those metals from reacting with the dithizone. Other possible sources of interference are stannous tin, thallium, and bismuth, but the amount of these elements in most natural materials is below the interference threshold.

Zinc reacts with dithizone at a pH of 4.5. In the presence of sodium thiosulfate, most of the elements that would interfere with the zinc determination are complexed and thus prevented from reacting with the dithizone. Although palladium and stannous tin react under the conditions of the test, their interference usually is unlikely, because palladium occurs naturally in very small amounts, and because tin, if present, is almost always in the stannic form. A positive error is obtained for samples containing 10 or more times as much cadmium, cobalt, nickel, or copper as zinc. In most samples the occurrence of these elements in such concentrations is improbable, and therefore interference from them in the zinc test would be exceptional. If more than 10 percent aluminum is present and the zinc content is 200 ppm or less, the zinc value obtained will be low.

The copper complex formed with 2,2′-biquinoline is not a strong complex. Ions that form strong complexes with copper, such as ammonium ion, prevent the reaction of copper and 2,2′-biquinoline and therefore should not be present during the test. If organic matter (such as humic acid) is present, which can be extracted by isoamyl alcohol, a yellow color will mask the color of the copper biquinoline complex. If samples of high organic content are preignited at 450°C, interference from organic compounds can be prevented.

COPPER, LEAD, AND ZINC IN PLANTS

Biogeochemical prospecting has been widely applied in the search for copper, lead, and zinc. Much work has been done on the use of plants in exploration for copper and zinc by Warren, Delavault, and Irish (1949, 1951, 1952) in the United States and Canada. Prominent among other workers who have prospected for copper and zinc by using plants are Harbaugh (1950) in the Tri-State district (Kansas, Missouri, and Oklahoma); Cannon (1955) in Orleans County, N.Y.; Marmo (1953) in Finland; and Vogt and others (1943) in Norway. The copper and zinc in plants have been determined by emission spectrography, by X-ray, and by colorimetric analysis. A field method for the determination of zinc in plants was first described by Reichen and Lakin (1949).

To prepare plant material for the determination of copper, lead, and zinc, the U.S. Geological Survey uses one of the ashing methods described on page 16. When a dry-ashing process is used, the ash obtained is ground, if necessary, so that it will pass through a 200-mesh sieve; after being sieved, it is mixed thoroughly. A 0.1-g portion of the ash is fused with 0.5 g potassium pyrosulfate and the melt is dissolved in 3 ml 6 *M* hydrochloric acid. The solution is diluted to 10 ml. Aliquots of this solution, or of the solution obtained from the wet-ashing procedure, are used for the determination of copper, lead, and zinc by the procedures given for soils and rocks.

ACID-EXTRACTABLE COPPER IN SOILS AND SEDIMENTS

The following procedure for the determination of acid-extractable copper in soils and sediments is given by Canney and Hawkins (1958). The copper that is extracted from a soil or sediment by cold hydrochloric acid is estimated by use of the colored copper 2,2′-biquinoline complex in an isoamyl alcohol extract. Although this extraction yields only about 10 to 30 percent of the total copper in most samples, it has been found that the pattern of analytical data revealed by its use is often more significant than the pattern of total copper; and because the method is rapid and requires only simple, easily portable items of equipment, it is ideally suited for use under rough field conditions, at the sample site if desired. Many data can be collected in a relatively short time because a single determination requires only about 2 minutes. The method has a limiting sensitivity of about 1 ppm, which means that a positive test can usually be obtained on most samples. The method is not recommended for samples containing appreciable quantities of decaying organic material, because soluble organic matter may dissolve in the organic solvent to yield a yellow solution that masks the pink color of the copper-biquinoline complex.

REAGENTS AND APPARATUS

Biquinoline reagent solution, 0.02-percent: Add 0.2 g 2,2′-biquinoline to about 900 ml isoamyl alcohol in a beaker. Warm on a steam bath in a well-ventilated area away from open flame until the biquinoline is dissolved. Allow solution to cool, and dilute to 1 liter with isoamyl alcohol. The solution should be colorless; if it is yellow, the reagent is impure and should not be used.

Buffer solution: Dissolve 400 g sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$), 100 g sodium tartrate ($Na_2C_4H_4O_6 \cdot 2H_2O$), and 20 g hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 1 liter of metal-free water. Adjust the pH of this solution with HCl or NaOH solutions, if necessary, to between 6 and 7, using pH test paper. To check for copper contamination place 10 ml of buffer in a culture tube, add 1 ml the biquinoline reagent, cap, and shake for 2 min. Absence of a pink coloration in the organic layer indicates that the solution is satisfactory for use. If contaminated, the buffer may be cleaned by the procedure given for the lead buffer solution on page 21.

Hydrochloric acid, $6M$: Add 500 ml conc. HCl to 500 ml water.

Standard copper solution, 100 μg copper per ml: Dissolve 0.2 g copper sulfate ($CuSO_4 \cdot 5H_2O$) in 500 ml $0.1M$ HCl. More dilute copper standard (10 μg per ml, and 1 μg per ml) can be prepared by dilution of appropriate aliquots of this copper standard (100 μg per ml) with $0.1M$ HCl.

Minimum equipment for reagents sufficient for 40 to 50 determinations at the sample site:

1 scoop, 0.2-g.
1 polyethylene dropping bottle, 2-oz, with attached cap, for dispensing $6M$ HCl. Determine the number of drops to equal 1 ml.
1 polyethylene dispensing bottle, 4-oz, for the biquinoline reagent.
1 polyethylene dispensing bottle, 16-oz, for the buffer solution.
Culture tubes, 22- by 175-mm, marked at volumes of 11 and 13 ml.
Polyethylene stoppers, for above culture tubes.
1 plastic standard rod (optional). See p. 13.

PROCEDURE

1. Place in a 22- by 175-mm culture tube 0.2 g (or one 0.2 g scoopful) of the fine fraction of a soil or sediment sample.
2. Add about 1 ml $6M$ HCl and slosh the sample in the acid for about 30 sec.
3. Add 10 ml buffer solution, 2 ml biquinoline reagent; then cap the tube with the polyethylene stopper, and shake the tube vigorously for about 30 sec.

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4. Allow the tube to stand until the organic layer separates sufficiently, then compare color of organic layer either with liquid biquinoline standards or a plastic standard rod.
5. To convert to parts per million, multiply by five the number of micrograms of copper found.

Preparation of standards

A series of copper standards for 0, 0.2, 0.4, 0.8, 1.5, 3, and 6 μg of copper is recommended. In a field laboratory, liquid biquinoline standards in culture tubes are satisfactory; for analyses at the sample site, however, use of a plastic standard rod is much more convenient.

To prepare liquid standards, place 1 ml of 6*M* HCl in each of a series of culture tubes; add to each the requisite amount of standard copper solution of appropriate concentration to produce the series suggested above; then follow the regular procedure starting with step 3. One set of standards should remain stable for several months provided the tubes are kept tightly capped to prevent evaporation of the isoamyl alcohol.

DISCUSSION

Relatively coarse organic matter in some samples may interfere by accumulating at the water-alcohol interface. If this happens, the debris can usually be removed from the interface and dispersed throughout the buffer by manually centrifuging the tube.

To increase sensitivity, if desired, the sample size can be increased, with the amounts of acid and buffer increased proportionately. Conversely, the upper range of the method can be extended, by decreasing the sample size or by increasing the volume of biquinoline reagent. In such cases different factors are required for conversion from micrograms of copper to parts per million.

A standard sample should be analyzed at the start of each day's work as a check on the reagents and standards to insure comparable results from day to day.

AMMONIUM CITRATE—SOLUBLE HEAVY METALS IN SOILS AND SEDIMENTS

The field method for the determination of heavy metals that are soluble in solutions of ammonium citrate is described in detail by Bloom (1955). An aqueous ammonium citrate solution is used at ambient temperature to extract heavy metals from a sample of soil or sediment, and a xylene or toluene solution of dithizone is used to estimate the concentration of heavy-metal ions. Although this method measures only a small fraction of the total metal content of a sample, geochemical dispersion patterns related to base-metal deposits are sometimes revealed more clearly than by methods that measure the total metal content.

The method is extremely rapid; a determination can be made in less than 1 minute. As only a few simple items of equipment are needed, the method is well adapted to field use because samples can be analyzed as rapidly as they are collected. Thus, a geologist's efficiency in finding and outlining economically important dispersion patterns or heavy metals is increased. The method has been widely used in geochemical prospecting.

REAGENTS AND APPARATUS

Xylene, reagent-grade: Occasionally a manufacturer's best grade of xylene may be unsatisfactory, as indicated when fresh dithizone solutions rapidly take on yellow hues caused by oxidation of the dithizone. Such xylene can sometimes be made satisfactory for use by distillation or by shaking it with small amounts of concentrated sulfuric acid, and freezing out water remaining after the acid wash.

Carbon tetrachloride (CCl_4), reagent-grade.

Dithizone solution, 0.01 percent in xylene: Dissolve 0.05 g dithizone in 500 ml reagent-grade xylene approximately 12 hr before using. Store the solution in a glass-stoppered Pyrex bottle that has been wrapped with paper or aluminum foil, and keep it cool.

Dithizone solution, 0.001 percent in xylene: Prepare by diluting 10 ml dithizone solution (0.01 percent) to 100 ml with xylene. This solution can be conveniently dispensed in the field from an aluminum-foil-wrapped polyethylene wash bottle. As this dilute solution is less stable than the stronger solution, only about 100 ml should be made up at one time, and care should be taken in the field to keep the container away from direct sunlight so far as possible.

Dithizone, 0.01 percent in carbon tetrachloride (CCl_4) (for purifying ammonium citrate solution): Dissolve 0.01 g dithizone in 100 ml of CCl_4.

Chloroform ($CHcl_3$), reagent-grade.

Ammonium hydroxide, metal-free.

Ammonium citrate solution: Dissolve 25 g ammonium citrate ($(NH_4)_2HC_6H_5O_7$) and 4 g hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in about 300 ml water. Add concentrated NH_4OH until testing with pH paper shows that the solution has a pH of about 7, and dilute to 500 ml with water. Place the solution in a separatory funnel and remove heavy metals by extraction of the aqueous solution with 15-ml portions of a CCl_4 solution of dithizone (0.01-percent) until the organic layer remains green. Extract the dissolved dithizone by shaking the aqueous solution with 25-ml portions of $CHCl_3$ until the latter is colorless. Then wash twice with CCl_4 to remove dissolved $CHCl_3$. Finally, adjust the pH of the solution to 8.5 by adding metal-free NH_4OH. This final adjustment of the pH should be made very carefully, because the rate of extraction of the metal dithizonates is dependent on pH.

1 separatory funnel, 1-liter, glass-stoppered.
2 graduated cylinders, glass-stoppered, 100-ml.
6 graduated cylinders, glass-stoppered, 25-ml.
2 polyethylene wash bottles, 16-oz.
1 polyethylene wash bottle, 8-oz.
2 dropping bottles, polyethylene, 2-oz.
1 scoop, 0.1-g.

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PROCEDURE

1. Place one scoopful (about 0.1 g) of the fine fraction of a soil or sediment sample into a 25-ml glass-stoppered cylinder and add 5 ml ammonium citrate solution and 1 ml dithizone solution in xylene (0.001 percent).
2. Shake the cylinder vigorously for 5 sec.
3. Allow the organic and aqueous phases to separate and observe the color of the xylene (upper) layer. If it is green, green blue, or blue, record as 0, ½, or 1 ml, respectively.
4. If the color is blue purple to red, titrate with about 1-ml increments of the xylene dithizone solution (0.001 percent), shaking for a few seconds after each addition until a blue color is obtained.
5. As an index of the heavy-metal content, record the volume of dithizone solution used. By titrating a series of solutions that contain known amounts of zinc, a calibration curve can be constructed from which the exchangeable-metal content can be obtained in parts per million, zinc equivalent.

DISCUSSION

If desired, other lighter-than-water solvents may be employed. Tuolene is one that is widely used.

To ensure comparable results in day-to-day use of this method, the frequent running of a standard sample whose exchangeable-metal content is known is highly recommended.

In areas where the exchangeable-metal content of most samples is unusually high, the strength of the work solution can be advantageously increased to 0.003 percent.

HEAVY METALS IN WATER

A complete description of the method of determining heavy metals in water and its application is given by Huff (1948). According to Huff, the sensitivity of the test permits the detection of 0.002 ppm zinc, 0.01 ppm lead, and 0.01 ppm copper in a 50-ml sample. Waters of high heavy-metal content can be analyzed by reducing the size of the sample taken for analysis. Organic matter in the water tends to cause stable emulsions to form between the organic solvent and water. These emulsions and zinc contamination are the most serious interferences in the use of the method. Although reagents of exceptional purity are required, only simple equipment is needed and the test can be made in a few minutes in the field. Thus the geologists can test water samples as he collects them and can follow anomalies without delay.

Because the reagent is very sensitive, the analysis is extraordinarily susceptible to contamination; it is mandatory that all apparatus be kept scrupulously clean. Check determinations should be made frequently.

REAGENTS AND APPARATUS

Acetic acid, 2*M:* Dilute 114 ml glacial acetic acid to 1 liter with metal-free water.

Sodium acetate solution, 2*M:* Dissolve 164 g sodium acetate ($NaC_2H_3O_2$) in metal-free water and dilute to 1 liter.

Acetate buffer solution: Mix 9 parts 2*M* sodium acetate with 1 part 2*M* acetic acid. Purify by shaking with successive portions of dithizone solution (0.01 percent) until the organic layer remains green.

Ammonium hydroxide, 2*M:* Dilute 127 ml conc. metal-free ammonium hydroxide to 1 liter with metal-free water.

Carbon tetrachloride (CCl_4), reagent grade.

Dithizone solution, 0.01-percent: Dissolve 0.05 g dithizone in 500 ml reagent-grade CCl_4. As sunlight and heat decompose the reagent, solutions should be stored in glass-stoppered bottles wrapped with aluminum foil and kept cool.

Dithizone solution, 0.0015-percent: Dilute 15 ml dithizone solution (0.01 percent) to 100 ml with reagent-grade CCl_4. This dilute solution is very susceptible to oxidation and should be protected from heat and sunlight as much as possible. The bottle used to dispense this reagent in the field should be wrapped with aluminum foil. To check for oxidation, place a few ml of the dithizone solution in a glass-stoppered graduated cylinder containing 20 to 30 ml metal-free water, make slighly alkaline with NH_4OH and shake for 10 to 15 sec. Observe the color of the organic layer. More than a slight tinge of yellow indicates that some oxidation has taken place, and the reagent should not be used.

Zinc standard solution (100 μg per ml): Dissolve 0.01 g reagent-grade zinc in 100 ml 0.1*M* HCl. More dilute standard solutions are prepared as needed.

Thymol blue indicator solution, 0.04-percent: Dissolve 0.04 g sodium salt of thymol blue in 100 ml water.

4 graduated cylinders, 100-ml, glass-stoppered.
1 graduated cylinder, 5-ml.
1 separatory funnel, 125-ml, glass-stoppered.
1 automatic pipet, 5-ml.
6 polyethylene dropping bottles, 2-oz, with attached cap.
1 polyethylene dispensing bottle, 8-oz.

PROCEDURE

1. Place 50 ml of the water sample in a 100-ml glass-stoppered graduated cylinder and add 5 drops acetate buffer solution and 5 ml dithizone solution (0.0015 percent).
2. Cap the cylinder and shake it vigorously for 1 min. Allow the phases to separate, and observe the color of the CCl_4 layer.
   - (a) If the color is intermediate between green and red (a mixed color caused by a combination of red metal-dithizonate and unreacted green dithizone), estimate the amount of metal present by reference to table 4, column 3, or compare with a standard zinc solution (see p. 23).
   - (b) If the color is red, clean the cylinder by rinsing with increments of metal-free water and the dithizone solution until the dithizone solution remains green. Then repeat the analysis using a smaller volume of sample until a mixed color is obtained.

TABLE 4.—*De*

Acidity of
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Mixed-color range
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TABLE 4.—*Description of colors obtained with heavy-metals tests on standard solutions*

[After Huff (1948)]

Acidity of extraction	Micrograms of metal in 50 ml of solution	Color of dithizonate in strong, white transmitted light [1]			
		Zinc	Copper	Lead	1:1:1 mixture of zinc, copper, lead
Mixed-color range; pH of about 5.5 obtained with acetate buffer.	20	Light purplish red.	Strong purplish red.	Light purplish red.	Light purplish red.
	15	---do---------	---do---------	Light red purple.	Do.
	10	---do---------	---do---------	Pale purplish blue.	Do.
	7	---do---------	---do---------	-------------	Do.
	5	---do---------	Pale purple----	Light blue green.	Light red purple.
	4	Light red purple.	Pale purplish blue.	-------------	
	3	Light purple---	Light blue green.	-------------	Pale blue.
	2	Pale blue------	Light bluish green.	Light bluish green.	Light blue green.
	1	Light blue green.	Light green----	-------------	Light bluish green.
	½	Light bluish green.	-------------	-------------	
	0	Light green----	Light green----	Light green----	Light green.
Monocolor range; pH of about 9.0 obtained by adding ammonium hydroxide to mixed color test.	1	Strong pink----	Moderate pink-	Moderate pink-	Strong pink.
	½	Weak pink	Faintest color detectable.	Faintest color detectable.	Weak pink.
	1/10	Faintest color detectable.	Colorless------	Colorless------	Faintest color detectable.
	0	Colorless------	Colorless------	Colorless------	Colorless.

[1] Color identification based upon Munsell notation (see "Munsell Book of Color," standard ed., Munsell Color Co., Inc., Baltimore, Md., 1929; also Judd, D. B., and Kelly, K. L., "Method of Designating Colors," National Bureau Standards Research Paper 1239, Sept. 1939). In the mixed-color range the colors all have about the same value but vary in hue and chroma, the intermediate hues being distinctly grayish whereas the end members have strong chroma; in the monocolor range the hue remains constant while the chroma and value change as the colors become fainter.

(c) If the color apparently remains unchanged, add 2 drops thymol blue indicator, add 2*M* NH_4OH dropwise until the indicator just turns from yellow to blue, then add 1 additional drop. Shake again for 15 sec and then estimate visually the amount of metal present by referring to table 4, column 3, monocolor range pH about 9.

3. Multiply the number of μg of metal found in 50 ml of sample by 20 to convert to parts per billion (1 ppb = 0.001 ppm).

PAPER-CHROMATOGRAPHIC METHOD FOR TRACES OF COPPER, COBALT, AND NICKEL IN SOILS

Hunt, North, and Wells (1955) and Stanton and Gilbert (1956) described a paper-chromatographic procedure for estimating the amount of copper, cobalt, and nickel in soils. A small aliquot from a hydrochloric acid solution of the pyrosulfate fusion of a soil sample is placed near one end of a strip of suitable paper. (See p. 33.) This end is lowered into a solvent mixture of methyl ethyl ketone, hydrochloric acid and water. The upward diffusion of this mixture through the paper separates the chlorides of copper, nickel, and cobalt into definite bands that become visible after treatment with rubeanic acid. Nickel appears on the paper as a blue-purple band just above the test spot; cobalt, as a brown band above the nickel; and copper, as on olive-green band above the nickel and below the brown ferric hydroxide at the solvent-mixture front. D. B. Hawkins (oral communication, 1957) reported that the exposure of the chromatogram to ammonia after treatment with rubeanic acid enhances the color of the metal rubeanates. The present method gives positive tests for 50 ppm or more of copper, cobalt, or nickel.

The sample is fused with potassium pyrosulfate, and the fused mass is dissolved in hydrochloric acid containing a little nitric acid, which is added to prevent double-band formation for copper. To obtain sensitivity, the volume of the sample solution must be kept small because the optimum quantity of test solution to be applied to the paper strip is 0.01 ml.

A critical step in the method is the drying of the paper after application of the sample solution. The water and hydrochloric acid content must be reduced to an optimum value. This is accomplished by heating the paper for 3 minutes in a dry beaker floated in a boiling water bath.

This method has been used successfully by the U.S. Geological Survey to outline copper and nickel mineral deposits on Yakobi Island, Alaska (R. M. Chapman, oral communication, 1957).

REAGENTS AND APPARATUS

Potassium pyrosulfate ($K_2S_2O_7$), reagent-grade, powdered.

Hydrochloric acid, reagent-grade, conc.

Nitric acid, reagent-grade, conc.

Nitric acid-hydrochloric acid solution: Dilute 25 ml conc. HNO_3 with about 100 ml metal-free water, add 250 ml conc. HCl, and dilute with solution to 500 ml with water.

Ammonium hydroxide, reagent-grade.

Ethyl methyl ketone (2-butanone), dry, reagent-grade.

Rubeanic acid solution, 0.1 percent: Dissolve 0.1 g rubeanic acid (dithiooxamide) in 60 ml ethyl alcohol and dilute to 100 ml with water.

Standard copper, cobalt, nickel (500 μg each element per ml): Dissolve 0.4050 g nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), 0.4037 g cobaltous chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and 0.3930 g cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) in 200 ml nitric acid hydrochloric acid mixture.

Solvent mixture: Transfer to a 25-ml graduated cylinder 15 ml ethyl methyl ketone, 3 ml conc. HCl, and 2 ml water. Mix and transfer to a 600-ml beaker and cover with a watchglass. Prepare 15 min before required because the vapor in the beaker must be in equilibrium with the solvent mixture to obtain good separation of the metals in the chromatogram.

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Filter paper, Whatman CRL/1: This paper comes in specially designed rectangular sheets (21.3 by 11 cm) with 11 slots cut in the paper parallel to the short side, leaving 12 strips 1.5 cm wide joined at the top and bottom.
Test tubes, 18- by 150-mm.
Beakers, glass, 600-ml.
Beakers, glass, 50-ml.
Watchglasses or petri dishes, 125 mm diameter.
Pipet, measuring, 10-ml, calibrated in 0.1 ml.
    micro, 0.01 ml.
Atomizer, all-glass, 50-ml.
Cylinder, graduated, 25-ml.

PROCEDURE

1. Transfer to an 18- by 150-mm test tube 0.2 g sample, add 0.5 g $K_2S_2O_7$, mix, and heat until a quiescent melt is obtained.
2. Allow the melt to cool, add 2.0 ml of the nitric acid-hydrochloric acid mixture, and heat for 10 min in a boiling water bath that is shallow enough to leave the upper end of the test tube cool.
3. Remove the tube from the bath and allow to cool. Prolonged standing or centrifuging may be required to insure a clear supernatant solution above the K_2SO_4 that crystallizes.
4. Prepare the solvent mixture as described above under "Reagents and apparatus," transfer to a 600-ml beaker, and cover with a watchglass.
5. With a micropipet, transfer 0.01 ml of the clear sample solution to a location near the end of one of the strips of a sheet of Whatman CRL/1 paper. Aliquots may be similarly placed on the remaining strips of each sheet of paper except on the outer strips, which cannot be used.
6. Form a cylinder from the sheet of filter paper, and fasten the upper corners with a paper clip. Place this cylinder, with sample spots lowermost, into a dry 600-ml beaker floating in a bath of boiling water.
7. After 3 min. has elapsed, transfer the paper cylinder to the beaker containing the solvent (prepared in step 4) and cover with a watchglass.
8. The solvent will diffuse slowly upward through the paper; 30 min. or more is required for it to reach the top of the strips. When the solvent has almost reached the top of the strips, remove the paper cylinder and allow it to dry in air for about 5 min.
9. Place cylinder in a 600-ml beaker containing a 50-ml beaker of ammonium hydroxide. Cover and leave 2 or 3 min.
10. Remove the paper clip, spread the chromatographic sheet on a clean paper blotter, and spray both sides with the rubeanic acid solution.
11. Again form the sheet into a cylinder, and place it in a 600-ml beaker containing a 50-ml beaker of ammonium hydroxide. Cover and leave for 2 or 3 min.
12. Compare the colored bands with appropriate standards, and multiply by 1,000 the μg of metal found in the sample, to obtain parts per million.

Preparation of standards

Transfer aliquots of 0.1, 0.2, 0.4, 0.8, 1.6, 3.0 and 6.0 ml, respectively, of the standard copper-cobalt-nickel solution to seven 10-ml volumetric flasks, 1 aliquot to the flask; add 2.5 g $K_2S_2O_7$ to each flask, dilute each to volume with the acid mixture, warm to dissolve the $K_2S_2O_7$, and shake each to mix the contents.

Place 0.01-ml aliquots of these standards on the successive strips of the Whatman CRL/1 paper as in step 5, one aliquot to a strip, and follow procedure through step 10 of the procedure. The number of µg of each metal on the 7 strips are 0.05, 0.1, 0.2, 0.4, 0.8, 1.5, and 3.0, respectively, and correspond to 50, 100, 200, 400, 800, 1,500, and 3,000 ppm of the metal in the sample.

COBALT IN SOILS

The field method for the determination of cobalt given below is taken from a procedure described by Almond (1953a). It is based on the reaction of cobalt with 2-nitroso-1-naphthol, which yields a pink compound soluble in carbon tetrachloride. Under the conditions of the test, copper and nickel also react with the reagent and are at least partially extracted by carbon tetrachloride along with cobalt 2-nitroso-1-naphtholate. However, as the 2-nitroso-1-naphthol complexes of nickel and copper are unstable in the presence of cyanide, these elements can be removed from the carbon tetrachloride extract by shaking it with a dilute cyanide solution. If the sample has a high iron content, the iron interferes with the test by forming a green precipitate that collects at the interface between the aqueous and organic phases. This precipitate cannot be separated easily. The method has been successfully used by the Geological Survey in geochemical investigations in several places, including the Blackbird cobalt district of Idaho (Canney and others, 1953).

REAGENTS AND APPARATUS

Sodium citrate solution, 10-percent: Dissolve 100 g sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) in 1 liter metal-free water.

Phosphate buffer solution, 2.2-percent: Dissolve 22 g sodium orthophosphate ($Na_2HPO_4 \cdot 12H_2O$) in 1 liter metal-free water.

Bromthymol blue indicator solution: Grind 0.1 g bromthymol blue in a mortar with 16 ml 0.01*M* NaOH and dilute to 250 ml with metal-free water.

2-nitroso-1-naphthol reagent solution, 0.01-percent: To 0.05 g 2-nitroso-1-naphthol add 10 drops of 2*M* NaOH. Add metal-free water dropwise while mixing with a glass rod. When the reagent is completely dissolved, dilute to 500 ml with metal-free water.

Potassium cyanide solution, 0.05-percent: Dissolve 0.5 g potassium cyanide (KCN) in 1 liter metal-free water. (*CAUTION.* See p. 5.)

Potassium pyrosulfate ($K_2S_2O_7$), fused powder, reagent-grade.

Standard cobalt solution, 100 µg per ml: Dissolve 0.04 g cobalt chloride ($CoCl_2 \cdot 6H_2O$) in metal-free water, add 1 ml conc. hydrochloric acid, and dilute to 100 ml in a volumetric flask. From this solution prepare more dilute standard solutions (10 µg per ml and 1 µg per ml) just before preparing a series of cobalt standards.

Hydrochloric acid, 1*M:* Dilute 83 ml conc. acid to 1 liter with metal-free water.

Ammonium hydroxide, conc., reagent-grade.

Sodium hydroxide, 2*M:* Dissolve 80 g NaOH in 1 liter metal-free water.

Carbon tetrachloride (CCl_4), analytical-grade.

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Culture tubes, 16- by 150-mm: Calibrate at 5 and 10 ml.
Separatory funnels, 125-ml.
Graduated pipets, 1- and 5-ml, graduated in tenths.
2 automatic pipets, 5-ml.
2 polyethylene dropping bottles.
3 volumetric flasks, 100-ml.
Polyethylene wash bottle, 250-ml.

PROCEDURE

1. Place 0.1 g (or a 0.1-g scoopful) sample in a 16- by 150-mm culture tube. Add 0.5 g $K_2S_2O_7$ flux to the tube.
2. Shake and rotate the tube to mix sample and flux, then fuse the mixture over a burner for 3 to 5 min.
3. Remove the tube from the heat and rotate it so that the melt cools in a thin film on the side of the tube.
4. When the tube is cool, add about 5 ml 1*M* HCl to the tube and place it in a hot water bath. Shake the tube intermittently, and crush the melt with a glass rod, if necessary, to reduce it to a powder.
5. Dilute the solution to 10 ml with water and mix the contents.
6. Transfer a 2-ml aliquot of this solution to a 125-ml separatory funnel.
7. To the separatory funnel add 1 ml sodium citrate solution (10 percent), 4 ml phosphate buffer solution, and 2 drops bromthymol blue indicator, and shake the funnel to mix the contents.
8. Add conc NH_4OH dropwise while shaking the funnel until the solution turns blue, then back titrate with 1*M* HCl to a faint yellow green, at which point the pH of the solution should be approx. 6.5.
9. Add 3 ml 2-nitroso-1-naphthol solution (0.01 percent), and 1 ml CCl_4 to the separatory funnel and shake the funnel for 1 min.
10. When the layers separate, drain the CCl_4 layer into a 16- by 150-mm culture tube containing 10 ml KCN (0.05 percent) solution.
11. Shake the tube for about 10 sec. and compare the color in the CCl_4 layer with the colors of similarly prepared standard solutions of known cobalt content.
12. Calculate the cobalt concentration in the sample according to instructions on p. 8.

Preparation of standards

A series of cobalt standards for 0, 0.2, 0.4, 0.8, 1.5, 3.0, and 6.0 μg of cobalt is recommended. To prepare the standards, place 1 ml of 1*M* HCl in each of a series of 125-ml separatory funnels, add to each the required amount of standard cobalt solution (1 μg per ml and 10 μg per ml), to produce the series suggested above, and then follow the regular procedure starting with step 7.

COBALT IN NATURAL WATERS

Traces of cobalt react with 2-nitroso-1-naphthol in slightly alkaline solution to yield a pink compound soluble in carbon tetrachloride. This reaction was used by Almond (1953b) as the basis for a simple method for determining cobalt in natural waters. The procedure described below will usually detect cobalt in water in amounts of as little as 1 ppb (0.001 ppm), and a determination in the field at the sample site need take no longer than 2 to 3 minutes. This method was used by the Geological Survey to study the dispersion of cobalt in the surface waters of the Blackbird cobalt district of Lemhi County, Idaho (Canney and others, 1953).

According to Almond, the conditions of the test are such that the reaction is nearly specific for cobalt. Nickel, however, may interfere, and its presence should be considered.

REAGENTS AND APPARATUS

Sodium citrate solution, 10-percent: Dissolve 10 g sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) in 100 ml water.

2-nitroso-1-naphthol, 0.01-percent: To 0.01 g 2-nitroso-1-naphthol, add 2 drops 2*M* NaOH. Add water dropwise while mixing with a glass rod. When the reagent is completely dissolved, dilute to 100 ml with water.

Ammonium hydroxide, (1+12): Mix 1 volume conc. NH_4OH with 12 volumes water.

Bromthymol blue: In a mortar, grind 0.1 g bromthymol blue with 16 ml 0.01*M* NaOH and dilute to 250 ml with metal-free water.

Carbon tetrachloride (CCl_4), analytical-grade.

Standard cobalt solution, 100 μg per ml: Dissolve 0.04 g cobalt chloride ($CoCl_2 \cdot 6H_2O$) in water, add 1 ml conc HCl and dilute to 100 ml with water. From this solution prepare as needed more dilute standard solutions containing 10 μg per ml and 1 μg per ml.

Culture tubes, 16- by 150-mm.

2 graduated glass cylinders, glass stoppered, 100-ml.

1 automatic pipet, 2-ml.

3 polyethylene dropping bottles, 2-oz, with attached cap.

3 volumetric flasks, 100-ml, with stopper.

Graduated pipets, 1-, 4-, and 10-ml.

PROCEDURE

1. To a 50-ml sample of water in a 100-ml glass-stoppered graduated cylinder, add 0.5 ml sodium citrate solution (10 percent), and 1 drop of bromthymol blue indicator solution, then NH_4OH (1+12) dropwise until the solution just turns blue.
2. Next add 1 ml 2-nitroso-1-naphthol reagent and 1 ml CCl_4; cap, and shake the cylinder for 90 sec.
3. After the phases have separated, discard most of the aqueous phase and pour the organic layer into a 16- by 150-mm culture tube. A pink color indicates the presence of cobalt. Compare with standards.
4. To express the concentration of cobalt in parts per million, divide the number of μg of cobalt found by the volume of the sample taken.

Preparation of standards

A series of cobalt standards for 0, 0.1, 0.25, 0.50, 1.0, 2.0, and 5.0 μg cobalt is recommended. To prepare each standard, add to about 50 ml metal-free water in a 100-ml glass-stoppered graduate the requisite amount of standard cobalt solution and then follow the above procedure starting with the addition of the sodium citrate solution. The series of 7 standards may be conveniently stored in seven tightly stoppered 16- by 150-mm culture tubes and should be stable for a month or more.

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DISCUSSION

For field use, the sodium citrate and 2-nitroso-1-naphthol solutions may be dispensed from polyethylene dropping bottles that have been roughly calibrated to determine the number of drops that will dispense the requisite amount of reagent. The carbon tetrachloride should be measured fairly accurately.

Should the color of the organic layer be deeper than that of the highest standard, the determination may be repeated using a smaller volume of sample; or, alternatively, additional known amounts of carbon tetrachloride can be added until the color of the organic layer falls into the range of the standard series.

NICKEL IN SOILS, ROCKS, AND PLANTS

Nickel in the prepared sample of soil or rock, or of plant ash, is put into solution by fusing a portion of the sample with potassium pyrosulfate and dissolving the melt with hydrochloric acid. Ash of vegetation is obtained by using one of the procedures described on page 16. Nickel reacts with α-furildioxime to form a yellow complex that is insoluble in water but soluble in several organic solvents; the stable nickel (II) complex is extracted with benzene (Gahler and others, 1951; Stanton and Coope, 1958). Optimum color development occurs with a pH range of 8.5 to 9.5; below or above this range, extraction is slow and incomplete. A satisfactory pH is obtained by using a buffer of ammonium citrate and ammonium hydroxide. Because excessive amounts of ammonium citrate or hydroxide prevent color formation and extraction of nickel, the size of the sample aliquot is limited. Although cobalt forms a colored complex with α-furildioxime, it interferes in this nickel determination only when the cobalt-nickel ratio exceeds 12:1. Such a cobalt-nickel ratio is unlikely in most samples, but should it exist, results would be affected only by an error of about 10 percent. Copper and ferrous iron are other sources of interference in the determination of nickel, but they interfere only when the sample contains an exceptionally high ratio of iron and (or) copper to nickel.

REAGENTS AND APPARATUS

Potassium pyrosulfate ($K_2S_2O_7$), fused powder.

Hydrochloric acid, 2*M*.

Nickel buffer solution: Dissolve 60 g ammonium citrate $[(NH_4)_2HC_6H_5O_7]$ in about 200 ml metal-free water. Add 130 ml conc. NH_4OH, then dilute to 1 liter with metal-free water.

α-furildioxime solution (0.2 percent). Dissolve 0.2 g α-furildioxime in 15 ml absolute ethyl alcohol, and dilute this solution with benzene to 100 ml.

Standard nickel solution (100 μg per ml): Dissolve 0.2 g clear uneffloresced crystals of nickel chloride ($NiCl_2 \cdot 6H_2O$) in 500 ml 0.1*M* HCl. From this solution prepare standard solutions (10 μg per ml and 1μg per ml) prior to preparing the series of nickel standards.

Culture tubes, 16- by 150-mm, each marked at 5-ml and 10-ml capacities.

Scoops, 0.1 and 0.5-g.

Pipet, automatic, 5-ml.
- automatic, 2-ml.
- volumetric, 2-ml.
- 1-ml, graduated in tenths.

PROCEDURE

1. Weigh or scoop 0.1 g sample into a 16- by 150-mm culture tube.
2. Add 0.5 g $K_2S_2O_7$ to the tube, heat to fuse the flux and sample, and continue heating for about 2 min after the flux melts.
3. Remove the tube from the flame and rotate the tube so that the melt cools in a thin film on the side of the tube. When the tube is cool, add 5 ml 2*M* HCl and place the tube in a hot water bath until the melt has disintegrated.
4. Allow the tube to cool, then dilute the sample solution to 10 ml with water.
5. Transfer a suitable aliquot (not more than 2 ml) of the sample solution to a 16- by 150-mm culture tube that contains 5 ml nickel buffer solution.
6. Add 1 ml α-furildioxime solution, stopper the tube, and shake for at least 1 min.
7. Compare the color of the benzene layer with colors of benzene layers in similarly prepared standards.
8. Calculate the nickel concentration in the sample according to instructions on page 5.

Preparation of standards

A series of nickel standards for 0, 0.5, 1, 2, 4, 8, 15, 30, 60, and 100 μg of nickel is recommended. To prepare the standards, place 1 ml 2*M* HCl and 5 ml nickel buffer in each of a series of 16- by 150-mm culture tubes, add to each the required amount of nickel solution to produce the series suggested above, and then follow the regular procedure starting with step 6.

ANTIMONY IN SOILS AND ROCKS

A complete discussion of the field method for the determination of antimony in soils and rocks is given by Ward and Lakin (1954). The powdered sample is fused with bisulfate, and the fused mass is leached with moderately strong hydrochloric acid. The antimony is oxidized to the pentavalent state and subsequently extracted into isopropyl ether from a dilute acid solution. The isopropyl ether extraction separates antimony from bismuth, chromium, cobalt, lead, and tungsten, but not from iron, which is usually present in relatively large amounts. The ether layer is shaken successively with mild reducing agents and dilute acid to isolate the antimony from interferences; and, finally, with rhodamine B to form a fine dispersion of red-violet rhodamine B chloroantimonate which behaves for the most part like a true solution.

As much as 100 ppm of gallium in the sample does not interfere. (Sandell, 1959, p. 271.)

As little as 0.5 to 1 ppm of antimony can be determined. More than 15 ppm of antimony can be determined by using a smaller aliquot of the sample solution or by dilution of the ether phase.

The method has been tested under field conditions in both the Colorado Front Range and in the Coeur d'Alene district of Idaho. It was used successfully in geochemical exploration for antimony in Alaska (Sainsbury, 1957).

REAGENTS AND APPARATUS

Flux, fused sodium bisulfate ($NaHSO_4$): Prior to use, heat in a porcelain casserole and fuse gently for 5 min. Cool and crush cake.

Hydrochloric acid, 6*M*.

Hydrochloric acid, 1*M*.

Hydrochloric acid–glycerine mixture: Add 20 ml glycerine to 100 ml 6*M* HCl.

Standard antimony solution (1,000 μg per ml): Dissolve 0.274 g antimony potassium tartrate in 100 ml 6*M* HCl.

Standard antimony solution, 20 μg per ml: Dilute 2 ml standard solution (1,000 μg per ml) to 100 ml with 6*M* HCl.

Ceric sulfate solution, 5.2 percent: Dissolve 5.2 g tetrasulfato ceric acid $[H_4Ce(SO_4)_4]$ in 100 ml 0.5*M* H_2SO_4.

Hydroxylamine hydrochloride solution, 1-percent: Dissolve 1 g hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 100 ml water.

Hydroxylamine hydrochloride–hydrochloric acid solution, 1-percent: Dissolve 1 g $NH_2OH \cdot HCl$ in 100 ml 1*M* HCl.

Isopropyl ether: Practical grade is suitable provided it is peroxide free. Saturate with 1*M* HCl (*CAUTION.* See p. 5.)

Rhodamine B reagent, 0.02-percent: Dissolve 0.02 g rhodamine B (tetraethyl rhodamine) in 100 ml 1*M* HCl.

Sodium sulfite solution, 1-percent: Dissolve 1 g sodium sulfite (Na_2SO_3) in 100 ml water.

Filter paper, ashless, for finest precipitate, as No. 42 Whatman.

Funnels, small, 35-mm inside diameter at top.

Mortar and pestle.

Pipets:

- 1 0.1-ml, calibrated in hundredths.
- 2 5-ml, automatic type.

Test tubes, 18- by 150-mm.

Separatory funnels, Squibb-type, 125-ml.

Tubes, 14- by 80-mm outside diameter, flat-bottom.

PROCEDURE

1. Fuse 0.2 g sample with 1 g flux in 18- by 150-mm tube.
2. Add 6 ml 6*M* HCl–glycerine mixture to fused mass, and heat tube in hot water bath until melt disintegrates.
3. Remove tube from bath and add 1 ml Na_2SO_3 and 3 ml HCl–glycerine mixture.
4. Filter the solution through No. 42 Whatman filter paper and collect the filtrate in 125-ml separatory funnel.

5. Rinse the residue from the tube onto filter paper with 2 separate 3-ml portions of hot HCl–glycerine solution, then pour 2 ml hot water through filter paper.
6. Cool filtrate in funnel to 25°C, then add 3 ml ceric sulfate solution. Shake funnel to mix contents.
7. Add 10 drops aqueous $NH_2OH \cdot HCl$ to funnel and shake it to mix contents.
8. Keep the solution cool; and add 40 ml water and 5 ml isopropyl ether to the solution in the separatory funnel. Shake the funnel for 30 sec.
9. Allow the phases to separate and discard the aqueous phase.
10. Wash the ether with 2 ml $NH_2OH \cdot HCl$–hydrochloric acid solution, and finally, with 2 ml 1*M* HCl.
11. Add 2 ml rhodamine B reagent solution to the ether in the separatory funnel and shake the funnel for 10 sec.
12. Discard the rhodamine B reagent solution, and pour 3 ml of the ether from the top of the separatory funnel into a flat-bottomed tube.
13. Compare the color in the ether with the color of similarly prepared standards of known antimony content. This color is stable for at least 6 hrs.
14. Calculate the antimony concentration in the sample according to instructions on p. 8.

Preparation of standards

1. Add, respectively, 0, 0.2, 0.4, 0.8, 1.5, and 3 μg of antimony to 6 separatory funnels, each containing 6 ml HCl–glycerine solution, by pipetting suitable aliquots from a standard antimony solution.
2. Add 1 ml ceric sulfate to the contents of the separatory funnel and shake the funnel to mix the contents.
3. Add 2 to 4 drops aqueous $NH_2OH \cdot HCl$ and 17 ml water.
4. Continue with step 8 in procedure starting with addition of isopropyl ether.

DISCUSSION

If the ether phase containing the antimony-rhodamine B complex has to be diluted to permit matching with one of the suggested standards, the diluted ether phase must again be shaken with the rhodamine B reagent before a valid comparison can be made.

After the bisulfate fusion, calcium and other alkaline earths may precipitate as sulfates in the moderately concentrated hydrochloric acid. The precipitates occlude antimony, and on alkaline rocks the results may be low. However, these sulfates are soluble in glycerine, and the hydrochloric acid–glycerine mixture recommended is satisfactory in preventing antimony losses.

ARSENIC IN SOILS

The method for determining arsenic in soils described by Almond (1953c) is a confined-spot procedure using a modified Gutzeit apparatus in which, by the action of zinc in a hydrochloric acid solution, arsenic (III) is reduced to arsine (AsH_3), and the evolved arsine gas is reacted with mercuric chloride to form a yellow-to-orange compound. As this colored compound slowly

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decomposes, the test spots change in color; consequently, artificial standard spots must be prepared.

The sample is partly dissolved by molten potassium hydroxide in a test tube or nickel crucible. Although prolonged heating of the sample with potassium hydroxide would effect complete solution of most samples, it would also dissolve the glass test tube. Experience has indicated that heating the mixture until it is fluid renders most of the arsenic acid-soluble. The hydrogen sulfide evolved with the arsine is removed by reaction with lead acetate on glass wool through which the gases are passed. The black lead sulfide formed by the reaction serves as an indicator for renewing the lead acetate-coated glass wool.

REAGENTS AND APPARATUS

Lead acetate-coated glass wool: Dissolve 15 g lead acetate [$Pb(C_2H_3O_2)_2 \cdot 3H_2O$] in 100 ml water and 3 ml glacial acetic acid. Steep in this solution for 15 min as much glass wool as is conveniently covered by the solution, then remove and allow to dry. Fill the lower section of glass pipe with this dried glass wool. Store excess glass wool in stoppered bottle.

Hydrochloric acid, conc.

Stannous chloride ($SnCl_2 \cdot 2H_2O$), 10-percent: Dissolve 10 g stannous chloride in 100 ml conc. HCl, and transfer to a stoppered bottle.

Standard arsenic solution (1,000 μg arsenic per ml): Dissolve 0.13 g arsenic trioxide in 2 ml 1*M* NaOH, dilute with water to about 50 ml, make slightly acid by adding 3 ml 1*M* HCl, and dilute to 100 ml. From this standard solution prepare more dilute solutions as needed.

Mercuric chloride paper: Dissolve about 25 g mercuric chloride ($HgCl_2$) in 100 ml ethyl alcohol. Place some filter paper (Black Ribbon, S and S No. 589) in the solution and steep for 1 hr. Remove, and allow the paper to dry in the air. Cut in disks ½ inch in diameter and store in a box.

Potassium hydroxide pellets, (KOH) reagent-grade.

Modified Gutzeit apparatus (see fig. 4): To assemble the apparatus, place the female portion of the aluminum coupling on one section of the glass pipe and insert the unflanged end of the pipe into the rubber stopper. Pack the tube with lead acetate–coated glass wool. Place a disk of the $HgCl_2$ reagent paper on the coupling containing the second glass tube. Insert the rubber stopper into the test tube when the solution is prepared for AsH_3 evolution. The apparatus is conveniently held upright by a funnel rack. For efficient operation in mass-production determinations, 24 units of the apparatus are required. Additional test tubes are required for fusion of the samples. Only 2 to 4 fusions may be made in each test tube before it must be discarded. When the black lead sulfide formed by the reaction has discolored the lower half of the glass wool, the glass wool should be removed from the apparatus and replaced by fresh glass wool.

PROCEDURE

1. Weigh or scoop 0.1 g of sample, and transfer to a 25- by 150-mm test tube.
2. Add 8 pellets (about 0.8 g) of KOH.
3. Heat the tube containing sample and KOH over a burner for about 1 min. Remove the tube from the flame and rotate the tube so that the melt

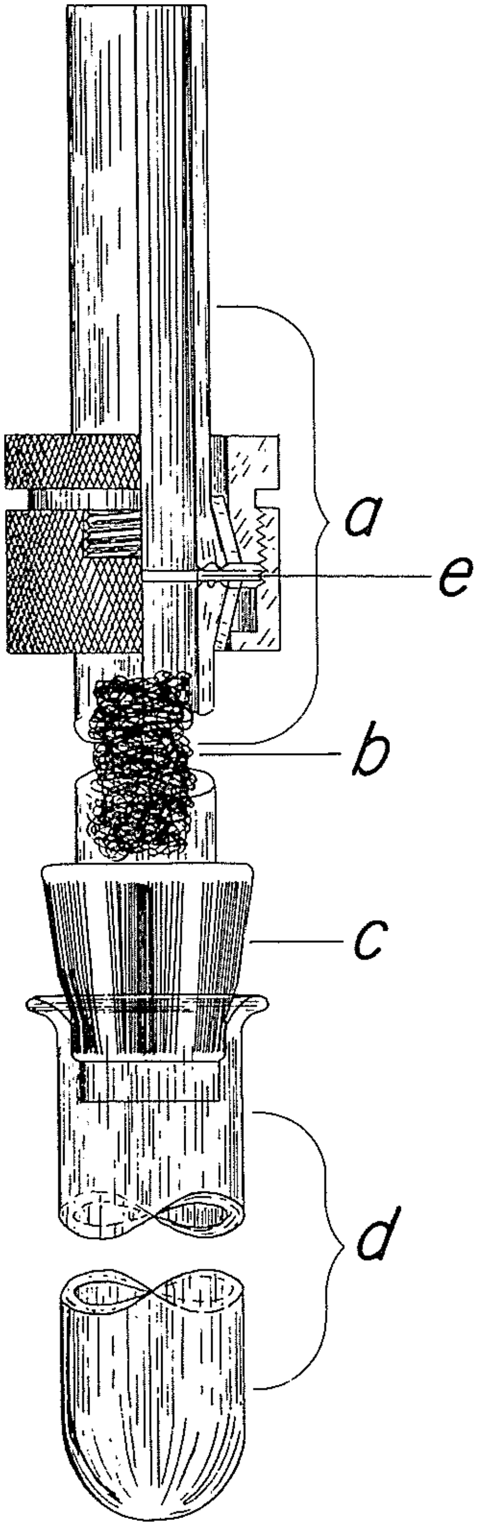

FIGURE 4.—Modified Gutzeit apparatus. *a*, two sections of glass pipe with aluminum coupling, inner diameter 0.25 inch; *b*, glass wool coated with lead acetate; *c*, No. 4 rubber stopper with center hole 0.5 inch in diameter; *d*, test tube with rim, 25- by 150-mm; *e*, mercuric chloride reagent paper, disks 0.5 inch in diameter.

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will cool in a thin film on the side of the tube. Because KOH attacks glass, continuing to heat the tube after the flux has melted should be avoided.

4. When the tube is cool, add 3 ml water to the contents and let stand until the melt disintegrates (approximately 30 min).
5. Add 3 ml conc. HCl, then 4 ml water. Shake the tube to mix the solution.
6. Transfer all of the sample solution or a suitable aliquot to another 25- by 150-mm test tube. If the aliquot is 4 ml or less, add 3 ml conc. HCl. If the aliquot is 5 to 10 ml, it is not necessary to put in additional conc. HCl; however, enough acid should be present so that the hydrogen formed on the addition of zinc sweeps out all of the AsH_3. Use of all the sample solution gives a positive test for 10 ppm arsenic in the sample.
7. Add 0.5 ml $SnCl_2$ solution and mix the solution. This solution should not be left standing, because any silica present will form a gel.
8. Add 2 to 4 g mossy zinc, and immediately attach the test tube to the rubber stopper on the modified Gutzeit apparatus.
9. After 1 hr remove the disk of reagent paper and compare as soon as possible with a standard series of spots.
10. Calculate the arsenic concentration in the sample according to instructions on p. 8.

Preparation of standards

Artificial standard series. For the series 1, 2, 4, 8, and 16 μg of arsenic, prepare artificial standard spots from chrome-yellow and deep chrome-yellow watercolors. Mix deep chrome-yellow watercolor with 2 ml of water in a small beaker. Paint on filter paper and allow the paper to dry. Prepare several shades by varying the number of coats of watercolor per spot. Then add 0.5 ml water to the beaker and again paint several shades on the filter paper. Prepare shades of chrome yellow in a similar manner.

Prepare three 1-μg arsenic spots by adding 1 μg of arsenic to each of three 25- by 150-mm test tubes containing 3 ml conc. HCl and 4 ml water, and proceed with step 7. Compare each spot with the dry watercolor paper and punch out the spot that most nearly matches the arsenic spot. Select the average (midcolor) spot as representing 1 μg of arsenic. Repeat the same process for each of the remaining standards of the series.

DISCUSSION

Many of the heavy metals in amounts of 50 mg or more interfere with the arsenic test, but their presence in soils in such high concentrations is most unlikely even in mineralized areas. Errors may be caused by arsenic that remains behind instead of being swept out of the test tube, and by arsine adsorption on the lead acetate. Although variation in the rate of hydrogen evolution causes errors in the conventional "strip test," they are much less serious in the confined-spot test described above. The difference in values between the arsenic content of soil in a mineralized area and that of soil in an unmineralized area is normally so great that there is little danger that the prospector will be misled by the small variations in value resulting from the errors implicit in this method. Leaks in the apparatus that allow arsine to escape without coming in contact with the mercuric chloride will cause serious errors, but this can be avoided. The method is useful for obtaining semiquantitative data on materials containing 10 ppm or more of arsenic.

BARIUM IN SOILS AND ROCKS

The sample of soil or rock that is to be tested for barium is powdered, fused with a modified carbonate flux, and the fused mass leached with hot sodium carbonate solution to remove water-soluble sulfates and carbonates. The barium carbonate formed during the fusion is dissolved in dilute hydrochloric acid and the barium precipitated as the sulfate in an aqueous medium having nearly constant ionic strength. The turbidity of the solution is compared with that of standard barium sulfate precipitated in the same manner. As described, the method is useful over a concentration range of 500 to 10,000 ppm of barium, but by increasing the sample size (for example, to 0.5 g) and using a proportionate amount of flux, the lower value of the concentration range is near 200 ppm of barium.

The method has been used successfully in Arkansas to prospect for barite (D. A. Brobst, written communication, 1959).

REAGENTS AND APPARATUS

Acetic acid (1+1). Equal parts by volume of glacial acetic acid and water.

Chloroform ($CHCl_3$), reagent-grade.

Flux: Equal parts by weight of sodium carbonate (Na_2CO_3) and potassium nitrate (KNO_3), ground to pass 80-mesh sieve and mixed well.

Hydrochloric acid, 4*M*.

Potassium sulfate (K_2SO_4), ground to pass 300-mesh sieve.

Sodium carbonate solution (Na_2CO_3), 5-percent aqueous.

Sodium chloride solution: Dissolve 60 g salt (NaCl) in 250 ml water. Filter to remove any turbidity.

Sodium diethyldithiocarbamate, 1-percent aqueous solution: Filter.

Standard barium solution, 100 μg per ml: Dissolve 0.0178 g barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 100 ml water. Filter to remove any turbidity.

Culture tubes, 16- by 150-mm.

Cylinders, graduated, 100-ml, glass-stoppered.

Filter paper, very fast, ashless, such as No. 41 Whatman.

Glass wool.

Separatory funnels, 60-ml.

Stevens extraction tubes: These are made by constricting, near one end, a glass tube 170 mm long and 7 mm in inside diameter, and packing the resulting small bulb with fine glass wool to serve as a filtering medium.

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PROCEDURE

1. Fuse 0.2-g sample with 1.0 g flux in a culture tube until brown fumes of nitrogen dioxide appear.
2. As soon as these fumes are no longer visible—about 3 min—cool, and add 5 ml Na_2CO_3 reagent.
3. Place tube in hot water bath for 15 min.
4. Place Stevens Extractor (Lakin, Almond, and Ward, 1952) into culture tube, bulb end down, and filter solution into extractor by inserting deflated syringe in upper end of extractor. Discard filtrate.
5. Add 5 ml Na_2CO_3 reagent to residue in culture tube, heat for a few min, and filter solution as in step 4. Discard filtrate.
6. Add 5 ml 1.5*M* HCl to tube and filter through glass wool into extractor.
7. Transfer HCl filtrate to a 60-ml separatory funnel. Add 1 ml sodium diethyldithiocarbamate and 5 ml $CHCl_3$. Shake funnel 30 sec and drain organic layer.
8. Filter aqueous phase through No. 41 Whatman filter paper into 100-ml graduated cylinder containing 5 ml 1.5*M* HCl and 8 ml NaCl solution.
9. Add water to 40-ml mark, then add 20 ml acetic acid. Add 0.5 g K_2SO_4. Stopper and mix.
10. Shake stoppered cylinder at frequent intervals over 10-min period.
11. Compare turbidity of samples with standards and calculate the barium concentration in the sample according to instructions on p. 8.

Preparation of standards

1. By pipetting suitable aliquots of the standard barium solution, add 0, 100, 200, and 300 μg of barium respectively to 4 graduated cylinders, each containing 8 ml NaCl solution, 10 ml 1.5*M* HCl, and 20 ml acetic acid (1+1).
2. Dilute volumes to 60 ml with water and proceed with addition of K_2SO_4 in step 9.

DISCUSSION

Turbidimetric methods are less accurate than colorimetric methods and they are usually avoided in trace analysis. The barium method is no exception to this general statement, but under uniform conditions and within a given concentration range it is moderately useful.

The turbidity is due to the absorption of the incident light by the small particles of barium sulfate. The absorption depends on the particle size, which varies with the manner of addition of the precipitant, temperature, time of standing, and electrolytes.

The method is selective but not specific. Other elements (as, for example, lead and strontium) may accompany the barium, and the results may be too high. Lead is removed by the carbamate extraction, and strontium interference has not been found to be serious.

TRACES OF BISMUTH IN ROCKS

A complete discussion of the method for determining traces of bismuth in rocks is given by Ward and Crowe (1956). The pulverized sample is fused with pyrosulfate and the fused mass is treated with hot 8*M* nitric acid. Ethylenediaminetetraacetic acid, disodium salt is added and the pH is increased with ammonia and alkali cyanide. At a pH of around 10 to 11, bismuth reacts with carbamate to form a yellow complex that can be extracted into chloroform. The absorbance of the bismuth carbamate in chloroform can be measured instrumentally, or the chloroform solutions from samples can be compared visually with those obtained from standard bismuth solutions. The procedure as written is applicable to rocks containing 20 to 160 ppm bismuth.

REAGENTS AND APPARATUS

Ammonium hydroxide (NH_4OH), specific gravity 0.90.
Bismuth standard solution, 1,000 μg per ml: Dissolve 0.5 g bismuth metal in 500 ml conc. HNO_3.
Bismuth standard solution, 10 μg per ml: Dilute 1 ml of the standard solution (1,000 μg per ml) to 100 ml with water.
Chloroform ($CHCl_3$), boiling-range minimum 95 percent between 59.5° and 61.5°C.
Ethylenediaminetetraacetic acid, disodium salt (EDTA).
Nitric acid, 8*M*.
Potassium pyrosulfate ($K_2S_2O_7$).
Sodium cyanide (NaCN), 5-percent aqueous. *CAUTION* (see p. 5.)
Sodium diethyldithiocarbamate, 1-percent aqueous solution.
Beaker, 60-ml.
Cotton, absorbent.
Filter paper, 9-cm, retaining medium-sized particles, such as No. 1 Whatman.
Funnels.
Funnel, separatory, 60-ml.
Pipet, serological, 10-ml graduated.
pH test paper, short-range, pH 5 to 6.
Tubes, flat-bottom, 14- by 80-mm outside dimensions.

PROCEDURE

1. Fuse 0.5 g sample with 1.5 g $K_2S_2O_7$ in 60-ml beaker.
2. Cool, add 2 ml 8M HNO_3, and heat until incipient boiling.
3. Add 8 ml water, heat to boiling and add 1 g solid EDTA.
4. Add ammonia drop by drop until pH of sample solution is 5 to 6. Test externally with pH paper.
5. Add 5 ml NaCN and filter, collecting filtrate in the separatory funnel.
6. Add 1 ml ammonia to filtrate and shake to mix.
7. Add 1 ml carbamate reagent and 5 ml $CHCl_3$. Shake funnel 1 min.
8. Through a cotton tampon in funnel stem, drain organic layer into a tube or cuvet.
9. Compare with standards.
10. Calculate the bismuth concentration in the sample according to instructions on p. 8.

Preparation of standards

To a series of 5 separatory funnels each containing 8 ml water and 1 g solid EDTA, add, using the bismuth standard solution (10 μg per ml), no bismuth

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to first , 10 μg to second, 20 μg to third, 40 μg to fourth, and 80 μg to fifth, and proceed with step 4.

DISCUSSION

At a pH of 11, mercury (II), palladium (II), silver, copper (II), and thallium (III) form carbamates that are more stable than bismuth carbamate (Bode and Tusche, 1957), but in an alkaline medium such as that described, when cyanide and EDTA are added only bismuth forms a stable carbamate.

Mixing aqueous solutions of EDTA and cyanide prior to use results in side reactions that decrease the effectiveness of the mixture. In fact, aqueous solutions of EDTA become ineffective in a relatively short time; hence, the solid is added directly to the sample solution.

CHROMIUM IN SOILS AND ROCKS

A method useful for determining the chromium content of samples containing more than 100 ppm chromium has been described by Wood and Stanton (1956) and also by Sandell (1959, p. 391). This method depends upon the oxidation of chromium to chromate by fusion of the sample with sodium hydroxide and sodium peroxide. A hot-water leach of the fused melt dissolves the chromate and removes it from the insoluble hydrated oxides formed during the fusion. The chromium is thus separated from most of the cations yielding colored solutions that would mask the yellow color of the chromate. The majority of the metals that form soluble salts give colorless solutions that do not interfere with the test. Although uranium, cerium, gold, and the platinum metals give colored solutions, these elements may usually be disregarded as they are unlikely to be present in the sample in amounts sufficient to interfere in the test. During the fusion, manganese is oxidized to manganate, but interference resulting from it is avoided because the manganate is reduced to hydrated manganese dioxide by adding alcohol to the hot-water leach of the melt. Copper may be present in the filtrate, imparting a faint blue color to the solution.

REAGENTS AND APPARATUS

Sodium hydroxide, pellets.

Sodium hydroxide solution, 2*M*: Dissolve 80 g NaOH in metal-free water and dilute to 1 liter.

Sodium peroxide (Na_2O_2).

Ethyl alcohol, 95-percent.

Chromium standard solution (1,000 μg per ml): Dissolve 0.283 g potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 100 ml with water.

Chromium standard solution (100 μg per ml): Dilute 10 ml chromium standard solution (1,000 μg per ml) to 100 ml with water.
Nickel crucibles, 30-ml.
Nickel tongs.
Filter paper, 9-cm hardened filter paper of close texture, such as No. 50 Whatman.
Funnels, 65-mm diameter.
Scoop, 0.1-g capacity.
Spatula.
Culture tubes, 16- by 150-mm.
Pipet, 1-ml, graduated.
Glass stirring rods, 5-mm diameter.

PROCEDURE

1. Weigh or scoop 0.1 g sample and transfer it to a nickel crucible.
2. Add 5 pellets (0.5 g) NaOH, and with a spatula add about 0.25 g Na_2O_2 to the crucible.
3. Heat cautiously over a moderate flame and continue heating for about 1 min after a quiescent melt is obtained. If the heating is too rapid or if the flame is too high, spitting of the sample will cause loss of some of the material heated.
4. Allow the melt to cool, then add 10 ml of a 10-percent solution of alcohol in water to the crucible, and bring the solution to boiling. Scrape the bottom of the crucible with a glass stirring rod to insure that the melt is disintegrated. To minimize loss of volume, avoid excessive boiling, but completely disintegrate the melt.
5. Filter the solution through a 9-cm dry filter paper into a dry 16- by 150-mm culture tube. Compare the yellow of the filtrate with that of standard solutions. Multiply by 10 the number of μg found, to convert to parts per million of chromium.
6. If the color of the sample solution is deeper than that of the highest standard, transfer a suitable aliquot of the solution to another 16- by 150-mm culture tube. Then add 2 ml $2M$ NaOH solution and dilute to 10 ml with water and compare with standards.

Preparation of standards

Transfer, respectively, 0, 10, 20, 40, 80, 150, and 300 μg of chromium from the standard chromium solution (100 μg per ml) to each of seven 16- by 150-mm culture tubes. Add 2 ml of $2M$ NaOH to each tube and dilute the solutions to 10 ml with water. Shake the tubes to mix the solutions.

GERMANIUM IN COAL AND ROCKS

The following rapid semiquantitative laboratory method for the determination of traces of germanium in coals and rocks (Almond and others, 1955) is based on the distillation of germanium tetrachloride from a hydrochloric acid sample solution and turbidimetric estimation of a germanium phenylfluorone complex. Coal samples are ashed in a muffle furnace; rocks are treated with hydrofluoric acid to volatilize much of the silicon, and the residue is fused with a mixture of potassium bisulfate and potassium per-

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sulfate. The coal ash or the fused residue of the rock is dissolved in hydrochloric acid. These treatments dissolve the germanium without loss. The method gives useful data on material containing 4 ppm or more of germanium.

The distillation of germanium tetrachloride from a 6*M* hydrochloric acid solution can be accomplished in about 15 minutes for six samples in a simple distillation assembly. As the reaction of germanium with phenylfluorone is slow and incomplete in strong acid solutions, it is necessary to dilute an aliquot of the 6*M* hydrochloric acid distillate to 0.6*M* HCl before reacting with the reagent. To obtain complete reaction of germanium, an excess of phenylfluorone must be added. The presence of excess yellow reagent together with the pink insoluble germanium phenylfluorone complex results in an orange-colored solution whose color increases in intensity with increasing amounts of germanium. The distillation separates germanium from many interfering elements, especially gallium, titanium, tin, antimony, molybdenum, and iron (Cluley, 1951). When iron is present in quantities 10 times that of germanium, it interferes with the test; therefore, extreme care must be exercised to keep free of iron both the distillate and all vessels used after the distillation. Erroneous results are most commonly due to contamination by a few micrograms of iron after distillation.

Gum arabic is used as a protective colloid to stabilize the colloidal germanium complex, but it is only partly effective. Visual comparison of the sample solutions with the standard series may be made 1 hour after mixing, but should be done within 3 hours because, on prolonged standing, the germanium phenylfluorone complex precipitates.

REAGENTS AND APPARATUS

Phenylfluorone solution, 0.03-percent: Dissolve 0.03 g phenylfluorone in 85 ml ethyl alcohol and 5 ml 2.6*M* H_2SO_4 by warming on a steam bath; remove, then dilute to 100 ml with ethyl alcohol.

Gum arabic reagent, 0.05-percent: Add 0.05 g gum arabic to 100 ml metal-free water and warm until it dissolves.

Potassium bisulfate-potassium persulfate fusion mixture: Mix equal weights of these two reagents.

Sodium hydroxide solution, 0.1*M*: Dissolve 4 g NaOH in 1 liter metal-free water.

Hydrochloric acid, conc., reagent-grade.

Hydrochloric acid 6*M*: To 2 liters metal-free water add 2 liters conc. HCl.

Hydrofluoric acid, 48-percent: *CAUTION.* (See p. 5.)

Standard germanium solution, 100 μg per ml: Dissolve 0.144 g germanium dioxide in 20 to 25 ml 0.1*M* NaOH and dilute to 1 liter.

Standard germanium solution, 1 μg per ml: Dilute 10 ml standard solution (100 μg per ml) to 1 liter with metal-free water.

Litmus paper.
Culture tubes, 16- by 150-mm; marked at 10 ml.
Cylinders, graduated, 25-ml.
Pipets, 1-, 5-, 10-ml; graduated in tenths.
Platinum crucible, 45-ml.
Furnace, muffle; thermostatically controlled.
Aluminum dishes: Made from aluminum foil (may be used for containers to hold coal during ashing).
Germanium distillation unit (see fig. 5). The distillation flask is a modified 125-ml Erlenmeyer wash bottle. The normal delivery tube of the wash bottle is cut off and sealed; the normal pressure tube is bent downward to form an inverted U. A water-cooled condenser, 20 cm in length, is connected to the open tube of the flask with tygon or similar tubing, a glass tube, and rubber stopper. The distillate is collected in 25-ml graduated cylinders.

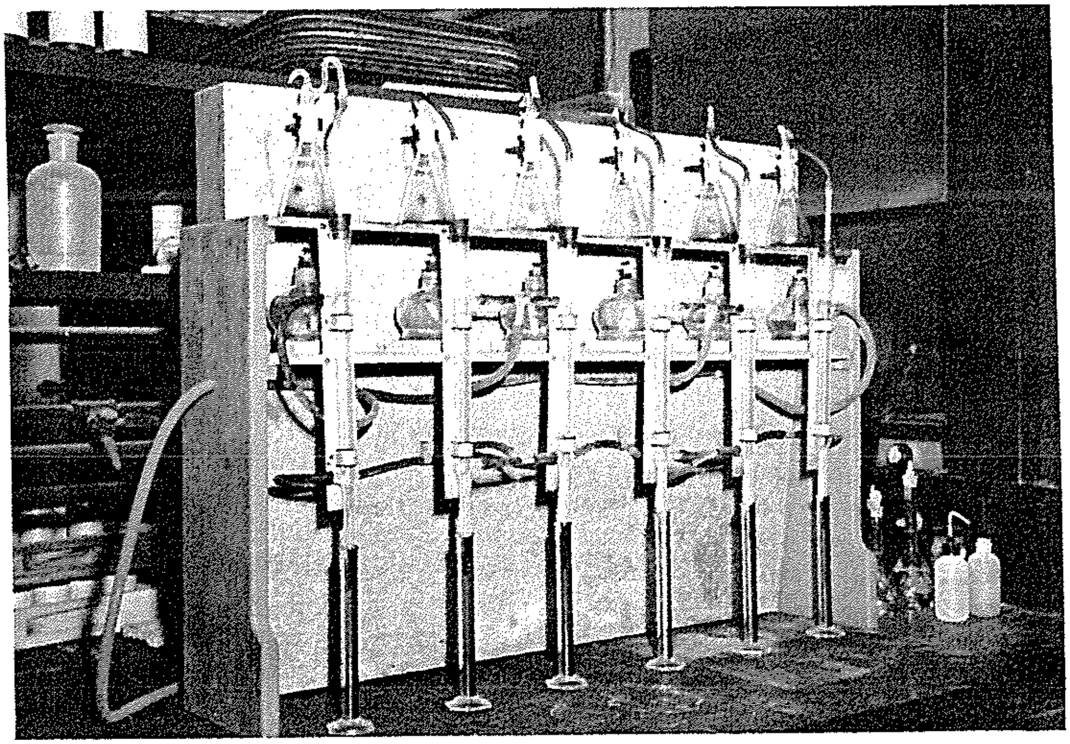

FIGURE 5.—Germanium distillation unit.

Six of these units may conveniently be mounted on a two-shelf rack as illustrated. Alcohol lamps or gas microburners may be used for a heat source.

PROCEDURE

Sample preparation and distillation

Rocks

1. Weigh 0.25 g (as much as 1 g may be used) of sample and transfer it to a platinum evaporating dish.
2. Moisten the sample with water, add 10 to 15 ml HF to the dish, and slowly evaporate the acid to dryness in a hood.
3. Add about 1.5 g potassium bisulfate–potassium persulfate fusion mixture. Heat the sample and flux until a clear melt is obtained.
4. When the dish is cool, add 10 ml of 6*M* HCl to the dish, and transfer the acid and melt to a distillation flask.

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5. Add 10 ml more $6M$ HCl to the dish, stir the acid with a glass rod, and transfer the acid to the flask. The melt will go into solution when heated. Because of the volatility of germanium tetrachloride (boiling point 86°C), HCl solutions of the sample must not be heated until in the assembled still.
6. Connect the distillation flask to the water-cooled condenser, apply heat, and collect 10 ml distillate. Use a 25-ml graduated cylinder as a receiver.

Coal

1. Weigh 0.5 g coal sample and transfer to an aluminum dish.
2. Place the dish in a muffle furnace which is at a temperature below 200°C. Raise the temperature 50° every half hour until the temperature is 550°C. Leave the muffle at 550°C for about 2 hr, then remove the dish and let it cool.
3. Transfer the ash into a distillation flask, add 20 ml $6M$ HCl, and distill at least 10 ml into a 25-ml graduated cylinder.

Estimation of germanium

1. Record exact volume of distillate.
2. Transfer a 1-ml aliquot of the distillate to a 16- by 150-mm culture tube.
3. Add 1 ml gum arabic solution, and then dilute this solution to 10 ml with metal-free water.
4. Add exactly 0.5 ml phenylfluorone solution, shake the tube to mix the solution, and then let the solution stand for 1 hr.
5. Compare the color of the solution with standards prepared at the same time as unknowns.

Preparation of standards

1. Transfer, respectively, 0.2, 0.4, 0.8, 1.5, 3, and 6 ml germanium standard solution (1 μg per ml) to a series of 16- by 150-mm culture tubes.
2. To each tube add 1.0 $6M$ HCl, 1 ml gum arabic solution, and dilute these solutions to 10 ml.
3. Add exactly 0.5 ml phenylfluorone solution to each tube, shake the tubes to mix the solutions, and then let the solutions stand for 1 hr.

Calculation

The calculation of parts per million (ppm) of germanium in the original sample may be done simply by application of the following formula:

$$\text{Ge (ppm)} = \frac{\text{Milliliters of distillate} \times \text{micrograms found in 1 ml of distillate}}{\text{Weight of sample, in grams}}$$

IRON

Iron is not often determined in soils and rocks for the purpose of prospecting; however, analysis of these materials for iron is useful to basic geochemical studies in establishing relations that are useful in prospecting. Two methods for the determination of iron are described, but neither is a field method. In both methods hydrofluoric acid in platinum vessels is used to decompose the sample, and the procedures used to estimate the iron concentration employ apparatus not commonly used in the field. The colorimetric method using orthophenanthroline is most useful for samples containing less than 1 percent iron; the volumetric method using dichromate is more suitable for samples that contain more than 1 percent iron.

IRON IN SOILS, ORTHOPHENANTHROLINE METHOD

The colorimetric method described for the determination of iron is derived from the work of Walden, Hammett, and Chapman (1931), who showed that an orange-red complex is formed between ferrous iron and orthophenanthroline. The method is almost the same as that described by Sandell (1959). Soil samples are ignited to expel organic matter, then digested with sulfuric and hydrofluoric acids; the residue is dissolved in hydrochloric acid. Although the sample-digestion procedure attacks many iron minerals, it fails to decompose certain other minerals; for example, magnetite, ilmenite, and tourmaline (Hillebrand and others, 1953). If it is suspected that the samples contain these minerals, or if after the acid digestion the sample solution appears to be incomplete, an additional digestion procedure is carried out.

An aliquot of the sample solution is diluted with water and the iron is reduced to Fe(II). Orthophenanthroline is added, and after standing for 1 hour the colored solutions are diluted and the color concentration determined photometrically at 515 mμ. The iron content of the sample is determined by using a standard calibration curve. The lower limit of detection is approximately 50 ppm iron and the method can be used for samples containing as much as 20 percent iron. One man can analyze approximately 40 samples per day for iron.

REAGENTS AND APPARATUS

Sulfuric acid, conc. reagent-grade.

Sulfuric acid, 9*M*: Slowly pour 500 ml conc. H_2SO_4 into a reagent bottle containing 500 ml water. Place the reagent bottle in a cold water bath until the solution is cooled, then stopper.

Hydrofluoric acid, 48-percent, reagent-grade. (*CAUTION*. See p. 5.)

Hydrochloric acid, conc., reagent-grade.

Hydrochloric acid, 1*M*: Dilute 83 ml conc. acid to 1 liter with water.

Potassium pyrosulfate ($K_2S_2O_7$), fused-powder, reagent-grade.

Buffer solution: Dissolve 153 g sodium acetate ($Na_2C_2H_3O_2 \cdot 3H_2O$) in about 500 ml water. Add 30 ml glacial acetic acid and dilute the solution to 1 liter with water. The pH of the solution should be approximately 4.5.

Hydroquinone, 1-percent solution: Dissolve 1 g of hydroquinone in 100 ml of buffer solution. Keep under refrigeration and discard if coloration appears.

Orthophenanthroline, 0.5-percent solution: Dissolve 0.5 g orthophenanthroline monohydrate in 100 ml water; warm to effect solution. Store in refrigerator; discard if coloration appears.

Standard iron solution (100 μg per ml): Dissolve 0.010 g electrolytic iron in 10 ml 4*M* HNO_3, boil to expel oxides of nitrogen, and dilute to 100 ml

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Platinum evaporating dishes, 20- to 50-ml.

Laboratory tongs, platinum-tipped.

Stirring rod, platinum.

Pipet, 0.1-ml; graduated in 0.01 ml.
1.0-ml; graduated in 0.1 ml.

Pipet, volumetric, 1-, 2-, and 10-ml.

Flasks, volumetric, 25- and 100-ml.

Colorimeter or spectrophotometer.

PROCEDURE

1. Weigh 0.100 g soil sample into a 50-ml platinum evaporating dish.
2. Ignite the sample over a burner for about 10 min to oxidize organic matter, then allow the dish to cool.
3. Wet the sample with about 1 ml $9M$ H_2SO_4, then add about 8 ml 48-percent HF. Stir the sample in the dish with a platinum stirring rod.
4. Allow the dish to stand at room temperature overnight.
5. Transfer the dish to a hotplate and bring the contents to incipient dryness. If solution of sample was incomplete, include the additional digestion procedure described below in steps a and b.
   a. Add approximately 0.2 g $K_2S_2O_7$ to the residue in the platinum dish and fuse over a burner.
   b. Allow the dish to cool before continuing with step 6.
6. Add 10 ml $1M$ HCl to the dish and warm to dissolve residue.
7. Transfer the sample solution in the platinum dish to a 100-ml volumetric flask. Rinse the dish with several 10-ml portions of water, transferring the washings to the volumetric flask. Dilute contents of flask to 100 ml with water and mix well.
8. Transfer a suitable aliquot (1.0 ml) to a 25-ml volumetric flask containing 3 or 4 ml water.
9. Add 1 ml hydroquinone solution and 1 ml orthophenanthroline solution, in that order. The buffer solution containing hydroquinone serves to adjust the pH to 4.5 and to reduce the iron.
10. Allow the flask and contents to stand for 1 hr; then dilute to 25 ml with water, and mix.
11. Transfer a portion of the solution to a photometer tube and obtain the transmittancy of the solution at 515 $m\mu$.
12. Using the standard calibration curve, determine the iron concentration corresponding to the transmission of the solution and calculate the iron content of the sample.

Preparation of standard calibration curve

1. Transfer suitable aliquots, containing 1 to 60 μg iron, to 25-ml volumetric flasks, using for a reagent blank one additional flask to which no iron is added.
2. Add 3 to 4 ml water to each flask and proceed with steps 9 thru 11 above.
3. Prepare the standard calibration curve by plotting percentage transmittance versus iron concentration on semilog graph paper or absorbance versus iron concentration on linear graph paper.

DISCUSSION

The method described is applicable to most soils and many rocks. Several divalent metals, including cadmium, mercury, and zinc react with orthophenanthroline to give slightly soluble colored complexes (Fortune and Mellon, 1938). The large excess of reagent added in the method usually compensates for this source of interference. Interference by certain other metals is obviated by maintaining the pH at approximately 4.5. The most serious interference results from bismuth and silver, which in small concentrations react with orthophenanthroline to give precipitates.

IRON IN ROCKS, DICHROMATE TITRATION METHOD

The determination of iron in rocks by dichromate titration is a rapid laboratory method that involves the titration of ferrous iron with potassium dichromate, using diphenylamine sulfonic acid as an indicator. The indicator was recommended for volumetric analysis by Knop (1924). The sample is digested with 9*M* sulfuric acid and 48-percent hydrofluoric acid. Addition of hydrochloric acid produces yellow ferric chloride, which is then reduced with stannous chloride to the ferrous form as indicated by the disappearance of the yellow color. Boric acid is added to complex the fluoride present, and sulfuric acid is added in order to obtain a sharper end point. Excess stannous chloride solution is oxidized to stannic chloride by the addition of mercuric chloride (Scott, 1950). The aqueous solution is titrated with potassium dichromate, using diphenylamine sulfonic acid as an indicator, until a blue color persists for 20 to 30 seconds. The method can be used for samples containing more than 0.02 percent iron.

REAGENTS AND APPARATUS

Sulfuric acid, concentrated, reagent-grade.
Sulfuric acid, 9*M*: Pour slowly 500 ml conc. H_2SO_4 into a reagent bottle containing 500 ml water.
Hydrofluoric acid, 48-percent, reagent-grade. (*CAUTION.* See p. 5.)
Hydrochloric acid, concentrated, reagent-grade.
Hydrochloric acid, 1*M*: Dilute 83 ml conc. HCl to 1 liter with water.
Phosphoric acid (H_3PO_4), 85-percent, reagent-grade.
Indicator solution: Dissolve 0.1 g barium diphenylamine sulfonate in 500 ml 85-percent H_3PO_4 and mix well.
Mercuric chloride solution, saturated: Add mercuric chloride ($HgCl_2$) to 100 ml water; shake during addition until some salt remains undissolved as proof of saturation.
Stannous chloride solution: Dissolve 10 g stannous chloride ($SnCl_2 \cdot 2H_2O$) in 100 ml conc. HCl.
Potassium dichromate ($K_2Cr_2O_7$), reagent-grade.
Potassium dichromate solution: Dissolve 3 g $K_2Cr_2O_7$ in 2 liters water. (Cal-

culate iron equivalence of the dichromate solution by titrating a standard ferrous iron solution in the same manner as the sample.)

Standard ferrous iron solution, 0.1-percent iron: Dissolve 0.7020 g ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$] in water and dilute to 100 ml.

Boric acid (H_3BO_3), reagent-grade, crystal.

PROCEDURE

1. Weigh 0.500 g sample into a 50-ml platinum evaporating dish.
2. Add about 2 ml water to wet the sample. Then add 2 ml 9*M* H_2SO_4 and about 10 ml 48-percent HF. Stir the contents of the dish with a platinum stirring rod.
3. Allow the dish to stand 2 to 4 hrs, then place it on a steam bath and evaporate the contents to incipient dryness.
4. Add 10 ml 1*M* HCl and continue heating until the residue is dissolved.
5. Remove the dish from the steam bath and add $SnCl_2$ solution dropwise until the yellow color disappears, then add exactly 2 drops in excess.
6. Transfer the sample solution to a 600-ml beaker containing 400 ml water, 5 g boric acid, and 5 ml conc. H_2SO_4.
7. Add 2 ml $HgCl_2$ solution to the beaker and 10 ml indicator solution.
8. Titrate the sample solution with $K_2Cr_2O_7$ solution to a blue color that remains visible for 20 to 30 sec.
9. Calculate the iron content from the titer.

DISCUSSION

The volumetric method described is not as sensitive as the colorimetric method for iron but has good precision over a wider range of iron concentration. Vanadium interference is obviated since the vanadium is reduced to the quadrivalent state in the procedure (Hillebrand and others, 1953). More than a slight excess of stannous chloride must be avoided, because excessive mercurous chloride may be produced, leading to high values. The blue color obtained at the end point will not persist longer than 20 to 30 seconds owing to the slow oxidation of mercurous chloride; hence, it is advisable initially to make several determinations for detection of the end point.

MANGANESE IN SOILS AND ROCKS

The determination of manganese in soils and rocks is based on the oxidation of manganese to permanganate in acid solution (Willard and Greathouse, 1917). The method is sensitive, rapid, and well suited to field use. The samples are fused with an acid flux and the melt digested with nitric acid, which readily decomposes most of the manganese minerals. A portion of the sample solution is further acidified and the manganese oxidized to permanganate by potassium periodate. The characteristic purple permanganate color developed is compared visually with standard solutions to estimate the manganese concentration.

The method is relatively free from interferences. The high acid concentration can be varied within rather wide limits, and excess periodate does not affect the color intensity. Standard solutions remain stable for several months.

The lower limit of detection is approximately 50 ppm manganese, and the method can be used for samples containing as much as 30 percent manganese. One man can make approximately 100 determinations per day.

REAGENTS AND APPARATUS

Potassium pyrosulfate ($K_2S_2O_7$), fused powder, reagent-grade.
Potassium periodate (KIO_4), crystal, reagent-grade.
Phosphoric acid (H_3PO_4), 85-percent, reagent-grade.
Sulfuric acid, concentrated, reagent-grade.
Nitric acid, concentrated, reagent-grade.
Nitric acid, 4*M*: Dilute 250 ml conc. HNO_3 to 1 liter with water.
Standard manganese solution, (100 μg per ml) : Carefully weigh 0.0100 g electrolytic manganese metal into a 150-ml beaker, and add 10 ml 4*M* HNO_3. When the metal has dissolved, boil the solution for a few minutes to expel oxides of nitrogen. Allow the solution to cool, then transfer it to a 100-ml volumetric flask. Rinse the beaker with several 10-ml portions of water, transferring the washings to the volumetric flask. Dilute to 100 ml with water and mix well before using.
Culture tubes, 16- by 150-mm.
Pipet, 0.1-ml; graduated in 0.01 ml.
  0.1-ml; graduated in 0.1 ml.
  5.0-ml; graduated in 0.1 ml.
Pipets, volumetric, 1.0- and 2.0-ml.
Sample scoop, 0.1-g.
Flux scoop, 0.5-g.

PROCEDURE

1. Weigh or scoop 0.1 g sample and transfer it to a dry 16- by 150-mm culture tube.
2. Add 0.5 g $K_2S_2O_7$ flux and alternately rotate and tap the tube to mix the sample and flux.
3. Fuse the sample for 2 to 3 min after the flux is molten. If a liquid melt is not obtained on heating, extra flux may be added to the tube.
4. Remove the tube from the flame and rotate the tube so that the melt cools in a thin film on the sides.
5. When the tube is cool, add 3 ml 4*M* HNO_3 and place the tube in a boiling water bath until the melt is reduced to a fine powder. Intermittent shaking of the tube or crushing of the melt with a glass rod will hasten this process.
6. Remove the tube from the hot water bath, and when cool dilute the sample solution to 10 ml with water. Place a cork stopper or thumb over the culture tube and shake to mix; allow the solution to settle.
7. Transfer a suitable aliquot (5.0 ml) to a clean 16-by 150-mm culture tube. If the aliquot is less than 2 ml, add 1 or 2 ml 4*M* HNO_3 before proceeding.
8. To the culture tube containing the aliquot, add 0.5 ml conc. H_2SO_4 and 0.5 ml conc. H_3PO_4, shaking the tube after each addition.

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9. Add about 0.2 g KIO_4 and place in a boiling water bath for 15 min. Shake the tube intermittently during the 15 min.
10. Remove the tube from the water bath; when cooled, dilute the solution to 10 ml with water. Cover the top of the culture tube and shake to mix the solution.
11. Estimate the manganese concentration of the solution in micrograms by visually comparing the color obtained with the color of the most nearly matching manganese standard solution.
12. Calculate the manganese concentration in the sample according to instruction on p. 8.

Preparation of standards

1. Transfer, respectively, 0, 0.05, 0.1, 0.2, 0.4, 0.8, 1.5, and 3.0 ml standard manganese solution (100 μg per ml) to eight 16- by 150-mm culture tubes. This standard series will contain 0, 5, 10, 20, 40, 80, 150, and 300 μg manganese.
2. To each of 8 culture tubes add (shaking the tube after each addition) 2 ml $4M$ HNO_3, 0.5 ml conc. H_2SO_4, and 0.5 ml conc. H_3PO_4.
3. Add about 0.2 g KIO_4 to each tube, and place in a boiling water bath for 15 min. Shake each tube intermittently during the 15 min.
4. Remove the tubes from the water bath; when cooled, dilute each solution to 10 ml with water. Cover each tube and shake to mix.

DISCUSSION

Most of the common reducing ions are removed either in the pyrosulfate fusion or when the sample is boiled with HNO_3. Many metal ions that might precipitate in weak acid solution (for example, silver, lead, and mercury remain dissolved because of the high acid concentration. The most common interference is that caused by metal ions that impart a color of their own to the solution; that is, copper, nickel, cobalt, chromium, uranium, and iron (III). As much as 0.02 mg per ml of copper, nickel, cobalt, and uranium can be tolerated (Mehlig, 1939). Interference due to iron (III) is obviated by formation of the colorless complex ion with phosphoric acid (Snell and Snell, 1959). The effect of chromate ion is minimized by the high acid concentration; however, the presence of small amounts of bismuth and tin result in turbidity in the final solution (Sandell, 1959). Chloride, which decolorizes the permanganate ion, is largely expelled in the pyrosulfate fusion.

TRACES OF MERCURY IN SOILS AND ROCKS—CAMP- AND SAMPLE-SITE DETERMINATION

The complete procedure for determining traces of mercury in soils and rocks is given in detail by Ward and Bailey (1960). The powdered sample is heated at low heat with ammonium iodide; the unreacted material is dumped from the tube, and the sublimate on the inner walls of the tube is dissolved in an acetate buffer.

Dithizone is added, and in the presence of EDTA and thiocyanate, mercuric dithizonate is extracted into an immiscible solvent away from possible interferences such as bismuth, copper, gold, silver, and tin. The phases are separated and excess dithizone is removed with dilute ammonia, leaving an orange mercuric dithizonate in the organic solvent. By estimating color intensities between standards, one can determine as little as 2.5 ppm of mercury.

The iodide volatilization is effective on samples containing cinnabar, but it has not been adequately tested on other mercury minerals.

The method has been tested around known ore bodies in California, Nevada, and Texas, and the results confirm its usefulness in exploration for new ore bodies in similar geologic environments.

REAGENTS AND APPARATUS

Ammonia (NH_4OH), 0.4*M*, metal-free.

Ammonium iodide (NH_4I), reagent-grade.

Ammonium thiocyanate (NH_4SCN), reagent-grade.

Buffer, sodium acetate–acetic acid solution: Generally, the buffer is prepared by mixing 10 ml 2M acetic acid with 5 ml 2*M* sodium acetate; however, as different batches of sodium acetate may have either a greater amount of alkali than the stoichiometric requirement or a variable amount of water, the volume ratio of the 2*M* acetic acid and the aqueous sodium acetate has to be adjusted to produce the desired pH. The correct volume ratio can be determined by titrating a given volume of 2*M* acetic acid with the aqueous sodium acetate until the pH of the mixture is 4.

Complexing agent: A mixture of 5 g hydrazine sulfate and 10 g EDTA.

Dithizone, 0.01-percent: Dissolve 0.01 g purified reagent in 100 ml reagent-grade chlorofrom ($CHCl_3$).

Dithizone, 0.0015-percent: Mix 15 ml dithizone solution (0.01 percent) in chloroform with 85 ml soltrol.

Ethylenediaminetetraacetic acid, disodium salt (EDTA).

Mercury standard A, 1,000 μg per ml: Dissolve 0.1354 g reagent-grade mercuric chloride ($HgCl_2$) in 100 ml 0.5*M* H_2SO_4.

Mercury standard B, 10 μg per ml: Dilute 1 ml standard A to 100 ml with 0.5M H_2SO_4. This standard is stable for at least 3 months at ordinary temperatures.

Soltrol: A high-boiling nonvolatile solvent composed mostly of isoparaffinic hydrocarbons and marketed by Phillips Petroleum Co. In most areas this solvent can be used as shipped; however, if desired, solvent can be freed of trace metals by shaking as much as 250 ml once with 10 ml of 0.5*M* H_2SO_4 and then removing the acid by shaking successively 3 times with 50-ml portions of metal-free water.

Culture tubes, 18- by 150-mm.

Scoop, 0.5-g.
  0.1-g.

Pipets, automatic, 5-ml, plunger-type.

Separatory funnels, 60-ml, Squibb-type.

PROCEDURE

1. Mix 2 small scoops (0.2 g total) sample and 1 small scoop NH_4I in a culture tube and heat mixture at low heat for 1 min. Cool.
2. Invert tube and dump loose solid material.
3. Holding tube upright, add 10 ml buffer, 1 large scoop of complexing agent, and 1 small scoop NH_4SCN, and dissolve.
4. Transfer contents of tube to separatory funnel and add 1 ml dithizone solution (0.0015 percent).
5. Shake funnel 1 min. Drain and discard aqueous phase.
6. Add 5 ml water and shake funnel 10 sec. Drain and discard aqueous phase.
7. Add 5 ml 0.4*M* metal-free ammonia and shake funnel 5 sec. Drain and discard aqueous phase.
8. Compare color of organic layers with color of standards.
9. Calculate the mercury concentration in the sample according to instructions on page 8.

Preparation of standards

To each of four 60-ml separatory funnels add 10 ml acetate buffer, 0.1 g EDTA, and the appropriate amount of standard B—none to first funnel, 1 μg mercury to second, 2 μg to third, 4 μg to fourth. Proceed as above, starting with step 4.

DISCUSSION

Mercury standards are unsatisfactory for field use because of the possible decomposition of the mercuric dithizonate when exposed to heat and sunlight. Aqueous solutions of Orange II, an azo dye, are moderately stable and the color closely resembles that of mercury dithizonate. Recently, this dye has been incorporated in a thermosetting resin to provide a stable and sturdy artificial plastic standard. The preparation of these is described on page 15. Plastic standards are sturdy enough for rough field use and they are stable for more than a year.

MOLYBDENUM IN SOILS AND ROCKS, CARBONATE FUSION METHOD

A complete discussion of the carbonate fusion method for determining molybdenum is given by Ward (1951b). After the soil or rock sample is fused in a test tube with a modified carbonate flux, the water-soluble molybdenum reacts with thiocyanate under reducing conditions in dilute hydrochloric acid to form an amber-colored complex not readily visible in the aqueous solution. A small volume of isopropyl ether is used to extract and concentrate the complex; after separation of the organic solvent as a shallow layer on the aqueous solution, as little as 0.005 μg molybdenum per ml of aqueous solution is readily visible.

The carbonate fusion and the subsequent aqueous leach separate molybdenum from practically all of the iron, copper, and other elements which form insoluble hydroxides. Tungsten interference is largely prevented by the addition of tartrate. Rhenium reacts with thiocyanate and may interfere if present in sufficient quantities. Large amounts of uranium, vanadium, and niobium may interfere, but the acid concentration is too low for an appreciable reaction of vanadium and niobium with thiocyanate. Moreover, niobium is easily hydrolyzed and therefore not very soluble in the aqueous leach.

REAGENTS AND APPARATUS

Flux: Mix equal parts by weight of sodium carbonate (Na_2CO_3) and potassium nitrate (KNO_3) and grind to pass an 80-mesh sieve.
Hydrochloric acid, concentrated, reagent-grade.
Isopropyl ether. (*CAUTION.* See p. 5): If ether is peroxide free, on the day it is to be used shake it with one-tenth its volume of equal amounts of stannous chloride ($SnCl_2$) and potassium thiocyanate (KSCN) reagents.
Phenolphthalein indicator solution, 1-percent: Dissolve 1 g phenolphthalein in 100 ml alcohol.
Potassium nitrate solution, 10-percent: Dissolve 10 g in 100 ml water.
Potassium thiocyanate solution, 5-percent: Dissolve 5 g salt in 100 ml water. Prepare fresh daily.
Sodium tartrate ($NaHC_4H_4O_6 \cdot H_2O$), powdered, reagent-grade.
Standard molybdenum solution, 100 μg per ml: Dissolve 0.075 g pure molybdic acid anhydride in 1*M* NaOH, dilute with water, add 1*M* HCl until solution is just acid, then dilute to 500 ml with water.
Standard molybdenum solution, 1 μg per ml: Prepare daily by diluting 1 ml standard solution (100 μg per ml) to 100 ml with water.
Stannous chloride reagent, 10-percent: Dissolve 10 g $SnCl_2 \cdot 2H_2O$ in 17 ml conc. HCl, and dilute with water to a volume of 100 ml.
Culture tubes, 16- by 150-mm.
Flask, volumetric, 100-ml.
Scoop, 0.1-g.
Mullite mortar and pestle.
Pipets, 1- and 2-ml, graduated.
Stevens extractors. (See p. 44.)

PROCEDURE

1. Add 0.1 g sample to a 16- by 150-mm culture tube, then add 0.5 g flux. Shake the tube thoroughly to mix the sample and flux.
2. Heat and rotate tube over a burner to effect a sinter.
3. Cool tube, and add 4 ml metal-free water.
4. Put stoppered Stevens extractor into culture tube and place the tube in a boiling water bath for 5 min.
5. Remove the tube from the water bath and cool. Pipet a 1-ml filtered aliquot into a 16- by 150-mm culture tube marked at 5 ml.
6. Add 1 drop phenolphthalein solution to the aliquot, and then add 1*M* HCl, drop by drop, until the pink color disappears.
7. Add 0.5 ml KNO_3 solution and 0.2 g powdered sodium tartrate and shake to dissolve. Bring the volume of the solution to 5 ml with water.
8. Add the following reagents and shake the tube after each addition:
   0.5 ml conc. HCl.

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0.3 ml KSCN solution.
0.5 ml $SnCl_2$ solution.

9. Allow the tube to stand 1 min, then add 0.5 ml isopropyl ether; shake the tube vigorously for 10 sec.
10. Compare amber color of organic layer with that obtained from standard solutions.
11. Calculate the molybdenum concentration in the sample according to instructions on page 8.

Preparation of standards

Transfer, respectively, 0, 0.1, 0.2, 0.4, 0.8, 1.5, 3, and 6 μg molybdenum to a series of culture tubes, then follow procedure beginning with step 7 above.

DISCUSSION

Occasionally, the quantity of iron (III) leached from the carbonate residue exceeds the amount which can be reduced to iron (II) by the recommended procedure. A pink color forms when the thiocyanate is added to the sample solution. In such cases a few additional drops of stannous chloride reagent suffice to complete the iron reduction and restore the colorless solution. If the pink color develops in the isopropyl ether layer after extraction, additional drops of stannous chloride reagent are added and the test tube shaken again as in the first extraction.

MOLYBDENUM IN SOILS AND ROCKS, ACID DIGESTION METHOD

The soil or rock sample is digested over a low flame with a mixture of concentrated sulfuric and nitric acids. Sufficient hydrochloric acid saturated with citric acid is added to inhibit the effects of the other acids; from such a medium, molybdenum (VI) is readily extracted into isoamyl acetate, which then floats on top of the aqueous layer and separates from the residue of the unattacked sample. An aliquot of the organic layer containing the molybdenum (VI) is shaken with a dilute hydrochloric acid solution containing tin (II) and thiocyanate. During the shaking a series of reactions take place with the resulting formation of the amber-colored molybdenum (V) thiocyanate in the shallow organic layer. As described, the method is applicable to soils and rocks containing 2.5 to 40 ppm molybdenum.

The acid digestion is effective on most molybdenum minerals such as molybdenite and powellite. In fact, in highly weathered materials—soils, for example—molybdenum is present largely in the sexivalent state and the addition of nitric acid is unnecessary. However, hot sulfuric acid alone is ineffective on molybdenite. Iron, tungsten, vanadium, and rhenium interfere in this method, but tin (II) reduces iron to the ferrous form, which does not form a colored thiocyanate. Citric acid largely prevents the interference of tungsten and vanadium. Rhenium is usually not present in soils or rocks to a great extent; however, it reacts similarly to molybdenum and its presence should not be discounted, especially in so-called high-molybdenum materials.

REAGENTS AND APPARATUS

Ammonium thiocyanate solution (NH_4SCN), 5-percent: Dissolve 5 g of the salt in 100 ml water. Prepare fresh daily.
Citric acid, reagent-grade.
Hydrochloric acid, concentrated.
Isoamyl acetate, reagent-grade.
Nitric acid, concentrated.
Standard molybdenum solution (100 μg per ml): Dissolve 0.075 g pure molybdic acid anhydride in 1*M* NaOH, dilute with water, add 1*M* HCl until solution is just acid, then dilute to 500 ml with water.
Standard molybdenum solution (50 μg per ml): Prepare every 2 to 3 days by mixing equal volumes of the standard solution (100 μg per ml) and water.
Stannous chloride solution, 10 percent: Dissolve 10 g $SnCl_2 \cdot 2H_2O$ in 17 ml conc. HCl and dilute with water to 100 ml. Prepare fresh daily.
Sulfuric acid, concentrated.
Reagent No. 1: Dissolve 40 g citric acid in 100 ml 6*M* HCl.
Reagent No. 2: To 50 ml water add 5 ml conc. HCl, 5 ml NH_4SCN solution and 5 ml $SnCl_2$ solution. Prepare fresh daily.
Pipets, 0.5-, 1-, and 5-ml, graduated in tenths.
Culture tubes, 18- by 150-mm.

PROCEDURE

1. To 0.1 g sample in an 18- by 150-mm culture tube, add 1 ml conc. H_2SO_4 and 1 drop conc. HNO_3.
2. Heat tube over alcohol lamp for ½ min and cool.
3. Add 4 ml reagent No. 1 and 1 ml isoamyl acetate; stopper, and shake contents of tube for ½ min.
4. While the tube stands to allow the phases to separate, prepare another culture tube by adding to it 5 ml reagent No. 2.
5. From the first tube, transfer 0.5 ml of separated isoamyl acetate to the second tube containing reagent No. 2; stopper, and shake the tube for 10 sec.
6. Compare amber color of isoamyl acetate layer with that obtained from standards.
7. Calculate the molybdenum concentration in the sample according to instructions on page 8.

Preparation of standards

1. Add, respectively, 0, 0.005, 0.01, 0.02, 0.04, 0.06, and 0.08 ml standard molybdenum solution (50 μg per ml) to a series of 7 tubes, each containing 5 ml reagent No. 2.
2. Add 0.5 ml isoamyl acetate to each tube; stopper, and shake tube for 10 sec.

DISCUSSION

The final step in the procedure frequently results in a pink color in the organic layer presumably due to iron (III) thiocyanate. The addition of as much as 0.5 ml stannous chloride solution followed by a 10-second shaking of the tube may be necessary to remove the pink color. In rare cases more than 0.5 ml stannous chloride may seem necessary, but such amounts will increase the acid concentration and result in a less stable amber color of the molybdenum thiocyanate.

MOLYBDENUM IN PLANTS

A complete discussion of this method for the determination of molybdenum in plants is given by Reichen and Ward (1951). The fresh plant material, usually leaves, is heated over a field stove until only a gray to black ash remains. A sample of this ash is fused with lithium nitrate to complete the oxidation, and the fused mass is leached with dilute hydrochloric acid. In such a medium, after addition of stannous chloride, molybdenum will react with thiocyanate to form an amber-colored complex easily extractible into isopropyl ether. The ether separates as a shallow layer on top of the aqueous solution and thus concentrates the molybdenum complex to permit easy comparison with standards. Generally, vanadium, tungsten, and rhenium are not present in sufficiently large quantities to interfere.

The method is not designed to detect the small differences in the molybdenum content of plants that are caused by the health of the plant, soil moisture, and other factors. It does, however, permit measurement of differences as small as 0.25 μg in the plant ash, which are significant in geochemical prospecting. The method has been used in biogeochemical prospecting in California by Carlisle and Cleveland (1958).

REAGENTS AND APPARATUS

Ammonium hydroxide solution, $1M$: Dilute 6.6 ml conc. NH_4OH, specific gravity 0.90, to 100 ml with metal-free water.

Hydrochloric acid, concentrated, reagent-grade.

Hydrochloric acid, $1M$: Dilute 8.3 ml conc. HCl to 100 ml with metal-free water.

Isopropyl ether, practical grade, free of peroxides (see p. 5): If the ether is peroxide free, saturate it with $SnCl_2$ and KSCN by shaking with a solution containing equal volumes of these reagents equivalent to 10 percent of the volume of ether.

Lithium nitrate ($LiNO_3$), reagent-grade.

Phenolphthalein solution, 1.0-percent: Dissolve 1 g phenolphthalein in 100 ml alcohol.

Potassium nitrate solution (KNO_3), 10-percent: Dissolve 10 g of the salt in 100 ml water.

Potassium thiocyanate solution (KSCN), 5-percent: Dissolve 5 g of the salt in 100 ml water.

Standard molybdenum solution, 100 μg per ml: Dissolve 0.075 g pure molybdic acid anhydride in 3 ml of 1*M* NaOH solution; dilute with water, make slightly acid with 0.1*M* HCl, and make up to 500 ml with water.

Standard molybdenum solution, 2 μg per ml: Dilute 2 ml standard solution (100 μg per ml) to 100 ml with water. Prepare fresh daily.

Stannous chloride solution, 10-percent: Dissolve 10 g $SnCl_2 \cdot 2H_2O$ in 17 ml conc. HCl and dilute to 100 ml with water.

Microbalance, torsion type, capacity 75 mg (see p. 9): A scoop, previously calibrated by weighing a measured amount of ash, can be used under field conditions in place of the balance.

Dishes, evaporating, 60 ml, platinum.

Scoop, 0.25-cc; for measuring lithium nitrate.

Tongs, platinum-tipped.

Pipets:
- 1-ml; graduated in 0.1 ml.
- 1-ml; graduated in 0.01 ml.
- 2-ml; graduated in 0.5 ml.
- 5-ml; graduated in 0.1 ml.

Tubes, culture, 16- by 150-mm; calibrated at 5 ml mark.

PROCEDURE

1. Ash the fresh plant material by heating in a platinum dish over the stove. Mix ash.
2. Fuse 25 mg ash with 1 scoop $LiNO_3$ in calibrated culture tube.
3. Dissolve whitish melt in 1 ml 1*M* HCl, add 1 drop indicator and 1*M* NH_4OH dropwise to faint pink. Add water to 5-ml mark.
4. To a series of 11 culture tubes add, respectively, the following amounts of the molybdenum standard (2 μg per ml): None to first tube, 0.5 μg to second tube, 1.0 μg to third tube, and continue, increasing the amount in each tube by 0.5 ml increments; the last tube should contain 5 μg of molybdenum. Add water to 5-ml mark.
5. To both samples and standards add 0.6 ml conc. HCl, 0.5 ml KSCN, 1 ml $SnCl_2$. Shake tube after each addition.
6. To all samples and standards, add 1 ml isopropyl ether, stopper the tubes, and shake each for 15 sec.
7. Within 30 min. compare the amber-colored ether layer over sample solutions with that obtained over standard solutions.
8. Calculate the molybdenum concentration in the ash according to instructions on p. 8 using ash weight in place of sample weight.

DISCUSSION

The field burning of the plant material does not leave a white ash. The ignition must be completed, as incompletely burned organic material imparts a brownish color, resembling that of the molybdenum complex, to the isopropyl ether in the subsequent extraction. The fusion of the charred material with a low-melting oxidizer like lithium nitrate completes the ignition, and the white fused mass easily dissolves in dilute acid, producing a colorless solution.

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NIOBIUM IN ROCKS

The complete laboratory method for the determination of niobium in rocks is given by Ward and Marranzino (1955). The sample is fused with potassium pyrosulfate, and the fused mass is extracted with hot tartaric acid. Strong hydrochloric acid is added to an aliquot of the tartaric acid solution, and the niobium is allowed to react with thiocyanate in an aqueous medium. The niobium thiocyanate is extracted into ethyl ether, and the ether phase is treated successively with portions of hydrochloric acid containing stannous chloride. The niobium thiocyanate remains in the ether phase, which is mixed with acetone to provide a stable solution whose absorbance is measured instrumentally. The quantity of niobium is determined by reference to a calibration curve. The niobium content can also be determined visually by comparison with standards. The procedure is applicable to rocks containing as little as 50 ppm of niobium. The method is subject to interference by large amounts of molybdenum and tungsten.

The fusion of the sample with pyrosulfate is effective on columbite, bauxite, some monazite, and nepheline syenite; it is less effective, however, on some euxenite and wolframite samples.

REAGENTS AND APPARATUS

Acetone, A.C.S. grade.

Ethyle ether, peroxide-free (*CAUTION.* See test for peroxides, p. 5.) Immediately before use, shake the ether with 1/20 its volume of stannous chloride reagent.

Ammonium thiocyanate solution (NH_4SCN), 20-percent: Dissolve 20 g NH_4SCN in 100 ml water (prepare fresh solution daily).

Hydrochloric acid-tartaric acid solution: Dissolve 15 g tartaric acid in 100 ml 9*M* HCl.

Potassium pyrosulfate ($K_2S_2O_7$), fused-powder, reagent-grade.

Stannous chloride solution, 10-percent: Dissolve 10 g $SnCl_2 \cdot 2H_2O$ in 17 ml conc. HCl, then dilute to 100 ml with water (prepare fresh solution every other day).

Standard niobium solution, 200 μg per ml: Prepare by fusing 0.0286 g niobium pentoxide (Nb_2O_5) with 1.5 g $K_2S_2O_7$ in a porcelain—or preferably a vitreosil—crucible. Dissolve the fused mass in 1*M* tartaric acid and make up to 100 ml with 1*M* tartaric acid.

Standard niobium solution, 20 μg per ml: Prepare by diluting 10 ml standard solution (200 μg per ml) to 100 ml with 1*M* tartaric acid and mixing thoroughly.

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

Cuvets.

Mortar and pestle.

Pipets, 1-ml, 5-ml, and 10-ml, each graduated in 0.1 ml.

Separatory funnels, 60-ml.

Test tubes, 16- by 150-mm.

PROCEDURE

1. Mix 0.2 g sample with 4 g $K_2S_2O_7$ in test tube, and fuse mixture for 15 min. Cool.
2. Add 10 ml 1*M* tartaric acid, and break up fused mass with glass stirring rod.
3. Place tube in boiling water bath 2 to 3 min. and then pipet a 1-ml aliquot of the clear supernatant liquid into 5 ml hydrochloric acid-tartaric acid reagent in a 60-ml separatory funnel.
4. Mix contents of funnel, and cool to 20°C.
5. Add 5 ml NH_4SCN solution, and mix.
6. Add 5 ml ethyl ether to funnel, and shake mixture for 30 sec.
7. When phases have separated, drain and discard aqueous phase; add 5 ml $SnCl_2$, and shake the funnel 20 sec. Drain, discard aqueous layer, and repeat this step.
8. Transfer ether phase to 10-ml volumetric flask, add acetone to mark, and mix.
9. Transfer to a cuvet, read absorbance of solution at 385 $m\mu$ on a spectrophotometer and ascertain the number of micrograms of niobium present by reference to a standard curve, or visually compare absorbance of sample with the absorbance of standard niobium solution added to 10 ml 1*M* tartaric acid as in step 2 and taken through remainder of procedure.

DISCUSSION

If stannous chloride is added directly to the hydrochloric acid–tartaric acid solution before the ether extraction, vanadium is reduced and forms a yellow-colored thiocyanate, which is extracted along with niobium. The above procedure avoids this by extracting the thiocyanates of iron, niobium, and other elements into the ether and then reducing the iron to iron (II), whose thiocyanate is not only colorless but is also preferentially soluble in the aqueous phase.

PHOSPHORUS IN SOILS AND ROCKS

The method described below for the determination of phosphorus is based on the colorimetric method first proposed by Misson (1908). It depends on the reaction of orthophosphate with a mixture of vanadate and molybdate in acid solution. The yellow complex formed, presumably molybdivanadophosphoric acid, provides the basis for colorimetric measurements.

The sample is fused with an acid flux and the melt digested with nitric acid. Vanadate-molybdate reagent is then added to a portion of the sample solution, and a yellow color develops on standing. The color thus obtained is compared visually with the color of standard solutions to determine the phosphorus concentration in the samples.

The method is relatively free from interferences. Acid concentration must be controlled because it affects the color development.

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A masking orange-yellow color is developed if the hydrogen ion concentration is less than 0.2*M*, and development of the yellow color of the molybdivanadophosphoric acid is slow at concentrations above 1.6*M* (Kitson and Mellon, 1944). An excess of vanadate and molybdate is required for complete color development; however, additional reagent has no effect on the color. Standard solutions remain stable for approximately 2 weeks.

The lower limit of detection is approximately 50 ppm phosphorus, and the method can be used for samples containing as much as 20 percent phosphorus. One man can analyze about 100 samples per day for phosphorus.

REAGENTS AND APPARATUS

Potassium pyrosulfate ($K_2S_2O_7$), fused-powder, reagent-grade.
Nitric acid, concentrated, reagent-grade.
Nitric acid, 4*M*: Dilute 250 ml conc. HNO_3 to 1 liter with water.
Vanadate-molybdate reagent:
  A. Dissolve 1.25 g ammonium metavanadate (NH_4VO_3) in 400 ml 8*M* HNO_3
  B. Dissolve 50 g ammonium molybdate ($(NH_4)_2MoO_4$) in 400 ml water.
    Combine solutions A and B, dilute to 1 liter with water, and mix.
Standard phosphorus solution, 50 μg per ml: Dissolve 0.5782 g sodium phosphate ($Na_2HPO_4 \cdot 12H_2O$) in 800 ml water. Add 20 ml conc. HNO_3, and dilute to 1 liter with water. Mix well before using.
Tubes, culture, 16- by 150-mm.
Pipets:
  0.1-ml; graduated in 0.01 ml.
  5.0-ml; graduated in 0.1 ml.
  Volumetric, 1.0- and 2.0-ml.
Flux scoop, 0.5-g.

PROCEDURE

1. Weigh or scoop 0.1 g sample and transfer it to a dry 16- by 150-mm culture tube.
2. Add 0.5 g $K_2S_2O_7$ flux to the tube and alternately rotate and tap the tube to mix the sample and flux.
3. Heat to fuse the sample and continue heat for 1 min after the flux is molten.
4. Remove the tube from the flame and rotate so that the melt cools in a thin film on the sides.
5. When the tube is cool add 2 ml 4*M* HNO_3, and place the tube in a boiling water bath until the melt is reduced to a fine powder.
6. Remove the tube from the boiling water bath; when cool, dilute the sample solution to 10 ml with water. Insert a cork in the tube or hold the thumb over the top and shake to mix the solution, then allow the residue to settle.
7. Transfer a suitable aliquot (0.1 to 5.0 ml) to a clean 16- by 150-mm culture tube.
8. Add 2 ml vanadate-molybdate reagent to the tube and dilute to 10 ml with water.
9. Stopper the culture tube, shake, then allow the solution to stand for 30 min.

10. Estimate the phosphorus content of the solution, in μg, by visually comparing the color obtained with the color of the most nearly matching phosphorus standard solution.
11. Calculate the phosphorus concentration in the sample according to instructions on page 8.

Preparation of standards

1. Transfer, respectively, 0, 0.04, 0.08, 0.16, 0.3, 0.6, 1.2, and 2.4 ml standard phosphorus solution (50 μg per ml) to eight 16- by 150-mm culture tubes. This standard series will contain 0, 2, 4, 8, 15, 30, 60, and 120 μg phosphorus.
2. Add 0.2 ml 4*M* HNO_3 and 2 ml vanadate-molybdate solution to each of the 8 culture tubes.
3. Dilute each tube to 10 ml with water. Cover the tubes, shake, and allow to stand 30 min. before use.

DISCUSSION

Most of the phosphorus minerals are readily attacked by the pyrosulfate fusion. Some phosphate may be lost if the fusion is prolonged or the temperature of the fusion is too high. Certain cations, such as bismuth (III), thorium (IV), arsenic (V), and anions such as chloride and fluoride, may interfere in the test by delaying color development. Unless these interfering ions are present in large concentrations, however, the color will develop if the solution stands for 30 minutes (Snell and Snell, 1959). The interference from large amounts of silica (more than 25 ppm) can be removed by evaporation of the sample with perchloric acid (Snell and Snell, 1959). Tin may cause a turbidity in the final solution (Kitson and Mellon, 1944).

SELENIUM IN HIGHLY SELENIFEROUS MATERIALS

The presence of selenium usually cannot be visually recognized in minerals in which it is concentrated; therefore, a simple field test for selenium is a very desirable tool for the prospector and for the geologist who is evaluating prospects or mines. On the Colorado Plateau, selenium commonly is present in sulfide minerals, especially in the pyrite and galena associated with uranium ores (Coleman, 1956). Oxidation of these sulfides produces a red elemental selenium halo about the ore. The selenium content of the sulfide ores and of the host rock containing the elemental selenium halos may be as high as 2 to 2.5 percent.

Many efforts have been made to determine selenium quantitatively in soils and rocks, but none of them has been wholly satisfactory. Gooch and Peirce (1896) observed that selenium can be separated from tellurium by distillation as selenium tetrabromide. Noyes and Bray (1927) used this distillation in their systematic qualitative analysis of the rarer elements. Robinson

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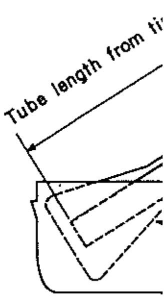


FIGURE 6.—I

and his coworkers (1934) developed methods for the determination of selenium in pyrite, soils, and plant material, using the distillation of selenium tetrabromide.

In Robinson's method, the selenium tetrabromide that is distilled from a constant-boiling solution of hydrobromic acid may be accompanied by arsenic, some germanium, tin, and antimony. The distillate, diluted with water to 4*M* acid, is treated with sulfur dioxide, hydroxylamine hydrochloride, or sodium sulfite to reduce the selenium to the elemental form, thus giving a specific test for selenium. The colloidal precipitate of elemental selenium obtained by the action of a reducing agent on dilute solutions of selenium is a light pink to orange red. As the concentration of selenium increases, the precipitate becomes darker red. This precipitate eventually takes on a purple tinge and ultimately changes to a dark red or black amorphous form, which settles to the bottom of the beaker.

For field use, the proposed rapid test for selenium (Lakin, 1959) has two advantages over the well-established laboratory methods of analyses outlined above; first, the simplicity of the still (see fig. 6); and, second, the elimination of the necessity to transport liquid bromine, through preparation of bromine–hydrobromic acid solution in the field by means of the well-known reaction between sodium bromate and hydrobromic acid. The transportation of bromine is hazardous, a fact that has heretofore prevented the field distillation of selenium.

With oxidized materials the practical range of the proposed rapid field test is from 50 to 1,000 ppm; the range can be extended downward to 10 ppm by allowing the precipitated selenium to

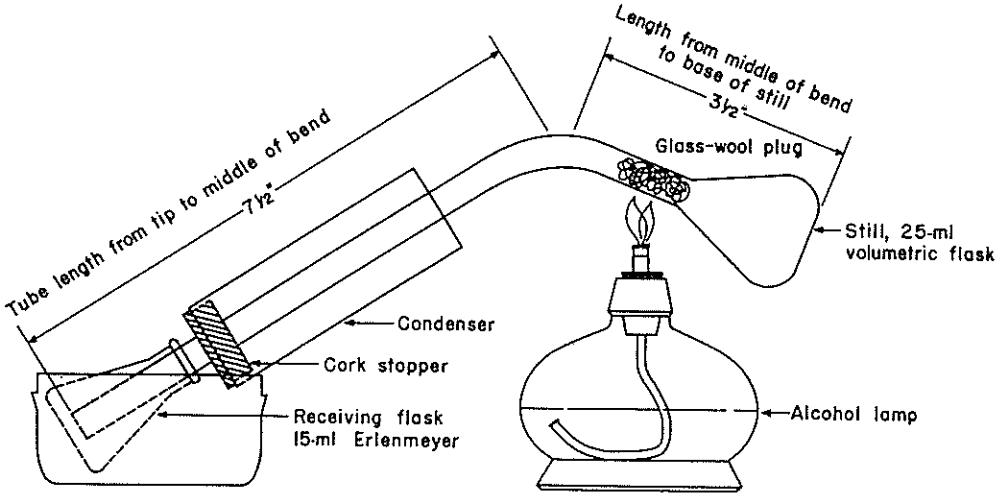


FIGURE 6.—Dimensional drawing of a field selenium still, showing position of still in use.

stand overnight. A somewhat more tedious method is necessary for sulfide ores and for materials containing organic matter, such as carbonaceous shales. The sensitivity for the sulfide ores and carbonaceous shales is approximately 50 ppm; the upper limit is determined by how small a sample one wishes to take.

REAGENTS AND APPARATUS

Hydrobromic acid–bromine reagent: In a 250-ml beaker dissolve 1.5 large scoops (1.5 g) sodium bromate ($NaBrO_3$), in 10 ml water. In one continuous operation, rapidly pour 90 ml conc. HBr into the bromate solution. The rapid addition of HBr is necessary to provide sufficient volume to dissolve the bromine produced during the initial violent reaction and to prevent its loss. Transfer the solution to a glass-stoppered bottle and keep it cool. The reagent contains approximately 1.5 percent bromine.

Nitric acid–mercuric nitrate reagent: Dissolve 1 large scoop (1.0 g) mercuric oxide (HgO) in 100 ml conc. HNO_3.

Standard selenium solution, 500 μg per ml: Dissolve 500 mg reagent-grade selenium in 200 ml hydrobromic acid–bromine reagent. Warm in water bath to insure solution of the selenium, and dilute to 500 ml with water. The final solution must be colored red with an excess of bromine.

Sulfuric acid, concentrated.

Sodium sulfite (Na_2SO_3).

Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$).

Pipet, 1-ml; graduated in 0.1 ml.

Large scoop, 1-g.

Small scoop, 0.2-g.

Glass wool.

Selenium still. (See fig. 6.)

Erlenmeyer flasks, 15-ml.

Beakers, 30-ml.

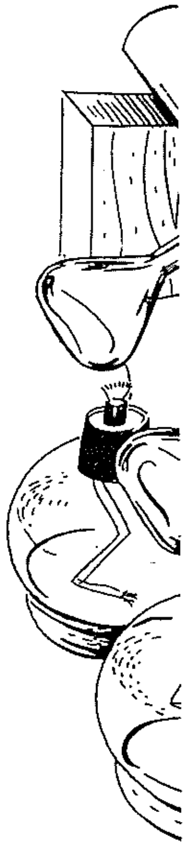
Selenium still rack. (See fig. 7.)

Metal dish, 8 cm in diameter and 4 cm high.

PROCEDURE

Materials exclusive of sulfides and highly organic samples

1. Add a large scoop sample (approx. 1 g) to the dry still through the condenser tube and tap gently.
2. Wash the condenser tube down with 1 ml water, followed by 2 ml H_2SO_4. If the material to be tested is limestone or if it contains large amounts of carbonate, add the H_2SO_4 slowly to allow the reaction to proceed without undue violence.
3. Cool the contents of the still by immersing it in cold water. When cool, add 5 ml hydrobromic acid–bromine reagent.
4. With a pliable plastic tube push a small plug of glass wool down the condenser about 1 inch past the bend in the condenser, so that the glass wool is well below the uppermost part of the still when the latter is placed in the distillation rack (see fig. 6). Push the condenser tube through the cork in the condenser sleeve, place the still in the distillation rack, and fill the condenser sleeve with cold water.
5. Add about 10 drops water to the receiving flask (15-ml Erlenmeyer flask), place the flask in a metal dish containing 50 ml cold water, and insert



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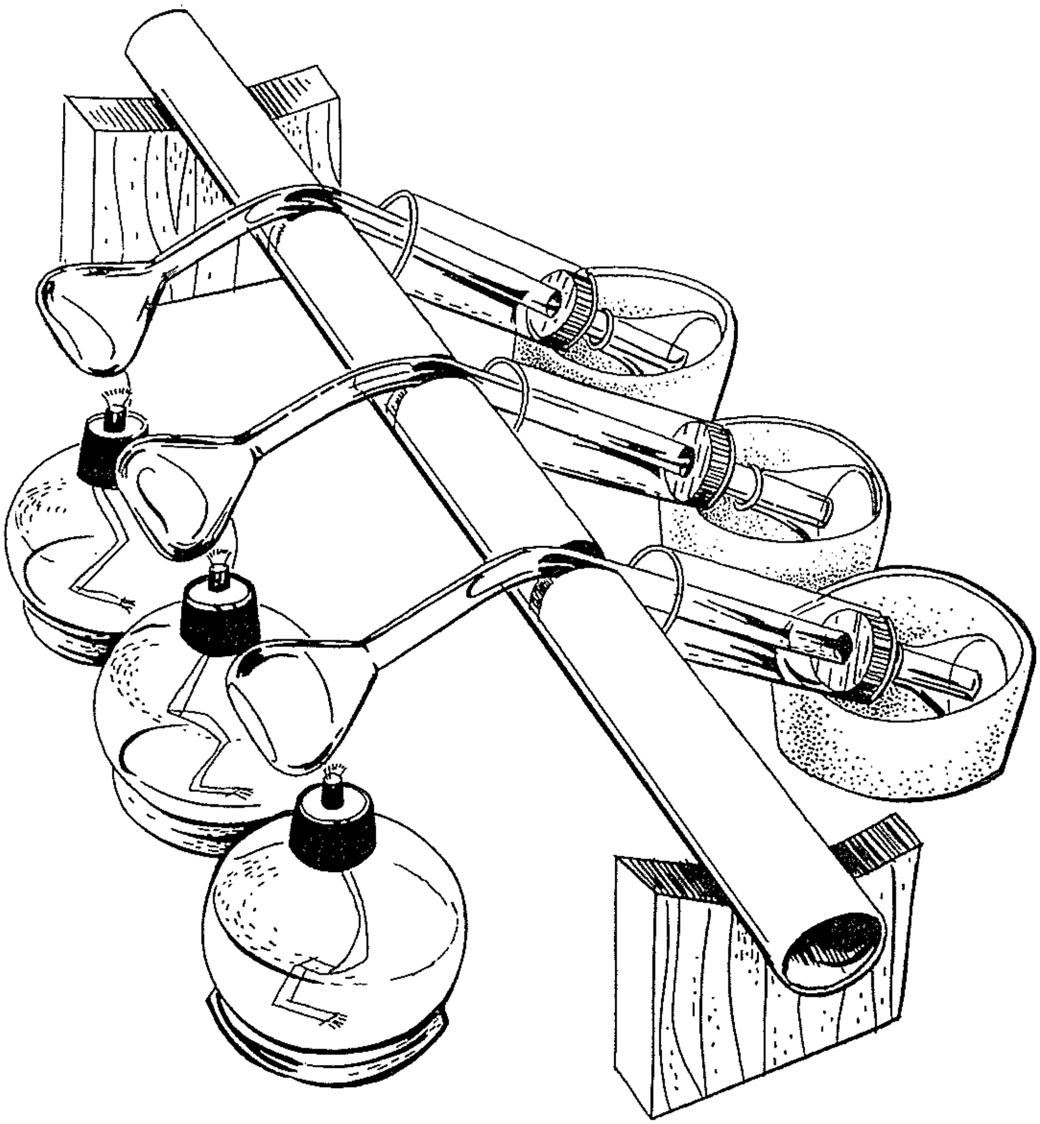

FIGURE 7.—Simple distillation rack supporting three stills.

the condenser tip of the still in the receiving flask until the condenser tip dips below the surface of the water.

6. Light the alcohol lamp and place it under the still adjacent to the condenser so that the flame heats the glass-wool plug and just touches the liquid. During this stage of heating, red fumes of bromine distill over and condense in the receiving flask.
7. After a few moments, slowly push the flame under the liquid charge in the still to increase the heat and cause HBr to distill.
8. When about 3 or 4 ml have distilled, extinguish the alcohol lamp and remove the receiving flask. Add water to the distillate to adjust the volume to 6 ml.
9. Add about 0.05 g Na_2SO_3 to reduce the excess bromine, a state which is indicated by the disappearance of the red color. To reduce the selenium, heat the flask until it is distinctly warm. It is essential that an excess of Na_2SO_3 be present throughout this step.
10. Add 1 small scoop (0.2 g) $NH_2OH \cdot HCl$; after 15 min. estimate the selenium content, in micrograms, of the sample solution, by visually

comparing the pink turbidity obtained with that of the most nearly matching selenium standard.

11. Calculate the selenium concentration in the sample according to instructions on page 8.

Sulfide-bearing samples

1. Place a small scoop (approx. 0.2 g) sample in a 30-ml beaker.
2. Add 2 ml nitric acid-mercuric nitrate reagent and heat the mixture over an alcohol lamp until the brown oxides of nitrogen are evolved copiously. Set aside until the reaction subsides and then heat again.
3. Repeat this cycle until the evolution of oxides ceases. One can conveniently handle 5 to 10 samples by intermittently heating them. If the sample is largely sulfide, it may be necessary to add 1 ml more of nitric acid-mercuric nitrate reagent to bring the sample into solution.
4. When the sulfide appears to be dissolved (usually in about 20 min.) evaporate the solution almost to dryness, then add 2 ml H_2SO_4 and heat to white fumes.
5. Cool and transfer the sample solution to a still, wash down with 1 ml of water, cool again, and then add 5 ml hydrobromic acid-bromine reagent, rinsing first the beaker and then the condenser with each reagent. Place the glass-wool plug in the condenser and proceed with the distillation previously described.

Materials containing large quantities of organic matter

For the determination of selenium in materials such as carbonaceous shales that contain organic matter, the procedure is the same as that followed for sulfides. A 1-g sample can be used, however, if the material contains less than 20 percent organic matter.

Preparation of standards

Prepare a series of selenium standards as follows. From the selenium standard solution (500 μg per ml) transfer 0.0, 0.1, 0.2, 0.4, 0.8, and 2.0 ml, respectively, to six 15-ml Erlenmeyer flasks. This standard series will contain 0, 50, 100, 200, 400, and 1,000 μg selenium. Add 2 ml of hydrobromic acid–bromine reagent to each flask and with water dilute each standard to 6 ml. Add an excess of Na_2SO_3 and warm each flask until the red color of the bromine disappears; then add a small scoop $NH_2OH \cdot HCl$ and set aside. Fresh standards must be prepared daily.

SULFATE IN NATURAL WATERS

The procedure used for the determination of sulfate in natural waters is a slight modification of the one described by Fritz and Yamamura (1955). The sulfate ion is determined by a rapid titration with barium perchlorate in an 80-percent alcohol medium in the apparent-pH range from 2.5 to 4.0 Thorin [2(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid], an indicator for excess barium ions, is used to detect the end point, which is indicated by a color change from yellow to pink. Preliminary passage of the sample through a cation-exchange column serves the dual purpose of removing interfering cations that form colored complexes with thorin and of adjusting the apparent pH so that it is

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within the range given above. Sulfate concentrations as low as 3 ppm can be measured, and a single determination takes only 3 to 5 minutes. The equipment required can be simplified so that determinations are easily made at the sample site.

Although the method has been used in geochemical prospecting work in several localities, it is not considered completely tested and therefore should be used with caution until it is more definitely shown that satisfactory results can be obtained with it. Phosphate ion interferes seriously, but, except in unusual instances, the amount of phosphate in natural waters is usually so low that it can be ignored as a source of serious error.

REAGENTS AND APPARATUS

Ethyl alcohol, 95-percent.

Barium perchlorate solution, 0.005*M*: Dissolve 1.68 g barium perchlorate [$Ba(ClO_4)_2$] in 200 ml of water and dilute to 1 liter with ethyl alcohol. Adjust the apparent pH to about 3.5 with perchloric acid.

Thorin indicator solution, 0.025-percent: Dissolve 0.025 g thorin [2(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid] in 100 ml alcohol.

Hydrochloric acid, 6*M*: Mix equal volumes conc. HCl and water.

Sulfate standard solutions, 100 μg sulfate ion per ml: Dissolve 0.181 g potassium sulfate (K_2SO_4) in metal-free water and dilute to 1 liter.

Ion-exchange column, glass tube about 1 inch in diameter and 6 inches long. Pack about half the length of the tube (3 in.) with a cation-exchange resin (hydrogen form) such as Dowex 50. As necessary, this resin may be rejuvenated with 6*M* HCl and then washed with water until the resin is free of acid.

Erlenmeyer flasks, 250-ml.

Graduated glass cylinder, 100-ml.

Microburet.

Polyethylene dropping bottles, 2-oz., with attached cap.

PROCEDURE

1. Pass the water sample through the ion-exchange column and discard the first 30 to 40 ml. Measure 10 ml of the next portion into a 250-ml flask, and add 40 ml ethyl alcohol.
2. Add 1 drop thorin indicator solution and then titrate with 0.005*M* $Ba(ClO_4)_2$ solution, taking the first permanent change from yellow to pink as the end point. Swirl the contents of the flask during the titration. Record in milliliters the volume used.
3. To express the sulfate concentration in parts per million, multiply the volume of $Ba(ClO_4)_2$ solution used by the number of micrograms of sulfate equivalent to 1 ml of $Ba(ClO_4)_2$, and divide by the volume of the aliquot used (usually 10 ml).

Standardization of the barium perchlorate reagent

1. Pass through the column about 100 ml of the sulfate standard containing 100 μg per ml. Discard the first 30 to 40 ml of effluent, but save the remainder.
2. Meaure three 10-ml aliquots of the effluent into separate 250-ml flasks each containing 40 ml ethyl alcohol.

3. Add 1 drop thorin indicator solution to each flask, and titrate each with 0.005*M* $Ba(ClO_4)_2$ to the first permanent pink. Calculate the average number of milliliters required from the three individual values.
4. Divide 1,000 by this average value to obtain the number of micrograms of sulfate equivalent to 1 ml of $Ba(ClO_4)_2$ reagent used.

DISCUSSION

The pH of the effluent is a measure of the effectiveness of the cation-exchange column. The pH of the effluent should be checked with a pH meter occasionally, especially with waters whose chemical characteristics are unknown, to ensure that the exchange column is functioning properly. The number of samples that can be passed through the column before it requires rejuvenation depends on their salinities.

For use in the field, the barium perchlorate reagent can be dispensed with fair precision from a dropping bottle instead of a buret. If a wide range of sulfate content is expected, it is convenient to prepare a number of standard barium solutions of different strengths. Each dropping bottle must be individually standardized against standard sulfate solutions.

SMALL QUANTITIES OF TIN IN SOILS AND ROCKS

A rapid, relatively simple, and moderately accurate method for the determination of small quantities of tin in soil and rocks, described by Wood (1956) and modified by Marranzino and Ward (1958), is based on two reactions: (a) the volatilization of stannic iodide, accomplished by heating the sample with ammonium iodide; and (b) the subsequent reaction of quadrivalent tin with 4,5-dihydroxyfluorescein. The procedure was field tested at Majuba Hill, Nev., with moderate success, and is applicable to samples containing 5 to 100 ppm tin; with modifications it can be used on samples containing larger amounts of tin.

REAGENTS AND APPARATUS

Ammonium iodide, fine crystals.

Buffer solution: Dissolve in 500 ml metal-free water 50 g monochloroacetic acid ($CH_2ClCOOH$), 50 g chloroacetic acid, sodium salt ($CH_2ClCOONa$), and 25 g hydroxylamine hydrochloride ($NH_2OH \cdot HCl$).

Cyclohexanone-*o*-dichlorobenzene reagent: Mix 46 ml cyclohexanone, A.C.S. grade, with 50 ml *o*-dichlorobenzene, commercial grade.

4,5-dihydroxyfluorescein reagent, 0.02-percent: Dissolve 0.02 g in 50 ml 95-percent reagent-grade ethyl alcohol, heat to dissolve, and dilute to 100 ml with ethyl alcohol.

Hydrochloric acid-ethyl alcohol reagent: Mix 2*M* HCl with an equal volume of ethyl alcohol, A.C.S. grade.

Standard tin solution, 1,000 μg per ml: Dissolve 0.100 g tin metal in 50 ml hydrobromic acid, A.C.S. grade. Add 0.5 g potassium bromate ($KBrO_3$),

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swirl to bring about solution. If the color due to free bromine fades as the tin goes into solution, add another 0.5 g KBrO$_3$. Dilute to 100 ml with HBr.

Standard tin solution, 10 µg per ml: Dilute 1 ml standard solution (1,000 µg per ml) to 100 ml with metal-free water. Prepare fresh every 4 hrs.

Culture tubes, 16- by 150-mm, calibrated at 10 ml.

Scoops, 0.5- and 0.2-g.

Pipets:
  0.1-ml, calibrated in 0.01 ml.
  5-ml, calibrated in 0.1 ml.
  1.0-ml, volumetric.
  Automatic, two 5-ml, one 2-ml.

Spatula, small porcelain.

Sublimation tube, 180 mm in length and 10 mm in diameter, with a bulb 20 mm in diameter blown on one end.

PROCEDURE

1. Place 0.2 g sample with 0.5 g ammonium iodide in the bulb of the sublimation tube. Mix the contents by alternately rotating the tube and tapping it gently.
2. Heat the tube over a moderate flame until the mixture is quiescent, then let the tube and sample cool.
3. Add 5 ml hydrochloric acid–ethyl alcohol reagent.
4. Heat the tube very gently and swirl the contents until all of the sublimate is in solution. Do not allow the solution to boil.
5. Let the tube and contents stand for 15 min or until all of the undecomposed sample settles to the bottom of the bulb.
6. Transfer a 2-ml aliquot of the clear solution to a 16- by 150-mm test tube.
7. Add 5 ml buffer solution, heat gently over a flame until the solution is colorless. Do not boil.
8. If the sample has a high iron content, as is indicated by a pink solution, add another 2 ml buffer solution, and again heat the solution gently.
9. Cool the contents of the tube to 25°C, and dilute the solution to 10 ml.
10. Add 1 ml of 4,5-dihydroxyfluorescein reagent, and shake the tube 5 or 6 times to mix the contents.
11. Within 2 min., add 2 ml cyclohexanone-*o*-dichlorobenzene reagent, stopper the tube with a cork, and shake vigorously for 60 sec. Allow the phases to separate.
12. Compare the pink color produced in the unknowns with the standard series and calculate the tin concentration in the sample according to instructions on page 8.

Preparation of standards

To seven 16- by 150-mm test tubes, add, respectively, 0, 0.05, 0.1, 0.2, 0.4, 0.8, and 1.5 ml of the standard tin solution (10 µg per ml). This standard series will contain 0, 0.5, 1, 2, 4, 8, and 15 µg of tin. Add 5 ml buffer solution to each tube, dilute to 10 ml, and proceed from step 8 above.

DISCUSSION

The procedure has been used on samples containing cassiterite with results sufficiently accurate to indicate areas of tin mineralization. The procedure has been tried successfully on material containing 2 μg of tin in the presence of 10,000 μg of iron, 200 μg of antimony, 100 μg of titanium, or 100 μg of molybdenum and tungsten.

TITANIUM IN ROCKS

The rapid laboratory method described below for the determination of titanium depends on the reaction of Tiron (disodium-1,2-dihydroxybenzene-3, 5-disulfonate) to produce an intense yellow color with titanium in solution. The reagent was first applied to the determination of titanium by Yoe and Armstrong (1947).

The samples are digested with hydrofluoric acid and fused with potassium pyrosulfate. After solution of the fused mass with sulfuric acid, Tiron reagent is added to an aliquot of the sample solution and the pH is adjusted. A buffer solution is added to maintain the pH at 4.5, and a reducing agent is added to destroy the colored iron complex. The concentration of color due to titanium is determined photometrically at 410 mμ, and the titanium content of the sample is then calculated using a standard calibration curve.

The lower limit of detection is approximately 100 ppm titanium, and the method can be used for samples containing as much as 20 percent titanium.

REAGENTS AND APPARATUS

Sulfuric acid, 1.7*M*: Pour 100 ml conc. sulfuric acid into 1,000 ml water and mix.

Hydrofluoric acid, 48-percent, reagent-grade. (*CAUTION.* See p. 5.)

Ammonium hydroxide, conc., reagent-grade.

Potassium pyrosulfate ($K_2S_2O_7$), fused-powder, reagent-grade.

Sodium hydrosulfite ($Na_2S_2O_4 \cdot 2H_2O$), dry-powder, reagent-grade.

Tiron (disodium-1,2-dihydroxybenzene-3,5-disulfonate), dry-powder, reagent-grade.

Tiron solution, 4-percent: Dissolve 4 g Tiron in water and dilute to 100 ml with water.

Buffer solution: Dissolve 40 g ammonium acetate ($NH_4C_2H_3O_2$) in water, add 15 ml glacial acetic acid, and dilute to 1 liter with water. The pH of the buffer is approximately 4.5.

Standard titanium solution, 500 μg per ml: Weigh 3.68 g potassium titanium oxalate [$K_2TiO(C_2O_4)_2 \cdot 2H_2O$], into a 500-ml Kjeldahl flask, and add 8 g ammonium sulfate [$(NH_4)_2SO_4$], and 100 ml conc. H_2SO_4. Gradually heat to boiling and boil for 10 min. Cool and pour the solution into 700 to 800 ml water. After cooling, dilute to 1 liter with water.

Standard titanium solution, 10 μg per ml: To a 100-ml volumetric flask add 0.8 g ammonium sulfate [$(NH_4)_2SO_4$]; put into solution with 20 to 30 ml H_2O. Add 10 ml conc. H_2SO_4. Cool and add 2 ml standard titanium solution (500 μg per ml). Dilute to 100 ml with water.

Flask, Kjeldahl, 500-ml-capacity.

Platinum evaporating dishes, 50-ml-capacity.

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Tongs, platinum-tipped.
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Pipets:
  0.1-ml, graduated in 0.01 ml.
  1.0-ml, graduated in 0.1 ml.
  Volumetric, 1-, 2-, and 5-ml.
Cylinders, graduated, glass-stoppered, 25-ml.

PROCEDURE

1. Weigh 0.100 g sample and transfer it to a 50-ml platinum evaporating dish.
2. Moisten the sample with water and add about 10 ml hydrofluoric acid (48-percent) to the dish. Stir the contents of the dish with a platinum stirring rod.
3. Place the dish on a steam bath and evaporate the contents to dryness.
4. Remove the dish from the steam bath, add 1 g $K_2S_2O_7$ to the residue, and fuse over a burner.
5. Allow the dish to cool; then add about 20 ml H_2SO_4 (1.7*M*), and warm to dissolve the residue.
6. Transfer the sample solution from the platinum dish to a 100-ml volumetric flask. Rinse the dish with two 10-ml portions H_2SO_4 (1.7*M*), combining the washings with the sample solution in the volumetric flask. When cool, dilute the solution to volume with H_2SO_4 (1.7*M*) and mix well.
7. Transfer a suitable aliquot (1 or 2 ml) to a 25-ml glass-stoppered graduated cylinder and add 5 ml Tiron solution.
8. Adjust the pH to 5 to 7 by adding conc. NH_4OH dropwise. The color of the Tiron-iron complex will change from blue green to violet at this pH.
9. Add 15 ml acetate buffer, which serves to further adjust and maintain the pH at 4.5.
10. Dilute the solution to 25 ml with water, stopper, and mix.
11. Add 25 to 50 mg $Na_2S_2O_4 \cdot 2H_2O$ powder to the solution; then stopper and invert the cylinder once.
12. After 5 min., but before 15 min., transfer a portion of the solution to a cuvet and obtain the transmittancy at 410 mμ in a spectrophotometer.
13. Using the standard calibration curve, determine the titanium concentration corresponding to the transmittance of the solution, and calculate the titanium content of the sample.

Preparation of standard calibration curve

1. Transfer suitable aliquots containing 1 to 60 μg of titanium to 25-ml glass-stoppered graduated cylinders, using 1 additional cylinder, to which no titanium is added, for a reagent blank.
2. Add 5 ml Tiron solution to each cylinder and proceed with steps 8 through 12, above.
3. Prepare the standard calibration curve by plotting percentage transmittance versus titanium concentration on semilog graph paper or absorbance versus titanium concentration on linear graph paper.

DISCUSSION

The intensity of the yellow-colored Tiron-titanium complex is unchanged over the pH range 4.3 to 9.6 (Yoe and Armstrong, 1947). Interference due to iron is obviated by reduction of iron (III) to iron (II) and determination of titanium at pH 4.5 (Sandell, 1959). Chromium, copper, molybdenum, vanadium, and tungsten interfere by forming colored complexes with Tiron. Interference by certain other elements that consume reagent is largely overcome by using an excess of Tiron.

Although the color of the titanium complex is reported to remain stable for 2 weeks, more reproducible results are obtained if the transmittancy is determined within the prescribed time limit. Vigorous agitation of the solution after addition of sodium hydrosulfite is to be avoided, because the blue color of the ferric iron–Tiron complex may reappear as a result of oxidation by exposure to air.

TUNGSTEN IN SOILS

The method for the determination of tungsten in soils is given by Ward (1951a). The powdered sample is sintered with a modified carbonate flux in an ordinary test tube and the sinter is leached with hot water. An aliquot of leachate is treated with stannous chloride and potassium thiocyanate in nearly concentrated hydrochloric acid. The yellow tungsten thiocyanate, which forms rapidly at a temperature of 90° to 100°C, is extracted from the cool solution into a small volume of isopropyl ether. The ether separates as a shallow layer on top of the aqueous solution and permits ready detection of as little as 1 μg of tungsten or even less, depending on the volume of the extractant.

The carbonate fusion followed by an aqueous leach separates tungsten from iron, titanium, and other elements that form insoluble hydroxides. Large amounts of molybdenum interfere by extracting along with tungsten, but the amber-colored molybdenum thiocyanate can usually be bleached by increasing the hydrochloric acid concentration of the aqueous phase and shaking the tube as in the initial extraction. Rhenium reacts similarly to molybdenum, but it is rare and therefore can probably be ignored in most samples. As much as 1,000 μg of vanadium imparts no color to the organic layer.

REAGENTS AND APPARATUS

Flux: Mix by weight 5 parts of sodium carbonate (Na_2CO_3), 4 parts of sodium chloride ($NaCl$), and 1 part of potassium nitrate (KNO_3); grind the mixture to pass an 80-mesh sieve.

Hydrochloric acid, conc., reagent-grade.

Isopropyl ether: Practical grade is suitable provided peroxides are absent. (See p. 5.) Immediately before use, shake the ether with one-tenth its

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volume of equal parts of potassium thiocyanate (KSCN) solution and a stannous chloride ($SnCl_2 \cdot 2H_2O$) solution in approximately 2*M* HCl.

Potassium thiocyanate solution, 25-percent: Dissolve 25 g KSCN in 100 ml water.

Standard tungsten solution, 100 μg per ml: Dissolve 0.09 g sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$) in water and dilute to 500 ml.

Standard tungsten solution, 10 μg per ml: Dilute 10 ml standard solution (100 μg per ml) to 100 ml with water. Prepare fresh daily.

Stannous chloride solution, 10-percent: Dissolve 10 g $SnCl_2 \cdot 2H_2O$ in 100 ml conc. HCl.

Scoop, 0.25-g.

Mortar and pestle.

Pipet, 1-ml and 5-ml, graduated in 0.1 ml.

Culture tubes, 16- by 150-mm.

PROCEDURE

1. Mix 0.25 g sample with 1.25 g flux in a 16- by 150-mm culture tube, and sinter.
2. Cool tube, add 5 ml water, and place in boiling-water bath.
3. Use stirring rod to break up sinter, and then remove tube from water bath. Cool.
4. Transfer a 1-ml aliquot of supernatant liquid to another culture tube calibrated at 5 ml. Add water to mark.
5. Add 4 ml $SnCl_2$ and 0.5 ml KSCN, shaking tube after each addition.
6. Place tube in boiling-water bath for about 5 min or until H_2S evolves moderately.
7. Remove tube from bath, cool, and add 0.5 ml KSCN and 0.5 ml isopropyl ether. Stopper tube and shake it vigorously.
8. Compare the tungsten thiocyanate color in the ether layer with color of standards.
9. Calculate the tungsten concentration in the sample according to instructions on page 8.

Preparation of standards

To a series of 6 culture tubes add the following amounts of the tungsten standard (10 μg per ml): none to first tube, 0.1 ml to second tube, 0.4, 0.8, 1.5, and 3.0 ml, respectively, to the remaining tubes. This standard series will contain 0, 1, 4, 8, 15, and 30 μg tungsten. Dilute standards to 5 ml with water and proceed with step 5 above.

URANIUM IN SOILS AND ROCKS

The method described below for the determination of uranium was developed by Hunt and others (1955) and afterward was modified for use in dry climates by Thompson and Lakin (1957). It depends upon the separation of uranium by means of paper chromatography and the estimation of the amount of uranium present from the appearance of the colored uranium ferrocyanide complex on the paper. The sample is digested with a 4*M* nitric acid solution containing aluminum nitrate. Microaliquots of this solution are placed on CRL/1 chromatographic paper and dried.

The separation of the uranium is accomplished with a mixture of ethyl acetate, nitric acid, and water. As the ethyl acetate mixture moves upward through the paper, the uranyl nitrate in the aliquot moves with the solvent front away from the other ions, which remain where the aliquot was placed. After the separation, the paper is dried and sprayed with a solution of potassium ferrocyanide to produce a band of brown uranium ferrocyanide. Because the width of the band and the intensity of its color are proportional to the amount of uranium present, the band is compared in those respects with standard bands previously prepared. The suggested procedure is applicable to samples containing 4 to 1,200 ppm uranium. By means of the proposed method, the uranium in 60 samples of soils and sedimentary rocks can be determined in an 8-hour day by using inexpensive and easily obtainable reagents and equipment.

REAGENTS AND APPARATUS

Nitric acid, conc.
Nitric acid–aluminum nitrate solution: Dissolve 60 g aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] in 100 ml 4*M* HNO_3.
Standard uranium solution, 1,000 μg per ml: Dissolve 0.211 g uranyl nitrate hexahydrate [$UO_2(NO_3)_2 \cdot 6H_2O$] in 100 ml nitric acid–aluminum nitrate solution.
Ethyl acetate.
Solvent mixture: Place 30 ml ethyl acetate, 3.5 ml conc. HNO_3, and 10 ml water in a 600-ml beaker, cover beaker with a watchglass, and let stand for 20 min before using.
Aluminum nitrate, crystalline.
Hydrofluoric acid, 48-percent.
Potassium ferrocyanide solution [$K_4Fe(CN)_6 \cdot 3H_2O$], 5-percent: Dissolve 5 g $K_4Fe(CN)_6 \cdot 3H_2O$ in 100 ml water.
Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$], crystalline.
Chromatographic paper, Whatman CRL/1.
Ignition tubes, 16- by 125-mm.
Cylinders, graduated, 50- and 10-ml.
Beakers, 600-ml.
Dishes:
    Platinum, 50-ml.
    Porcelain, 50-ml.
Stirring rod, plastic.
Watchglasses, 125-mm-diameter.
Bottle or atomizer for indicator spray.
Scoop, 1-g.
Flasks, volumetric, 250- and 10-ml.
Pipets:
    Serological, 0.1- and 1-ml, graduated.
    Micro, 0.01- and 0.05-ml.
    Volumetric, 1- and 2-ml.
Desiccator, inside diameter 150-mm.

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PROCEDURE

1. Weigh or scoop 1 g sample and transfer it to a 16- by 125-mm ignition tube. For samples containing more than 1,200 ppm uranium, 0.1 g can be used.
2. Add 2 ml $HNO_3 \cdot Al(NO_3)_3$ solution and digest the sample for 1 hr in a boiling water bath. Either centrifuge the sample or allow sufficient time for the insoluble residue to settle.
3. With a micropipet withdraw an appropriate aliquot (0.01 or 0.05 ml) of the supernatant sample solution; starting about 1.5 cm from the bottom of one of the strips on a sheet of Whatman CRL/1 chromatographic paper, spread the aliquot evenly across the strip. Follow the same procedure to place 10 sample aliquots on each sheet of paper, using the same size aliquot on all the strips of any one sheet.
4. Fasten the top corners of the paper together with a paper clip to form a cylinder, place upright in a desiccator containing satd. $Mg(NO_3)_2$ solution and leave for at least 30 min.
5. After the aliquots have dried, remove paper cylinder from desiccator and place cylinder upright (with the aliquots at the bottom) in the 600-ml beaker containing the solvent mixture.
6. Leave the paper cylinder in the beaker until the solvent front has risen at least 2 cm above the area wetted by the sample aliquot, but not above the top of the slit.
7. Remove the paper from the beaker, unfold, allow the ethyl acetate (solvent mixture) to evaporate, and spray the chromatogram with $K_4Fe(CN)_6$ reagent.
8. Compare the brown ferrocyanide complex of uranium with a standard uranium chromatogram.
9. Calculate the uranium concentration in the sample according to instructions on page 8.

Preparation of standards

1. Prepare dilute uranium standard solutions by adding 0.1, 0.2, 0.4, 0.8, 1.5, 3, and 6 ml, respectively, of standard uranium solution (1,000 μg per ml) to a series of 10-ml volumetric flasks—0.1 ml to the first flask, 0.2 ml to the second flask, and relative amounts to the remaining flasks—and making volume up to mark with $HNO_3 \cdot Al(NO_3)_3$ reagent.
2. Place 0.01-ml aliquots from the dilute standard uranium solutions on chromatographic paper, one aliquot from one standard solution to each strip, and allow to dry one-half hour in desiccator.
3. Place paper in solvent and continue as with samples.
4. These standard bands contain, respectively, 0.1, 0.2, 0.4, 0.8, 1.5, 3.0, and 6.0 μg of uranium.

DISCUSSION

Samples that contain a large amount of organic material should be ignited in a porcelain dish for about 15 minutes prior to sample digestion. Otherwise large amounts of organic material produce a yellow color at the solvent front and interfere with the estimation.

Dilute nitric acid alone does not extract all of the uranium from resistant minerals, especially if the element is in the silicate lattice. A hydrofluoric–nitric acid digestion is preferable with such minerals.

The drying of the aliquot after it has been placed on the chromatographic paper is important. If the aliquot is not dried properly, the bands will not be uniform and the amount of uranium present will be difficult to estimate. The desiccator containing the saturated magnesium nitrate has the correct humidity at room temperature for drying the chromatograms.

Aluminum nitrate is added to the nitric acid digesting solution to prevent the interference of anions, especially phosphate. Because of changes in composition, the solvent mixture is satisfactory to use for a maximum of about 3 hours only, or for no more than 5 sheets of paper. The chromatograms need not be sprayed immediately. They should be compared with standards as soon as possible after spraying, however, because the excess potassium ferrocyanide solution sprayed on the chromatogram is oxidized by air to a yellowish blue color that overshadows the brown of the uranium complex.

URANIUM IN NATURAL WATERS

The method for the determination of uranium in natural waters is fully described by Ward and Marranzino (1957). The procedure eliminates the necessity for transporting bulky water samples from field to laboratory and the time-consuming evaporation of samples preliminary to analysis. Under field conditions, the uranium is separated from a water sample by means of a phosphate collector and, after a paper-chromatographic separation, is determined by reaction with ferrocyanide.

The method was tested under field conditions in Karnes County, Tex., where the area of uranium mineralization was detected by determining the uranium content of the streams.

REAGENTS AND APPARATUS

Ammonium hydroxide, conc., reagent-grade.

Ethylenediaminetetraacetic acid, disodium salt (EDTA), 5-percent-aqueous.

Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$], reagent-grade: A saturated aqueous solution is used as the desiccant for drying aliquots from sample and standard solutions.

Nitric acid, specific gravity 1.42, reagent-grade.

Nitric acid–aluminum nitrate reagent: Dissolve 80 g [$Al(NO_3)_3 \cdot 9H_2O$], reagent-grade, in mixture of 25 ml conc. HNO_3 and 75 ml water.

Potassium ferrocyanide [$K_4Fe(CN)_6 \cdot 3H_2O$], 5-percent-aqueous.

Phosphate reagent: ($Na_2HPO_4 \cdot 12H_2O$), saturated aqueous solution.

Solvent mixture: To a clean dry 600-ml beaker, add in this order:—30 ml reagent-grade ethyl acetate, 6 ml conc. HNO_3, and 0.5 ml water. Swirl to obtain clear solution and cover. The mixture can be used immediately, and it is good for 4 to 5 chromatograms or 4 hrs, whichever involves the shorter time.

Standard uranium solution 1,000 μg per ml: Dissolve 0.211 g uranyl nitrate [$UO_2(NO_3)_2 \cdot 6H_2O$] in 100 ml of $HNO_3 \cdot Al(NO_3)_3$ reagent.

Atomizer.

Beaker, 600-ml.

Crucibles, porcelain No. 0, high-form.

Desiccators, 150 mm in diameter: For efficient operation 2 or more are required, 1 for standards and 1 for samples.

Filter apparatus (see fig. 8): To assemble, connect Tygon tubing *b* with inverted vial *d*. Drop into *b* a circular piece of filter paper 2.5 cm in diameter so that it covers the small holes in *d*. Prepare in water a slurry with one ashless tablet. Pour slurry into plastic cylinder *b*; pulp *c* will collect on filter paper.

Paper, filter, qualitative such as Whatman No. 1, cut in 2½-cm circles for retention of paper pulp in filter apparatus described above.

Paper tablets, ashless, such as Whatman.

Paper, Whatman CRL/1 chromatographic: Ten chromatograms can be made on each sheet.

Micropipets, 0.01-ml and 0.02-ml.

Pipet, 10-ml, graduated, calibrated in 0.1 ml.

pH test paper, long range for pH 1 to 6 and short range for pH 5.8 to 6.2.

PROCEDURE

1. Pour a 500-ml sample of natural water into a 600-ml beaker. Add 2 ml conc. HNO_3.
2. Add conc. NH_4OH dropwise until the pH is 2.5.
3. Add phosphate reagent until the pH is 5.9 to 6.1. If a precipitate forms with the addition of phosphate, add EDTA solution dropwise while stirring the sample solution until the precipitate redissolves, and then titrate the sample solution drop by drop, alternately, first with phosphate reagent and then with EDTA until the pH is 5.9 to 6.1.
4. Pour into polyethylene bottle *a*; attach bottle *a* to prepared filter apparatus (*b* connected with *d*).
5. Suspend *a* and remove cork from bottom so that water filters through paper pulp *c*. When filtration is complete, remove bottle *a* from rest of apparatus. (If determination is not to be made immediately, stopper tube *b* with stopper *e*.)
6. For immediate determination, transfer the paper pulp together with the filter paper to a porcelain crucible. Add 4 to 5 drops of conc. HNO_3 and dry on hotplate.
7. Heat over open flame until only a white ash remains. Cool.
8. Add 0.5 ml conc. HNO_3 to the ash, heat gently to dryness, and ignite to expel nitric oxide fumes. Cool.
9. Repeat the addition of conc. HNO_3. Police the sides of the crucible with a small glass stirring rod and evaporate the liquid in the crucible to dryness.
10. Dissolve all residue in the cool crucible in 0.2 ml $HNO_3 \cdot Al(NO_3)_3$ reagent and warm gently for 20 sec. Avoid boiling.
11. Transfer a 0.02-ml aliquot of the warm sample solution to a strip of the chromatographic paper approximately three-fourths inch from the edge of the sheet. (Do not use the end strips.)
12. Fashion the sheet into a cylinder with the strips in vertical position and fasten at corner with a paper clip.

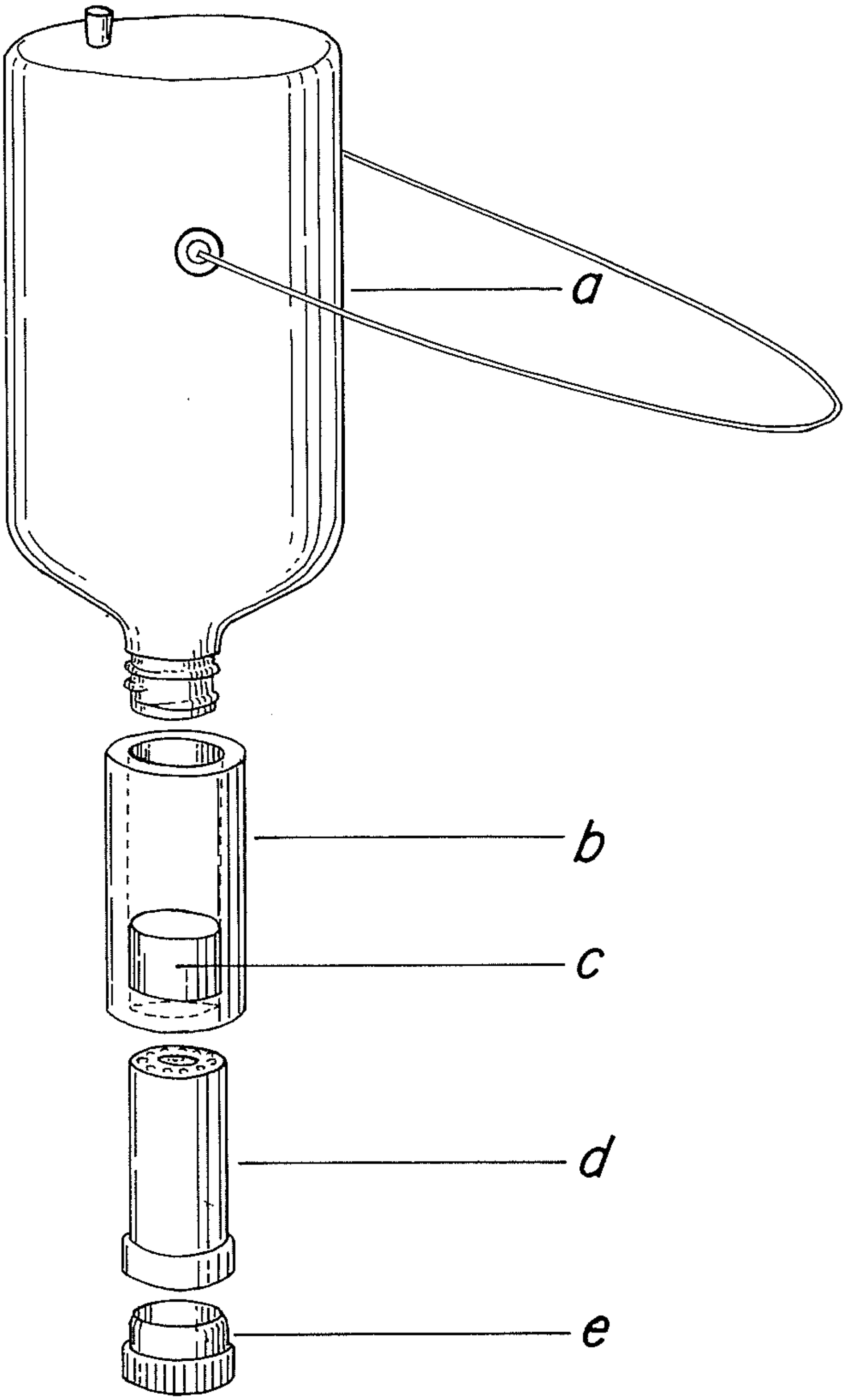

FIGURE 8.—Filter apparatus used for the determination of uranium in natural waters. *a*, polyethylene bottle, 16-oz. capacity, with small hole in the bottom which is stoppered with a cork; *b*, Tygon tubing of proper dimension to fit closely over the neck of bottle *a*; *c*, paper pulp; *d*, plastic vial, with holes drilled in the bottom and of a size to fit securely into the Tygon tubing; *e*, stopper of proper size to fit plastic vial and the Tygon tubing.

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13. Store the sheet in a desiccator over a saturated $Mg(NO_3)_2$ solution for at least 30 min.
14. Remove paper from desiccator and place lower end of the paper in the solvent mixture. Allow solvent to rise through the dried sample aliquot to within 1 inch of the top of the paper.
15. Remove strip from solvent, dry, and spray both sides of the paper with $K_4Fe(CN)_6$ reagent.
16. Compare chromatograms of samples with those of matching standard solutions to determine uranium content of aliquot.
17. Multiply by 20 the uranium content of the standard chromatogram, or by estimated value between bands, in order to convert to parts per billion (1 ppb = 0.001 ppm) in original sample.

Preparation of standards

1. Prepare dilute uranium standard solutions by adding 0.1, 0.2, 0.4, 0.8, 1.5, 3, and 6 ml, respectively, of standard solution, 1,000 μg per ml, to a series of 10-ml volumetric flasks—0.1 ml to the first flask, 0.2 ml to the second flask and relative amounts to the remaining flasks,—and making volume up to mark with $HNO_3 \cdot Al(NO_3)_3$ reagent.
2. Place 0.01-ml aliquots from the dilute standard uranium solutions on chromatographic paper, one aliquot from one standard solution to each strip, and allow to dry one-half hour in desiccator.
3. Place paper in solvent and continue as with samples.
4. These standard bands contain, respectively, 0.1, 0.2, 0.4, 0.8, 1.5, 3.0, and 6.0 μg of uranium.

DISCUSSION

Certain mine waters and saline waters tend to give low values. This is due in part to the abundance of the dissolved salts present in the waters that are collected by either the phosphate or by the paper pulp. Muddy water should be allowed to settle before a 500-ml portion is used; otherwise, the mud will collect on the filter-paper pad and will interfere with the ignition of the paper.

URANIUM IN VEGETATION

A modification of a paper-chromatographic method (Hunt, North, and Wells, 1955) permits the rapid determination of uranium in ashed vegetation. The ash of the plant sample is dissolved in concentrated nitric acid and evaporated to dryness; the residue is dissolved in dilute nitric acid and the uranium extracted with ethyl acetate. The ethyl acetate extract is burned, the small residue dissolved in dilute nitric acid–aluminum nitrate reagent, and the uranium determined by its reaction with ferrocyanide after a paper chromatographic separation. (A. P. Marranzino, written communication, 1959.)

The procedure was field tested at a prospect near Marshall Pass, Colo., where the values obtained by analysis of the vegetation indicated the presence of uranium mineralization.

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REAGENTS AND APPARATUS

Aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$], reagent-grade.
Ethyl acetate, reagent-grade.
Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$], reagent-grade.
Nitric acid, conc., specific gravity 1.42, reagent-grade.
Nitric acid, $0.5M$: Mix together 8 volumes of conc. HNO_3 and 92 volumes of water.
Nitric acid–aluminum nitrate reagent: Add 25 ml conc. HNO_3 to 75 ml water and dissolve 80 g $Al(NO_3)_3 \cdot 9H_2O$ in the solution.
Potassium ferrocyanide [$K_4Fe(CN)_6$], 5-percent, aqueous.
Solvent mixture: In this order, put into a clean dry 600-ml beaker 30 ml ethyl acetate, 6 ml conc. HNO_3, and 0.5 ml water. Swirl to obtain a clear solution, and cover. This solution is good for 4 hr or 4 chromatograms, whichever involves the shorter time.
Standard uranium solution, 1,000 μg per ml: Dissolve 0.211 g uranyl nitrate [$UO_2(NO_3)_2 \cdot 6H_2O$] in 100 ml $HNO_3 \cdot Al(NO_3)_3$ reagent.
Atomizer.
Crucibles, porcelain No. 0, high form.
Desiccator, 150 mm in diameter.
Evaporating dishes, porcelain No. 00A, and No. 3.
Flasks, volumetric, 10-ml.
Funnels, separatory, 60-ml.
Paper, chromatographic, Whatman CRL/1.
Micropipets, capacity 0.01 and 0.02 ml.
Measuring pipet, calibrated in 0.1 ml.

PROCEDURE

1. Weight 1 g of ash into a No. 00A porcelain evaporating dish. (For procedure see page 8.
2. Add 2 to 3 drops water and 5 ml conc. HNO_3, mix contents, and evaporate to dryness.
3. Add 5 ml HNO_3 ($0.5M$) and 9.5 g $Al(NO_3)_3 \cdot 9H_2O$. Heat gently to effect solution.
4. Transfer the solution to a 60-ml separatory funnel; with 1 ml of $0.5M$ nitric acid, wash any residue from the evaporating dish into the separatory funnel.
5. Add 10 ml ethyl acetate, shake approximately 60 sec, allow the phases to separate, and discard the aqueous phase.
6. Decant the ethyl acetate extract into a No. 0 porcelain crucible, ignite, and burn to dryness.
7. Cool the crucible, add 0.3 to 0.4 ml conc. HNO_3. Police the crucible with a small glass rod, and evaporate the acid solution to dryness.
8. Cool the crucible, add 0.2 ml $HNO_3 \cdot Al(NO_3)_3$ reagent, and dissolve all of the residue by heating gently for approximately 20 sec. Avoid boiling.
9. Transfer a 0.02-ml aliquot of the warmed solution to one of the strips on a sheet of Whatman CRL/1 chromatographic paper approximately ¾ inch from the edge of the sheet. (Do not use the end strips.)
10. Fashion the sheet into a cylinder with the strips in vertical position and fasten at corner with a paper clip.
11. To dry, place the sheet in a desiccator over a satd. solution of $Mg(NO_3)_2$ for at least 30 min.

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12. Remove the sheet from the desiccator and immerse the aliquot end in the solvent mixture previously prepared in the 600-ml beaker and replace cover on beaker.
13. Allow the solvent to rise through the dried aliquot to within 1 inch of the top of the slotted paper.
14. Remove the paper from the solvent and dry. Spray the solvent area lightly on both sides of the paper with $K_4Fe(CN)_6$ reagent.
15. To determine the uranium content of the aliquot, compare the bands from samples with those from standard solutions.
16. Calculate the uranium concentration in the ash according to instructions on page 8, using ash weight instead of sample weight.

Preparation of standards

1. Prepare a series of dilute standard uranium solutions by adding 0.1, 0.2, 0.4, and 0.8 ml, respectively, of the standard uranium solution (1,000 μg per ml) to 1-ml volumetric flasks—0.1 ml to the first flask, 0.2 ml to the second flask and relative amounts to the remaining flasks, making volume up to the mark with $HNO_3 \cdot Al(NO_3)_3$ reagent.
2. Place a 0.01-ml aliquot of each of the standard solutions containing respectively, 10, 20, 40, and 80 μg per ml, on a strip of a chromatographic sheet, one aliquot to a strip.
3. Dry the sheet in a desiccator for at least 30 min and continue as described above.

DISCUSSION

Field determination by a paper chromatographic method offers distinct advantages over others: (a) the same reagents and apparatus are used as for the field estimation of uranium in soils and rocks (Thompson and Lakin, 1957) and in waters (Ward and Marranzino, 1957); (b) the apparatus is portable, inexpensive, simple to use, and independent of electrical power; and (c) the estimation is not affected by contaminants frequently found in plant ash. In the procedure, all of the uranium and many of the leached metals are extracted into the ethyl acetate (Grimaldi, and others, 1954). Since the final estimation of the uranium content is determined chromatographically, contaminants such as iron, vanadium, niobium, and other elements offer no interference, and therefore preliminary removal of these elements is not necessary.

VANADIUM IN SOILS AND ROCKS, PHOSPHOTUNGSTATE METHOD

The method described for vanadium is based on a reaction first used for the determination of vanadium by Willard and Young (1928), in which yellow phosphotungstovanadic acid is formed when phosphoric acid and sodium tungstate are added to an acid solution containing vanadium.

The samples are fused with an acid flux, and the melt is digested with hydrochloric or nitric acid. A portion of the sample solution is further acidified with nitric acid and boiled, then phosphoric acid and sodium tungstate are added. The solution is heated to hasten color development, and the colors obtained are compared visually with standard solutions to estimate the vanadium concentration.

Most vanadium minerals yield readily to the acid attack (Hillebrand and others, 1953). The sodium tungstate concentration and the phosphoric acid concentration may be varied within rather wide limits (Sandell, 1959). Standard solutions will remain stable for about 1 week. The lower limit of detection is approximately 50 ppm vanadium, and the method can be used for samples containing as much as 20 percent vanadium. One person can analyze approximately 100 samples per day for vanadium.

REAGENTS AND APPARATUS

Potassium pyrosulfate ($K_2S_2O_7$), fused-powder, reagent-grade.
Phosphoric acid H_3PO_4, 85-percent, reagent-grade.
Nitric acid, conc., reagent-grade.
Nitric acid, 4*M*: Dilute 250 ml of conc. HNO_3 to 1 liter with water.
Sodium tungstate solution, 5-percent: Dissolve 5 g sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) in water and dilute to 100 ml with water.
Standard vanadium solution, 100 μg per ml: Dissolve 0.2295 g reagent-grade ammonium metavanadate (NH_4VO_3) in a solution containing 30 ml 4*M* HNO_3 and about 100 ml water. When the salt is dissolved, dilute the solution to 1 liter with water and mix well before using.
Culture tubes, 16- by 150-mm.
Pipets:
  0.1-ml, graduated in 0.01 ml.
  1.0-ml, graduated in 0.1 ml.
  10-ml, graduated in 0.1 ml.
  Volumetric, 1-, 2-, and 5-ml.

PROCEDURE

1. Weigh or scoop 0.1 g sample and transfer it to a dry 16- by 150-mm culture tube.
2. Add 0.5 g $K_2S_2O_7$ flux, and alternately rotate and tap the tube to mix the sample and flux.
3. Heat over the flame of a laboratory burner or gasoline stove, and continue heating for 2 to 3 min after the flux is molten.
4. Remove the tube from the flame and rotate the tube so that the melt will cool in a thin film on the side.
5. When the tube is cool, add 3 ml 4*M* HNO_3 and place the tube in a boiling water bath until the melt is reduced to a fine powder.
6. Remove the tubes from the water bath and, when cool, dilute the sample solution to 10 ml with water. Stopper the culture tube with cork or thumb and shake to mix; allow the residue to settle.

7. Transfer a suitable aliquot (usually 2 ml) to a clean 16- by 150-mm culture tube.
8. To the aliquot add 1 ml conc. HNO_3 and boil for approximately 5 sec.
9. Add 0.3 ml conc. H_3PO_4 and 2 ml sodium tungstate solution (5 percent).
10. Dilute the solution to 10 ml with water; stopper the culture tube and shake to mix.
11. Place the culture tube in a boiling water bath for 10 min.
12. Remove the tube from the water bath and estimate the vanadium concentration of the solution in micrograms by visually comparing the color obtained with the color of the most nearly matching vanadium standard solution.
13. Calculate the vanadium concentration in the sample according to instructions on page 8.

Preparation of standards

1. Transfer, respectively, 0, 0.03, 0.05, 0.1, 0.2, 0.4, and 0.8 ml of standard vanadium solution (100 μg per ml) to seven 16- by 150-mm culture tubes. This standard series will consist of 0, 3, 5, 10, 20, 40, and 80 μg of vanadium.
2. To each of the 7 culture tubes add 1 ml conc. HNO_3 and bring each solution to a boil for approximately 5 sec.
3. Add 0.3 ml conc. H_3PO_4 and 2 ml sodium tungstate (5 percent) to each tube.
4. Dilute each solution to 10 ml with water; stopper each culture tube and shake to mix.
5. Place the tubes in a boiling water bath for 10 min.
6. Remove the tubes from the water bath and, when cool, place a cork stopper in each tube to avoid evaporation.

DISCUSSION

Most of the common reducing ions are expelled or oxidized in the pyrosulfate fusion or when the sample is boiled with nitric acid. Molybdenum forms a colored complex with the phosphotungstic acid, but only when present in relatively large concentrations (Wright and Mellon, 1937). Iron interference is obviated by formation of the colorless complex with phosphoric acid. The most important source of interference in the method is from colored ions; of these, however, only chromium is likely to occur in sufficient quantities to produce an interfering color.

VANADIUM IN ROCKS, THIOCYANATE METHOD

A chance observation made during the study of a niobium procedure (Ward and Marranzino, 1955) suggested a method that seemed promising as a means for rapid field determination of small amounts of vanadium. It was observed that when vanadium, in 9*M* sulfuric acid, was reduced by stannous chloride in the presence of citrate and ethylenediaminetetraacetic acid (EDTA), the lower valence form reacted with thiocyanate to produce a yellow ether-extractable complex ion. The reacting form is presumably vanadium (III), because the yellow color of the solution is unlike that of solutions of other valence forms that might be produced during the reduction (Ward and Marranzino, 1953; Lovering and others, 1956).

The method was tested under field conditions in the southern Black Hills of South Dakota. Although the testing was limited and results may be different in areas of different geology, the coincidence of radioactivity anomalies with abnormal concentrations of vanadium suggests that this method for determination of vanadium may be useful in locating mineralized zones.

REAGENTS AND APPARATUS

Ethyl ether, reagent-quality. (*CAUTION*. See p. 5.) Before use, shake 100 ml ethyl ether with 5 ml $SnCl_2$ reagent.

Ethylenediaminetetraacetic acid, disodium salt (EDTA) solution, 2-percent: Dissolve 2 g of the salt in 100 ml water.

Potassium thiocyanate solution, 20-percent: Dissolve 20 g potassium thiocyanate (KSCN) in 100 ml water. This solution must be prepared fresh daily.

Sodium citrate solution, 10-percent: Dissolve 10 g sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) in 100 ml water.

Sodium hydroxide, 2.5*M*: Dissolve 10 g sodium hydroxide (NaOH) in 100 ml water.

Standard vanadium solution, 1,000 μg per ml: Dissolve 1.785 g pure vanadium pentoxide (V_2O_5) that has been previously ignited at 500°C in 20 ml 2.5*M* NaOH. Neutralize with 9*M* H_2SO_4, add 28 ml conc. H_2SO_4, and dilute to 1 liter with water.

Standard vanadium solution, 100 μg per ml: With water dilute 10 ml standard solution (1,000 μg per ml) to 100 ml.

Stannous chloride reagent: Dissolve 15 g stannous chloride ($SnCl_2 \cdot 2H_2O$) in 100 ml conc. HCl. Prepare this solution every other day.

Sulfuric acid, 9*M*: Add conc. H_2SO_4 to an equal volume of water.

Culture tubes, 16- by 150-mm.

Scoop, 0.1-g.

Pipets:
  Automatic, 2- and 5-ml.
  1-ml, graduated in 0.1 ml.
  10-ml, graduated in 0.1 ml.

PROCEDURE

1. To a 16- by 150-mm culture tube, add 0.1 g sample and 1 ml 9*M* H_2SO_4; heat until the mixture begins to boil vigorously. (If the soil or rock sample contains appreciable amounts of organic matter, prolong the acid digestion by allowing the boiling to continue about 20 sec.)
2. Remove tube from heat and allow to cool.
3. Add, shaking tube after each addition, 4 ml sodium citrate solution, 2 ml EDTA solution, and 3 ml $SnCl_2$ reagent.
4. Cool contents of tube and add 2 ml KSCN solution. Shake tube.
5. Cool, add 2 ml ethyl ether; stopper the tube with a cork and shake tube for 20 sec. (If a brown scum collects in the ether layer, the scum probably

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is a result of residual organic matter; add 1 to 2 ml of water to test tube. *Do not shake tube.* The ether layer will rise into a clear part of the tube, and thus separate from the scum.)

6. Compare color intensity with either artificial standards prepared previously, or with vanadium standards prepared as shown below.
7. Calculate the vanadium concentration in the sample according to instructions on page ....

Preparation of standards

Label eight 16- by 150-mm test tubes respectively in the sequence of letters *a* through *h*, and add, to each, 1 ml 9*M* H_2SO_4. To each tube add the appropriate amount of vanadium from standard solutions (1,000 μg per ml or 100 μg per ml) as shown below; then follow steps 3, 4, and 5 of procedure.

Standard	Volume of standard solution		Vanadium content	
	Milliliters	Standard solution —	Micrograms	Percent[1]
a	0		0	0
b	0.3	100 μg per ml	30	.03
c	.6	do	60	.06
d	1.5	do	150	.15
e	.3	1000 μg per ml	300	.3
f	.5	do	500	.5
g	1.0	do	1,000	1.0
h	2.0	do	2,000	2.0

[1] Corresponding to 0.1-g sample.

DISCUSSION

Molybdenum, tungsten, niobium, and uranium are possible sources of interference because they react with thiocyanate to form colored compounds extractible with ether. Under the conditions of the test for vanadium, however, the amber color of the molybdenum thiocyanate will fade within half an hour, and the vanadium content may be estimated at that time. In the presence of citrate, small quantities of tungsten are sufficiently complexed to prevent interference. Niobium, if present, interferes. Although uranium (VI) reacts with thiocyanate to form a yellow complex similar to that of vanadium (III), uranium is not considered to be a serious source of interference because only a small quantity of uranium thiocyanate is extracted by the ether.

SPECTROGRAPHIC ANALYSIS FOR USE IN GEOCHEMICAL EXPLORATION

The following method is useful for determining simultaneously 34 elements on a single sample of rock, soil, or mineral. It is modified from an earlier semiquantatative procedure (Myers, Canney, and Dunton, 1956). The modification consists of capping

TABLE 5.—*Compounds and concentration range used in synthetic standards*

Standard	Percent	Elements	Compound	Matrix[1]
1	1.0–0.0001	Cu, Zn, Pb, Co, Ni, Mn, and Zr.	CuO, NiO, Co_3O_4, PbO, ZrO_2, Mn_3O_4, ZnO.	6:4:0.1 ratio of quartz, microcline, and iron oxide.
2	1.0–0.0001	V, Mo, Sn, Y, Cr, and Sc.	V_2O_5, Cr_2O_3, Y_2O_3, MoO_3, SnO_2, Sc_2O_3.	Do.
3	1.0–0.0001	Ge, Ag, Be, Ga, Sr and Ba.	GeO_2, Ag_2O, BeO, Ga_2O_3, $SrCO_3$, $BaCO_3$.	6:4:0.1 ratio of quartz, perthite, and iron oxide.
4	1.0–0.001	B, Ti, As, La, and Tl.	H_3BO_3, TiO_2, As_2O_3, La_2O_3, Tl_2O_3.	Do.
5	1.0–0.001	Cd, Bi, In, Sb, and Tl.	CdO, Bi_2O_3, Sb_2O_4, In_2O_3, Tl_2O_3.	Do.
6	10.0–0.01	U	U_3O_8	Do.
7	1.0–0.001	Nb, Ta	Ta_2O_5, Nb_2O_5	Do.
8	10.0–0.001	Mg	MgO	Do.
9	10.0–0.01	Fe	Fe_2O_3	9.117 g quartz, 0.884 g Al_2O_3, and 0.1 g of Co_3O_4.
10	20.0–0.01	Si	SiO_2	8.8 g Al_2O_3, 1.0 g Na_2CO_3, and 0.2 g Fe_2O_3.

[1] The matrix may contain different kinds of quartz, microcline, or perthite, depending on the trace-element content.

the sample-graphite mixture advocated in the earlier procedure with 20 mg of a 1:5 mixture of calcium carbonate and graphite. This addition promotes a smoother burning arc which minimizes sample loss and results in better precision.

The sensitivity obtained under average conditions is given in table 1 of this compilation.

PREPARATION OF STANDARD POWDERS

The standard mixtures were prepared from spectrographically pure chemical compounds in a matrix whose composition approximates that of the material being analyzed. Geologic materials vary widely in composition, and a single matrix is not universally applicable. At the expense of a small amount of accuracy a matrix with a composition resembling that of an average granite can be used for most of the applications of this method. Thus, the 10 series of standard mixtures described in table 5 are prepared in a matrix resembling granite. This matrix is essentially the same as that described by Gordon and Murata (1952) and by Bastron, Barnett, and Murata (1960).

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concentrated standard mixture—1 percent, except for mixtures Nos. 6, 8, 9, and 10—with the specified matrix to prepare a series of standards for the different orders of magnitude suggested as a useful concentration range. The concentration in each order of magnitude differs by a common factor, the cube root of 10 in these series. Thus, the series of standards for cobalt would contain respectively the following amounts of the element: the first standard, 1 percent; the second standard, 0.464 percent; the third, 0.215 percent, and so forth. These numbers are rounded off respectively to 1, 0.5, 0.2, and 0.1. The ranges within an order of magnitude are 1.0 to 0.5, 0.5 to 0.2, and 0.2 to 0.1. In practice, the logarithmic midpoints of these ranges are calculated, rounded off similarly; the concentration of an element is always reported with one of the following numbers: 1.0, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1. Thus, the reported value for the concentration of a given element will always be one of these numbers expressed as a power of 10 depending on the relative concentration of the element.

The blackness of a line is a logarithmic function of the quantity of the element producing the line, and the voluntary assignment of numbers to the midpoints of the above concentration ranges is not valid; nevertheless, because the differences between the assigned number and the actual value are small, the former numbers are used as convenient approximations in geochemical exploration.

EQUIPMENT AND OPERATING CONDITIONS

Spectrograph: A 1.5-meter Wadsworth-mounted grating spectograph, fixed position, with dispersion of 5.4 A per mm over the spectral range from 2,060 to 4,840 A in the second order.
Slit width, 20 $m\mu$.
Intensity control: Rotating sector 15 percent with 18-percent quartz filter.
Source: Direct current with open-circuit potential of 230 v from 5-kw 230-v d-c motor generator with maximum arc-current output of 18 amp. Resistances in series are used to control and limit the arc current.
Upper electrode: Graphite rod, ⅛ inch in diameter and 1.5 inches long.
Lower electrode: Preformed electrode, ¼ inch in diameter with thin-walled cavity.
Exposure: Burned to completion for 120 sec.
Emulsion, 35-mm film, type 3–0.
Processing: Films are developed in D–19 developer for 3.5 min at 20°C, fixed, washed in running water for 5 min, and air dried.
Photometry: Comparator with 20 × magnification.

ANALYTICAL PROCEDURE

1. The sample to be analyzed is reduced to a dry powder equivalent to minus-200 mesh. A 10-mg portion is then mixed with 20 mg pure graphite powder (grade Sp–2) and transferred into the cavity of the preformed electrode. The sample-graphite mixture is packed into the electrode

cavity with an aluminum tapping rod, to pack the charge tightly. Twenty mg of a spectrographically pure calcium carbonate-graphite mixture (1:5) is placed on top of the charge and the same tapping technique is repeated.

2. An initial excitation of 3 amp is effected by bringing the electrodes together. Then the arc gap is opened to approximately 5 mm and at the same time the arc current is increased to 12 amp. The sample is burned to completion in about 120 sec. Standards are arced in the same manner.
3. The processed film on which the spectra of the samples are recorded is compared to a standard film in a comparator of 20 × magnification.

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