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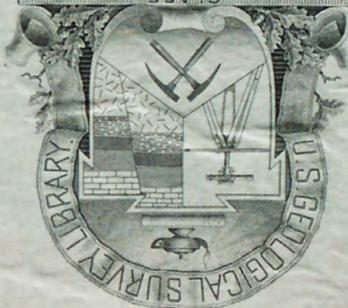
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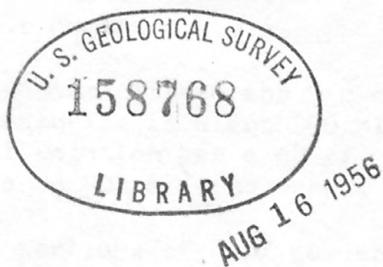
also carried in stock in the following sizes

	HIGH	WIDE	THICKNESS		HIGH	WIDE	THICKNESS
1523	9 inches	7 inches	$\frac{3}{8}$ inch	1529	12 inches	10 inches	$\frac{1}{2}$ inch
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290 Determination of Readily Soluble Copper, Zinc, and Lead in Soils and
242 Rocks; Nitric Acid Extraction

by
1913
Harold Bloom and H. E. Crowe 1872
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Introduction

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

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

Reagents

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

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

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

Reagent B (for zinc).

(1) Weigh 125 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and bring into solution with about 400 ml water. Purify by shaking with 15-ml portions of 0.01 percent dithizone solutions until the CCl_4 layer is green. Remove dithizone by successive extractions with small portions of CCl_4 .

(2) Add 60 ml of glacial acetic acid to about 400 ml water. Weigh out 306 g of sodium acetate $\cdot 3\text{H}_2\text{O}$ and dissolve in the acetic acid solution. Purify as described above.

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

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

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Released 19543

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

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

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

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

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

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

Hydroxylamine hydrochloride. Use best grade obtainable.

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

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

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

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

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

Ammonium citrate, 10 percent. Dissolve 100 g $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$ in about 400 ml of water. Purify by shaking with successive portions of 0.01-percent dithizone until the carbon tetrachloride layer is green. Remove dithizone by successive extractions with small portions of CCl_4 . Dilute to 1 liter.

Preparation of standard solutions

Copper, 0.01 percent (100 micrograms per ml). Dissolve 0.2 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water; add 50 ml of 1N HCl and dilute to 500 ml with water.

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

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

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

Lead, 0.01 percent (100 micrograms per ml). Dissolve 0.016 g of dried $\text{Pb}(\text{NO}_3)_2$ in water containing 1 drop of conc. HNO_3 , and dilute to 100-ml volume with water.

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

Apparatus

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

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

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

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

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

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

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

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

2 separatory funnel holder.

1 separatory funnel, 2 liter (Pyrex).

1 separatory funnel, 125 ml (Pyrex).

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

Test tube brushes.

1 spatula.

1 camel's hair brush.

4 dropping bottles. 250-ml size

1 wash bottle, polyethylene, 500-ml size.

6 400 ml beakers.

4 glass stirring rods.

1 2-liter Pyrex bottle for storing reagent B.

2 500-ml Pyrex bottles.

8 1-liter Pyrex or polyethylene bottles.

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

6 25-ml graduate cylinders with ground glass stoppers.

3 100-ml graduates.

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

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

Balance. Sensitivity 2 mg.

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

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

1 porcelain pipette holder.

Procedure

Weigh 0.1 gram sample (minus 80 mesh) and transfer to a 16x150 mm culture tube previously marked at 10 ml volume. Add 3 ml of 1+3 H_2O_2 to the tube and digest for 1 hour on the hot plate. If, during the digestion, the volume gets very low, add some water to prevent dryness. If solution bumps, insert an anti-bump glass tube. Remove the tube from the heat, bring volume to the 10-ml mark with water, close with thumb and mix by inverting the culture tube. Allow the solution to settle for about 15 minutes. From this solution run zinc, lead, and copper as follows:

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

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

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

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

A 1-microgram lead standard is a weak pink color and corresponds to 50 ppm when the above procedure is followed. A visual estimation of a pink color containing more than 3 micrograms of lead is difficult. Either increase or decrease the aliquot depending upon the concentration of the pink layer.

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

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

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

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

References Cited

- Almond, Hy and Morris, H. T., 1951, Geochemical techniques as applied in recent investigations in the Tintic district, Utah: Econ. Geology, v. 46, p. 608-625.
- Lakin, H. W., Stevens, R. E., and Almond, Hy, 1949, Field method for the determination of zinc in soils: Econ. Geology, v. 44, p. 296-306.
- Matviak, M., 1951, On the prevention of bumping: Chemist Analyst, v. 40, p. 64-65.
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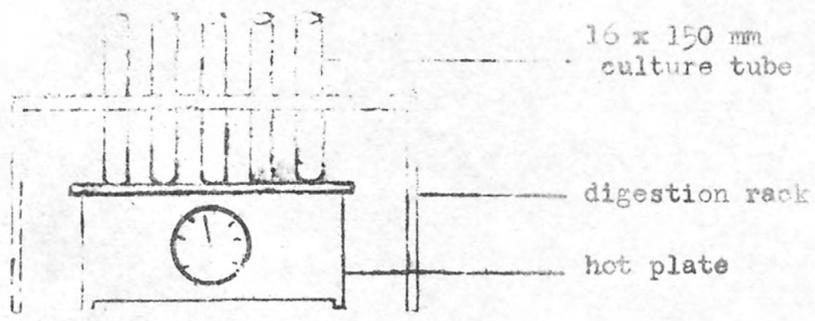
Conversion of micrograms per aliquot to parts per million in samples

(Based on 0.1 g sample diluted to 10 ml)

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

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

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



16 x 150 mm
culture tube

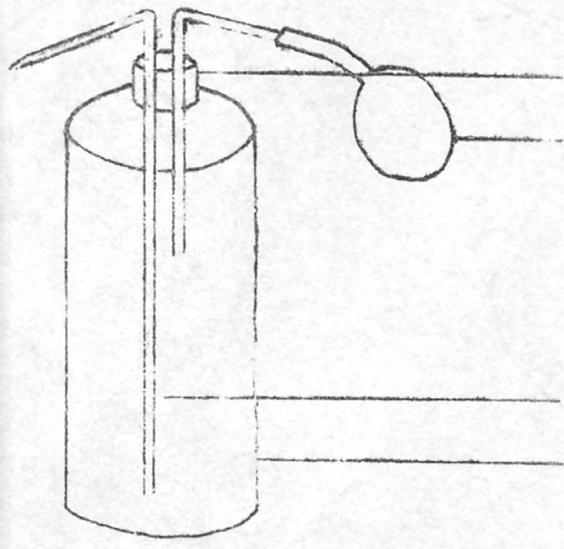
digestion rack

hot plate



anti-bump
glass tube

II



Two hole stopper

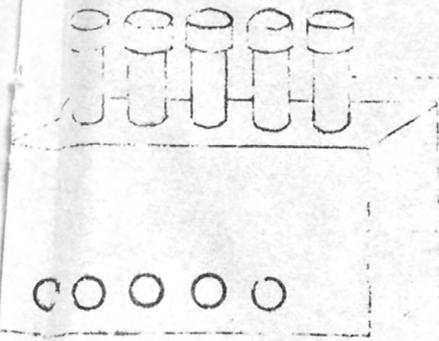
Rubber bulb

glass tubing

1 pint thermos bottle

II

III



screw capped culture tube

wood block



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