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Field and Laboratory Methods used
by the
Geological Survey of Canada in Geochemical Surveys
No. 5 COLD EXTRACTABLE "HEAVY METAL"
IN SOIL AND ALLUVIUM

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DEPARTMENT OF ENERGY, MINES AND RESOURCES

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INTRODUCTION

To meet requests the Geological Survey of Canada is preparing a series of papers describing methods of analysis suitable for geochemical surveys, giving a complete list of the equipment and reagents required and a detailed step-by-step account of the procedure employed.

The tests described are based on those published in the scientific literature, in some cases slightly modified to speed production. Geochemical prospecting, detailed sampling procedures, and the interpretation of the analytical data are not discussed here. For a review of such topics the reader is referred to "The Principles of Geochemical Prospecting" by Hawkes (1957), "Principles of Geochemical Prospecting" by Ginzburg (1960), and "Geochemistry in Mineral Exploration" by Hawkes and Webb (1962).

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PRELIMINARY REMARKS

This test is one of the simplest and most useful available to a prospector interested in applying geochemistry to mineral exploration. It is based on the reaction of dithizone (diphenylthiocarbazone) with a large group of metals, giving strongly coloured reaction products. This reagent and its chemical reactions are described in detail by Sandell (1959, pp. 139-176). The method given below was first described by Bloom (1955) as a rapid and simple test for determining "heavy metals" at the sample site, and has been slightly modified by members of the Geological Survey of Canada. The heavy metals determined as a group include copper, lead, zinc, nickel, cobalt, silver, and tin, but in practice, the metal determined is chiefly zinc. This is only one of a number of tests for the determination of heavy metals, but we have found it to be simple and satisfactory.

The precautions necessary in trace-element work are discussed briefly in publication No. 1 of this series (G.S.C. Paper 59-3). Some additional remarks however, may be made for tests such as this, which are designed for use at the sampling site.

In handling wet sample material, avoid contaminating the sample with metal derived from such objects as brass buckles, watch bands, and coins. For instance, a considerable quantity of metal can be carried on the fingers from coins in the pocket, and this is readily transferred to the cork of the analysis tube, leading to incorrect results.

Select the finest material possible. In a sample of stream sediments, for instance, as much of the silt fraction as possible should be included. Pebbles, twigs, and other coarse particles should be removed from soil and stream-sediment samples. Where the field test gives a high value, a larger sample should be collected in a paper or plastic bag for careful analysis in a laboratory. It should be remembered, however, that the results obtained by a laboratory analysis are not directly comparable with those obtained by this field test.

NOTES ON THE METHOD

This method of geochemical prospecting is based on the premise that some of the metal in a sample of soil or stream sediment is loosely attached to the surfaces of the mineral grains or organic materials. This adsorbed or 'loosely bonded' metal, which may amount to as much as 20 per cent of the total metal in the sample, may be removed by leaching the sample with a dilute solution of ammonium citrate, or even water. The heavy metal thus removed is then determined by reacting it with dithizone to form a coloured product. The colour produced is a measure of the metal content of the sample.

Because the method is designed for rapidity and ease of use in the field, samples are not weighed but are measured with a small scoop. A scoopful of the sample is placed in the analysis tube with five millilitres (ml) of the ammonium citrate buffer solution. The function of the buffer solution is to dissolve the 'loosely bonded' metal referred to above, and to maintain the acidity of the sample solution at a pH of 8.5, the point at which the dithizone reacts most rapidly and completely with the greatest number of heavy metals. The buffer solution contains hydroxylamine hydrochloride to prevent iron from interfering with the test. Five millilitres of a dithizone-benzene solution is then added to the tube. The tube is corked and shaken vigorously for exactly 30 seconds. The benzene layer is allowed to separate and is observed for a colour change which may range from the original bright green to red, through the sequence, blue-green, blue, blue-purple, and purple. Any colour other than green is an indication that the sample contains an appreciable quantity of metal. Additional amounts of the dithizone-benzene solution are added with shaking until a standard colour, or end point, usually blue, is reached. The amount of dithizone required to reach this point is then a measure of the cold extractable heavy-metal content of the sample.

ANALYTICAL PROCEDURE

Determination of Heavy Metal

1. To a clean test tube add one scoopful of fine soil or sediment (approximately 0.5 gram).
2. Add buffer from a polyethylene wash bottle to the 5-ml mark on the test tube, then add 5 ml of dithizone-benzene solution. Cork and shake vigorously for 30 seconds.

3. Allow the benzene layer to separate at the top of the liquid. A colour change may be noticed between green (original colour) and red. If the colour is blue-green or green the determination is finished. Record the weight of sample and the amount of dithizone-benzene solution used.
4. If the colour is on the red side of the blue-green end point, add an additional 5 ml of dithizone solution, and shake for 10 seconds. Continue adding dithizone, 5 ml at a time, and shaking until the blue-green colour is obtained. Record the weight of sample taken and the volume of dithizone in benzene solution required to reach the end point.
5. The values obtained may be plotted on the map as mls of dithizone and contoured in this form. Alternatively, the approximate amount of metal in the sample may be calculated from the following formula:

$$\frac{1}{\text{wt. of sample}} \times \frac{\text{ml of dithizone}}{5} = \text{ppm (parts per million),}$$

e.g. if a 0.5-gram sample is taken, and it requires 20 ml of dithizone to reach the blue-green colour, the sample contains

$$\frac{1}{0.5} \times \frac{20}{5} = 8 \text{ ppm.}$$

6. It is possible to determine larger amounts of metal by taking a smaller sample. In order to do this, the sample scoop should contain a second hole of 0.2-gram capacity. Should a second determination be necessary because of the high metal content of the sample, clean the test tube and cork as directed by step 11 under "(C) Buffer Solution", in the section below, and proceed with the second determination using a 0.2-gram sample. Calculate the value in parts per million as before, remembering to use a sample weight of 0.2-gram instead of 0.5-gram.
7. At the end of each determination, when the blue-green colour has been reached, the tube and cork are free of metal and require no further cleaning. The contents of the tube are shaken and emptied, and the next determination can be started directly.

Preparation of Equipment and Working Solutions

(A) Dithizone-Chloroform Solution (0.2% W/V)

1. Weigh 0.1 gram of dithizone on a torsion balance using paper or aluminum foil.
2. Transfer to a 50-ml, stoppered, graduated cylinder.
3. Add chloroform to the 50-ml mark and shake vigorously for at least 5 minutes.
4. Cover the cylinder with brown paper or aluminum foil and store in a cool place.

(B) Dithizone-Benzene Solution (0.001% W/V)

1. Pipette 2.0 ml of the dithizone-chloroform solution (0.2% W/V) into a 500-ml graduated cylinder.¹

Note: Use the pipette only for dithizone solutions. Both the pipette and cylinder must be clean and dry.

2. Dilute with benzene to the 400-ml mark. This solution should be prepared fresh daily in an amount sufficient for the day's work. If the colour shows any change from the original intense green the solution should be discarded.
3. Transfer the solution to a 500-ml polyethylene wash bottle and keep in the dark and as cool as possible. The wash bottle may be covered with black paper or aluminum foil.

(C) Buffer Solution

1. Weigh 200 grams of ammonium citrate, and 32 grams of hydroxylamine hydrochloride, and put into a 600-ml beaker.
2. Fill the beaker with metal-free water and warm with stirring to dissolve.
3. Transfer to a 1-gal polyethylene bottle, previously calibrated at 2 litres (2,000 ml) and dilute with metal-free water to 2 litres.

¹ For health reasons, organic solvents should not be pipetted by mouth. Use either a pipette filler or a rubber bulb.

4. Add concentrated ammonium hydroxide until the pH is 8.5 (about 105 ml). Determine the pH with pH papers.
5. Measure out 10 ml of 0.2 per cent dithizone-chloroform solution and dilute to 100 ml with benzene, using the graduated cylinder.
6. Shake the buffer solution with two successive 50-ml portions of the dithizone solution in a separatory funnel. Allow the dithizone solution to separate cleanly after each addition and drain off the buffer into its polyethylene bottle. The last addition of dithizone should remain green when the buffer is pure.
7. Shake the buffer solution with two successive 100-ml portions of chloroform in the separatory funnel. Separate as before, by draining off the chloroform layer.
8. Shake the buffer with one 50-ml portion of benzene. The benzene layer should now be light green.
9. Drain the buffer into the polyethylene bottle and dilute to 4 litres with metal-free water (mark bottle previously). Readjust the pH to 8.5 with concentrated ammonium hydroxide if necessary.
10. Prepare the analytical test-tubes as follows: Carefully pipette 5 ml of water into the test-tube using the 5-ml volumetric pipette. Mark the level on the tube with a glass-marking diamond or tungsten-carbide pencil. Continue adding water in 5-ml increments, marking the tube until the entire length has been calibrated. Prepare at least one spare tube in case of breakage.
11. Clean the tubes and corks by following the steps of the analytical procedure but without a sample. Continue to clean the tubes and corks until the last portion of dithizone added remains green. Tubes may be cleaned of metal contamination in the field at any time by following this procedure.

EQUIPMENT

In the following list of equipment and chemicals required for this heavy-metal test, equipment is listed under two headings—laboratory and field. The laboratory equipment includes all items required for the preparation of the working solutions used in the test. Under field equipment are listed all items specifically required to perform the test at the sample site. All equipment and chemicals may be purchased from one of the companies listed under "Laboratory Equipment and Supplies" in the yellow pages of the telephone book.

The approximate cost of the items, at 1963 prices, is \$265; a large part of this amount is taken up by the two balances listed. Costs will be considerably reduced if the user enlists the assistance of a local high-school chemistry teacher, druggist, or assay office in preparing the working solutions.

Laboratory

Torsion balance, 500-mg capacity, sensitive to 1 mg, or any other type of balance of similar capacity and sensitivity.

Reagent balance, 1-gram capacity.

Glass-writing diamond or tungsten-carbide pencil.

Stainless-steel spatula, 4-inch blade.

Mixed-resin demineralizing unit. (Note: Metal-free water must be used in the preparation of reagents, rinsing, etc.)

One 1-gal polyethylene bottle.

One 600-ml beaker.

One 500-ml graduated cylinder.

One 2-litre Squibb type separatory funnel. (Note: Stopcock grease must not be used on the stopcock of the funnel, therefore, after use the funnel must be thoroughly rinsed and the stopcock left loosely in place to prevent binding.)

One 50-ml, stoppered, graduated cylinder.

One 5-ml volumetric pipette.

One 2-ml volumetric pipette.

One roll pH paper (pH 2-10).

Field

Three pyrex test-tubes, rimless, 18 x 150 mm, fitted with select-quality cork stoppers.

Two 500-ml polyethylene wash bottles.

One sample scoop, made from a bar of lucite plastic or aluminum, $1/2 \times 3/8 \times 3$ inches. A hole is drilled at one end of the bar approximately $1/4$ inch in diameter by $3/16$ inch deep to contain 0.5 gram of sample. The size of hole may be determined by trial and error. A second hole approximately $3/16$ inch in diameter by $1/8$ inch deep should be drilled in the other end of the bar to contain 0.2 gram of sample.

One stainless-steel spatula with 4-inch blade.

Reagents Required for 1,000 Determinations

1 gram diphenylthiocarbazone (dithizone), A.C.S. reagent-grade or equivalent.

300 grams ammonium citrate (diabasic), A.C.S. reagent-grade or equivalent.

50 grams hydroxylamine hydrochloride, A.C.S. reagent-grade or equivalent.

300 ml ammonium hydroxide, A.C.S. reagent-grade or equivalent.

8 litres benzene, A.C.S. reagent-grade or equivalent.

1 litre chloroform, A.C.S. reagent-grade or equivalent.

Other solvents such as xylene and toluene may be used in place of benzene. Obtain only reagent-grade solvents: cheaper, commercial-grade solvents are not satisfactory and should not be used.

Precautions

1. Metal-free water must be used exclusively in this test. This may be obtained by passing clean tap water through a resin demineralizing column. Occasionally, clean stream or spring water may be found to be very low in metal and may be used in place of metal-free water.
2. Keep the cork used in the analysis tube from becoming contaminated. Never touch the lower part of the cork with the fingers. At no time should a finger be used to cover the tube in place of a cork.

3. Some soil and stream-sediment samples may contain appreciable quantities of organic matter. This may cause difficulties in the analysis by discolouring the dithizone solution or by preventing the two liquids in the tube from separating. The separation of the two liquids in such a case may be aided by laying the tube on its side for several minutes. This will usually cause enough separation for the colour to be detected.
4. In some samples the amount of metal determined will depend directly on the length of time the tube is shaken. For this reason, the amount of shaking must be the same in every case. Only in this way will the results be comparable.
5. It has been found that with samples high in copper, a brownish colour in the benzene layer results, rather than the normal red. This should be taken as a positive result and more dithizone solution added.
6. Colour-blind persons will find it difficult, if not impossible, to perform this test satisfactorily.