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PAPER 63-29

FIELD AND LABORATORY METHODS USED BY
THE GEOLOGICAL SURVEY OF CANADA
IN GEOCHEMICAL SURVEYS

No. 4

A LABORATORY METHOD FOR DETERMINING ANTIMONY IN
SOILS AND ROCKS

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DEPARTMENT OF
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GEOLOGICAL SURVEY OF CANADA IN GEOCHEMICAL SURVEYS

NO. 4 ANTIMONY

INTRODUCTION

This paper continues the series outlining the methods used in geochemical surveys and gives a complete list of the equipment and reagents required and a detailed step by step account of the procedures employed for the determination of traces of antimony in soils and rocks.

The method described was originally published by Ward and Lakin (1954). To speed production certain steps have been slightly modified.

No attempt will be made to discuss the principles of geochemical prospecting, field sampling procedures, or the interpretation of the analytical data obtained. For a review of such topics the reader is referred to the first three works noted below in the bibliography.

SELECTED BIBLIOGRAPHY

Ginzburg, I. I.

1960: Principles of Geochemical Prospecting; Pergamon Press, London.

Hawkes, H. E.

1957: Principles of Geochemical Prospecting; U. S. Geol. Surv., Bull. 1000-F.

Hawkes, H. E., and Webb, J. S.

1962: Geochemistry in Mineral Exploration; Harper and Row, New York.

Sandell, E. B.

1959: Colorimetric Determination of Traces of Metals, 3rd ed., pp. 258-265, Interscience Inc., New York.

Ward, F. N., and Lakin, H. W.

1954: Determination of Traces of Antimony in Soils and Rocks; Anal. Chem., vol. 26, No. 7, pp. 1168-1173.

Ward, F.N., Lakin, H.W., Canney, F.C., et al.
1963: Analytical Methods Used in Geochemical Exploration
by the U. S. Geological Survey; U.S. Geol. Surv.,
Bull. 1152.

SUMMARY AND GENERAL REMARKS ABOUT METHOD

The sample of rock or soil is fused with potassium pyrosulphate and the cooled melt is dissolved in 6 molar hydrochloric acid. Any Sb (IV) present is reduced to Sb (III) with sodium sulphite, and all the Sb (III) is then oxidized to Sb (V) with ceric sulphate. Hydroxylamine hydrochloride is added to reduce iron to the ferrous state and to reduce the excess ceric sulphate. The antimony (V) is then extracted with iso-propyl ether. Rhodamine B reagent is added and the optical density of the red-violet antimony complex that develops is measured at 550 millimicrons using a suitable colorimeter. The number of micrograms of antimony in the sample is determined from a standard curve. If a colorimeter is not available, the concentration of antimony in the samples can be determined visually by matching with standards.

To achieve reproducible results with the method the timing is of the utmost importance. Once the test solution has been treated with ceric sulphate solution (see step 13 under analytical procedure) the time schedule as indicated in the procedure must be rigidly followed. The oxidized antimony hydrolyses to a form that does not react with rhodamine B, and this may give rise to low and erratic results if a regular time schedule is not maintained.

Metal-free water obtained by passing distilled water through a resin demineralizing column must be used for making up all reagents and solutions and for rinsing glassware. All glassware used in the test should be of a hard borosilicate type such as pyrex.

If no colorimeter is available, visual standards can be used. However, this reduces the productivity of the method as time must be spent each day in preparing a fresh set of standards.

If a colorimeter is used to measure the intensity of the antimony-rhodamine B complex, it is advisable to check the calibration curve periodically as the value of the readings obtained may decrease with the aging of the tungsten lamp. This is indicated by a gradual change in the gradient of the standard curve. When the tungsten lamp is replaced, a new standard curve should be plotted.

If arsenic (III), gold, or thallium (I) are present in the sample in large amounts, they may interfere with the method and give erroneous results.

SAMPLE PREPARATION

Soil and Sediment Samples

Equipment

Kraft paper sample envelopes made with water-resistant glue, approximately 6" x 3"

Oven or other means of drying samples

Porcelain pestle and mortar, 100-mm diameter

Set of 6 non-contaminating sieves ranging from 20 to 200 mesh per lineal inch

This set should include an 80-mesh sieve. The sieves can be constructed from a length of 3-inch plastic tubing and 4-inch squares of Swiss bolting silk.

Stiff paint brush, 1 1/2"

Sample-bag numerator

Procedure

1. Dry the sample in its original envelope, either in the air or in an oven at about 100°C.
2. Crush sample lightly with a pestle and mortar and sieve onto a sheet of glossy paper.
The minus-80-mesh fraction is satisfactory for most purposes, but the best mesh size should be determined for each project.
Clean the pestle, mortar, sieve, and paper with a stiff brush after each sample.
3. Transfer sieved fraction to a numbered sample envelope and discard oversize.
1 gram of sieved sample is adequate for most analytical requirements.

Rock Samples

Equipment

Steel plate and pestle

Agate mortar and pestle or power mortar

Specimen vials, with plastic molded caps, 10 gram capacity

Procedure

1. Break the sample into small uniform pieces.
2. Roll and mix thoroughly on a large sheet of paper.
3. Cone and quarter to obtain about 10 g of sample.
4. Grind in an agate mortar or power grinder to a fine powder.
Sample should be fine enough to pass a 200-mesh sieve.
5. Transfer sample to a specimen vial and mix thoroughly by shaking vial.

ANALYTICAL PROCEDURE

Equipment required

Torsion balance, 500 mg capacity, sensitive to 1 mg

Reagent balance, 1 kg capacity

Stainless steel spatula, 4" blade

Stainless steel spatula, 8" blade

Water still and mixed resin demineralizing column

2 aspirator bottles, pyrex or polyethylene, 5 gal

Tygon tubing

Screw clips

Glass-writing diamond

Plastic scoop, 1 g capacity, made by drilling a small hole in a lucite bar

Electric hot plate, 10" x 12"

Fit hot plate with a 1" rim of asbestos board and cover with 1/2" to 3/4" layer of sand. Attach a rack to support 25 test tubes (16 x 150 mm) on the sand tray

Suitable gasoline stove covered with wire mesh to support about 6 tubes in the flame or alternatively a multiple burner unit with a suitably designed rack

Glass rod, pyrex

Rack to hold about 30 test tubes (16 x 150 mm) with asbestos base

100 test tubes, rimless, pyrex, 16 x 150 mm

4 reagent bottles, polyethylene, 200 ml

2 reagent bottles, polyethylene, 100 ml

2 reagent bottles, polyethylene, 1 litre

1 reagent bottle, polyethylene, 1 gal

1 cylinder, measuring, pyrex, 50 ml

1 cylinder, measuring, pyrex, 1 litre

1 beaker, pyrex, 100 ml

3 beakers, pyrex, 600 ml

3 wash bottles, polyethylene, 500 ml

2 pipettes, graduated, serological, pyrex, 1 x 0.01 ml

2 pipettes, graduated, serological, pyrex, 5 x 0.1 ml

1 pipette, graduated, serological, pyrex, 10 x 0.1 ml

5 separating funnels, Squib, pyrex, 125 ml

1 separating funnel, Squib, pyrex, 250 ml

2 shaking racks

These should be constructed of some non-contaminating metal (e. g. aluminum) with clips for holding 5 x 125 ml separating funnels (Figure 1).

4 automatic pipettes to deliver 2 ml

2 automatic pipettes to deliver 5 ml

12 corks, 7/8" diameter at narrow end

Laboratory clock with a sweeping second hand

6 clamps

6 retort stands

1 ring, 3" diameter

1 oven for drying tubes

1 flask, volumetric, pyrex, 1 litre

2 flasks, volumetric, pyrex, 100 ml

Colorimeter and 1/2" diameter cells

1 thermometer, -20° to 110°C

1 funnel, filtering, pyrex, 65 mm diameter

Reagents required for 1,000 determinations

1,000 g potassium pyrosulphate, fused, powdered, analytical grade

10 litres concentrated hydrochloric acid, analytical grade

10 g sodium sulphite

200 g ceric sulphate

8 litres iso-propyl ether, analytical grade

0.5 g rhodamine B (tetraethyl rhodamine)

140 ml concentrated sulphuric acid, analytical grade

0.5 g antimony potassium tartrate, analytical grade

1 box filter paper, Whatman No. 1, 11 cm diameter

Preparation of equipment and reagents

1. Number the test-tubes with a glass-writing diamond and calibrate at the 3 ml, 5 ml, and 10 ml levels.
2. Prepare a 1M hydrochloric acid solution by diluting 82.5 ml of concentrated acid to 1,000 ml with metal-free water in a cylinder.
3. Prepare a 6M hydrochloric acid solution by adding 1,000 ml of concentrated acid to 1,000 ml of metal-free water.
4. Prepare a 1% aqueous hydroxylamine hydrochloride solution by dissolving 2 g of hydroxylamine hydrochloride in 200 ml of metal-free water.
5. Prepare a 1% hydroxylamine hydrochloride solution in 1M hydrochloric acid by dissolving 2 g of hydroxylamine hydrochloride in 200 ml of 1M hydrochloric acid.
6. Prepare a 0.5M sulphuric acid solution by cautiously adding 14 ml of concentrated acid to 486 ml of metal-free water.
7. Prepare a 3.3% ceric sulphate solution by dissolving 16.5 g of ceric sulphate in 500 ml of 0.5M sulphuric acid.
8. Prepare a 1% sodium sulphite solution by dissolving 1 g of sodium sulphite in 100 ml of metal-free water. Prepare this solution freshly once a week.
9. Prepare a 0.02% rhodamine B solution by dissolving 0.04 g of rhodamine B in 200 ml of 1M hydrochloric acid. Warm slightly and filter if necessary.
10. Shake, in a 250 ml separating funnel, sufficient iso-propyl ether for a day's operation, with successive 25 ml portions of ceric sulphate solution until the yellow colour remains after shaking for 1 minute. Then destroy the excess ceric

sulphate with 1 ml of aqueous 1% hydroxylamine hydrochloride and discard the aqueous layer. Shake with two 25 ml portions of water followed by 25 ml of 1M hydrochloric acid. Stopper the funnel and leave the ether standing over the hydrochloric acid, until required. This treatment should be repeated daily.

11. Prepare a standard antimony stock solution containing $100 \mu\text{g/ml}$ by dissolving 0.274 g of antimony potassium tartrate in 1,000 ml of 6M hydrochloric acid.
12. Prepare an antimony solution containing $5 \mu\text{g/ml}$ by pipetting 5 ml of the stock solution into a 100 ml volumetric flask and diluting to the mark with 6M hydrochloric acid. This solution should be prepared freshly once a week or whenever the standard curve is checked.
13. Tie the glass stoppers around the necks of the separating funnels.

Procedure

1. Weigh 0.2 g of the sieved or finely ground sample into a numbered test tube.
Operate in batches of 20 to 25 samples. Note sample and test-tube number.
2. Add 1.0 g of potassium pyrosulphate by means of a scoop.
3. Mix the flux and sample by tapping the bottom of the tube on the palm of the hand.
4. Heat the tube in a flame until frothing ceases, remove from the flame, and rotate the tube to spread the melt in a thin layer around the sides of the tube.
5. Allow to cool and add 5 ml of 6M hydrochloric acid.
Dispense from a wash bottle.
6. Heat the tube gently on the sand tray until the melt breaks up into separate particles, taking great care that the solution does not boil.
7. Remove the tube from the sand tray and add 1 ml of 1% sodium sulphite solution.

8. Make up to the 10 ml level with 6M hydrochloric acid. Mix the contents of the tube thoroughly and allow to settle overnight.
9. Decant the solution into a 125 ml separating funnel.
Operate in batches of 5 using the shaking rack to support the separating funnels.
10. Wash the sides of the tube and residue with 3 ml of warm 6M hydrochloric acid, allow to stand a few minutes, and decant the solution into the separating funnel with the previous solution.
11. Repeat step 10, with 3 ml of warm 6M hydrochloric acid and then with 2 ml of warm water.
12. Cool the solution to below 25°C by running cold water over the funnels or by placing them in a refrigerator.
13. Add 5 ml of ceric sulphate solution, mix, and leave for 30 seconds.
14. Add 1 ml of aqueous 1% hydroxylamine hydrochloride solution and leave for 1 minute.
15. Add 45 ml of cold metal-free water and cool again, (if necessary) to below 25°C.
If possible previously cool the water in a refrigerator.
16. Add 5 ml of iso-propyl ether, stopper the funnel, and shake for 1 minute. Allow to stand for 5 minutes.
17. Drain off all but 0.5 ml of the aqueous phase, and add 2 ml of 1% hydroxylamine hydrochloride in 1M hydrochloric acid. Shake for 5 seconds.
18. Allow the phases to separate then discard the aqueous phase. Add 2 ml of 1M hydrochloric acid and shake for 5 seconds.
19. Discard the aqueous phase, add 2 ml of the 0.02% rhodamine B solution, and shake for 20 seconds.
20. Discard the aqueous phase and transfer the ether phase to a clean dry colorimetric tube.

21. Measure the optical density of the solution at 550 millimicrons against a reference solution of iso-propyl ether. If the reading is greater than the highest calibration standard, pipette a suitable volume of the ether solution into a clean colorimetric tube and dilute as necessary with a known amount of iso-propyl ether. Record the dilution.
22. Using the optical density reading obtained above determine the number of micrograms of antimony corresponding to this value from a previously established standard curve (see below). Calculate the antimony content of the sample in parts per million.

Sb content (ppm) =

$$\frac{\mu\text{g of Sb corresponding to optical density reading} \times \text{dilution (if any)}}{\text{Sample weight taken (g)}}$$

23. Rinse the separating funnels with 1M hydrochloric acid followed by metal-free water.

Preparation of standard curve

Add 15 ml of 6M hydrochloric acid to each separating funnel followed by 1 ml of 1% sodium sulphite solution and 2 ml of metal-free water. Pipette 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 ml of the 5 $\mu\text{g/ml}$ antimony solution into each separating funnel and proceed as in steps 12 to 21. The standard colours range from colourless through increasing intensities of red-violet corresponding to an antimony content of 0 to 3.5 micrograms. Plot a graph of optical density against micrograms of antimony. This should be a straight line.

Check the colorimetric tubes against each other at 550 millimicrons and reject any that are not optically matched at this wavelength.

If a colorimeter is not available a set of 5 standards can be prepared as above, and the colour obtained from the unknown samples can be matched against these visually. The standards must be prepared freshly each day.

Productivity

20 to 25 analyses per 8-hour man-day.

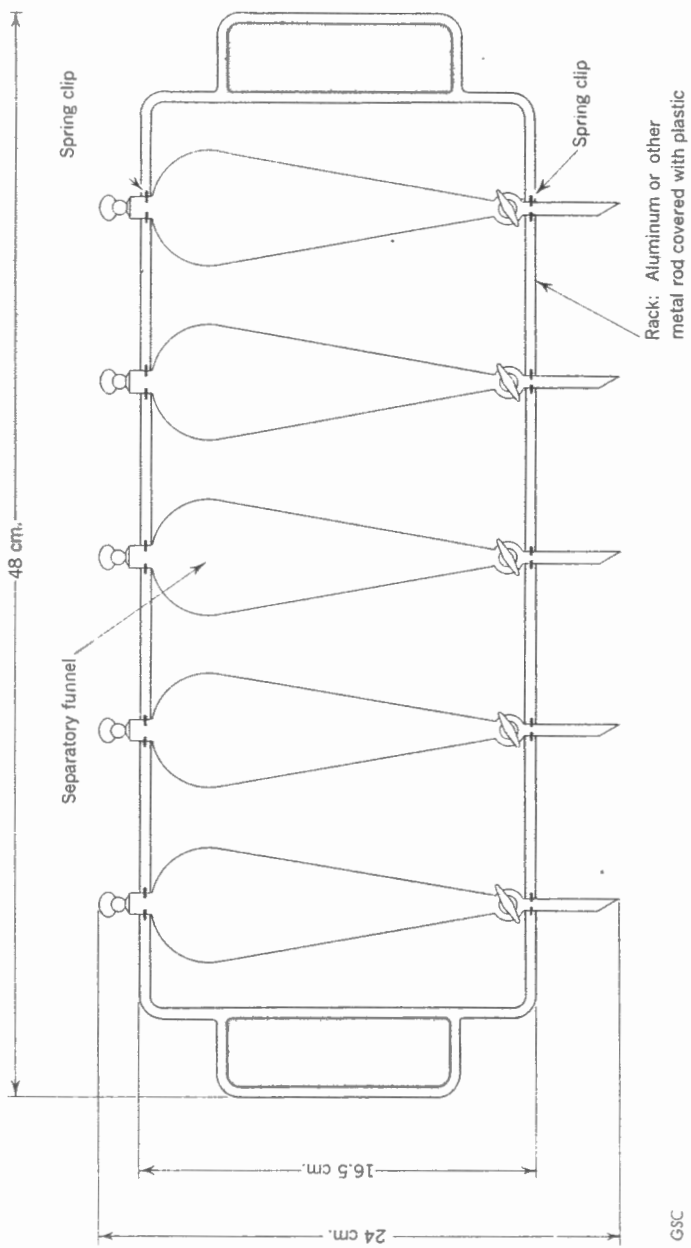


Figure 1. Support rack for shaking separatory funnels

ROGER DUHAMEL, F. R. S. C.
QUEEN'S PRINTER AND CONTROLLER OF STATIONERY
OTTAWA, 1963

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