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Field and Laboratory Methods used by
the Geological Survey of Canada
in Geochemical Surveys

No. 3. METHOD FOR DETERMINING ARSENIC

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INTRODUCTION

This paper is a continuation of the series outlining the methods of analysis used, listing the equipment and reagents required and giving a step by step account of the procedures.

The tests described are based on those published in the scientific literature, in some cases slightly modified to speed production. Geochemical prospecting, sampling procedures, or 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 Ginsburg (1960), and "Geochemistry in Mineral Exploration" by Hawkes and Webb (1962).

Selected Bibliography

Almond, Hy.

- 1953: Field Method for Determination of Traces of Arsenic in Soils; Anal. Chem., vol. 25, No. 11, p. 1766.

Geochemical Prospecting Research Centre, Royal School of Mines,
London

- 1962: Determination of Arsenic in Soil, Sediment, and Rock Samples, Tech. Comm. No. 20.

Ginsburg, I. I.

- 1960: Principles of Geochemical Prospecting; Pergammon 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.

Lachele, C. E.

- 1934: Rapid Method for Determination of Small Amounts of Arsenic; Ind., Eng. Chem., Anal. Ed., vol. 6, No. 4, p. 256.

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

1952: Compilation of Field Methods Used in Geochemical
 Prospecting by the U. S. Geological Survey; U.S. Geol.
 Surv., Circ. 161.

Stanton, R.E., and Gilbert, M.A.

1956: Preliminary Treatment of Soil and Sediment Samples
 for Analysis; Imperial College of Science and Technology,
 Geochemical Prospecting Research Centre, London,
 Tech. Comm. No. 1.

Remarks about Contamination

Contamination from reagents and equipment and careless working habits may lead to faulty and sometimes misleading results. One of the principal causes of inaccuracy in trace analytical work is contamination from outside sources. It is essential to run one or two blanks with every batch of analyses, coupled with two or three standard samples covering a suitable range of values. Once the value of these samples has been established, any result that falls outside the limits of accuracy of the method or any increase in the metal content of the blank requires investigation. The source of the error should be found before proceeding with further analyses, and if necessary the entire batch should be repeated.

As it is not expedient to carry out the analyses in duplicate, the analyst has no way of detecting a chance result that might be questionable. Accordingly he must rely on the geologist to ask for a repeat determination on any sample where the result does not seem to fit the geological pattern. In general it is a good practice to repeat, as a routine procedure, any analysis falling above a certain level. This value should be settled in consultation with the geologist and will vary from one project to the next. Such a policy will ensure that time and money are not wasted in the investigation of apparently anomalous areas that are due entirely to faulty analyses.

Some of the sources of contamination and a few suggestions on how to avoid them are discussed in the following.

Metal-free water must be used for all tests. Pass distilled water through a demineralizing column to remove the last traces of metal.

Pyrex or a similar hard borosilicate-type glassware is essential; soft glass is a source of heavy metal contamination. All glassware and polyethylene reagent bottles should be washed with strong hydrochloric acid and then thoroughly rinsed with metal-free water before use. Test-tubes should be cleaned with a brush, rinsed with metal-free water, and dried in an oven. When in use they should be kept covered whenever possible.

Stopcock grease can give rise to contamination and should not be used. Extreme caution must be taken with all metal components on the equipment used to ensure that they do not come in contact with any of the solutions. Whenever a new item is introduced into the laboratory, the danger of contamination must be carefully considered.

Care must be taken with stoppers and corks. Corks should always be placed on the bench top-end down, never on their sides. It is advisable to tie glass stoppers to flasks, separatory funnels, and cylinders. Pipettes must not be placed carelessly on laboratory benches. A porcelain pipette support or some suitably designed non-contaminating rack should be used. The enamel filling used in the etching on the outside of certain brands of hard-glass pipettes has been found to be a serious source of lead contamination.

PRINCIPLE OF THE METHOD

A weighed amount of the sample is fused with potassium hydroxide and leached with metal-free water. The resulting alkaline solution is acidified with hydrochloric acid and then diluted to 10 millilitres with metal-free water.

An aliquot of this solution is transferred to an arsine generator (Figure 1) and, in the presence of stannous chloride, the arsenic is liberated as arsine by the action of nascent hydrogen. The nascent hydrogen is produced when zinc pellets are added to the acidified aliquot. The arsine and any other liberated gases are allowed to pass upward through a column packed with glass wool impregnated with lead acetate. The lead acetate is used to trap hydrogen sulphide that may be liberated from the solution. The gases then pass through a piece of mercuric-chloride paper, clamped in place over the top of the column. The arsine coming in contact with the paper imparts a yellow stain, the intensity of which is a measure of the quantity of arsenic in the original aliquot. The stained part of the paper is then compared with artificially prepared standards.

SAMPLE PREPARATION

Soil and Sediment Samples

Equipment

Kraft paper sample envelopes made with water-resistant glue, approximately 6 x 3 inches. These are required for collection of stream sediments and soils.

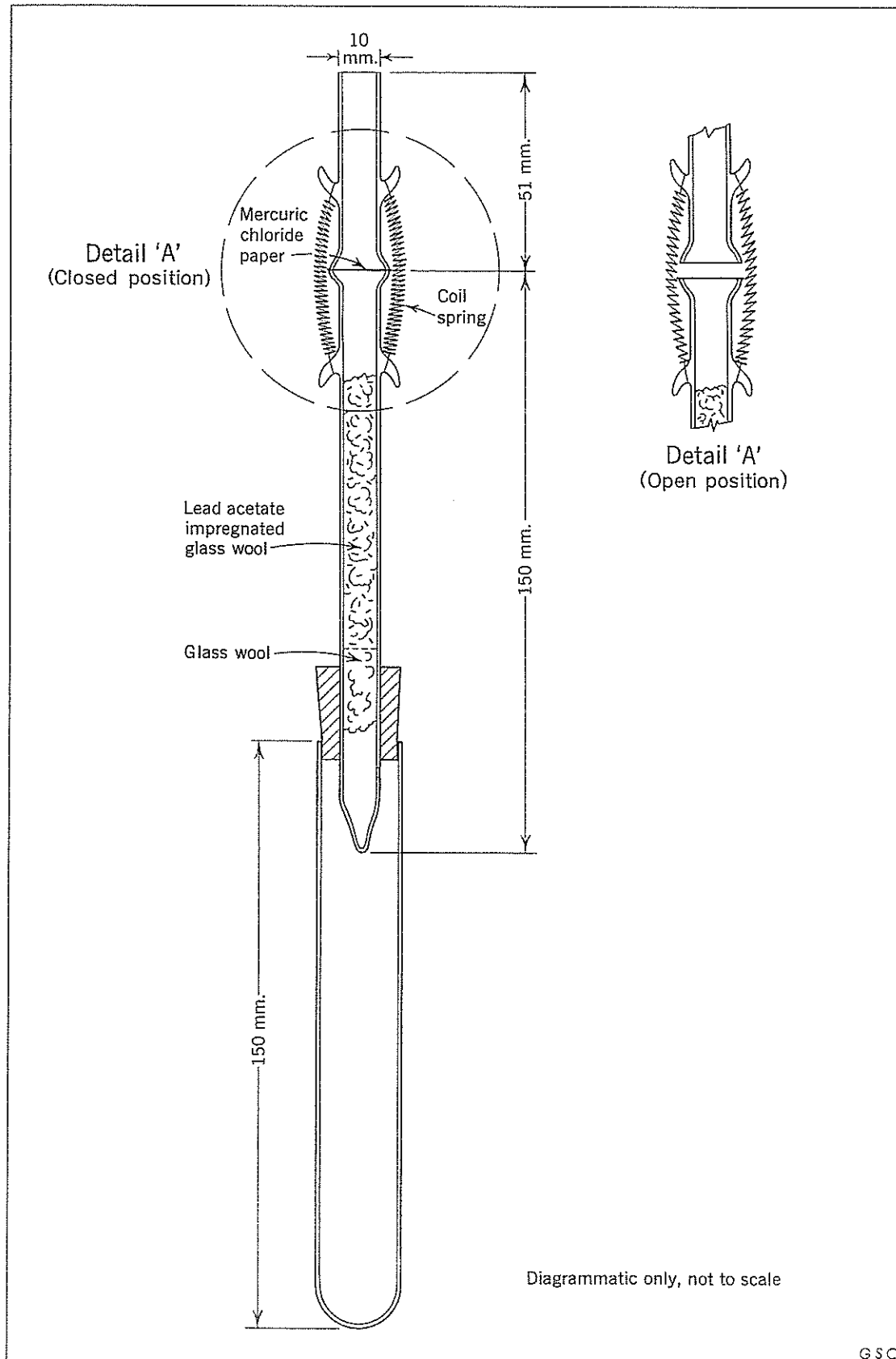


Figure 1. Gutzeit apparatus

Oven for drying samples.

Porcelain mortar and pestle, 75 to 100 mm in diameter.

Set of non-contaminating sieves, including 80-mesh- and 200-mesh-per-lineal-inch sieves.

Stiff paint brush, 1 1/2 inches.

Indelible marking pen.

Specimen vials with plastic moulded caps, 10-g capacity.

Procedure

1. Dry the sample in its original envelope at 100°C, preferably overnight.
2. Crush the sample lightly with a pestle and mortar, and sieve onto glossy paper. The minus-80-mesh fraction is satisfactory for most purposes, but the best mesh size should be determined for each project. Thoroughly clean the pestle, mortar, sieve, and paper with a stiff paint brush after each sample.
3. Transfer sieved fraction to a numbered specimen vial and discard oversize.

Rock Samples

Equipment for Procedure A

Steel plate and pestle.

Agate mortar and pestle or power mortar.

Specimen vials with plastic moulded caps, 10-g capacity.

Equipment for Procedure B

Chipmunk jaw crusher.

Braun pulverizer fitted with ceramic plates.

Small ceramic ball-mill which can be attached to a paint shaker.

Procedure A

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.
6. Clean mortar and grinder with a stiff paint brush.

Procedure B

1. Break a 2- or 3-pound sample into pieces about 2 inches in diameter.
2. Pass the sample through a Chipmunk crusher to produce pieces about 1/4 inch in diameter.
3. Then pass the sample through a ceramic disc pulverizer. This yields a powder of about minus-60 mesh.
4. Place the sample on a large sheet of paper and roll and mix thoroughly.
5. Place a scooped sample of about 10 g in a ceramic ball-mill attached to a paint shaker and shake for 1/2 hour.
6. Transfer sample to a specimen vial and mix thoroughly by shaking.
7. Clean crusher, grinder, and ball-mill with a stiff paint brush and finally remove any small particles by directing a stream of compressed air at the jaws, plates, etc.

ANALYTICAL PROCEDURE

Laboratory Equipment for Arsenic Test

Torsion balance, 500-mg capacity, calibrated in 1-mg divisions.

Reagent balance, 1-kg capacity.

Glass-writing diamond.

Stainless-steel spatula, 4-inch blade.

Stainless-steel spatula, 8-inch blade.

Water-still and mixed-resin demineralizing unit. Metal-free water must be used in all tests; also for making up standards, buffer solutions, and for rinsing etc.

2 polyethylene aspirator bottles, 5-gallon capacity.

Tygon tubing.

2 racks to hold 30 test-tubes (18 x 150 mm) each.

3 racks to hold 10 test-tubes (18 x 150 mm) each.

Suitably designed data sheets for recording results.

Pyrex glass rod, 3 inches long.

60 nickel crucibles (20-ml capacity).

4 Meker burners equipped with rings and triangles.

Miscellaneous items: tongs, wax pencils, glass cutting file, cork borers, stop-clock, test-tube brushes, wiping tissue, porcelain pipette supports, scissors, No. 2 rubber stoppers.

30 Gutzeit tubes. The Gutzeit tubes used in this test (Figure 1) are designed in such a manner that after the arsine and hydrogen are liberated, the gases pass through a tube containing glass wool impregnated with lead acetate and thence through a confined spot on mercuric chloride paper.

Each tube has two sections consisting of pyrex glass tubing (O. D. = 10 mm, and I. D. = 6 mm). The lower section is 15.0 mm long and the upper section 51 mm. The two tubes abut one another with ground surfaces and are held in place by a pair of 1 1/2-inch-long coil springs attached to lugs fused to the sides of the tubes.

The bottom end of the lower section is closed. A port 1/8 inch in diameter, is located 3/4 inch from the bottom. A hole is drilled in a rubber stopper (size No. 2) and the lower section is inserted into the stopper so that the port just appears below the stopper.

Reagents Required for 1,000 Determinations

600 g potassium hydroxide.
3,500 ml concentrated hydrochloric acid.
15 g lead acetate.
10 ml glacial acetic acid.
100 g mercuric chloride.
60 g stannous chloride.
100 g glass wool.
500 ml ethyl alcohol.
4 g sodium hydroxide.
1 g arsenic trioxide.
5 kg zinc shot.
50 sheets of S and S #589 filter paper (9-cm diameter).
6 g mossy tin metal.

Preparation of Reagents and Equipment

Stannous Chloride Solution

Place 10 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 90 ml of concentrated hydrochloric acid, add 1 g of mossy tin and stir until stannous chloride is dissolved and evolution of hydrogen ceases. Dilute to 100 ml with concentrated hydrochloric acid.

Lead Acetate Solution

Dissolve 15 g of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ in metal-free water, add 1 ml of glacial acetic acid and dilute to 100 ml with metal-free water.

Mercuric Chloride Solution

Dissolve 10 g of HgCl_2 in 40 ml of ethyl alcohol.

N Sodium Hydroxide Solution

Dissolve 4 g of NaOH in metal-free water and dilute to 100 ml.

N Hydrochloric Acid Solution

Dilute 8.3 ml of concentrated hydrochloric acid to 100 ml with metal-free water.

Arsenic Solutions

1000 μ g/ml Solution—Dissolve 0.132 g of arsenic trioxide (As_2O_3) in 2 ml of N sodium hydroxide solution. Add 4 ml of N hydrochloric acid solution and dilute to 100 ml with metal-free water.

100 μ g/ml Solution—Dilute 10 ml of the 1000 μ g/ml solution to 100 ml with metal-free water.

5 μ g/ml Solution—Dilute 5 ml of the 100 μ g/ml solution to 100 ml with metal-free water.

Lead Acetate Impregnated Glass Wool

Thoroughly saturate the glass wool with lead acetate solution, drain and dry.

Mercuric Chloride Paper

Soak 10 to 12 filter papers in 40 ml of alcoholic mercuric chloride solution, contained in a Petri dish, for 1 hour. Remove the papers and allow them to dry on watch glasses. Cut the papers into squares, 1 x 1 cm. Care must be taken not to use the edges of the circles when cutting out the squares.

Preparation of Gutzeit Tubes

Remove the upper section of the Gutzeit tube and insert a small plug of glass wool, 1 cm long, in the lower section. Position this plug about 1 cm above the port. Insert lead-acetate-impregnated glass wool in such a manner that it rests on top of the plug and extends upward to a height of 8 cm. Next clamp the upper part of the Gutzeit tube in place with the two coil springs.

Caution: Do not pack the column too tightly as this will reduce the gas flow. If packed correctly it should not be difficult to blow through the tube.

Preparation of Test-tubes

Number sixty test-tubes and calibrate at the 10-ml level, using a glass-writing diamond pen.

Sample Extraction

1. Weigh 0.1 g of the sieved sample into a nickel crucible. Operate in batches of sixty.
2. Moisten the sample with three or four drops of water.
3. Add approximately 0.5 g of potassium hydroxide. (For each bottle of the reagent, determine the average number of pellets to give approximately 0.5 g of the reagent. Five or six pellets generally weigh 0.5 g.)
4. Heat gently until dry and then fuse for 2 minutes over a Meker burner.
5. Allow the melt to cool and then add about 3 ml of metal-free water.
6. Loosen the melt by scraping the bottom of the crucible with a pyrex glass rod.
7. Transfer the contents of the crucible to a test-tube. Use a glass rod to facilitate pouring into the tube.
8. Add 3 ml of concentrated hydrochloric acid to the crucible. Stir well with a glass rod and pour the contents carefully into the test-tube.
9. Wash down the inside of the crucible two or three times with metal-free water and adjust the volume of the liquid in the test-tube to 10 ml with the washings.
10. Mix well and then proceed with the test.

Determination of Arsenic

1. Pipette an aliquot of 5 ml into a test-tube. If 5 ml proves to be too large a volume, pipette a 2-ml aliquot and add 2 ml of concentrated hydrochloric acid. Work in batches of thirty.

2. Fit the mercuric chloride papers into the Gutzeit tubes. This is accomplished by drawing the two sections about 2 mm apart and inserting a piece (1 x 1 cm) of the treated paper between the two ground-glass surfaces. It is unnecessary to remove the springs. After the papers are installed, proceed rapidly with the succeeding steps.
3. Add 0.5 ml of stannous chloride solution. If the yellow colour due to ferric iron is not discharged, add a few extra drops.
4. Dilute to 10 ml with metal-free water.
5. Add five pellets (about 2 g) of zinc to the solution, quickly insert a Gutzeit tube, and leave for 1 hour in a dark place.
6. Remove the mercuric chloride paper and compare the spot immediately with the artificial standards. (Speed is essential in comparing the spots as they begin to fade about 5 minutes after being exposed to light.)
7. Repeat the test on a smaller aliquot if the colour of the spot exceeds the top standard.
8. Arsenic content (ppm) =
$$\frac{\mu \text{ g of matching standard} \times 10}{\text{sample weight (g)} \times \text{volume of test solution used (ml)}}$$

Preparation of Standards

1. Pipette aliquots of 0.0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 ml of the 5 μ g/ml arsenic standards into eight test-tubes. These volumes of standard arsenic solution correspond to 0.0, 0.25, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 μ g of arsenic respectively.
2. Add 2 ml of concentrated hydrochloric acid and proceed as in steps 2, 3, 4, and 5 of the procedure.
3. Paint various shades of chrome-yellow and deep-chrome-yellow water paints on filter paper to match those obtained in step 2 above. Allow the paint to dry thoroughly.
4. Cut a piece of white cardboard into a rectangle 1 $\frac{3}{4}$ x 9 inches. Punch seventeen holes $\frac{3}{16}$ inch in diameter at $\frac{1}{2}$ -inch intervals along its length.
5. The artificial standards are to be affixed on the back of the cardboard and viewed through the holes. The first and alternate holes are left blank.

6. In the second hole attach with scotch-tape a piece of white untreated filter paper similar to that used in the test.
7. View through the third hole the spot produced by 0.25 μ g of arsenic and match it with the correct shade of painted filter paper.
8. Cut out the correct shade and affix it behind the cardboard so that it is viewed through the fourth hole.
9. Continue this procedure with the remainder of the standards.
10. When comparing spots produced by unknown samples, view them through the blank holes.

Productivity

When weighing and fusing in batches of sixty and using thirty Gutzeit tubes at a time, the arsenic content of sixty samples can be determined in a 7 1/2-hour man-day.

Accuracy

The standard of accuracy attained in this test depends a great deal on the skill and experience of the analyst. Considerable practice is required in detecting the slight variations in shade from one standard to the next. For the average operator, a mean accuracy of the order of \pm 25 per cent can be obtained.