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Field and Laboratory Methods used by the
Geological Survey of Canada in Geochemical Surveys
No. 9. TIN IN SOILS AND STREAM SEDIMENTS

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DEPARTMENT OF ENERGY, MINES AND RESOURCES

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ABSTRACT

A test for tin suitable for soil and stream geochemical prospecting is described. The method is based on the reaction of tin with gallein after volatilization of the tin as stannic iodide.

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FIELD AND LABORATORY METHODS USED BY THE GEOLOGICAL
SURVEY OF CANADA IN GEOCHEMICAL SURVEYS
NO. 9
TIN IN SOILS AND STREAM SEDIMENTS

INTRODUCTION

To meet requests the Geological Survey of Canada is preparing a number of papers describing methods of analysis suitable for geochemical surveys, in which are 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. For a review of such topics the reader is referred to Hawkes (1957), Ginzburg (1960), and Hawkes and Webb (1962).

Preliminary Remarks

With recent advances in the price of tin in world markets, interest in the metal is increasing. To meet the need for a test for tin suitable for soil and stream sediment geochemical prospecting, the Geological Survey of Canada has examined and tested a number of currently available analytical methods. The one outlined has been found, in our experience, to give a satisfactory sensitivity combined with adequate precision.

The method for tin given below was first described by Wood (1956) and modified subsequently by Stanton and McDonald (1961). Further modifications have been made by the writer while using the test in Africa and in Canada.

While it is not intended to give a detailed account of geochemical prospecting for tin, a few comments are required. It is important to remember that tin is most commonly found in soils and stream sediments as the mineral cassiterite. Cassiterite is a mineral of high specific gravity (6.8-7.1) and this property affects its behaviour in soils and in stream sediments. Where, in the case of stream sediment sampling, one would normally collect samples of silt-sized material, when prospecting for tin a more coarse fraction should be collected. In many cases it is desirable to sieve these samples into two fractions (i. e. -20 to +80 and -80 mesh) and determine tin on both fractions. This aspect is considered by Tooms and Kaewbaidhoon (1961).

The high specific gravity of cassiterite also affects its behaviour in the sieved sample. If the sieved samples are moved around and disturbed to any degree, there will be a tendency for the cassiterite (and other heavy minerals) to settle towards the bottom of the container. Thus a sample weighed from the top of the container may give erroneously low results for tin. Care must be taken to mix the entire contents of the container before weighing out the sample.

Notes on the method

The Method is based on the reaction of tin with gallein (4, 5 - dihydroxy-fluorescein) after volatilization of the tin as stannic iodide. The weighed sample is mixed with ammonium iodide in a test tube and heated in a Bunsen flame. Tin in the sample is volatilized as stannic iodide which condenses on the cold part of the tube. The stannic iodide is dissolved in dilute HCl and an aliquot taken for determination. A chloroacetate-chloroacetic acid buffer is added to maintain the pH at between 2.0 and 2.5. The buffer also contains ascorbic acid to reduce any iodine to iodide and to maintain iron in the ferrous state, in which form it will not react with gallein. Gallein is added and reacts slowly with any tin present imparting a pink colour to the solution. This colour is compared with standards, and the amount of tin in the original sample is calculated:

A number of elements, including copper, iron, manganese, titanium, antimony, molybdenum and tungsten, are known to react with gallein, and hence can interfere with the test. Of these, copper and manganese are completely suppressed by the iodide attack. Titanium, molybdenum, and tungsten may lead to high results, but this interference can be detected by the purplish colour given by these elements to the final solution. In most samples they are not appreciably extracted by the iodide attack. At times iron interferes when the buffer recommended by Stanton and McDonald is used. This difficulty can generally be traced to poor quality hydroxylamine hydrochloride used as a reducing agent in the buffer, and to a higher pH (2.65) of the buffer than that recommended by Wood (1956). Hydroxylamine hydrochloride is rather unstable and tends to deteriorate with time. Accordingly, in this test, ascorbic acid has been substituted for hydroxylamine hydrochloride as the reducing agent, as it has been found to control effectively even those samples where iron is a major constituent. In addition, the pH of the buffer has been lowered to approximately 2.4, and no further interference from iron has been experienced. During the development of the test, several stream sediment samples were analyzed which contained lead in the 0.5 to 1 per cent range. On addition of the buffer to a 1 ml aliquot of sample solution, a bright yellow reaction product was formed in the solution. The nature of this product has not yet been determined, but its presence prevented satisfactory determination of tin. However, when a smaller aliquot of sample solution was taken the interference was less marked, and it was possible to determine tin satisfactorily.

It has been found during development of the method that the iodide concentration is a factor of some importance. Iodide has the effect of partially suppressing the reaction of tin with gallein. When standards were prepared without iodide, as recommended by Stanton and McDonald, difficulty was experienced in matching samples containing iodide with these standards. Absorbance readings on standards containing 5 μ g of tin were approximately 15 per cent lower when iodide was present. Thus it is desirable that the iodide content of samples and standards be approximately the same.

ANALYTICAL PROCEDURE

Determination of Tin

1. To a clean dry test-tube (18 x 180 mm) add a weighed sample of 0.25 g of soil or stream sediment.
2. Add 0.5 g ammonium iodide with a plastic scoop and mix thoroughly.
3. Heat gently over a Bunsen flame, holding the tube nearly horizontally or use fusion rack described in the Appendix. Care must be taken to avoid loss of fumes, by keeping the upper part of the tube as cool as possible. Continue heating after fuming has ceased until the sample is at a dull red heat.
4. When the tube is cool add, by means of an automatic pipette, 5 ml of 1N HCl and warm to dissolve all the sublimed material on the sides of the tube. Any deposit not readily dissolved must be broken up with a polyethylene stirring rod.
5. When the sample solution has settled (at least 15 minutes) pipette 1 ml of the clear sample solution into a test-tube (16 x 150 mm) graduated at 5 ml.
6. Add buffer from a polyethylene wash bottle to the 5 ml mark and mix. If all colour of iodine is not immediately cleared, warm gently. If the solution is still not colourless add a small amount of solid ascorbic acid and shake to dissolve. The solution should now be colourless.
7. Add 0.1 ml of gallein reagent solution, shake gently to mix and allow to stand for at least 15 minutes.
8. Compare with standards prepared as directed below.
9. Calculate tin concentration in parts per million using the formula:
$$\frac{a \times 5}{b \times c} = \text{Sn (p. p. m.)}$$
where a = micrograms of Sn in matching standard
b = weight of sample in grams
c = aliquot taken in ml.
10. Should the sample be higher than the highest standard, take a smaller aliquot, add blank iodide solution (for preparation see below) to bring the sample volume to 1 ml and proceed with steps 6 to 10 above.

Preparation of Standards

1. In three test-tubes (18 x 180 mm) marked one, two, and three add 0.5 g of ammonium iodide. Heat over a Bunsen flame until the ammonium iodide has all sublimed.

2. Dissolve the iodide sublimate in tubes one and two in 5 ml of 1N HCl. These two tubes contain blank iodide solutions.
3. Dissolve the sublimate in tube three by adding 5 ml of tin standard containing 5 µg/ml of Sn with a volumetric pipette.
4. To 10 test-tubes (16 x 150 mm) add 0.0; 0.05; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8 ml of iodide - standard solution from tube three.
5. Bring the volumes up to 1 ml using blank iodide solution from tubes one and two by adding 1.0; 0.95; 0.9; 0.8; 0.7; 0.6; 0.5; 0.4; 0.3 and 0.2 ml of the blank iodide solution.
6. Add 4 ml of buffer to each tube.
7. Add 0.2 ml gelatin solution.
8. Add 0.1 ml gallein solution, mix, and let stand at least 15 minutes before use. These standards should be stable for approximately one week.

Preparation of Reagents

1. Buffer Solution: Dissolve 15 grams sodium hydroxide in 400 ml of metal-free water in a beaker calibrated at 1 litre. When dissolved cool this solution to below 20° C. Dissolve 106 grams chloroacetic acid in 400 ml of metal-free water. Immerse the beaker containing the NaOH solution in a cold water bath and slowly add the chloroacetic acid solution with stirring, keeping the temperature around 20° C. When mixing is complete, add 5 grams of ascorbic acid, stir to dissolve, and dilute to 1 litre with metal-free water. This buffer has a pH of approximately 2.4. The life of the buffer solution is increased by keeping in a cool dark place, preferably in a refrigerator.
- 2* Gallein Solution: Dissolve 0.1 gram gallein in 100 ml of ethyl alcohol, with gentle heating. Filter through a Watman No. 41 filter paper into a measuring cylinder. Note the volume and dilute with an equal volume of metal-free water. Store in a plastic bottle.
3. Gelatin Solution: Dissolve 0.5 gram of gelatin powder (reagent grade) in 100 ml metal-free water, warming to dissolve. Store in a plastic bottle and keep cold. The solution may require heating in a water bath before use.
4. 1N HCl: Dilute 42 ml of concentrated HCl to 500 ml with metal-free water. Store in a plastic bottle. Larger quantities of this acid solution may be made up if desired.

*Note: The test described here is a monocolour one. It may be made a mixed colour one by dissolving 0.03 gram of methylene blue in 200 ml of water with gentle heating, and adding an equal volume of this to the gallein-alcohol solution in place of metal-free water. The colour range then will be from green through grey to pink.

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5. 6N HCl: Dilute 250 ml of concentrated hydrochloric acid to 500 ml with metal-free water. Store in a plastic bottle.
6. Standard Tin Solution: 100 $\mu\text{g}/\text{ml}$ - In a beaker dissolve 50 mg pure tin metal powder (reagent grade) in 50 ml concentrated HCl with heating. Transfer to a 500 ml volumetric flask, rinsing the beaker once with 6N HCl. Dilute the solution to 500 ml with 6N HCl.
7. Standard Tin Solution: 5 $\mu\text{g}/\text{ml}$ - Measure 5 ml of the 100 $\mu\text{g}/\text{ml}$ tin solution into a 100 ml volumetric flask using a volumetric pipette. Dilute to 100 ml with 1N HCl. Prepare this solution immediately prior to preparation of standards.

Equipment Required

Torsion balance, 500 mg capacity sensitive to 1 mg
Reagent balance, 1 Kg capacity
Fluorescent titration illuminator
Glass writing diamond
Glass marking grease pencil
Stainless steel spatula, 4-inch blade
Stainless steel spatula, 8-inch blade
Water still and mixed resin demineralizing column or other source of metal-free water
Aspirator bottle, polyethylene, 5 gallons
Tygon tubing
Screw clips for tubing
Bunsen burner and gas supply
Filter funnel stand
Two racks to hold 50 test tubes (18 x 180 mm) each, with asbestos base
Rack to hold 50 test tubes (16 x 150 mm)
Rack to hold 10 test tubes (16 x 150 mm)
Plastic scoop, 0.5 and 1.0 gram capacity, made by drilling a hole in either end of a lucite bar, 2½ inches by ½ inch by ½ inch
Two polyethylene bottles, 500 ml capacity
Two polyethylene wash bottles, 500 ml capacity
Polyethylene bottle, 1 litre capacity
Two polyethylene bottles, 250 ml capacity
Polyethylene stirring rod, 12 inches by 1/4 inch
Ten corks, size 4, select quality
One box Watman's filter paper, No. 41, 9 cm circles
Beaker, Griffin low form, 1000 ml
Beaker, Griffin low form, 400 ml
Beaker, Griffin low form, 250 ml
Graduated cylinder, 500 ml
Graduated cylinder, 100 ml
Volumetric flask, 500 ml
Volumetric flask, 100 ml
Automatic pipette, to deliver 5 ml
Two serological pipettes, 1 ml calibrated in 1/100 ml

Serological pipette, 2 ml calibrated in 1/10 ml
Volumetric pipette, 5 ml
Filter funnel, 60°
*Test tubes, pyrex rimless, 18 x 180 mm, at least 150
*Test tubes, pyrex rimless, 16 x 150 mm, at least 75

Reagents required for 1,000 Determinations

Ammonium iodide, reagent grade, 600 grams
Gallein (4, 5 - dihydroxyfluorescein), 1 gram
Chloroacetic acid, reagent grade, 600 grams
Sodium hydroxide, reagent grade, 100 grams
Ascorbic acid, reagent grade, 30 grams
Gelatin, powdered, 1 gram
Tin metal, reagent grade, 30 mesh, 1 gram
Ethyl alcohol, absolute 500 ml
Hydrochloric acid, concentrated, reagent grade, 1 litre

Additional Notes and Precautions

1. The test as described is sensitive to 2 ppm Sn. This limit may be lowered to 0.5 ppm by taking a 1 gram sample with 1 gram ammonium iodide. If this sensitivity is required, care must be taken to increase the amount of iodide in the standards accordingly.
2. When aliquots smaller than 1 ml are taken the volume should be made up to 1 ml with blank iodide solution before adding buffer. For this purpose it is well to have several tubes of blank iodide solution prepared in advance, as described under preparation of standards.
3. Much of the success of the test depends on the efficiency with which the sample is attacked with ammonium iodide. It is important that as little as possible of the fumes be allowed to escape. The test tube should be held nearly horizontally, and as small a part of the tube heated as possible.
4. Once the fused sample has been leached with 1N HCl, the determination of tin should be carried out as soon as possible. The sample solution should never be allowed to sit overnight or for any appreciable time prior to determination of tin in the solution.

*Note: Number the 18 x 180 mm tubes 1 to 100 with a writing diamond. Keep 50 as spares. Number 50 of the 16 x 150 mm tubes 1 to 50 and calibrate at 5 ml. Fit 10 of the 16 x 150 mm with corks numbered 0; 0.25; 0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5; 4.0; and calibrate the tubes at 5 ml. Keep 15 as spares.

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APPENDIX

One of the greatest difficulties in carrying out the tin test described herein is the problem of obtaining reproducible results during the fusion process. With experience and proper care reproducible fusions can be successfully carried out without elaborate apparatus. However, the danger of loss of sublimate is great when samples are heated strongly. Conversely, inadequate heating may result in tin not being liberated from the sample. In order to make the fusion somewhat easier the following apparatus was designed.

Apparatus

The fusion apparatus (see Fig. 1) consists of a circular tray of copper 9 inches in diameter and $2\frac{1}{2}$ inches deep. In the centre is a well $2\frac{1}{2}$ inches in diameter. Four copper tubes of $\frac{7}{8}$ -inch inside diameter pass through the tray at 90-degree intervals from the outside into the inner well. In these tubes the sample test-tubes are placed. The inner well is lined with thin asbestos sheet with holes to fit the sample test tubes snugly. The tray is fitted with a water inlet made of $\frac{1}{2}$ -inch copper tubing containing small holes, which is arranged around the bottom of the tray. Near the top of the tray is a $\frac{1}{2}$ -inch tube which serves as a water outlet. Figure 2 is a detailed drawing of the apparatus.

Use

The tray described above is placed on a laboratory tripod ring stand. A Fisher burner is centred below the well in the centre of the tray. The water inlet is connected to the tap by means of a length of plastic tubing, while a length of $\frac{1}{2}$ -inch tubing connected to the outlet carries the overflow to the drain. The water is turned on slowly, adjusted to keep the tray full, and allowed to become cold. If running water is not available the inlet and outlet tubes may be corked and the tray filled with ice and water.

Test tubes (18 x 180 mm) containing sample and ammonium iodide are placed in each of the horizontal tubes of the tray so that they project into the central well for approximately $\frac{3}{4}$ -inch. The burner is lit and the fusion proceeds. As each fusion is finished the tube is withdrawn and another inserted in its place. During the fusion it is possible to heat the sample tubes to a bright red heat while the portion of the sample tube remaining within the tray remains cold to the touch.

Although this technique works satisfactorily and makes it possible to fuse four samples at the same time, care must be taken not to bring the heated tubes into contact because they will fuse together. In use the following technique has been found to be more satisfactory, but is not as rapid. Instead of fusing the four tubes at the same time the sample tubes are heated one at a time in rotation. Each test-tube is inserted into its hole so that the tip just shows through into the central well. Then one by one, each tube is pushed about 1 inch into the flame. When the fusion is finished the tube is returned to its original position to cool, and another is inserted into the flame. As each tube cools it is replaced by a new sample tube awaiting fusion. Although, using this method, the fusions are done one at a time, approximately fifty samples can be fused in one hour without danger of sublimate loss. Care should be taken to keep a test-tube in each of the four positions while the flame is burning, otherwise moisture from the flame will condense inside the cold copper tube and crack a hot sample tube.



Figure 1. Fusion tray in operation

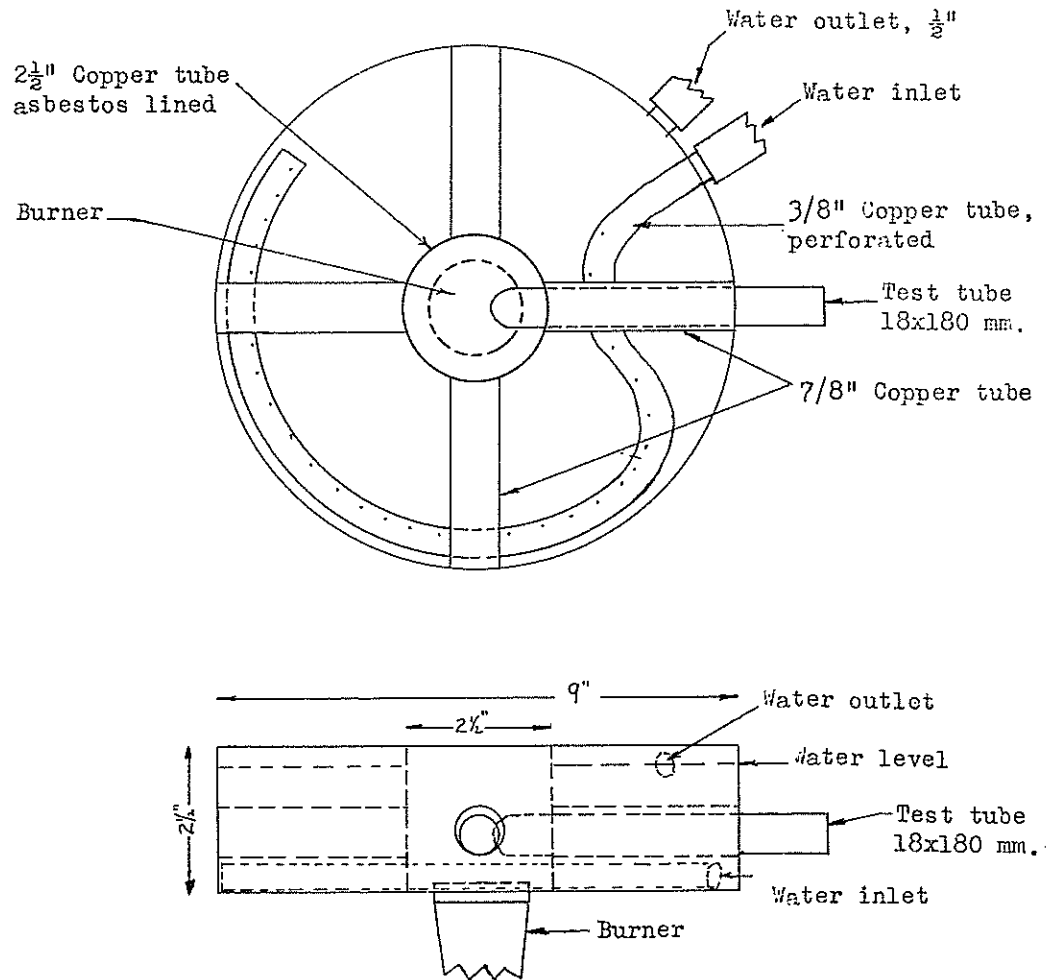


Figure 2. Fusion tray