Field Determination of Tin in Geochemical Soil and Stream Sediment Surveys*

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SYNOPSIS

A rapid method is described for the determination of tin in soils and sediments by means of gallein after decomposing the sample by heating it with ammonium iodide. The procedure may be used as either a mixed or a mono-colour method at the discretion of the analyst.

A FIELD METHOD FOR THE DETERMINATION of tin over the concentration range of 5 to 1250 ppm has been developed by Wood[1] for use in geochemical exploration. Marranzino and Ward[2] modified Wood's procedure by incorporating a solvent extraction stage, using a mixture of cyclohexanone and o-dichlorobenzene and covering the range 5–100 ppm. The present note describes a revised procedure whereby the lower limit of determination of the gallein method has been reduced to 0·5 ppm without recourse to a solvent extraction step; certain other improvements have also been made.

The procedure outlined below is a simple modification of Wood's method to cover the range 0·5 to 100 ppm on one aliquot from a 1-g sample; the range may be extended to 1000 ppm by use of a smaller aliquot. Visual comparison with a standard series may be facilitated by screening with methylene blue to give a mixed colour reaction, but the choice between mixed and mono-colour methods is a matter of personal taste which in no way affects the chemistry of the procedure. In preparing a standard tin solution, Wood dissolved the metal in hydrochloric acid, oxidized to stannic tin by addition of potassium bromate, and expelled bromine by boiling. The preparation of this solution is simplified by the fact that identical absorption spectra are exhibited by the tin-gallein complex at wavelengths ranging from 350 to 800 mμ, regardless of the initial valence state of the tin. Gelatine is added to the standard series to prevent precipitation of the tin-gallein complex. The mixed colour series ranges from green at zero through grey at 1·0 to 1·5 μg, to pink at 5 μg of tin, and it is stable for up to three weeks.

The acid leach solution employed by Wood contained 50 per cent of ethyl alcohol in order to achieve a rapid settling of the residue. Formation

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of the tin-gallein complex is retarded by alcohol, and the revised method, which employs a lower concentration of this reagent, reduces the effect to a minimum with only a slight increase in settling time.

Since there is a tendency for tin to be lost from the sample solution on long standing, it should be analysed during the day of preparation. This loss does not occur when the solution is filtered immediately after leaching, and it does not arise with standard tin solutions.

The method has also been applied to the analysis of rocks by Carmichael and McDonald.[3].

Productivity is 80 samples per man-day with a mean percentage accuracy of ± 25 at the 95 per cent probability level over the range 0·5 to 100 ppm.

Procedure

1. Mix 1 g of sample with 1 g of ammonium iodide in a Pyrex test-tube (18 by 180 mm). Heat the base of the tube until ammonium iodide ceases to sublime and the residue reaches a dull red heat. Keep the upper part of the test-tube as cool as possible to minimize loss of fume.

2. Leach by bringing to the boil with 5 ml of 1N-hydrochloric acid and allow the residue to settle.

3. Pipette a 1-ml aliquot into a test-tube (18 by 180 mm).

4. Dilute to 5 ml with buffer solution.

5. Warm until the iodine is reduced and then leave to cool.

6. Add 0·1 ml of reagent stock solution.

7. Mix and allow to stand for 10 min.

8. Compare with a standard series.

9. When the colour of a test solution is more intense than that of the highest standard, add the dilute reagent solution until the colour is grey, mix and allow to stand for 10 min before matching with the standards. When using the mono-colour reaction, dilute to within the middle of the range of the standard series.

10. If the test is still above the top standard, repeat from Step 3 with an aliquot of 0·1 ml, adding also 0·5 ml of 1N-hydrochloric acid.

11. The tin content in parts per million is obtained from the expression

$$\frac{b \times v \times d}{w \times a \times 5}$$

where b = matching standard (μg)

v = volume of final solution (ml)

d = volume of leach solution (ml)

w = weight of sample (g)

a = aliquot taken (ml).

Preparation of Standards

1. To 11 test-tubes add respectively 0, 0·05, 0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7, 0·8, and 1·0 ml of a standard solution containing 5μg of tin per ml.

2. To each of the first six test-tubes only, add 0·5 ml of 1N-hydrochloric acid.

3. Add 0·1 ml of gelatine solution.

4. Dilute to 5 ml with buffer solution.

5. Add 0·1 ml of stock reagent solution.

6. Mix and allow to stand for 10 min before using.

The standard range is 0, 0·25, 0·5, 1·0, 1·5, 2·0, 2·5, 3·0, 3·5, 4·0 and 5·0 μg of tin. If greater accuracy is required 0·75 and 1·25 μg standards may be included.

Preparation of Reagents

1. 1N-hydrochloric acid.—Mix 40 ml of the concentrated acid (sp. gr. 1·18) with 400 ml of water.

2. Buffer solution.—Dissolve 45 g of chloracetic acid, 75 g of sodium chloroacetate and 20 g of hydroxylamine hydrochloride in water and dilute to 1 litre.

3. Gelatine solution.—Dissolve 1 g in 100 ml of boiling water.

4. Stock reagent solution.—Dissolve 0·1 g of gallein in 100 ml of ethyl alcohol by heating gently, and filter through a Whatman No. 41 filter paper. Dissolve 0·03 g of methylene blue in 200 ml of water, warming gently. Combine the two solutions in equal proportions to provide the reagent stock solution. If the mono-colour reaction is preferred, dilute the gallein with an equal volume of water instead of methylene blue.

5. Dilute reagent solution.—Add 10 ml of stock reagent solution to 400 ml of buffer solution and 90 ml of 1N-hydrochloric acid and mix.

6. Standard tin solution.—Dissolve 50 mg of tin powder in 50 ml of concentrated hydrochloric acid and dilute to 500 ml with water. Dilute 5 ml of this solution to 100 ml with 1N-hydrochloric acid to give a solution containing 5 μg of tin per ml. Fresh dilute solution should be prepared from the strong solution each week.

REFERENCES

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