Rapid methods of tin determination for geochemical prospecting

W.W.S. YIM[1]

Abstract: Sampling errors and chemical interferences are largely responsible for many discrepancies in tin results obtained by various rapid geochemical techniques. For geochemical prospecting purposes it would be too expensive and time-consuming to analyse bulk samples, therefore, representative small samples must be used. However, measures for obtaining representative sub-samples are often neglected, thus rendering the results meaningless.

The merits and limitations of four geochemical methods currently in use for tin prospecting have been briefly assessed. The methods examined include the colorimetric technique, the emission spectrographic technique, the radioisotope X-ray flourescence technique and the atomic absorption technique. It is concluded that the atomic absorption method is superior to the other methods because it is more precise and that it is relatively free of chemical interferences. However, it is essential that the samples are free of calcareous material and that these samples are homogenised by grinding a representative portion of the original samples.

INTRODUCTION

The sampling problem of tin ores is well-known to mineral technologists, but this problem has been much neglected in geochemical prospecting. Since geochemical prospecting is used primarily to cut costs in mineral exploration, it would be expensive and time-consuming to analyse bulk samples. Therefore, representative small samples must be used. However, when small samples are used, whether the final results obtained are valid or not is doubtful.

Three semi-quantitative rapid methods are in use for tin determination in geochemical prospecting. Firstly, the emission spectrographic method (Nichol and Henderson-Hamilton, 1965), secondly, the colorimetric method (Stanton and MacDonald, 1961-2), which, according to Dunlop (1973), have a precision at the 95% confidence level of ±62.5% and ±23.5% respectively for soils and stream sediments in Cornwall. Finally, there is a method which involves the use of a portable radioisotope X-ray flourescence analyser (Bowie, *et al.* 1964-5), which according to Garson and Bateson (1967) at concentrations above the 150 ppm level, over 80% of the readings are within ±33⅓% of the mean. All three methods are affected to a greater or lesser extent by sampling errors and chemical interferences. The non-portable X-ray flourescence method is not considered here because it is a relatively slow method. This paper is based on findings from investigations made on sampling reproducibility and on existing geochemical methods suitable for tin determination in stream and marine sediment samples.

PROBLEMS IN SAMPLING

In general, there are two types of sampling errors. The first type of errors are those due to inherent inaccuracies of the method or due to bias in the analyst known as systematic errors. The second type is known as random errors which are due to sampling such as are introduced by taking dip samples from the sample container.

[1]Department of Geography & Geology, University of Hong Kong, Hong Kong.

Two common solutions for these errors are the use of standards based on the assumption that the errors affect both the known and unknown samples to the same degree; and the use of duplicates and/or more precise methods of analysis. However, these solutions only applied when the sample units used are representative of the sample population.

Sampling problems of cassiterite-bearing rocks, soils, stream and marine sediments are the result of, namely:

1. cassiterite normally occurs as discrete or monomineralic grains,

2. the high density of cassiterite (S.G.6.98–7.02), which results in its separation from other minerals by gravity,

3. the generally finer and variable grain size of cassiterite or cassiterite-bearing composite grains as compared with other mineral constituents present, and

4. the low abundance of cassiterite.

These factors acting in combination make it difficult to collect a representative sample. Therefore, in geochemical prospecting, the sample collected in the field must be sufficiently large, and during the sample preparation stage, measures must be taken to ensure that it is thoroughly homogenised before sub-sampling and weighing for tin determination.

There have been few investigations by geologists and geochemists on the sampling problem of earth materials. Edelman (1962) found that in an even-grained rock with a grain diameter of 1–2 mm, a representative sample requires a 1 kg sample weight, for it is necessary to have at least 10^7 grains if the specific gravity is 2.7. At 45 mesh and 70 mesh, the representative sample weights are 100 g and 20 g respectively. If less than 0.5 g sample is used in the geochemical analysis, it is necessary to grind 5 g of the 120 mesh fraction more finely (Kluman, 1967). In soils and sediments, cassiterite which is present as discrete mineral grains are more susceptible to sampling errors than other minerals, because of segregation due to its high specific gravity. Therefore a even larger sample than normal like those recommended by Gy (Ottley, 1966) will be necessary in order to obtain a representative sample. Gy proposed that in determining the weight of the sample required, the shape, particle size distribution, liberation and mineralogical composition factors should be taken into account.

Although the −80 mesh sample size fraction is widely used in geochemical prospecting, Tooms and Kaewbaidhoon (1961–2) have found that the +80 mesh size fractions may also be useful. However, in order that the sample will remain representative its weight collected in the field should increase with grain size. It is possible to estimate the number of cassiterite grains in different size fractions of a sample of soil or sediment by making a number of assumptions. The assumptions are, firstly, that all the tin is available as monomineralic cassiterite grains, secondly, all the grains within the sample are spherical and thirdly, the average density of the sample is 2.8. On the basis of these assumptions, it is possible to determine the number of cassiterite grains within any size fraction of a given diameter range and tin concentration. Table 1 shows the number of monomineralic cassiterite grains within each size fractions at different concentrations. The weight of a representative sample unit is dependent on the grain size as well as on the tin content. It can be seen that it is impossible to weigh out a representative sub-sample when only a fraction of a gram of the unground sample is used in the geochemical analysis. However, since composite grains of cassi-

TABLE 1

RELATIONSHIP BETWEEN GRAIN SIZE, TIN CONTENT
AND NUMBER OF CASSITERITE GRAINS IN 0.2 G UNGROUND SAMPLE,
BASED ON ASSUMPTION THAT ALL TIN IS PRESENT
AS DISCRETE CASSITERITE GRAINS

Grain Size (microns)		170–250	124–170	90–124	Under 90
Estimated No.	Minimum	8,727	27,757	71,521	187,056
of Grains	Maximum	27,756	71,520	187,055	>187,056
Tin Content ppm		No. of Grains			
100		0.4– 1.4	1.4– 3.6	3.6– 9.5	> 9.5
1,000		4 – 14	14 – 36	36 – 95	> 95
5,000		22 – 70	70 –181	181 –475	>475
10,000		88 –141	141 –363	363 –950	>950

terite may occur together with monomineralic grains, the sampling error is less than with monomineralic grains alone because the composite grains are lighter and segregation within the sample is less severe. Therefore, the samples collected in the field must be sufficiently large in size and should be ground to prevent inhomogeneity. Grinding of the samples may be done very rapidly to below 240 mesh by use of a Tema disc mill with grinding vessels of 10 cc, 50 cc, 100 cc or 250 cc capacity.

EXISTING METHODS OF TIN DETERMINATION

Out of the three existing methods of tin determination, the portable radioisotope X-ray flourescence method has the advantage in that it is rapid and non-destructive. A minimum of 20 g of sample was found to be necessary (Garson and Bateson, 1967) and grinding of the sample is essential in order to avoid gravitational concentration of cassiterite in the sample holder. Darnley and Leamy (1966) found that grinding will improve the sensitivity of the method as well as to obtain result consistency. However, the lower limit of detection of about 150 ppm (Garson and Bateson, 1967) is too high for geochemical prospecting purpose.

The relatively poor precision obtained by the emission spectrographic method and the colorimetric method may be accounted for mainly by sampling errors. These two methods commonly utilises 0.1 g and 1 g of the —80 mesh sample fraction respectively. Therefore, because of the small sample size and the inhomogeneity of the sample, the sampling errors may be very large. Although the 1 g sample used in the colorimetric method is less prone to sampling errors, tests with ground sample of variable weights up to 1 g attacked with 1 g ammonium iodide flux indicated that the best sample weight is around 0.2 g (Table 2). The residues from the first ammonium iodide attack were attacked a second time to determine the completeness of the first attack. However, the residues of the first attack were thoroughly washed with molar hydrochloric acid followed by deionised water to ensure that all soluble tin extracted had been removed. The results showed that the attack using a 0.2 g to 1 g sample to flux ratio is better than 90% efficient (Table 3).

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TABLE 2

RELATIONSHIP BETWEEN SAMPLE AND AMMONIUM IODIDE
RATIO ON SAMPLE WITH A MEAN COMPOSITION OF 3586 PPM TIN.
BASED ON TRIPLICATE ATOMIC ABSORPTION ANALYSIS.

Sample Wt.	Wt. NH₄I	Ratio	Mean	Range	Difference
g				ppm	
0.2	1	1:5	3600	3500–3700	200
0.5	1	1:2	3280	2960–3760	800
0.75	1	3:4	3005	2667–3467	800
1	1	1:1	3120	2840–3440	600

TABLE 3

EFFICIENCY OF AMMONIUM IODIDE ATTACK USING
A 0.2 G SAMPLE TO 1 G FLUX RATIO.

Sample No.	1st Attack	2nd Attack	Efficiency of 1st Attack %
	ppm		
1	2250	100	95.6
2	2500	200	92
3	4500	250	94.5
4	1800	< 50	97.3
5	6000	150	97.5

ATOMIC ABSORPTION METHOD

In recent years, atomic absorption spectrophotometry has played an increasingly important role in geochemical prospecting. The superiority of this technique, mainly due to its speed and better precision over the traditional techniques has already been described by Ward et al. (1969), Angino and Billings (1972) and others. However, because of the complex nature of geochemical samples, tin, always a difficult element to determine precisely at low concentrations, is subjected to chemical interferences. Allan (1963) reported a sensitivity of 0.4 ppm using a relatively low temperature air/ hydrogen flame which is prone to interferences, while Amos and Willis (1965) used a hotter nitrous oxide/acetylene flame which is less sensitive but seemingly without interference. Subsequently Bowman (1968) adopted this technique for analysing tin ores and concentrates, and Guru (1972) used a similar method for determining tin in sediments from the South China Sea. The procedure given below has been used for tin determination in soil, stream and marine sediment samples from Cornwall.

Analytical procedure

(1) Weigh 0.2 g of ground sample into a boro-silicate test tube (18×180 mm).

(2) Add 1 g of hand ground ammonium iodide (GPR grade) and mix thoroughly

(3) Heat over a low flame for 4–5 minutes, with frequent rotation and agitation of the tube until the ammonium iodide ceases to sublime, and the residue reaches a dull red colour.

(4) After cooling, add 5 ml of molar hydrochloric acid. Mix well and leach on a sand tray or in a water bath at 80 °C for 20 minutes.

(5) Dilute further if necessary with molar hydrochloric acid, mix well and leave to settle for 2 hours before spraying the solutions through the atomic absorption spectrophotometer.

Preparation of standards

(1) Stock tin standard 1000 ug/ml. Dissolve 1000 mg of tin powder (AR grade) in 100 ml of 10 molar hydrochloric acid and dilute to 1:1 with deionised water.

(2) Working standards. Prepare solutions for calibration by diluting the stock 1000 µg/ml tin standard to 2, 5, 10, 25, 50, 75 and 100 µg/ml of tin respectively with molar hydrochloric acid.

Operating Conditions

Instrument	Perkin Elmer atomic absorption spectrophotometer model 403
Wavelength	2246.1 Å
Slit Width	4
Lamp Current	30 mA
Burner Height	18
Flame	Nitrous oxide/acetylene
Flow Rate	Nitrous oxide 2.85 kg/cm²
	Acetylene 0.85 kg/cm²

The acetylene flow rate was adjusted to give the maximum 'red feather' without the flame being luminous. This was done in order to cut down carbon deposits forming in the burner slot, otherwise it would result in a decrease in sensitivity. In order to obtain the maximum absorption, the burner height was adjusted to a suitable level. The detection limit found was 2 µg/ml or a sample concentration of 50 ppm tin when using a digital readout and the calibration curve was linear up to 200 µg/ml (Fig. 1). No differences were found in the results when ammonium iodide was added to the standards. The precision, defined as two hundred times the standard deviation (s) divided by the concentration (c), 200 s/c, was determined by differences between duplicate determinations using the method of Thompson and Howarth (1973) (Table 4). It is possible to improve the sensitivity by using a graph recorder instead of the digital readout to isolate the background noise clearly. A plot of the results obtained for samples analysed in duplicate is shown in Fig. 2.

DISCUSSION

For marine sediment samples containing shells and similarly for calcareous rocks, soils and stream sediments, it is essential to remove the calcareous material with dilute acetic acid before the ammonium iodide attack. Table 5 illustrates the interference caused by the shell content in a marine sediment sample. If a sample with high calcareous content is decomposed by ammonium iodide, this reagent will attack the calcareous material in preference to the cassiterite, making the attack less efficient (Yim, 1975).
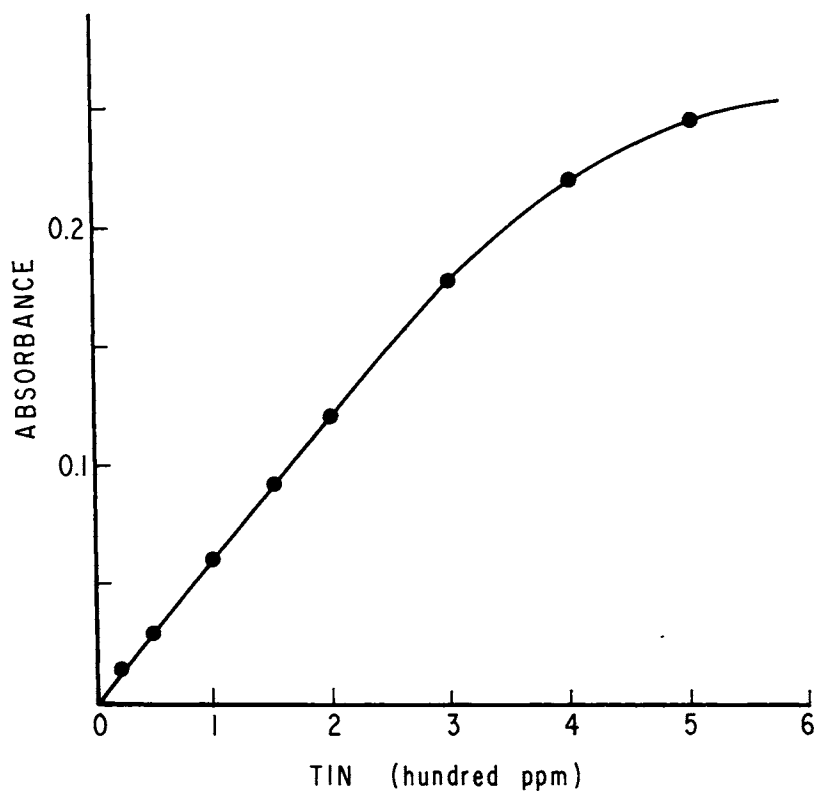
Fig. 1   Calibration curve for tin at 2246.1 Å in molar hydrochloric acid.

TABLE 4

RELATIONSHIP BETWEEN TIN CONCENTRATION AND
PRECISION OF ATOMIC ABSORPTION TECHNIQUE
BASED ON 197 DUPLICATES. (FROM YIM, 1975)

Tin Concentration ppm	Precision %
100	54.8
250	27.4
500	18.3
1,000	13.7
5,000	10.1
10,000	9.6
15,000	9.4

The precision of the atomic absorption method is superior over other geochemical methods of tin determination. Checks were made on the validity of the atomic absorption results using the volumetric method by titration with iodine following the reduction of tin using nickel (Pantony 1956). Fig. 3 shows that the atomic absorption results and the volumetric results are in agreement. On the other hand, comparison
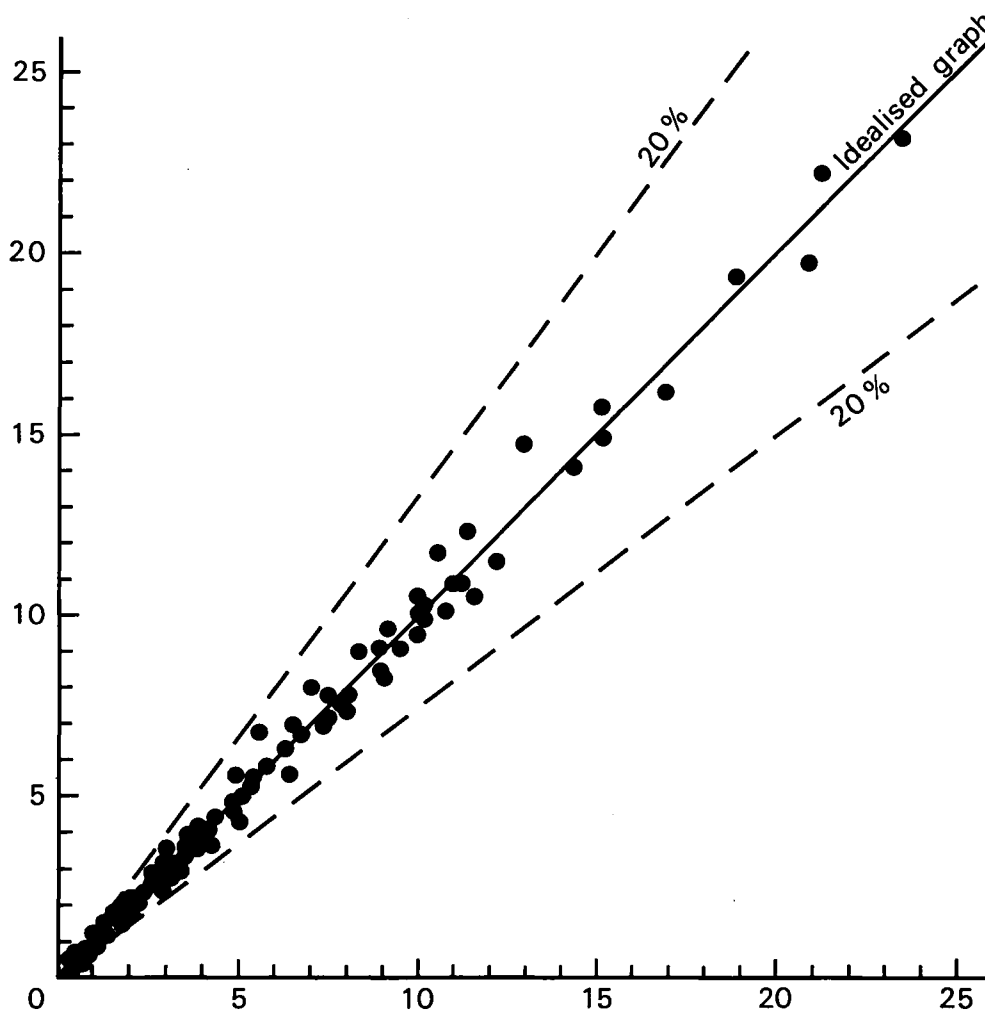
Fig. 2 Plot of tin results for 92 stream and marine sediment samples analysed in duplicate. (in thousands of ppm)

between results of the colorimetric method and the atomic absorption method (Fig. 4), suggests that the former method gave significantly higher results. The absence of values between 2000–3000 ppm for the colorimetric method indicates analytical error due to chemical interference. Since the samples with tin concentrations exceeding 3500 ppm have all been found to contain relatively high iron contnet, the narrow pH limits of 2.0 to 2.5 cannot be maintained due to incomplete reduction of ferric ions (Stanton and MacDonald, 1961–2), and a stronger buffer solution is required for complete reduction.

The results obtained by the emission spectrographic method for unground −80 mesh samples are, as expected, erratic compared to atomic absorption results for ground samples (Fig. 5). In addition to this, at high concentrations exceeding 4000

TABLE 5

RELATIONSHIP BETWEEN SAMPLE WEIGHT AND EFFICIENCY OF
AMMONIUM IODIDE ATTACK ON SAMPLE CONTAINING 32.5 PER CENT
SHELLS BY USE OF COLORIMETRIC METHOD. BASED ON
DUPLICATE ANALYSIS. (FROM YIM, 1975)

Sample Wt. g	Mean Assay Value of 1st Fusion	Mean Assay Value of Residue
	ppm	
0.1	875	190
0.25	640	320
0.5	200	700
0.75	17	500
1	<12.5	400
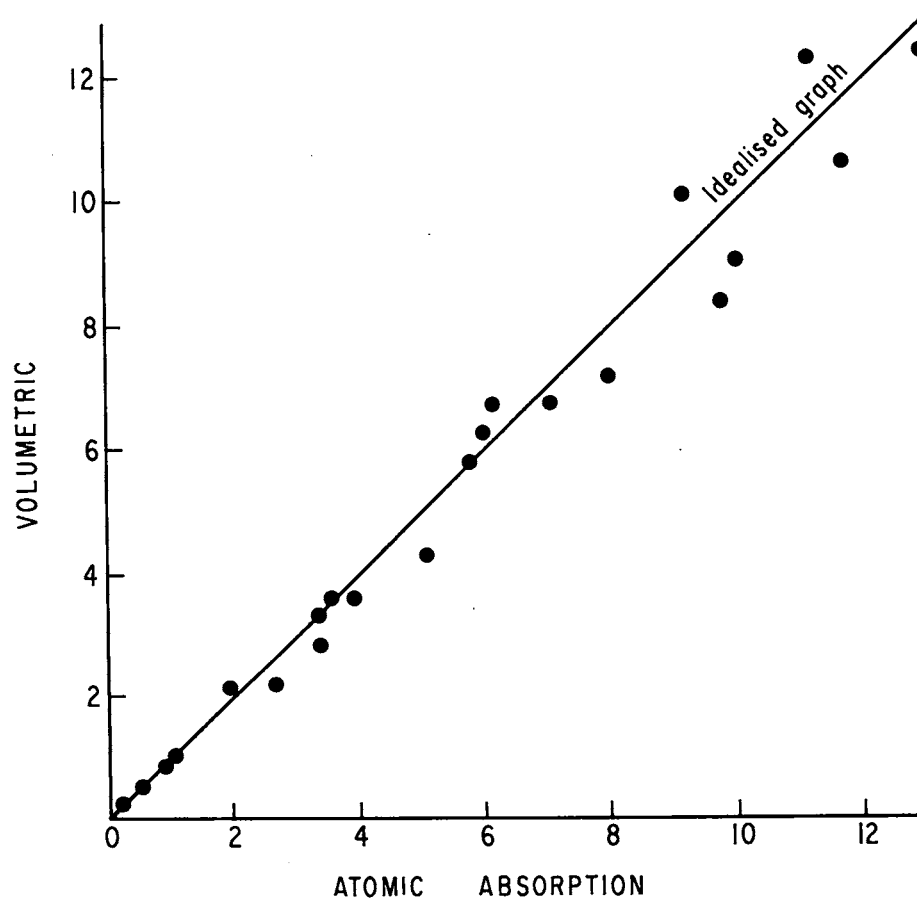
Fig. 3   Comparison between atomic absorption and colorimetric results. (in thousands of ppm)
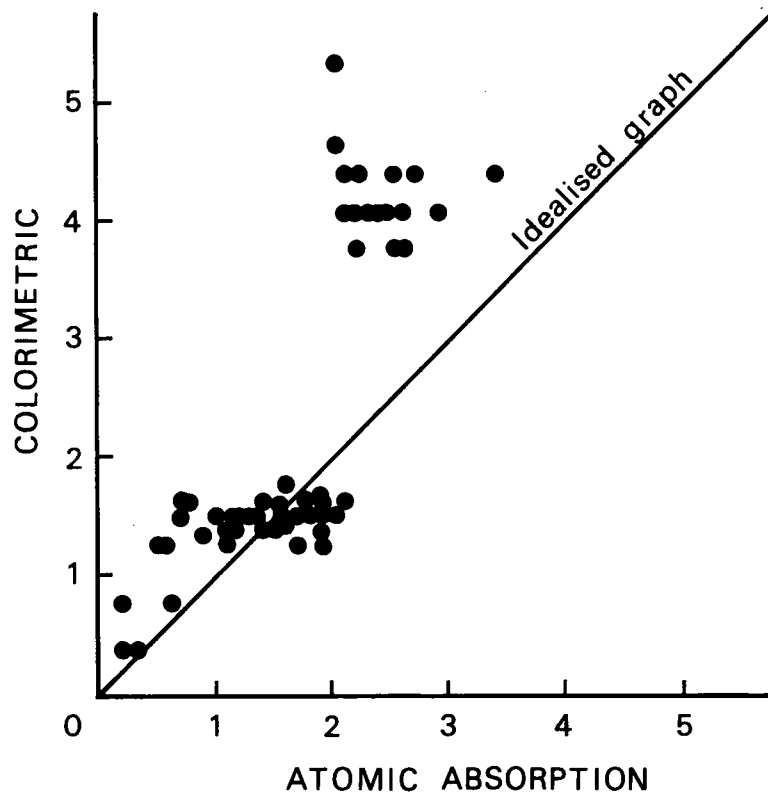
Fig. 4 Comparison between atomic absorption and colorimetric results. (in thousands of ppm)

ppm, the emission spectrographic results are higher than the atomic absorption results. This is likely to be the result of chemical interferences.

The productivity of the atomic absorption method is about 120 samples per man day excluding the time spent in sample preparation. This method compared to the emission spectrographic method is inexpensive especially when tin is the only element of interest. On the other hand, the colorimetric method has the major disadvantage in that it is subjective. It is likely that many laboratories using the colorimetric method do not take sufficient precautions to avoid sampling errors associated with using the −80 mesh unground sample, or, to follow the recommendation of Stanton and MacDonald (1961-2) in that the pH limits of 2.0 to 2.5 should be maintained. It is advisable to check the pH value of the buffer solution with a pH meter (Stanton, 1976).

A flow chart for the treatment of geochemical samples for tin determination is shown in Fig. 6. Kaewbaidhoon (1971) found that panning of alluvial sediments is preferable to conventional stream sediment geochemistry. Sampling errors are likely to be responsible for the erratic pattern of geochemical results compared to those obtained by panning. It is desirable to upgrade the tin content in the samples whenever possible by the removal of the barren fraction so as to cut down sampling errors. The separation point between samples with high tin content and low tin content may
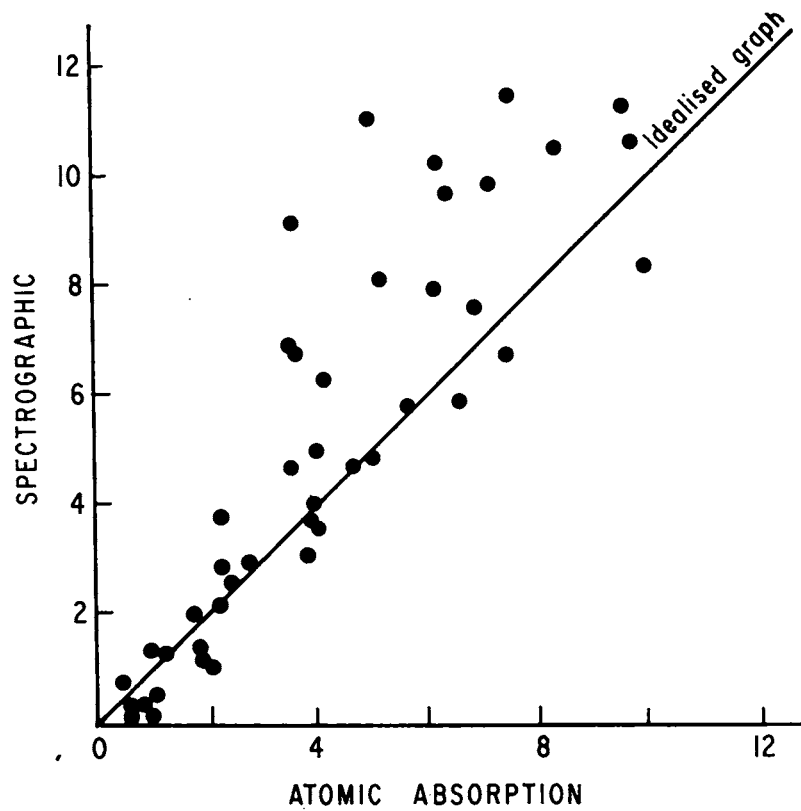
Fig. 5 Comparison between emission spectrographic results of unground –80 mesh samples and atomic absorption results of ground samples. (in thousands of ppm)
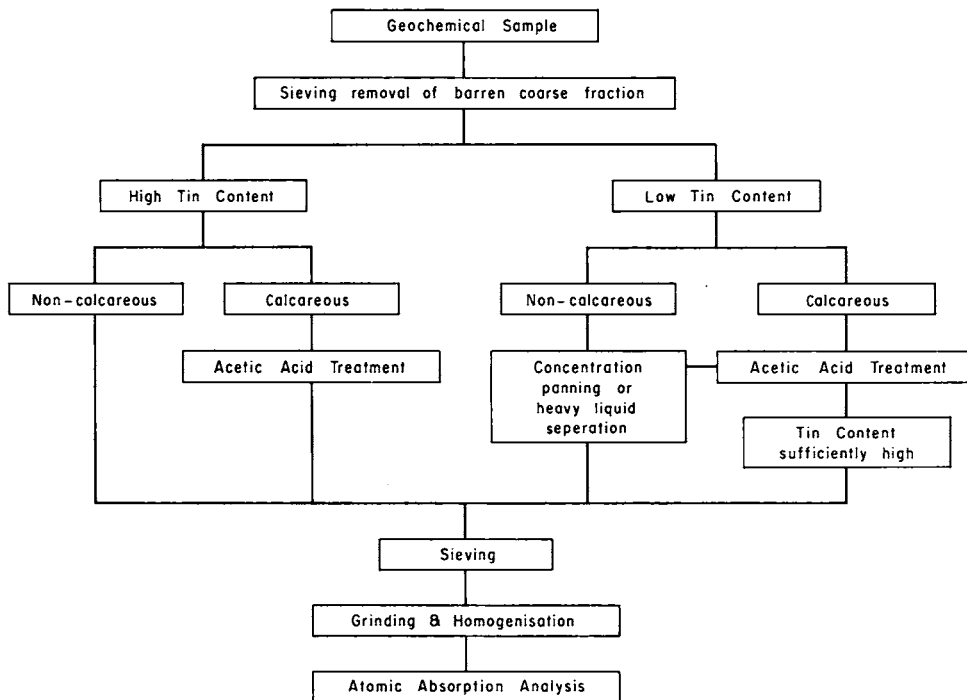

Fig. 6 Flow chart of sample treatment.

be determined during the orientation stage of the geochemical survey. For example, in the tin mining districts of Cornwall, the tin content in stream and marine sediments may be regarded as high since sufficient contrast can be found between background and anomalous values in the geochemical results without involving heavy mineral concentration methods like panning or heavy liquid separations.

CONCLUSIONS

Both sampling errors and chemical interferences are problems which deserve much more attention when applying rapid methods of tin determination in geochemical prospecting. The representative sample weight required should be determined during the orientation stage of the programme in order to avoid erratic results. Because of the low concentration of tin in the majority of the geochemical samples, it is desirable to pre-concentrate the sample to cut down sampling errors. Furthermore, it is necessary to split the sample representatively in all the sub-sampling stages, and, since the final sample weight used for tin determination is often small, a representative sample split must be homogenised by grinding in order to avoid segregation of cassiterite. The atomic absorption method outlined was found to be superior to the existing rapid methods of tin determination examined mainly because this method is found to be less prone to chemical interferences. However, in using this method, it is essential that calcareous material in the samples are removed beforehand.

ACKNOWLEDGEMENTS

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