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Field Determination of Cobalt in Soil and Sediment Samples*

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SYNOPSIS

A method for the determination of trace quantities of cobalt in soil and sediment samples is described. A thiocyanate complex of cobalt is extracted with amyl alcohol and compared with a series of standards similarly prepared.

A FIELD METHOD FOR THE DETERMINATION OF COBALT for use in geochemical prospecting was described by Almond and Bloom.[1] A confined spot test was used with 2-nitroso-1-naphthol as the reagent, when a lower limit of 10 ppm was achieved. Almond[2] subsequently developed a solvent extraction technique for this reagent, achieving a similar sensitivity. A paper chromatographic method with rubeanic acid as the spray reagent has been described by Hunt, North and Wells,[3] but in this case the lower limit of determination is 20 ppm and the method is often difficult to apply under field conditions. Ziegler and Glemser[4] described a procedure for the detection of cobalt as tri-*n*-butylammonium tetrathiocyanatocobaltiate; an analytical method based upon this was presented by Ziegler, Glemser and Preisler[5] and applied subsequently to steel analysis.[6] This procedure was adapted by Kranck[7] for the determination of cobalt in soil down to 5 ppm and used in a modified form by Jay[8] during geochemical dispersion studies in Northern Rhodesia. The method described below is based upon Kranck's work, and involves several radical changes in addition to improving the sensitivity to 1 ppm with an upper limit of 250 ppm from the same size of sample aliquot.

Procedure

1. Weigh 0·25 g of sieved sample into a borosilicate test tube.
   Operate with a batch of 100 samples.
2. Mix with 1 g of potassium bisulphate (fused, powder).
   Measure the bisulphate volumetrically with a perspex scoop.
3. Fuse until frothing has ceased and heat for a further 2 min.
   Use a primus stove fitted with an improvised attachment to support six test-tubes in the flame.
4. Allow the melt to cool and then add 5 ml of 0·5M-hydrochloric acid.
   Deliver the acid by means of an automatic dispenser.
5. Digest on a sand-tray until the melt has disintegrated.
6. Add 10 ml of buffer solution to a test-tube (16 × 150 mm).
   The tube should be calibrated at 10 and 12 ml.

[1] etc. See references at the end of the paper.

7. Pipette an aliquot of 2 ml into the test-tube.

8. Add 0·5 ml of tri-*n*-butylamine solution.

    Use an automatic pipette.

9. Cork the tube and shake vigorously for 1 min.

10. Compare the intensity of blue in the solvent phase with a set of standards (see below).

11. If the test solution shows a greater intensity than the highest standard repeat using a sample aliquot of 0·1 ml.

    Since acid must be added so that the equivalent of 2 ml of 0·5M-hydrochloric acid is present, dilute to the 12 ml mark with 0·5M-hydrochloric acid after adding the aliquot to the buffer solution.

12. The cobalt content in parts per million is obtained from the expression

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

where b = matching standard (μg) w = weight of sample (g)

       d = volume of leach solution (ml) a = aliquot taken (ml).

Preparation of Standards

1. To 22 test-tubes (16 × 150 mm) each containing 10 ml of buffer solution, add respectively 0, 0·05, 0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7, 0·8, 0·9 and 1·0 ml of a standard solution containing 5 μg of cobalt per ml, and 0·3, 0·35, 0·4, 0·5, 0·6, 0·7, 0·8, 0·9, 1·0 and 1·25 ml of a standard solution containing 20 μg per ml.

    The test-tubes should be calibrated at 10 and 12 ml.

2. Add 0·5M-hydrochloric acid to the 12-ml level.

3. Add 0·5 ml of tri-*n*-butylamine solution.

4. Cork the tubes and shake vigorously for 1 min.

    The zero standard should have a colourless solvent phase and the remainder increase uniformly in their intensity of blue.

Preparation of Reagents

1. *6M-hydrochloric acid.*—Mix 240 ml of the concentrated acid (sp. gr. 1·18) with 200 ml of water. Alternatively, the constant boiling mixture (6·11M) may be used.

2. *0·5M-hydrochloric acid.*—Mix 20 ml of the concentrated acid (sp. gr. 1·18) with 420 ml of water.

3. *Buffer solution.*—Dissolve 170 g of sodium acetate (tri-hydrate), 40 g of tetra-sodium pyrophosphate (deca-hydrate) and 5 g of hydroxylamine hydrochloride in water, add 140 ml of 6M-hydrochloric acid and dilute to 1 litre with water (solution A). Dissolve 360 g of potassium thiocyanate in water and dilute to 1 litre (solution B). Solutions A and B are mixed in the ratio 9 : 1 as required daily.

4. *Tri-*n-*butylamine solution.*—Mix together 90 ml of amyl alcohol (*n*- or *iso*-) and 10 ml of tri-*n*-butylamine. This solution should not be kept for longer than two to three days. The tri-*n*-butylamine must be colourless; it may develop a yellow tint with age.

5. *Standard cobalt solutions.*—Dissolve 202 mg of cobaltous chloride (hexahydrate) in water, add 25 ml of concentrated hydrochloric acid and dilute to 500 ml with water for a solution containing 100 μg of cobalt per ml. Dilute 20 ml of this solution with 0·5M-hydrochloric acid to 100 ml to give a solution containing 20 μg of cobalt per ml and dilute a further volume of 5 ml to 100 ml with 0·5M-hydrochloric acid to give a solution containing 5 μg of cobalt per ml. The two dilute solutions should be prepared freshly each week.

Decomposition of Samples

Using a paper-chromatographic method of analysis, Wood[9] found that results obtained after heating the sample with ammonium chloride agreed with those following fusion with potassium bisulphate, and suggested that the ammonium halide attack might provide a more convenient method of breaking down the sample. However, a more detailed comparison of these two forms of sample attack has shown that the ammonium chloride treatment does not give consistent results for cobalt. The mean accuracies (at the 95 per cent confidence level)[10] obtained on the same set of twelve samples were ± 20 per cent for potassium bisulphate and ± 50 per cent for ammonium chloride, the cobalt ranging from 5 to 120 ppm. This difference in accuracy would not be obvious when using the chromatographic method, which has a very poor precision for cobalt within this concentration range.

Extraction of the Cobalt Complex

An absorption spectrum has been plotted from 400 to 800 mμ and shows one maximum in this region, at a wavelength of 620 mμ. Beer's Law is obeyed from 0·2 to 50 μg per ml.

The reaction does not proceed in the complete absence of acetate, although as little as 7·5 mg of sodium acetate per ml of final aqueous solution will ensure complete reaction and extraction. Twenty times this concentration is necessary in order to maintain a pH value within the optimum range for the extraction of the thiocyanatocobaltiate complex. In the absence of other reacting ions this pH range is 1·0 to 5·2, but to minimize the degree of interference it is necessary to keep within the narrower limits of 4·5 to 5·2. The effect of pH variation on the recovery of added cobalt in the absence and presence of calcium and ferric ions is shown in Fig. 1.
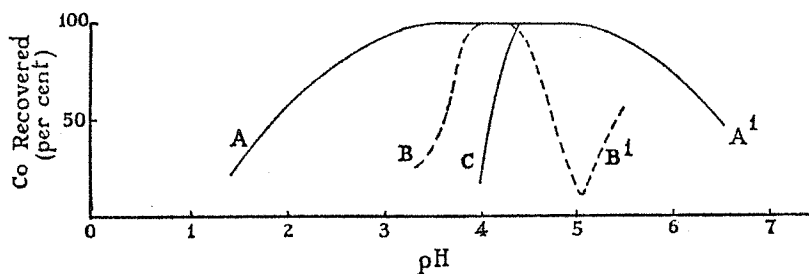

Fig. 1.—The effect of acidity on the recovery of cobalt.
AA^1 - Co 20 ppm; BB^1 - Co 20 ppm, Ca 10 per cent; CA^1 - Co 20 ppm, Fe 10 per cent.

When the optimum conditions are maintained, both sample and standard solutions will remain unchanged for a week. However, it is advisable to prepare fresh standards each day and store them in the dark when not in use, for although no deterioration due to age or light has been detected, it is possible that the stability of the thiocyanatocobaltiate solution in the organic phase may be influenced by trace impurities in the amyl alcohol.

Interference from Other Ions

The elements listed in Table I have been found to give no interference up to the stated concentration. The percentages quoted are related to complete solution of all the constituents of the sample, which is not necessarily the case in practice.

TABLE I.—*Elements causing no interference at the concentrations tested*

Element	%	Element	%	Element	%	Element	%
Fe	20	Ca	5	Cr	0·1	Mo	0·1
Al	20	Ti	0·7	Ni	0·1	W	0·1
Mn	20	Cu	0·7	Zn	0·1	V	0·1
				Pb	0·1		

For lateritic soils, the ammonium fluoride employed by Kranck as a sequestering agent for ferric ions has proved to be inadequate when optimum sensitivity is required. If the iron in solution exceeds the equivalent of 5 per cent of the original sample, it can only be masked by fluoride at the expense of sensitivity, since the cobalt reaction with thiocyanate would be suppressed slightly by an increase in the fluoride concentration. This limit is improved to 20 per cent when pyrophosphate is used, and there is also an improvement in the stability of the coloured organic phase. With fluoride, a trace of iron will enter the organic layer after the solvent extraction stage within one or two minutes of the phases separating. A yellow discoloration results which necessitates a further brief shaking immediately prior to matching with standards, a step that is unnecessary when using pyrophosphate.

The efficiency with which pyrophosphate masks iron in the presence of thiocyanate falls off sharply below pH 4·0 (see Fig. 1). The shaking time of 1 min is necessary for complete removal of interference from iron, even though cobalt alone can be extracted completely in 20 to 30 sec.

Interference from copper was prevented formerly by reduction with sodium thiosulphate. Under the weakly acid condition of the test this reagent has a tendency to decompose when mixed with the sample aliquot. A slight deposition of sulphur occurs, which either collects at the interface or disperses through the organic phase, imparting a yellow colour. This trouble is avoided by employing hydroxylamine hydrochloride as the reducing agent. For samples containing copper in excess of 0·7 per cent, the concentration of hydroxylamine hydrochloride can be increased proportionately, providing that the test is performed within the optimum range of pH.

The main limitation of the method arises from the fact that many pyrophosphates will precipitate and that there is great danger of these

precipitates carrying cobalt with them. Calcium is the main offender in this respect (see Table II) and it is unfortunate that the optimum range of pH in the presence of iron is different from that in the presence of calcium (see Fig. 1). The conditions of the aqueous test solution are in favour of the iron complexing with thiocyanate rather than pyrophosphate, and when

TABLE II.—*Recovery of cobalt in the presence of major components of soil samples*

Elements added	Percentage of each added element	Percentage of Co recovered from 20 ppm
Ca	2	100
	5	95
	10	80
	15	< 5
	20	< 5
Ca, Fe, Al, Mn .	1	100
	5	90
Fe, Al, Mn . .	5	100
	10	100

the latter is completely utilized in masking other elements (e.g. calcium or aluminium) even a trace concentration of iron will give discoloration in the amyl alcohol phase.

Performance

Results within ± 20 per cent at the 95 per cent confidence level[10] are easily achieved with very little experience, even in the concentration range
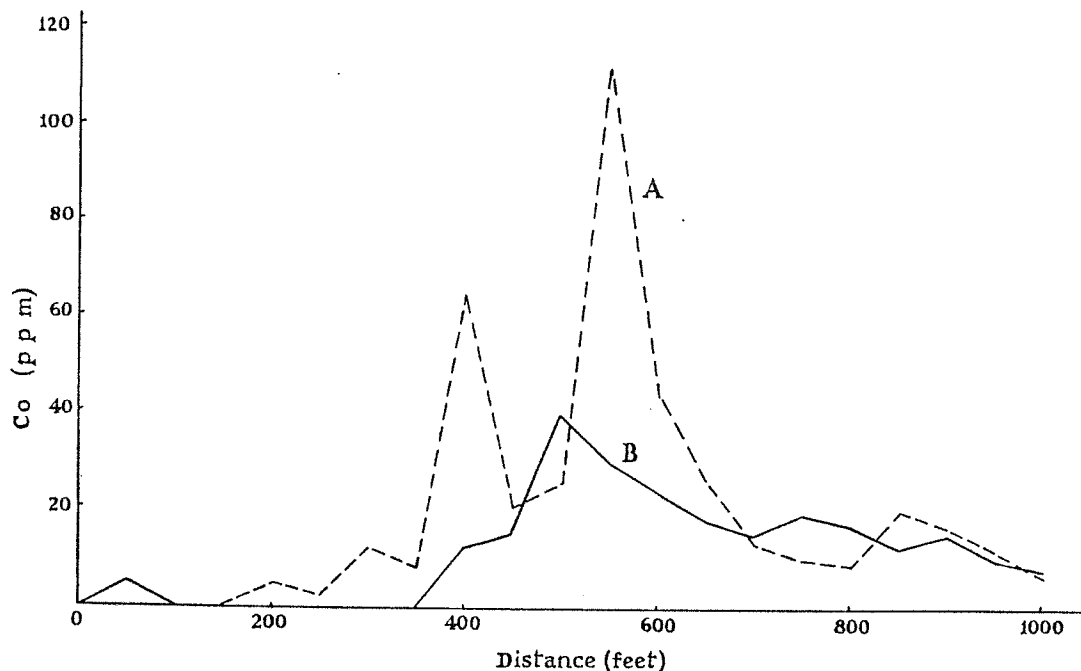

Fig. 2.—Traverse over freely drained soil at Chambishi, Northern Rhodesia. Sampled at, A, 3 in. and, B, 18 in. from surface.

1–50 ppm. The lowest standard represents 2·5 ppm, and cobalt may be detected down to 1 ppm. The range of 1 to 250 ppm is covered from a

sample aliquot of 2 ml and it may be extended to 5000 ppm by using an aliquot of 0·1 ml.

Fig. 2 depicts a traverse over freely drained soil at Chambishi, Northern Rhodesia.

Conclusions

The cobalt content of soil and sediment samples can be determined at concentrations varying from 1 to 250 ppm in the presence of iron up to 20 per cent. Within this range, 100 samples can easily be analysed per man-day to within ± 20 per cent at the 95 per cent confidence level, and the method is suitable for geochemical prospecting.

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