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A SEMIMICRO METHOD FOR THE  
DETERMINATION OF COBALT IN SOILS  
AND ROCKS: A FIELD TEST  
USING THE CHROMOGRAPH

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## ABSTRACT

A chromatographic method for the quantitative estimation of cobalt in soils and rocks is described. A 0.1 g sample is fused with potassium bisulfate and the fusion product extracted with 5 ml of citrate solution. A 0.2 ml aliquot of the sample solution is mixed with 0.1 ml of 2-nitroso-1-naphthol solution in the chromograph and the reddish brown cobalt nitroso-naphtholate that precipitates on the filter paper is compared with that of a standard series. Cobalt contents from 10 to 400 ppm in soil or rock can be determined to within  $\pm 40$  percent of the figure obtained spectrophotometrically in the laboratory.

## INTRODUCTION

In the course of the U. S. Geological Survey project to develop quick tests which can be carried out under field conditions, a satisfactory procedure has been found for determining cobalt, using 2-nitroso-1-naphthol as a confined spot test reagent.

Sensitive cobalt reagents are nonspecific. In order to determine the cobalt content of natural materials, a preliminary separation of the interfering elements is generally required. Before determining the cobalt content of a solution of plant material by the nitroso R salt method, Deijs and Feldmeyer (1949) separated the cobalt

from iron and copper with dithizone. Boyland (1946) suggested that all the metal complexes of 2-nitroso-1-naphthol be extracted into an organic solvent such as amyl alcohol or carbon tetrachloride. The immiscible organic phase can be separated from the aqueous phase and then in turn treated with concentrated hydrochloric acid or other acids which destroy the complexes of all the metals except cobalt. In the chromatographic spot test described here, 2-nitroso-1-naphthol is used to precipitate cobalt from complex solutions and the estimation is made without preliminary separation.

The chromograph, a device for making confined spots on reagent paper, was developed by Stevens and Lakin (1949) of the U. S. Geological Survey. The device is used "to confine areas of definite size on a strip of reagent paper fed through the apparatus, and to control automatically the rate of flow of test solution through the spot". The chromograph is used in this cobalt test to confine the precipitate resulting from the reaction of a cobalt solution with a solution of 2-nitroso-1-naphthol in a fixed area.

## REAGENTS

All reagents should be analytical grade. 2-Nitroso-1-naphthol. 0.01 percent. Dissolve 0.01 g 2-nitroso-1-naphthol in 100 ml of water to which 4 drops of N NaOH has been added.

Sodium hydroxide, N. Dissolve 40 g NaOH in water and dilute to 1 liter.

Potassium bisulfate. Pulverize in a mullite mortar.

Sodium citrate. Dissolve 50 g  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5\frac{1}{2}\text{H}_2\text{O}$  in water and dilute to 100 ml. Litmus paper, red.

Borate buffer. pH about 6.5. Dissolve 19 g  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  in 1 liter of water. Add 17 ml constant boiling HCl.

Sulfuric acid, N. Add 28.5 ml conc  $\text{H}_2\text{SO}_4$  to about 500 ml water and dilute to 1 liter.

Cobalt standard solution. 0.01 percent. Dissolve 0.40 g  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in water, add 1 ml of 1:1 HCl and dilute to 1 liter. Prepare more dilute solution from this stock solution.

Water. Water passed through the resin demineralizers now on the market is of satisfactory purity. The Bantam Demineralizer sold by the Barstead Still and Sterilizer Co. was used in this work.

#### EQUIPMENT

Gasoline stove. A Coleman "GI" pocket stove available in sports shops is satisfactory.

Fusion test tube rack. Constructed of two disks of sheet steel welded to a central supporting rod. Each plate has eight holes for test tubes; the holes in the bottom plate are small enough that the tubes will not slip through but large enough to permit the ready flow of heat.

Digestion rack. Similar in construction to that described for the fusion rack, but modified to fit into the utility cup of a Coleman "GI" pocket stove.

Filter sticks. Fuse a fritted pyrex disk of medium porosity on one end of a pyrex glass tube, 7 mm inside diameter and 130 mm long. (Developed by R. E. Stevens, U. S. Geological Survey)

Test tubes, 16 x 150 mm (marked at 10 ml), pyrex.

Dropping bottles. 6, pyrex.

Reagent bottles. 12, 250 ml, pyrex.

Balance. A torsion balance with a 0.01 g sensitivity is satisfactory.

Ear syringes. 6.

Pipettes. 2-0.5 ml, serological.  
2-2 ml, volumetric.  
2-5 ml, volumetric.

Filter paper. Whatman no. 50 cut in  $\frac{1}{2}$  in. strips.

Mullite mortar and pestle. Outside diameter of mortar 3 in.

#### PROCEDURE

1. Mix 0.1 g of finely ground soil or rock sample with 0.5 g pulverized potassium bisulfate in a pyrex test tube and fuse for 5 min. Cool, rotating the test tube so that the melt solidifies in a thin layer on the sides of the test tube.
2. Add 5 ml of the sodium citrate solution and digest in a boiling water bath until the lumps of flux are decomposed.
3. Add 1 small piece of litmus paper, then N sodium hydroxide dropwise until the litmus turns blue.
4. Add 2 ml of borate buffer, followed by N sulfuric acid to make the solution just acid. Dilute to 10 ml with water.
5. Place filter stick in test tube and apply suction to upper end of filter stick with an ear syringe.
6. Insert a strip of filter paper in the chromatograph and adjust the water level to the base of the connector tube (see fig. 2).
7. Transfer 0.2 ml of the filtrate in the filter stick (from operation 5) to the filter head of the chromatograph and add 0.1 ml of the 2-nitroso-1-naphthol reagent.
8. Open the stopcock to the rubber bulb and squeeze the bulb until the water column is at the top timing mark.
9. Turn the stopcock into position so that drainage takes place through the slow capillary.
10. After filtration is complete, add 1 drop of N sulfuric acid, and drain again.
11. Write the sample number adjacent to the spot on the paper.

Table 1.--Effect of pH on precipitation of elements with 2-nitroso-1-naphthol (citrate present).

pH	Quantity of precipitate from solutions of indicated percent concentration			
	Ni(0.1)	Fe(5)	Cu(0.1)*	Co(0.01)
1.0-2.0	absent	maximum	absent	absent
2.0-3.0	trace	moderate	absent	trace
3.0-3.5	trace	absent	absent	moderate
3.5-8.5	trace	absent	absent	maximum
8.5 plus	trace	absent	absent	trace

\*No copper precipitation with 2-nitroso-1-naphthol in presence of citrate.



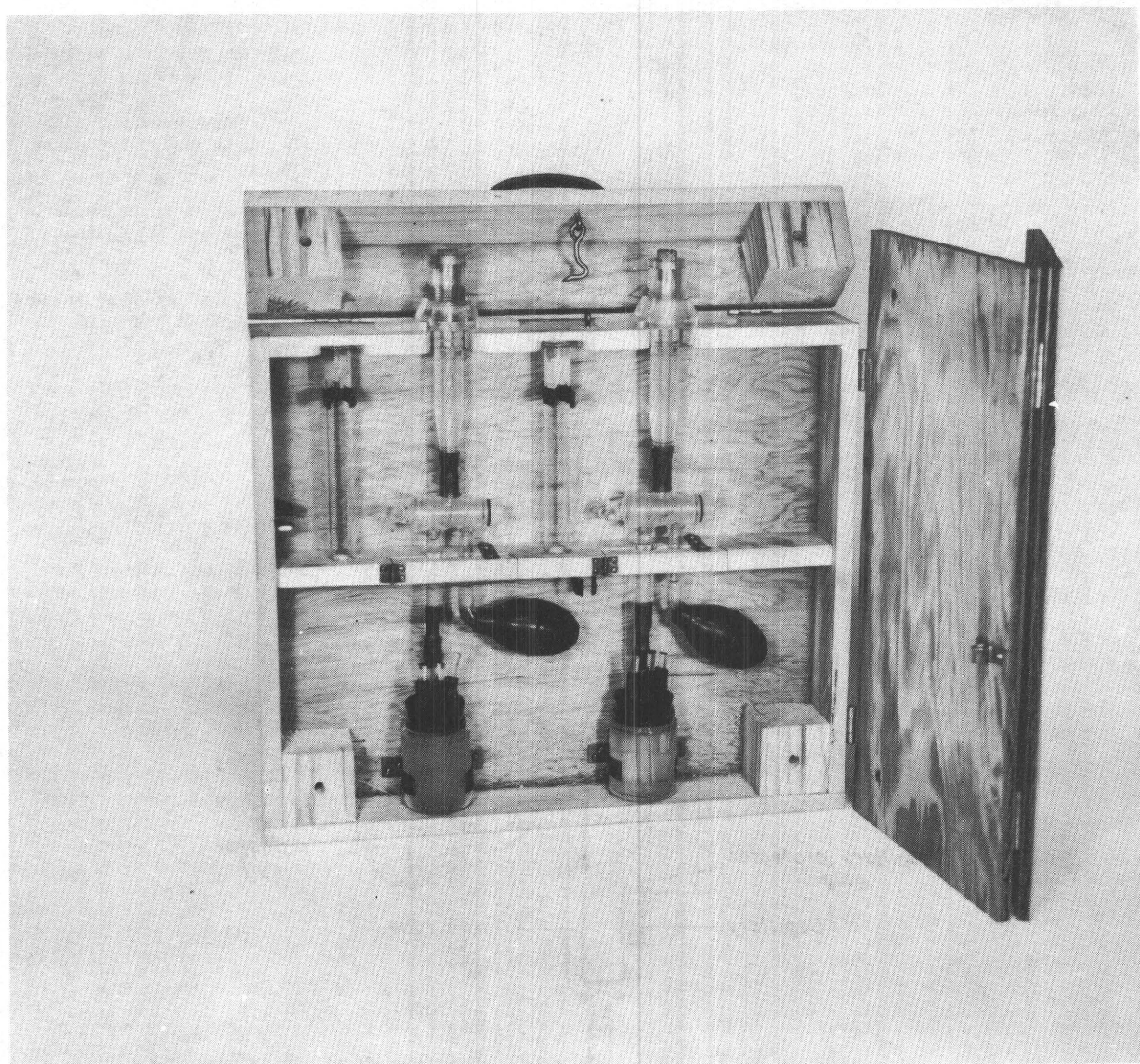


Figure 1. A chromograph set complete with case.

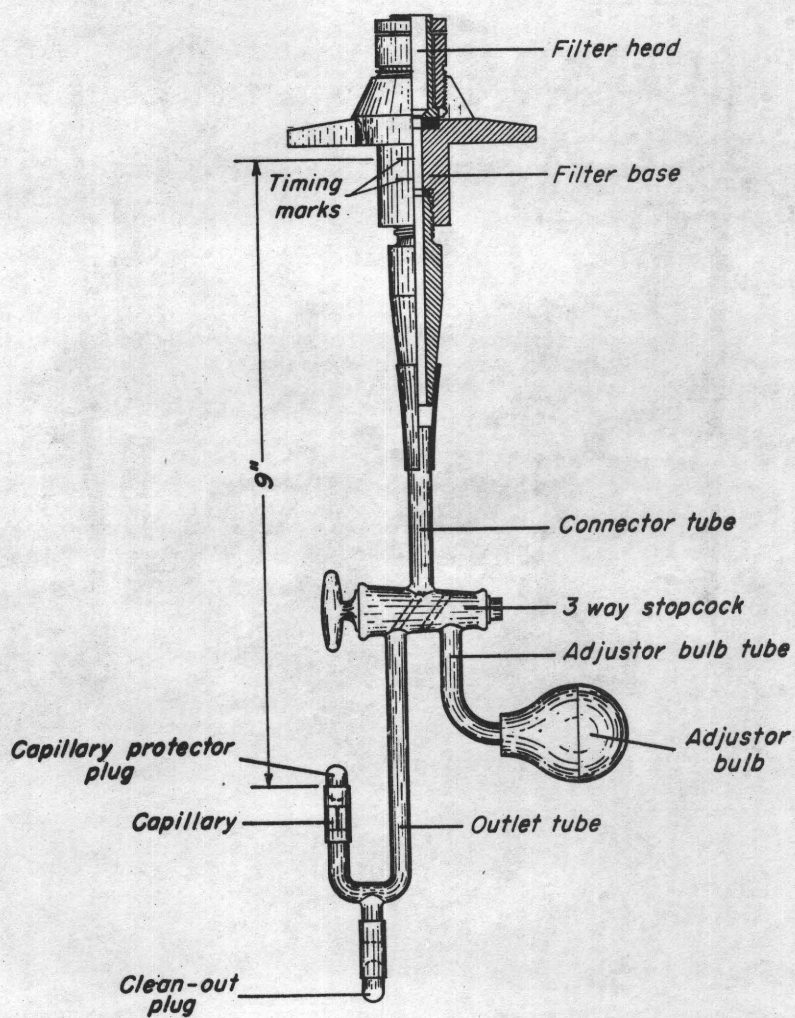


Figure 2. The chromatograph assembled showing on capillary.

12. Remove the strip of paper and allow the spot to dry.
13. Wash and dry the chromatograph head and parts that come in contact with the filter paper to remove traces of acid.
14. Compare the spots with spots of the standard series.
15. Repeat the test on those samples containing more than 400 ppm by diluting the sample solution.

Standard "spot" series: Prepare a series of spots ranging from 10 to 400 ppm as follows: To a series of 0.1 g cobalt-free soil samples, add 1, 3, 5, 8, 10, 20, and 40 micrograms of cobalt from standard cobalt solutions respectively. Evaporate to dryness over a steam bath. Add the flux, mix and prepare cobalt spots as described in operations 2 to 12.

### DISCUSSION

The direct fusion of soil or rock with potassium bisulfate is based on the Hillebrand - Lundell (1929) treatment of cobalt minerals in which cobalt minerals are broken up by a preliminary acid attack, followed by a fusion of the insoluble residue. To simplify the decomposition procedure, the acid attack was omitted.

Feigl (1946) describes spot test techniques for the detection of traces of cobalt with 2-nitroso-1-naphthol in the presence of iron and copper. He coprecipitates iron and cobalt as the phosphate and reduces copper (II) to copper (I). These steps reduce the sensitivity of the test about tenfold. In the chromatographic technique the interferences of copper and iron are eliminated by using a citrate solution at a controlled pH, and the test remains

Table 2.--A comparison of cobalt content of soils determined by spectrophotometric and chromatographic procedures.

Sample No.	Cobalt (ppm)	
	Spectrophotometric	Chromatographic
1	15	5
2	20	30
3	25	30
4	35	50
5	50	30
6	50	70
7	55	50
8	70	60
9	85	100
10	100	90
11	170	220
12	180	170
13	240	300
14	375	300
15	400	350

highly sensitive. The reddish-brown precipitate, cobalt nitroso-naphtholate, forms between pH 3.5 to pH 8.5. After filtration is complete, excess reagent is removed by washing with N sulfuric acid.

Color differences on spots containing from 0.02 to 0.8 micrograms of cobalt can be determined by the test described here. When a solution contains more than 0.8 micrograms of cobalt in the 0.2 ml aliquot, a spot of maximum intensity is formed, and a visual comparison with standard spots is not feasible; however, the concentration of cobalt in such a solution can be determined by dilution. Since the original sample weighed 0.1 g, a 0.2 ml aliquot from a 10 ml sample solution corresponds to 1/500 of a 1 g sample. The lowest detectable spot contains 0.02 micrograms of cobalt which corresponds to 10 ppm in the original soil; the highest comparable spot contains 0.8 micrograms of cobalt which corresponds to 400 ppm.

The effect of pH on precipitation of several elements is shown in table 1. The quantity of precipitate from a 0.1 percent nickel solution was small at any pH. A 5 percent iron solution gave strong dark colored precipitates below pH of 3, but above pH 3 no precipitate was formed. A 0.1 percent copper solution gave no precipitate in the presence of citrate.

### RESULTS

A comparison of the results obtained by two methods of analyses is given in table 2. In the laboratory (spectrophotometric) method, the sample was decomposed with perchloric acid. Copper was removed from an acid solution (pH 2.5 to 3.0) with dithizone. Cobalt was separated from iron by extraction with dithizone at pH 8. Cobalt dithizonate was destroyed with nitric acid, and the solution evaporated to dryness. The oxides were dissolved in acid and the cobalt in the solution estimated with nitroso R salt. The soils were high in copper and all contained large amounts of iron. Neither of these elements interfered. Except for sample no. 1, all results fall within 40 percent of each other. The greater number of steps required by the spectrophotometric method may lead to greater errors than those inherent in the simpler, chromatographic procedure. For the purpose of a quick test the chromatographic technique is accurate enough to compare the cobalt contents of soil samples in a given area. It is fast; one operator can do 25 to 30 determinations daily. Filtration is slow enough to allow time for the cobalt to react with the 2-nitroso-1-naphthol.

Copper and iron also react with 2-nitroso-1-naphthol, but the cobalt determination described here is successfully carried out directly even in the presence of large amounts of these elements. Citrate is used to prevent the precipitation of the copper salt of 2-nitroso-1-naphthol and the reaction with iron is prevented by carefully controlling the pH of the test solution (see table 1).

Traces of cobalt are determined by adding a test solution to a solution of 2-nitroso-1-naphthol in the head of the chromatograph (see fig. 1). The



solutions are mixed by squeezing the rubber bulb, which forces air to circulate the reagents through the sample solution. The mixed solution is filtered and the confined spot that remains is washed with acid and dried. It is then compared with a standard series of spots.

#### ACKNOWLEDGMENTS

Mr. H. E. Hawkes and Mr. T. S. Lovering, geologists of the U. S. Geological Survey, collected samples that were used in determining the cobalt content by the two methods.

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