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Field determination of nanogram quantities of mercury in soils and rocks

by

Margaret Hinkle, Kam Wo Leong,
and F. N. Ward

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3. Field determination of nanogram quantities of mercury in soils and rocks, by Margaret Hinkle, Kam Wo Leong, and F. N. Ward. 14 p. including 2 tables.

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Abstract

A method for determining nanogram quantities of mercury in geological materials is based on the catalytic effect of mercury on the reaction of ferrocyanide with nitrosobenzene to produce a violet-colored compound whose intensity is proportional to the mercury present. The mercury is released by heating a sample of soil or crushed rock to about 650°C. As little as 30 nanograms of mercury (30 parts per billion with 1 gram sample) can be detected. The reliability of the method is adequate to permit its use in geochemical surveys that utilize mercury as a pathfinder element.

Introduction

During the past several years, there has been considerable interest in the use of mercury as a pathfinder element for concealed hypogene deposits (Ginsburg, 1960; Hawkes and Webb, 1962). To measure the small amounts of mercury occurring in the halos around such deposits very sensitive spectrographic (Sergeev, 1961) and vapor absorption procedures (Hawkes and Williston, 1962; Vaughn and McCarthy, 1964) have been developed. Both types of measurement, however, require elaborate and expensive instrumentation, and this has tended to reduce the potential usefulness of mercury surveys in geochemical prospecting. Accordingly a simple chemical procedure is needed to offset the limitations imposed by the costly instrumantation.

The proposed procedure is based on the catalytic effect of mercury on the reaction of ferrocyanide with nitrosobenzene to produce a violet-colored compound whose intensity is related to the mercury concentration (Asperger and Murati, 1954). The color can be measured spectrophotometrically, with an instrument, or by visual comparison with standard solutions of known mercury content.

The method described here permits the determination of as little as 30 nanograms (3×10^{-8} grams) of mercury which is 30 ppb (parts per billion) with a 1-gram sample. Larger samples can also be used to achieve the determination of smaller contents but this is generally unnecessary because background amounts of mercury in most rocks is of the same order of magnitude (Turekian and Wedepohl, 1961).

Although the proposed method has not been completely tested and evaluated, the preliminary results are encouraging enough to warrant release, especially in view of the great interest in mercury as a pathfinder element.

Equipment

(Items of regular laboratory equipment such as pipets and volumetric flasks are not listed.)

Aluminum heating block with magnetic stirrer; combination is commercially available.

Magnets, 1/2-inch, Teflon-covered.

Pyrex test tubes, 16 x 150 mm.

Pyrex test tubes, 18 x 75 mm, prepared by cutting off top end of 18 x 150 mm tube, and fitting with female ℨ 14/20.

Rack, test tube.

Tube, delivery, length, 21 cm, bent at right angles and fitted with male ℨ 14/20.

Tube furnace, electric (alternatively a propane torch can be used as a heat source).

Water bath, constant-temperature.

Reagents

All reagents are prepared with demineralized water.

Acetate buffer: Dissolve 164 grams of anhydrous sodium acetate or 272 grams of the trihydrate in 1 liter of water. Add glacial acetic acid until the pH is 3.5, as measured by a pH meter.

Bromine-buffer reagent: Mix 10 ml acetate buffer, 5 ml bromine water saturated at room temperature and 85 ml water.

Ferrocyanide solution: Dissolve 0.422 grams $K_4Fe(CN)_6$ in water and dilute to 1 liter.

Nitrosobenzene solution: Dissolve 8 mg of nitrosobenzene in 90 ml water at 70° C (nitrosobenzene melts at 68°C); cool the solution and add 10 ml of acetate buffer.

Mercury standard: Dissolve 0.1354 g of reagent grade mercuric chloride in 100 ml of 1N sulfuric acid. This standard contains 1,000 micrograms mercury per ml. Prepare 100 µg per ml and 10 µg per ml standards by dilution with 1N H_2SO_4. These standards are stable for about 3 months at ordinary temperatures. A working standard of 1 µg per ml should be prepared fresh every day by diluting the 10 µg per ml standard with water.

Procedure

1. Place 0.1 to 0.5 gram of minus 40 mesh soil or rock sample into an 18 x 75 mm test tube, fit delivery tube and insert the end of tube containing the sample into a tube furnace maintained at a temperature of about 650°C.

2. Heat sample for 2 minutes and collect evolved vapors in 3 ml of bromine-buffer reagent contained in 16 x 150 mm test tube.

3. Remove sample tube from hot furnace, disconnect delivery tube, and rinse with 1 ml of bromine-buffer reagent. Add rinse to collecting reagent.

4. Place magnetic stirring bar in test tube containing collected vapors, insert tube in an aluminum heating block fitted over magnetic stirrer and heat test tube at 95°C until bromine distillation is complete and solution colorless. Heat an additional 2 minutes. Cool solution to 25°C and remove magnet.

5. Add 1 ml potassium ferrocyanide and 2 ml nitrosobenzene solutions to the contents of the test tube, mix, and place test tube in a water bath at 50°C for 45 minutes.

6. Remove tubes from water bath, cool rapidly, and compare with standard solutions by viewing axially. Alternatively, use a spectrophotometer to measure the absorbance at 528 mμ and ascertain the mercury content by reference to a previously established standard curve.

Calculation:

$$\text{ppb (parts per billion)} = \frac{\text{nanograms Hg}}{\text{sample weight (in grams)}}$$

Preparation of standard solutions:

Pipet aliquots of working standard (1 µg Eg per ml) into a series of test tubes as follows: none to first tube, 30 lambda to second, 50 lambda to third, 100 to fourth, 200 to fifth, 400 to sixth and 800 lambda to seventh tube. Add 4 ml of bromine buffer-reagent to each tube and continue with step 4 of procedure.

A possible mechanism suggested by Asperger, Murati, and Cupahin (1953) for the catalytic reaction is as follows:

$$Fe(CN)_6^{-4} \overset{H_2O}{\rightleftarrows} [Fe(CN)_5(H_2O)]^{-3} + CN^-$$

$$[Fe(CN)_5(H_2O)]^{-3} + C_6H_5NO \overset{Hg^{+2}}{\rightarrow} [Fe(CN)_5(C_6H_5NO)]^{-3} + H_2O$$

$$CN^- + H_2O \rightleftarrows HCN + OH^-$$

Other reactions such as the oxidation of the ferrocyanide or nitrosobenzene compete with the catalytic reaction whose rate is temperature dependent. A temperature of 50°C and a heating period of 45-60 minutes are optimum for the catalysis effect. At 60°C the reaction proceeded too rapidly and all standard solutions of a given series turned a uniform dark pink within 20 minutes. At a temperature of less than 50°C the catalytic reaction was too slow and air oxidation of ferrocyanide occurred.

Under uniform conditions of time and temperature the amount of colored compound formed is proportional to the mercury content. The absorbance of the colored compound however is directly proportional to the mercury concentration only with amounts of mercury up to about 100 nanograms in the final solution. Between 100 nanograms and about 400 nanograms the absorbance is not linear but nevertheless is sufficiently reproducible to permit valid measurements.

With mercury amounts greater than 400 nanograms the absorbance curve flattens, that is, the absorbances increase more slowly with mercury concentration, and differences in absorbance become difficult to measure except by changing the geometry of the system or by increasing the sensitivity of the detector. Use of spectrophotometric equipment allows changes in detector sensitivity, but the system geometry is more easily changed and in the range of 400 to 800 nanograms visual rather than instrumental comparisons are made by viewing the colored product axially. This mode takes advantage of the longer light path--5 cm--of the final solution in a test tube.

The color of the complex formed is stable for at least 30 minutes at room temperature and for as long as 90 minutes if the solutions are kept at refrigerator temperatures. The color fades rapidly if exposed to sunlight as reported by Asperger and Murati (1954).

Distillation of mercury from the soil or rock sample effects a separation from most elements which interfere with the subsequent estimation.

During heating, any sulfides present evolve small amounts of hydrogen sulfide and any organic matter decomposes. The hydrogen sulfide, as well as other decomposition products, decolorizes the bromine water and leads to losses of mercury because of the failure of the collecting solution to retain the mercury vapors. The use of small samples and the addition of iron filings to the sample mixture help to prevent the evolution of large volumes of hydrogen sulfide and thereby lessen the danger of loss during distillation.

The evolved mercury vapor was collected in different solutions such as bromide alone or bromide-buffer mixtures, and the best combination proved to be a mixture of saturated bromine water and buffer prepared as above. Under the experimental conditions given in the procedure no further pH adjustment is necessary and the excess bromine is eliminated by heating the test tube in a heating block and stirring vigorously.

Various techniques were tried to improve the distillation and recovery of mercury, such as the use of nitrogen to flush out the system, and the generation of gases in situ by heating decomposable compounds such as oxalic acid. The most consistent results were obtained by simply heating the crushed sample to about 650°C for 2 minutes in a 75-mm test tube fitted with a ♀ 10/14 to a delivery tube bent at a right angle to the test tube.

Results

The repeatability of the proposed procedure was tested by making 5 separate determinations on different soils and rocks all containing less than 1 part per million mercury. The range of the repeat determinations, the relative standard deviation, and the confidence limits at the 95-percent level are shown in table 1.

As a test of the validity of the catalytic method the results obtained thereby on different kinds of rocks and soils were compared with those obtained by the vapor absorption method (Vaughn and McCarthy, 1964). The comparison is given in table 2.

Table 1.--Repeatability of mercury determinations

Sample No.	Material	Mercury found (ppb)			Relative standard deviation (percent)
		High	Low	Mean and confidence limits at 95-percent level	
1	Flaky shale	50	30	38±10.0	21.2
2	Granite, fresh	100	70	80±15.2	15.3
3	Breccia (latite phonolite)	100	80	84±11.1	10.6
4	---do-----	110	90	100±12.4	10.0
5	Granite, altered	130	110	125±11.1	8.4
6	Shale	170	160	165±9.1	3.5
7	Limestone	950	860	907±36.3	3.5

Table 2.--Determinations of mercury by catalytic and vapor absorption methods

Sample No.	Material	Mercury content, ppb	
		Catalytic method	Vapor absorption method
1	Granite, fresh	20	40
2	Breccia (latite phonolite)	70	110
3	Granite, altered	200	290
4	Breccia (latite phonolite)	200	470
5	Limestone	2,000	5,090
6	Flaky shale	80	50
7	Alluvium	100	150
8	Weathered shale	80	200
9	----do----	180	300
10	Shale	100	300
11	Weathered shale	520	800
12	Shale	200	450

The differences observed by the two methods are due in part to differences in manner of standardization. Possible lack of homogeneity of samples is also a factor that is difficult to evaluate. Nevertheless, the results obtained by both methods are nearly interchangeable and thus it appears that the catalytic procedure is useful when the mercury content of soils and rocks is used as a parameter in geochemical exploration.

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