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# An Atomic-Absorption Method for the Determination of Gold in Large Samples of Geologic Materials

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By Gordon H. VanSickle and Hubert W. Lakin

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# AN ATOMIC-ABSORPTION METHOD FOR THE DETERMINATION OF GOLD IN LARGE SAMPLES OF GEOLOGIC MATERIALS

By Gordon H. VanSickle and Hubert W. Lakin

## Abstract

A laboratory method for the determination of gold in large (100-gram) samples has been developed for use in the study of the gold content of placer deposits and of trace amounts of gold in other geologic materials. In this method the sample is digested with bromine and ethyl ether, the gold is extracted into methyl isobutyl ketone, and the determination is made by atomic-absorption spectrophotometry. The lower limit of detection is 0.005 part per million in the sample. The few data obtained so far by this method agree favorably with those obtained by assay and by other atomic-absorption methods. About 25 determinations can be made per man-day.

## INTRODUCTION

The Heavy Metals program of the U.S. Geological Survey requires large numbers of gold analyses and an analytical capability to determine gold in very small amounts. Several rapid methods for gold determination that have been developed recently (Lakin and Nakagawa, 1965; Huffman and others, 1967; Thompson and others, 1968) have proved to be very useful for reconnaissance-type sampling of most areas (Erickson and others, 1966; Gott and McCarthy, 1966). However, these methods, which use samples weighing only 2–15 grams, are inadequate for the determination of the gold content of potential placer deposits because of the erratic distribution of particulate gold in these materials (Antweiler and Love, 1967; Clifton and others, 1967). Analysis of a larger sample (100 g) permits a more accurate determination of the gold content of such material. The 100-g sample also gives a detection limit for gold of 0.005 ppm (part per million), lower than that of the earlier methods, which have a detection limit of 0.02 ppm or more.

With the recent development of atomic-absorption spectrophotometry the measurement of gold has become simple and routine. Methods of sample dissolution vary. In a method described by Thompson, Nakagawa, and Van-Sickle (1968) a mixture of hydrobromic acid and bromine is used to solubilize the gold. The gold is then extracted into methyl isobutyl ketone (MIBK), and the gold concentration is determined by atomic-absorption spectrophotometry.

Shima (1953) described a method of leaching gold from large samples (100–500 g) with a mixture of bromine and ethyl ether and estimating the gold colorimetrically with dithizone.

The method which is proposed here, and which is a combination and modification of these two methods, results in a simple, reliable, sensitive, and low-cost analysis for gold in a large sample. The gold is dissolved by a mixture of bromine and ethyl ether and is extracted into MIBK; the gold concentration is then determined by atomic absorption.

We wish to acknowledge the help and advice of C. E. Thompson of Skyline Laboratories, Inc., and formerly of the U.S. Geological Survey. Arthur Kinkel, Paul Theobald, and Garland Gott of the U.S. Geological Survey provided the samples for our experimental work.

## REAGENTS AND APPARATUS

Bromine, reagent grade.

Ethyl ether, reagent grade. (Note: Because of the toxicity of bromine and the explosive nature of ethyl ether these reagents should be used only in a well-ventilated laboratory hood. They should be stored in a refrigerator.)

Hydrobromic acid, concentrated, reagent grade, distilled.

1.5 $N$ HBr: Dilute 172 milliliters of concentrated HBr to 1 liter with water.

0.1 $N$ HBr: Dilute 25 milliliters of concentrated HBr to 2 liters with water.

Methyl isobutyl ketone (MIBK), (2 methyl 4 pentanone), reagent grade.

Standard gold solution, 0.1 percent: Dissolve

exactly 1.000 g of gold in a solution of bromine in hydrobromic acid. Heat gently to expel excess bromine. Cool and dilute to 1 liter with concentrated hydrobromic acid.

Culture tubes, screwcap, 25 by 200 millimeters in size, with Teflon liner in screwcap.

Evaporating dishes, porcelain, 60 millimeters in diameter.

Glass jars, screwcap, 6 oz (ounces) in capacity. The caps must be noncorrosive. (We have had satisfactory results by lining each bakelite cap with a Teflon sheet.)

Spatula, porcelain, 6 inches in size.

Muffle furnace, electric.

Atomic-absorption spectrophotometer.

## PROCEDURE

1. Weigh 100 g of sample ground to −100 mesh and transfer it to a porcelain dish. Place the dish in a muffle furnace and heat at 700°C for 2 hours.

2. Cool and transfer the sample to a 6-oz glass jar. Add 1 ml bromine and 5 ml ethyl ether. Cap the jar tightly and shake vigorously to mix. Allow to stand for about 1 hour and shake intermittently.

3. Add 20 ml MIBK to mixture. Cap and shake vigorously to mix. Add more MIBK if necessary until the sample is completely wet and is the consistency of a soft mud ball.

4. Remove the cap and add approximately 10 ml 0.1 $N$ HBr to contents. Stir gently with a porcelain spatula. Continue to add 0.1 $N$ HBr in small increments and stir until the MIBK is separated.

5. Pour off the MIBK into a 25- by 200-mm screwcap culture tube containing 25 ml 0.1 $N$ HBr. Cap the tube and shake it for 30 seconds. Allow the phases to separate and aspirate the organic phase into an atomic-absorption spectrophotometer. Read the percent absorption and convert to concentration as directed for the particular instrument. The gold content, in parts per million, of the sample is equal to:

$$\frac{\mu g/ml \times (ml\ MIBK + ml\ ethyl\ ether)}{100}.$$

Add respectively 5, 25, 50, and 100 $\mu g$ of gold to four 100-ml volumetric flasks containing 25 ml 1.5 $N$ HBr. Add 50 ml MIBK and shake the flask for 1 minute. These MIBK solutions contain 0.1, 0.5, 1.0, and 2.0 $\mu g$ per ml gold.

## DISCUSSION OF PROCEDURE

In the roasting (step 1), organic carbon and sulfides should be completely oxidized. During the sample digestion (step 2), the capped glass jar must fill with brown vapors of bromine. The absence of bromine vapors indicates incomplete oxidation in step 1. An excess of bromine is required to ensure the solution of gold in the sample.

The 5 ml of ethyl ether originally added to the sample (step 2) dissolves in the MIBK and thus, for the calculation of the result, the volume of ethyl ether used in step 2 must be added to the volume of MIBK (step 3) used in the extraction.

The effectiveness of bromine and ethyl ether for the solution of gold is illustrated by the following experiments, which show that the solution rate is a function of the gold particle size. Three pieces of gold weighing a total of 69.4 milligrams (the largest piece was about 2 mm long and 1 mm in diameter) were placed in a 6-oz jar with 100 g of fine quartz sand. One ml bromine and 5 ml ethyl ether were added. The jar was capped, shaken, and allowed to stand for 1 hour. The gold pieces were then recovered and weighed; they were found to weigh 68.3 mg—a loss of 1.1 mg. The above procedure was repeated, and the pieces weighed after overnight digestion. By this time 32.2 mg had dissolved. Gold leaf, however, dissolves instantaneously in these reagents.

## PRECISION AND ACCURACY

The repeatability of the method was determined on four −100 mesh samples—three of phonolite breccia and one of gold- and monazite-bearing sand (table 1). The repeatability as measured by the relative standard deviation may be a function of the homogeneity of the samples. Pulverizing the −100 mesh sample in a ball mill for at least 1 hour would result in more uniform dispersal of the gold.

The gold content of 13 samples of oxidized

low-grade ore and two samples of sulfide ore from North Carolina has been determined by the atomic-absorption method in combination with four methods of sample solution (table 2): (1) Fire assay and aqua regia, (2) cyanide, (3) hydrobromic acid-bromine, and (4) bro-mine-ether as described here. The fire-assay method gives slightly higher gold content in materials containing less than 1 ppm than the bromine-ether procedure. Otherwise the agree-ment between the various methods is accepta-ble.

TABLE 1.—*Repeatability of the method*

| Sample | Description and locality | Number of determinations | Gold (ppm) | | | Standard deviation | Relative standard deviation (percent) |
|---|---|---|---|---|---|---|---|
| | | | Maximum | Minimum | Mean | | |
| CC–562 | Fractured phonolite breccia, Cripple Creek district, Teller County, Colo. | 6 | 0.56 | 0.34 | 0.46 | 0.074 | 16 |
| 567 | _____do_____ | 8 | .072 | .024 | .046 | .016 | 35 |
| 559 | _____do_____ | 6 | .018 | .009 | .015 | .0035 | 24 |
| ABK–045 | Gold and monazite placer sand, Moffat County, Colo. | 6 | 1.24 | .31 | .88 | .34 | 39 |

TABLE 2.—*Comparison of gold values obtained by four atomic-absorption methods*

[All samples from North Carolina, and sample numbers are preceded by K–. Fire-assay analyses by O. M. Parker, L. B. Riley, J. D. Mensik, and Claude Huffman, Jr., U.S. Geological Survey; cyanide and hydrobromic acid-bromine analyses by A. E. Hubert, U.S. Geological Survey]

| Sample | Description | Gold (ppm) | | | |
|---|---|---|---|---|---|
| | | Method of solution | | | |
| | | Fire assay and aqua regia (15-g sample) | Cyanide (100-g sample) | Hydrobromic acid-bromine (10-g sample) | Bromine-ether (100-g sample) |
| 12 | Rock chips and soil _____ | 0.7 | 0.4 | 0.8 | 0.62 |
| 13 | _____do_____ | .3 | .2 | .4 | .20 |
| 18 | _____do_____ | .3 | .3 | .7 | .28 |
| 19 | Saprolite _____ | .3 | .1 | .3 | .26 |
| 20 | Hard saprolite _____ | .2 | .08 | .4 | .14 |
| 21 | _____do_____ | .2 | .2 | .2 | .12 |
| 35 | Schistose (sericitic) saprolite _____ | 2. | 2.4 | 2.8 | 3.1 |
| 36 | _____do_____ | .6 | .7 | .8 | .65 |
| 57 | Red soil (B zone) _____ | .5 | .1 | .6 | .18 |
| 61 | Tuff saprolite _____ | .3 | .1 | .3 | .20 |
| 100 | Bedded tuff _____ | 1. | 1. | 1. | 1.2 |
| 130 | Rhyolitic tuff saprolite _____ | <.05 | <.02 | <.02 | .02 |
| 136 | Cellular gossan _____ | 5.5 | 3.2 | 5.6 | 6.8 |
| 109 | Pyritic rock _____ | 4. | 3.8 | 4. | 4.7 |
| 135 | Sulfide ore _____ | 7. | .5 | 3.9 | 4.6 |

## CONCLUSIONS

The method presented here is certainly not a replacement for the standard fire assay for gold; however, the simplicity, sensitivity, and lower cost of the method are distinct advan-tages.

We have emphasized the 100-g sample, but with a few modifications in the procedure and the equipment a much larger sample could be handled. The problems of grinding, roasting, extracting, and waste disposal by using a sam-ple much larger than the suggested 100-g size increase exponentially with the sample size.

Therefore, this method is a compromise between the need for analysis of larger samples and the ability to do larger numbers of samples easily. A method for routine analysis of samples as large as 1000 g has been developed by the Office of Marine Geology and Hydrology of the U.S. Geological Survey (H. E. Clifton, written com-mun, March 1968).

## REFERENCES

Antweiler, J. C., and Love, J. D., 1967, Gold-bearing sedimentary rocks in northwest Wyoming—a pre-liminary report: U.S. Geol. Survey Circ. 541, 12 p.

Clifton, H. E., Hubert, Arthur, and Phillips, R. L.,

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1967, Marine sediment sample preparation for analysis for low concentrations of fine detrital gold: U.S. Geol. Survey Circ. 545, 11 p.

Erickson, R. L., VanSickle, G. H., McCarthy, J. H., Jr., Nakagawa, H. M., and Leong, K. W., 1966, Gold geochemical anomaly in the Cortez district, Nevada: U.S. Geol. Survey Circ. 534, 9 p.

Gott, G. B., and McCarthy, J. H., Jr., 1966, Distribution of gold, silver, tellurium, and mercury in the Ely mining district, White Pine County, Nevada: U.S. Geol. Survey Circ. 535, 5 p.

Huffman, Claude, Jr., Mensik, J. D., and Riley, L. B., 1967, Determination of gold in geologic materials by solvent extraction and atomic-absorption spectrometry: U.S. Geol. Survey Circ. 544, 6 p.

Lakin, H. W., and Nakagawa, H. M., 1965, A spectrophotometric method for the determination of traces of gold in geologic materials, in Geological Survey research 1965: U.S. Geol. Survey Prof. Paper 525-C, p. C168-C171.

Shima, Makoto, 1953, Estimation of gold and silver contained in ores, study of rapid analysis for use in mines: Japan Analyst, v. 2, p. 96-98.

Thompson, C. E., Nakagawa, H. M., and VanSickle, G. H., 1968, Rapid analysis for gold in geologic materials, in Geological Survey research 1968: U.S. Geol. Survey Prof. Paper 600-B, p. B130-B132.