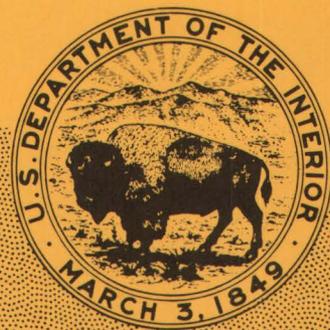


GEOLOGICAL SURVEY CIRCULAR 544



**Determination of Gold in
Geologic Materials by
Solvent Extraction and
Atomic-Absorption
Spectrometry**

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By Claude Huffman, Jr., J. D. Mensik, and
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United States Department of the Interior
STEWART L. UDALL, *Secretary*



Geological Survey
William T. Pecora, *Director*



First printing 1967
Second printing 1968

Free on application to the U.S. Geological Survey, Washington, D.C. 20242

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ABSTRACT

The two methods presented for the determination of traces of gold in geologic materials are the cyanide atomic-absorption method and the fire-assay atomic-absorption method. In the cyanide method gold is leached with a sodium cyanide solution. The monovalent gold is then oxidized to the trivalent state and concentrated by extracting into methyl isobutyl ketone prior to estimation by atomic absorption. In the fire-assay atomic-absorption method, the gold-silver bead obtained from fire assay is dissolved in nitric and hydrochloric acids. Gold is then concentrated by extracting into methyl isobutyl ketone prior to determination by atomic absorption. By either method concentrations as low as 50 parts per billion of gold can be determined in a 15-gram sample.

INTRODUCTION

The U.S. Geological Survey heavy metals program has instituted reconnaissance studies requiring rapid, precise, and sensitive methods for determining various elements in geologic materials. The determination of gold for this program has required methods more sensitive than the conventional fire-assay method. Lakin and Nakagawa (1965) described a spectrophotometric method for determining traces of gold in geologic materials; they found, however (oral commun., 1966), that thallium and iron interfere. Walsh (1955) has shown that atomic-absorption spectrometry is extremely well suited for direct determination of low concentrations of certain elements in solution, but until recently no work seems to have been undertaken for the determination of gold. Olson (1965) and Simmons (1965) used a cyanide solution to leach the gold from siliceous carbonate ores prior to estimation by atomic absorption. Tindall (1965) described an atomic-absorption method for the determination of gold in various types of samples dealt with in the copper mining industry. He used an aqua regia digestion followed by an organic extraction to concentrate the gold into a small volume. Strelow, Feast, Mathews, and Van Zyl (1966) applied an atomic-absorption method to the determination of gold in cyanide waste solutions. All these atomic-absorption methods have been used primarily for determining gold in the parts-per-million range.

This paper describes two rapid and precise atomic-absorption methods for gold determination currently used in the U.S. Geological Survey's Denver laboratory: the cyanide atomic-absorption method and the fire-assay atomic-absorption method. In developing these methods, sensitivity was stressed to enable geochemical prospecting for gold at the parts-per-billion level. Both methods can detect concentrations as low as 50 ppb (parts per billion) or 0.0015 ounce per ton of gold in a 15-gram sample.

In the cyanide method the sample is roasted and then treated with a sodium cyanide solution to dissolve the gold. The cyanide solution is acidified with hydrobromic acid and bromine water to oxidize the monovalent gold to the trivalent state. The gold is then concentrated by extracting into a measured volume of methyl isobutyl ketone (MIBK). The gold concentration is determined by an atomic-absorption spectrophotometer.

In the classical fire-assay method, the silver of the gold-silver bead obtained by cupellation is dissolved and the gold residue is determined gravimetrically. The sensitivity of this method is approximately 0.02 troy ounce per ton (600 ppb) on a 15-g (half assay ton) sample. In the proposed fire-assay atomic-absorption method the gold-silver bead from fire assay is dissolved in nitric and hydrochloric acids and then extracted into a small volume of organic solvent (MIBK) prior to estimation by atomic absorption. This procedure thus increases the sensitivity by about a factor of 10 when a 15-g sample is used. The sensitivity can be further increased by combining beads obtained from two fire-assay fusions of 30 g each of the same sample. With this technique about 15 ppb can be determined. This is about the limit imposed by reagent blanks.

REAGENTS

Standard gold stock solution, 400 ppm (parts per million) gold. Dissolve 0.200 g of gold metal in a covered beaker with 30 milliliters of aqua regia on a steam bath, remove cover, and evaporate to dryness. Heat on a hotplate until fumes from HNO_3 are no longer

present. Add 250 ml of (1:1) HCl to the beaker and digest on the steam bath to dissolve the gold salts. Transfer the solution to a 500-ml volumetric flask and dilute to volume with distilled water.

Sodium cyanide solution, 0.25 percent. Dissolve 5 g NaCN in 500 ml distilled water, add 2 drops of a 10-percent solution of NaOH, and dilute to 2,000 ml. The pH of this solution should be about 11.

Hydrobromic acid, 48-percent reagent grade.

Bromine water, saturated solution.

Calcium oxide powder, reagent grade.

Methyl isobutyl ketone (MIBK).

Santomerse S solution, wetting agent, (volume/volume in water, obtained from Chemical Co., St. Louis, Mo.

APPARATUS

Atomic-absorption spectrophotometer. A Elmer model 303 atomic-absorption spectrometer is used with the following instrument meters:

Wavelength: 2428 Angstroms.

Slit: 5 (3 millimeters, 20 Angstroms).

Source: Gold hollow cathode, 14 milliampere.

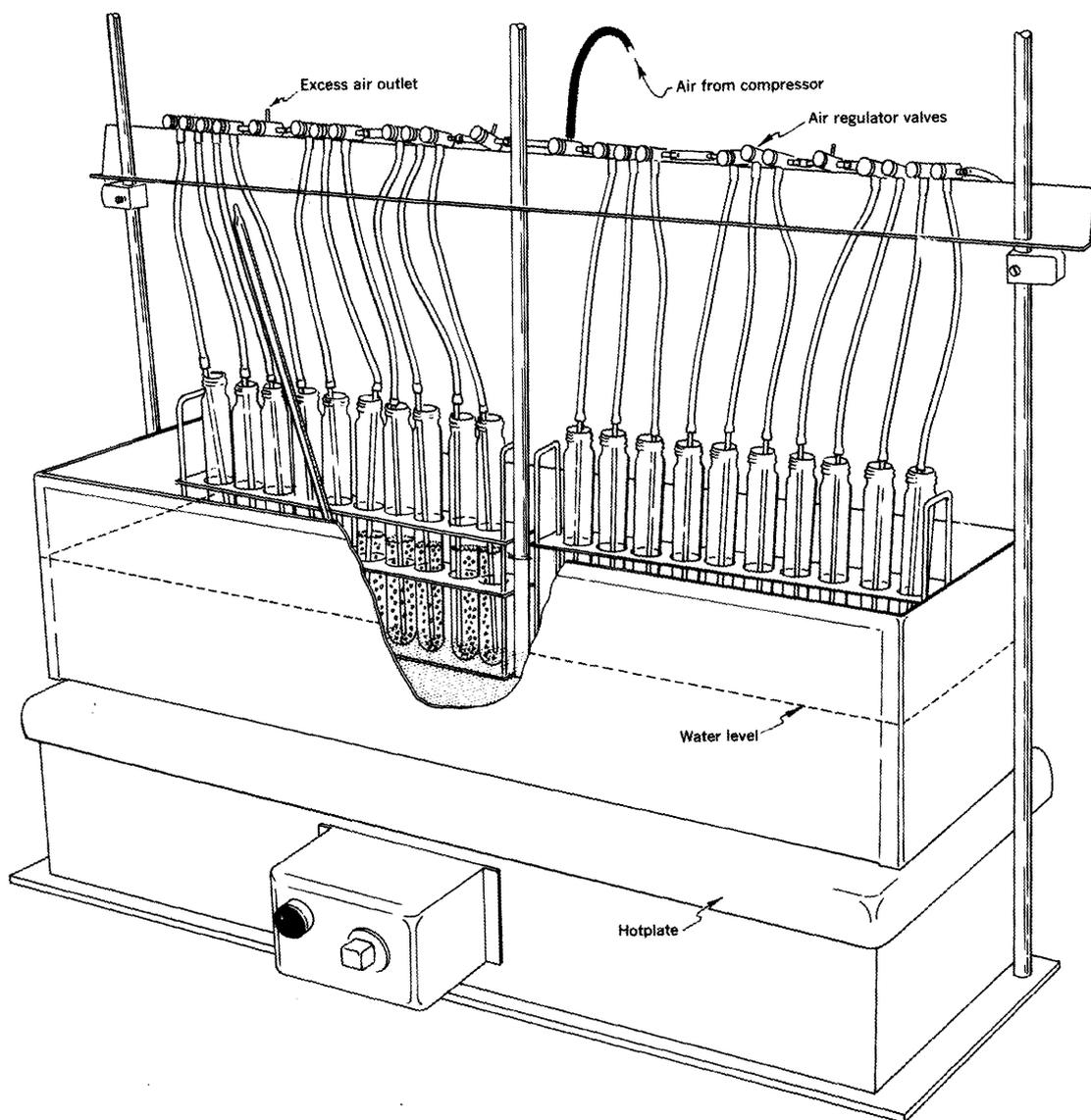


Figure 1.—Water bath equipped for aeration and constant temperature.

Acetylene: 9 pounds per square inch.

Air: 25 pounds per square inch.

Flame adjustments: With the burner lit, adjust the flow meters to approximately 2.8 on the acety-

lene and 3.0 on the air while aspirating water. Minor adjustments may be necessary to obtain a blue flame when the MIBK is aspirated.

Water bath equipped for aeration and constant temperature (fig. 1). The aeration device constructed in this laboratory consists of a compressor-vacuum pump capable of delivering air at one-third cubic foot per minute under a pressure of 15 pounds per square inch. This amount of air is more than sufficient for the 20 outlets shown in figure 1. The compressor supplies a group of air regulator valves (available from aquarium supply houses) which are connected to 3/16-inch-diameter Pyrex tubes by Tygon tubing. The valves are used to individually adjust the air supply to each sample. A steady air flow to the tubes is maintained by means of a small air tank and one or more bleed-off valves.

Constant-temperature water bath with magnetic stirrer (fig. 2). Teflon-coated 1/2-inch-diameter magnetic stirring bar.

Pyrex culture tubes, 25 by 200 millimeters, with poly-seal closure screw cap.

CYANIDE ATOMIC-ABSORPTION PROCEDURE

SAMPLE PREPARATION

Crush sample in a jaw crusher to less than 1/4-inch size, then split and grind a portion on ceramic plates set for less than 80 mesh. The sample is not sieved; a large portion of the sample will be less than 200 mesh.

1. Weigh a 2- to 15-g sample and transfer to a porcelain dish or crucible. Place the crucible in a cold muffle furnace and heat for 1 hour after the temperature reaches 600°C. Do not exceed 650°C because samples of high clay content may tend to sinter and thus trap the gold and prevent solution during the cyanide step.
2. Cool. Add 0.25 g CaO powder and mix thoroughly; transfer sample to a Pyrex culture tube. Add 30 ml of the 0.25-percent NaCN solution to the tube, place cap on the tube, and shake by hand to wet the entire sample. Place tube in an automatic shaker and shake for 15 minutes; let stand overnight.
3. Reshake to break up any cake formed in the bottom of the tube. Wash down sides of the tube with about 10 ml of the NaCN reagent. Add 4 drops of the 0.25-percent Santomerse S wetting agent to the tube and heat for 30 minutes in the water bath at 80°-85°C while aerating the sample (fig. 1).
4. If a 2-g sample is used, proceed to step 5. If a sample of more than 2 g is used, centrifuge the contents of the tube at 2,000 revolutions per minute for 5 minutes, then decant the liquid phase into another culture tube containing a magnetic

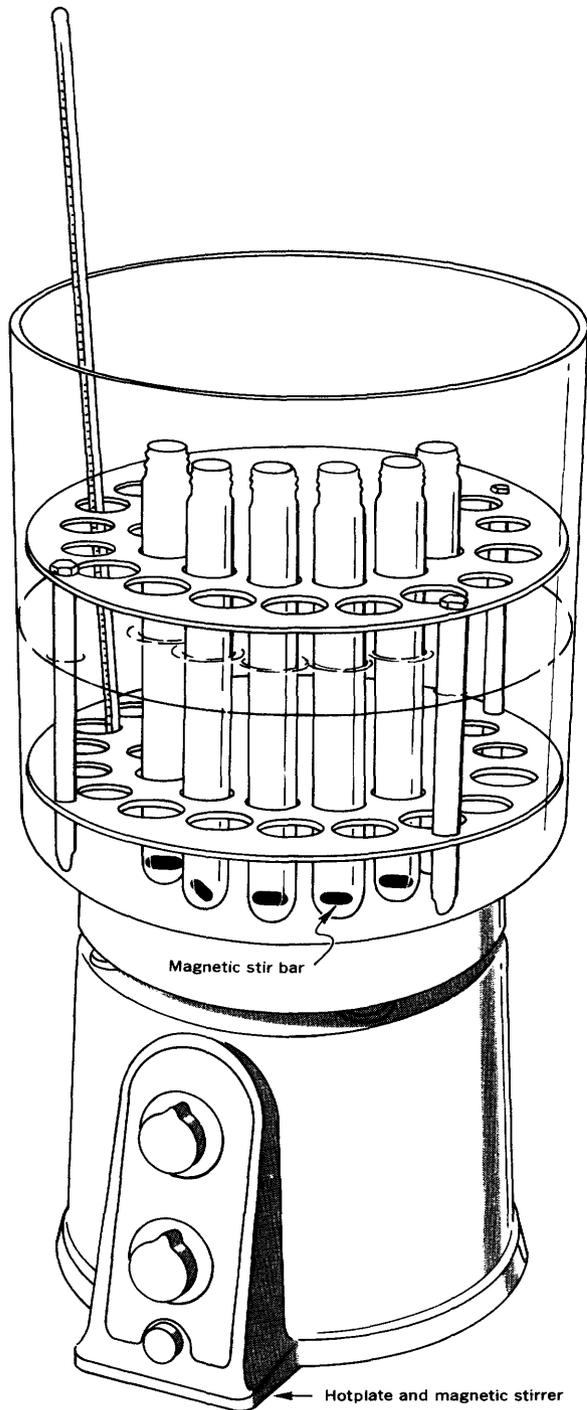


Figure 2.—Constant-temperature water bath with magnetic stirrer.

stirring bar. Wash the residue left in the first tube with 10 ml of the 0.25-percent NaCN solution containing 4 drops of saturated bromine water. Centrifuge again and combine wash solution with the original solution.

5. Add 5 drops bromine water and mix. Then, working under a well-ventilated hood, cautiously add 5 ml of 48-percent HBr. (CAUTION: Hydrogen cyanide gas is evolved.) Heat in a water bath equipped for magnetic stirring (fig. 2) for 30 minutes at 90°C.
6. Cool. Remove the stir bar with another magnet held outside the tube, add 10 ml MIBK, and shake for 1 minute. Centrifuge if step 4 has been omitted.
7. Measure the absorption of the MIBK phase along with reference standards (see following section, "Standardization") on an atomic-absorption spectrophotometer at a wavelength of 2428 Angstroms. Use a water-saturated solution of MIBK as a reference blank. To obtain a standard calibration curve, plot the absorption readings against gold concentration expressed as parts per million in the organic phase. The gold content of the sample in parts per million is equal to:

$$\frac{\text{gold in ppm in organic phase} \times 10 \text{ ml}}{\text{weight of sample in grams}}$$

If the sample has an absorbance greater than the 10 ppm standard, a dilution of the organic layer can be made. The dilution method is illustrated in the following example: Transfer a 2-ml aliquot of the organic phase to a tube containing about 30 ml of water and 2 ml of 48-percent HBr. Add 8 ml of MIBK, shake, and measure the absorption. This dilution factor of 5 will handle a 10-g sample containing as much as 50 ppm Au.

STANDARDIZATION

Prepare reference standards containing 0.1, 0.2, 0.4, 0.8, 1.0, 2.0, 4.0, 8.0, and 10.0 ppm Au in the organic phase for working curves by adding appropriate aliquots of a gold standard solution to a series of culture tubes. Add 2 ml of 48-percent HBr to each and adjust the volume to about 40 ml with water. Add 10.0 ml of MIBK and shake for 1 minute to extract the gold into the organic phase. Measure the absorption of these standards on the 1X or 10X scales of the atomic-absorption spectrophotometer. Periodically, standards can, and probably should, be checked by being subjected to the procedure starting with step 2. However, we have noted no difference in absorption readings between the standards taken through the entire procedure and those prepared as described.

FIRE-ASSAY ATOMIC-ABSORPTION PROCEDURE

The fire-assay method involves a fusion of ground ore with fluxes to form a slag phase and a metallic

lead phase. The lead collects any gold, platinum metals, or silver and settles out at the bottom when poured into a mold. After cooling, the slag is broken away from the lead button which is then put into the furnace in a cupel. The lead melts and is slowly oxidized by the hot air. The lead oxide wets the semiporous cupel material, generally bone ash, and is absorbed. The cupel material is not wet by the molten lead nor by the noble metals, which remain as a bead after the gradual absorption of the lead oxide.

The procedure for the further treatment of the bead is as follows:

1. Transfer the silver-gold bead obtained by fire assay to a 50-ml beaker.
2. Add 5 ml of (1:1) HNO₃, cover, and digest on a steam bath for 45 minutes. Uncover and evaporate the solution to about 2.5 ml.
3. Add 6 ml of concentrated HCl, cover, and let stand 20 minutes. Place beaker on steam bath and digest for 30 minutes, uncover, and evaporate to hard dryness.
4. Add 7 ml of concentrated HCl, cover, and digest on the steam bath until all salts are in solution. Uncover, add about 15 ml of water, and digest an additional 30 minutes.
5. Cool. Quantitatively transfer the solution to a Pyrex culture tube by washing beaker with about 10 ml of water. Add 2 ml of 48-percent HBr, mix, add 10 ml of MIBK, and shake tube for 1 minute.
6. Determine the absorbance of the organic phase along with reference standards prepared in the same manner as described in the cyanide procedure.

We routinely add 2 milligrams of silver in the fusion step. Precut lengths of lead rod, each containing this amount of silver, are obtainable commercially under the trade name Inquarts. Silver is important in this procedure for three reasons: (1) It has a protective effect and thus reduces gold losses during the cupellation step (Bugbee, 1940, p. 107), (2) it allows trace amounts of gold to be easily transferred from the cupel to a suitable container for analysis, and (3) the addition of silver provides a silver-gold bead that is easily dissolved. The ratio of silver to gold should be greater than 3:1 to allow dissolution of the bead; beads having lower ratios of silver to gold may be difficult to dissolve, even in aqua regia. For samples that contain sufficient silver, such addition is unnecessary; conversely, for samples that contain considerable gold, the addition of more than 2 milligrams silver may be necessary to attain this 3:1 ratio. The silver-gold bead is routinely weighed to allow an estimate or approximate check of the combined gold and silver content of the ore.

For a full discussion of the fire-assay method the reader is referred to Bugbee (1940) or Beamish (1966).

Table 1.—Comparison of gold values obtained by atomic-absorption methods and by the conventional gravimetric fire-assay method

[Gravimetric fire-assay by O. M. Parker and L. B. Riley. Atomic-absorption determinations by Claude Huffman, Jr., J. D. Mensik, and L. B. Riley]

Sample	Gold (ppm)			Sample description and locality
	Gravimetric fire assay	Atomic absorption		
		Fire assay	Cyanide	
96130 -----	4.8	4.8	4.3	Sulfide ore, White Pine mine, Jefferson County, Mont.
D223180 -----	10.3	11	10	Channel sample, Gold Anchor mine, Clear Creek County, Colo.
D119999 -----	13.7	16	15	Pyrite, Billy Goat mine, Okanogan County, Wash.
D100874 -----	15.8	18	14	Quartz pyrite ore, Phoenix mine, Clear Creek County, Colo.
D119971 -----	16.5	15	16	Quartz vein, Okanogan County, Wash.
D119956 -----	26.4	27	25	Mineralized quartzite, Okanogan County, Wash.

RESULTS

The accuracy of the two proposed atomic-absorption methods was first tested by analyzing a suite of six selected samples previously analyzed by the conventional gravimetric fire-assay method. The results (table 1) show good agreement between the two atomic absorption methods and the gravimetric fire-assay method. These samples were selected because they represent a wide variety of rock and ore types as indicated by semiquantitative spectrographic analysis. For example, sample D119956 contains 1.5 percent As, 7 percent Fe, and 0.07 percent Zn; sample D119971 contains >10 percent As, 10 percent Fe, and 0.03 percent Sb; sample D119999 contains >10 percent Fe, 5 percent Cu, and 0.2 percent Mn. About 90 percent of sample D100874 is estimated to be pyrite.

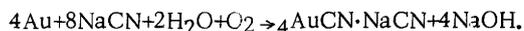
The cyanide atomic-absorption method has been thoroughly tested by routinely analyzing several hundred samples of varying composition. All samples that contained at least 0.5 ppm Au were reanalyzed by the fire-assay atomic-absorption method; in addition, many randomly selected samples containing less than 0.5 ppm Au were checked. Table 2 presents some of the data on 20 samples from Alaska and Nevada areas. The cyanide and fire-assay methods show concordant results.

SAMPLE DISSOLUTION, CYANIDE PROCEDURE

Simmons (1965) observed that low results were obtained on some samples if the ignition step was omitted prior to the cyanide treatment. We have confirmed his observation and routinely roast all samples.

The cyanide process has been used commercially for many years. The commercial processes are based on

the following chemical reaction:

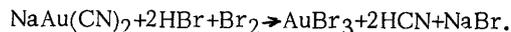


The amount of gold which can be dissolved in sodium cyanide solution depends on the amount of oxygen present (Jacobson, 1949, p. 554). The aeration device described in this paper supplies the oxygen for the preceding reaction and furnishes agitation to a large sample. It is desirable to keep the sample in a single tube during the entire analysis. In the initial stage of this investigation, 2-g samples were aerated conveniently by means of magnetic stirring. However, when we attempted to increase our sample size to 15 g we found that the magnetic stirrer would not sufficiently agitate the larger sample. The aeration device provides sufficient agitation of a 15-g sample.

EXTRACTION OF GOLD WITH METHYL ISOBUTYL KETONE

Methyl isobutyl ketone (MIBK) has been used extensively in atomic-absorption work to preconcentrate certain elements that show insufficient sensitivity in aqueous solution. Many authors favor this reagent because it has excellent flame characteristics and it is only slightly soluble in water (1.9 g per 100 ml).

We wish to emphasize that the gold is in the monovalent state after the cyanide treatment and will not be extracted quantitatively into the MIBK unless oxidized to the trivalent state. In this method the dicyanogold (I) ion is oxidized to the bromaurate (III) ion by the addition of bromine water and hydrobromic acid. The reaction is as follows:



The bromaurate (III) ion is then extracted quantitatively into MIBK prior to estimation by atomic absorption.

Table 2.—Comparison of gold values obtained by fire-assay atomic-absorption and cyanide atomic-absorption methods

[Analyses by Claude Huffman, Jr., J. D. Mensik, and L. B. Riley]

Sample	Gold (ppm)		Sample description
	Fire assay	Cya-nide	
D124654 ..	0.05	0.05	Altered rock.
ABH775 ..	.09	.07	Altered diorite.
D124913 ..	.09	.1	Altered zone.
ABH780 ..	.4	.3	Iron-stained quartz.
D124670 ..	.7	.8	Altered zone.
D124667 ..	.9	.8	Quartz vein.
D124665 ..	1	1	Altered zone.
D124943 ..	2	2	Massive sulfide vein.
ABH923 ..	2	2	Stained silicified quartzite.
D124916 ..	3	3	Sulfide replacement lenses.
ABH926 ..	4	4	Drusy quartz and iron oxide.
D124931 ..	7	5	Altered zone and quartz vein.
ABH871 ..	9	8	Gossan zone in quartzite.
D124676 ..	12	13	Quartz vein and altered zone.
D124675 ..	17	16	Quartz vein.
D124920 ..	27	27	Sulfide-bearing quartz-calcite vein.
ABH854 ..	44	40	Quartz, calcite, sulfides.
D124679 ..	52	58	Altered zone.
ABH832 ..	85	73	Iron-stained quartz.
D124681 ..	350	330	Altered zone.

Test solutions containing 1, 10, 50, and 100 micrograms of monovalent gold in 40 ml of cyanide solution were oxidized by adding 5 drops of saturated bromine water and 5 ml of 48-percent HBr, heated to expel hydrogen cyanide gas, cooled, and extracted with 10 ml of MIBK. All these test solutions showed by atomic-absorption spectrophotometry a recovery of greater than 95 percent in the organic phase.

Recently Strelow, Feast, Mathews, and Van Zyl (1966) confirmed our observation that monovalent gold in cyanide solution is not directly extractable with MIBK; they used $KMnO_4$ in HCl solution to oxidize the gold to the trivalent state.

Atomic-absorption methods for the determination of gold in solution are reasonably free from interferences. No effect from diverse ions has been noted in

this work. In the fire-assay bead method, silver is partially extracted into the MIBK, but has no effect on the gold determination. Strelow, Feast, Mathews, and Van Zyl (1966) also observed no interferences; they stated that Tl(III), Cr(VI), Mo(VI), As(V), Sb(V), Sn(IV), Se(IV), Te(IV), and Fe(III) are partially extracted but cause no interference with the determination of gold by atomic absorption.

CONCLUSIONS

The fire-assay separation combined with atomic absorption has two advantages over the classical fire-assay method: (1) It eliminates the tedious and critical steps of transferring, parting, annealing, and then weighing trace amounts of gold and (2) it provides greater accuracy and precision in low and fractional parts-per-million range.

We employ the more rapid cyanide method for scanning large numbers of samples for their gold content. Samples that show a gold content of greater than 1 ppm are then reanalyzed by the fire-assay atomic-absorption method to confirm the results.

REFERENCES

- Beamish, F. E., 1966, The analytical chemistry of the noble metals in International series of monographs in analytical chemistry [1st ed.]: New York, Pergamon Press, v. 24, 609 p.
- Bugbee, E. E., 1940, A textbook of fire assaying [3d ed.]: New York, John Wiley & Sons, Inc., 314 p.
- Jacobson, C. A., ed., 1949, Encyclopedia of chemical reactions: New York, Reinhold Pub. Corp., v. 3, 800 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.
- Olson, A. M., 1965, Gold assay by atomic absorption spectrophotometry: Perkin-Elmer Atomic Absorption Newsletter, v. 4, no. 5, p. 278-280.
- Simmons, E. C., 1965, Gold assay by atomic absorption spectrophotometry: Perkin-Elmer Atomic Absorption Newsletter, v. 4, no. 5, p. 281-287.
- Strelow, E. C., Feast, P. M., Mathews, C. J. C., and Van Zyl, C. R., 1966, Determination of gold in cyanide waste solutions by solvent extraction and atomic absorption spectrophotometry: Anal. Chemistry, v. 38, p. 115-117.
- Tindall, F. M., 1965, Silver and gold assay by atomic absorption spectrophotometry: Perkin-Elmer Atomic Absorption Newsletter, v. 4, no. 9, p. 339-340.
- Walsh, A., 1955, The application of atomic absorption spectra to chemical analysis: Spectrochim. Acta, v. 7, p. 108-117.