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A sensitive method for the determination of trace amounts of gold in geologic materials (soils, gossans, silicified limestones, etc.) would be useful in geochemical exploration for ore deposits of lead, bismuth, silver, copper, and zinc as well as for gold. Martinet and Cuper (1961) and Pakhomova and Vysotskaya (1963) have developed methods to meet this need. These methods yield satisfactory results but repeated evaporations, filtrations, precipitations and subsequent solution make the methods tedious and lengthy.

Several spectrophotometric methods for the determination of microgram quantities of gold have been published and reviewed critically by Sandell (1959), Beamish (1961), and Chow and Beamish (1963).

Recently, Daiev and Jordanov (1964) have determined 0.5 to 60 ppm gold in copper-, lead- and mixed-concentrates with N,N'-tetramethyl-o-tolidine as the color forming reagent. Cheng and Lott (1962) studied 4,4'-Bis(dimethylamino) thiobenzophenone (Thio-Michler's Ketone = TMK) and its related compounds as sensitive reagents for gold and concluded that TMK offers the highest sensitivity among the common colorimetric reagents for gold.

The separation of minute amounts of gold from the overwhelming quantities of other elements present in the large sample that is necessary to obtain a representative value is the difficulty inherent in all spectrophotometric methods for traces of gold in geologic materials. The ease of reduction of gold and its tendency to become adsorbed on glass and sample residue particles compound this difficulty. The method presented below offers a simple means of separation of gold and its subsequent measurement.

The gold and gold minerals in the sample are dissolved with concentrated hydrobromic acid and sodium bromate; the excess bromine resulting from the reduction of the bromate ion is expelled by evaporation; then the acid solution and the unattacked sample residue is transferred to a separatory funnel and sample solution is diluted to give a final acid concentration of about 3N. Two extractions of this solution and residue with ethyl ether yields a recovery of over 99 per cent of the gold in the ether phase. Subsequent wash of the ether with 1.5N hydrobromic acid removes the iron, silver, mercury, and most of the palladium extracted from the sample. The ether is evaporated to near dryness; the residue taken up in dilute ammonium acetate and shaken with a TMK solution in isoamyl alcohol to give a

red color whose intensity is proportional to the amount of gold in the sample. A five-gram sample is easily handled and 0.1 microgram of gold can be measured which gives a sensitivity of 0.02 ppm.

No attempt is made to bring the entire sample into solution. Any gold minerals completely enclosed in insoluble particles such as quartz would not be brought into solution and the analysis would be low. The sample must, therefore, be ground to a powder to insure a reasonable attack of the gold. As fine grinding may result in loss of gold by plating onto the grinding equipment, a reasonable compromise must be reached with each type of sample studied.

Hydrobromic acid, sodium bromate, and bromine are used to dissolve gold and gold minerals. Solution is just as complete as with aqua regia and tedious evaporations are avoided.

Although Goldschmidt (1954) gives .001 ppm for the abundance of gold in the lithosphere, De Grazia and Haskin (1964) suggest a crustal abundance of .0025 ppm. Their characteristic values of gold content obtained by a neutron activation method of analysis, range from .0024±.0018 ppm for acid igneous and metamorphic rocks, through .0047±.0016 for shales and .006±.0035 ppm for sandstone, to .012±.007 for pelagic clays. From this work it appears that a sensitivity of 0.02 ppm is 2 to 8 times the normal abundance of gold in various rock types. This sensitivity should reveal hydrothermal introduction of gold and give adequate data for mineral exploration.

Procedure

Sample solution

Roast 5 g of pulverized sample at red heat for 10 to 20 minutes in a porcelain dish. Transfer to a 150-ml beaker, mix thoroughly with about 2 g sodium bromate and wet with water. Rapidly pour 40 ml of concentrated hydrobromic acid* into the beaker containing the roasted sample and sodium bromate. Warm on steambath for one hour, then transfer to a hotplate and evaporate to a final volume of 20-25 ml.

Extraction

Transfer the entire contents of the beaker (solution and undissolved residue) to a 125-ml separatory funnel using 30 to 40 ml of water to effect the transfer and to dilute the acid to approximately 3N HBr. Add 50 ml ethyl ether, shake vigorously for 3 minutes and transfer the ether

*The rapid addition of hydrobromic acid is necessary to provide sufficient volume to dissolve most of the bromine produced during the initial violent reaction.

to another separatory funnel. Add 25 ml of ether to the aqueous sample solution and shake for 3 minutes. Combine the ether extracts and wash twice by shaking with 40- and 25-ml portions of 1.5N hydrobromic acid. If the second wash acid is colored a third wash is indicated.

Estimation

Put about 1 ml of water in a 150-ml beaker and add the ether phase from the extraction; evaporate on a steam bath until no odor of ether remains. Do not take to dryness. Dilute to 10 ml with water. To an aliquot in a 50-ml beaker add enough water to make the volume approximately 10 ml, add 2.5 ml NTA solution, mix thoroughly and adjust the pH to 3.0±0.2 with NH_4OH or H_3PO_4. Transfer the contents of the beaker to a 125-ml separatory funnel and add 3 ml of dilute thio-Michler's Ketone. Shake 3 minutes and allow phases to separate. Discard aqueous layer and wash organic phase with water. Drain off the water and add a few drops of ethyl alcohol to collect the last traces of water. Discard the water and transfer the organic phase to a cuvette and read the absorbance in a spectrophotometer at 545 mμ. Compare absorbance with standard curve to determine γ's of gold and convert to ppm.

Preparation of standard curve

To five 25-ml portions of 3N hydrobromic acid each containing 1 g iron as ferric bromide in separatory funnels add 0, 0.1, 0.5, 1.0, and 1.5 micrograms of gold and shake for 3 minutes with 25 ml of ethyl ether. Transfer the ether to another separatory funnel, add another 25-ml portion of ether to each aqueous phase and shake for 3 minutes. Combine the ether extracts and wash twice with 25-ml portions of 1.5N hydrobromic acid. Transfer the ether phases to 150-ml beakers containing 1 ml water, evaporate the ether on a steam bath and proceed as in estimation. Repeat several times and plot the average absorbance of 6 or more replicates vs the gold content to obtain a reliable curve for routine work.

Reagents

Standard gold solution (0.1 percent): Dissolve exactly 1.0000 g Au in HBr-Br_2 and heat gently to expel excess Br_2. Cool and dilute to 1,000 ml with conc. HBr.

Dilute gold solution (.0001 percent): Dilute 0.1 ml of 0.1 percent Au solution to 100 ml with 1.5N HBr. Prepare fresh daily.

Hydrobromic acid, concentrated, reagent grade, distilled.

Hydrobromic acid, 1.5N: Dilute 172 ml conc. HBr to 1 liter with water.

Reagents (cont'd)

Sodium bromate, powder, reagent grade.

Ethyl ether, reagent grade.

Nitrilo triacetic acid (NTA) solution (10 percent): To 10 g NTA in 50 ml water add NaOH pellets until solution is complete. Dilute to 100 ml with water. The pH of this solution should be about 3.3.

Thio-Michler's ketone: Dissolve 14.25 mg of 4,4'-bis(dimethylamino) thiobenzophenone in 400 ml isoamyl alcohol. Heat gently to hasten solution. Cool and dilute to 500 ml with isoamyl alcohol. Protect from light.

Dilute thio-Michler's ketone: Dilute 25 ml of stock solution to 75 ml with isoamyl alcohol. Keep cold and protect from light.

Isoamyl alcohol, reagent grade.

Extraction of gold with isopropyl and ethyl ethers

The extraction coefficient of gold from hydrobromic acid solutions with isopropyl ether and ethyl ether was investigated by McBride and Yoe (1948) for gold concentrations from 10 to 1,000 micrograms Au/ml. They recommended isopropyl ether and 2.0-2.5N hydrobromic acid for separation of gold from much iron. In order to determine the effectiveness of these solvents in extracting gold from solutions containing .0025 to .05γ gold/ml, the following experiments were made with gold(198) as a tracer. With equal volumes of the aqueous and organic phases the percent of gold extracted into the isopropyl ether increased from 15 percent with 0.5N hydrobromic acid through 45 percent with 2.5N acid to 86 percent with 5.5 and 6.0N hydrobromic acid. However, the presence of other ions increased the effectiveness of the extraction. With a stock solution containing 6.3 g Na, 18.3 g Mg, 48 g Al, 6 g K, 9 g Ca, 3.5 g Ti, 0.4 g Mn, and 18 g Fe per liter, the extraction of gold with isopropyl ether from 5N hydrobromic acid was 91 to 93 percent and from 6.5N acid was over 97 percent. This method is great! (oral communication, Davidson, 1964). At this high acidity most of the iron is extracted with the gold interfering with the subsequent measurement of gold.

Extraction of gold with ethyl ether is efficient at much lower acidities. With equal volumes of the aqueous and ether phases, 81 percent of the gold was extracted from 1N hydrobromic acid after a 1 minute shake and 88 percent from 1.5N acid. With the stock solution, described above, 87 percent was extracted from 1N acid and 95 percent from 1.5N hydrobromic acid. Very little ferric bromide is extracted under these conditions. With two 3 minute extractions

using equal volumes over 99 percent of the gold was extracted into the ether phase from 1.5N hydrobromic acid.

Adsorption of gold on sample residue

Gold is strongly adsorbed by the sample residue. Five samples of low grade ore from the Cripple Creek mining district, Cripple Creek, Colorado, were roasted, spiked with Au 198 as $AuBr_3$ and digested with hydrobromic acid and bromine. The samples were transferred to centrifuge tubes, centrifuged, and the supernatant liquid decanted. The residues were mixed thoroughly with 10 ml of water, centrifuged, the wash water decanted, and washed again with 10 ml of water. The residues contained from 41.5 to 64.4 percent of the radioactive gold with an average of 55 percent. When the hot concentrated hydrobromic acid was decanted from another sample residue 86 percent of the radio gold remained with the residue.

The answer to this problem is to make the ether extraction with the sample solution and residue in the separatory funnel. As the ether removes gold from the aqueous phase the adsorbed gold goes into solution. With gold 198 as a tracer added to samples and the unattacked sample residue and diluted acid solution extracted twice with ether, only 0.4 percent of the radio gold remained on the sample residue.

Interferences:

Several elements form colored compounds with thio-Michler's ketone. According to Cheng and Lott those elements are ruthenium(III), rhodium(III), iridium(III), mercury, silver, palladium, copper(I), and gold; however, in their proposed bromide-TMK procedure for auric gold only mercury, silver, and palladium represent interferences because the others do not form colored compounds in an organic medium. Neither mercury nor silver interfere in quantities up to 0.4 percent. Samples containing larger quantities of mercury could be tolerated since during the roasting process the mercury would be volatilized. Palladium forms a pink colored compound and becomes an interference in quantities greater than 300 γ.

Thallium(III) reacts at pH 3 with TMK to give a blue colored complex. The complex of thallium with NTA, however, is adequate to prevent interference with the gold determination except in samples unusually high in thallium. Only four samples out of over 1,200 analyzed in our laboratories contained sufficient thallium to cause interference. In these cases smaller sample aliquots were taken and no blue color was evident. With 2.5 ml of 10-percent solution of NTA 30 γ of Tl increases the absorbance at 545 mμ to give a value twice that obtained with 0.1 γ of gold.

Antimony is extracted by ethyl ether from 3N HBr solution and some remains in the ether phase. On dilution of the residue from the ether evaporation, hydrolysis of the antimony bromide yields a white precipitate which causes difficulty in taking an aliquot of the solution. This has been experienced only with high-grade antimony ores.

In addition to the above interferences cadmium and uranium were found to interfere--one milligram of either element gave a color equivalent to 0.1 microgram of gold.

Among the anions, Cheng and Lott reported that acetate, tartrate, chloride, sulfate, and dichromate had no effect on the determination of gold with TMK. The only interfering anion seems to be bromide and its presence diminishes the sensitivity of the method.

Bromine used in the digestion process of the sample can be a very serious interference if it is not entirely removed. A trace of bromine left in the sample solution is adequate to oxidize the TMK causing a green color. Boiling the hydrobromic acid-bromine solution of the sample eliminates the bromine.

Precision and accuracy

Table 1 shows the repeatability obtained with standard gold solutions run through the analytical procedure. These data may be used to draw a standard curve or the average absorbance of .018 per 0.1 microgram of gold may be used to calculate the gold content. The large relative standard deviation of the absorbance for 0.1 microgram of gold (26 percent) is expectable for the lower limit of a spectrophotometric procedure.

Another test of repeatability is shown in table 2. Three samples of gold ore were run repeatedly by the TMK method. Five gram samples were extracted with ethyl ether and appropriate aliquots of the aqueous acetate solution were taken to react with TMK. The variation between replicate determinations on these gold ores are greater than the variation obtained with standard gold solutions (table 1). It is reasonable to assume that these larger differences reflect differences in the gold content of the respective 5 g subsamples used for analysis.

The gold content obtained by the TMK method in a number of gold ores is compared with that obtained by fire assay in table 3. The TMK method is designed to determine gold in the range 0.02 to 3.0 ppm, but analyzed samples are not available in this range. However, the data in table 3 indicate the method is adequate to screen samples for gold and to determine if further sampling and fire assays are desirable. The method provides a simple, rapid, reasonably accurate procedure for determining gold in the range 0.02 to 3 ppm thus bridging the gap between fire assay and neutron activation procedures.

Table 1.--Repeatability of method using standard gold solutions in ferric bromide. Data represent nine replications at each gold concentration.

Gold taken γ (Micrograms)	Absorbance of gold TMK at 545 mμ*				Relative standard deviation percent	Absorbance per 0.1 γ Au
	Minimum	Maximum	Average	Standard deviation		
0.1	.010	.031	.0195	.0052	26.	.0195
0.5	.079	.095	.087	.0046	5.4	.0175
1.0	.157	.185	.1725	.0083	4.8	.0172
1.5	.243	.300	.272	.0168	6.1	.0181
						Avg. .0181

*The absorbance of the gold solutions were measured against their respective blank solutions as the null solution.

Table 2.--Repeatability of TMK method on gold ore samples from Clear Creek County, Colorado

Lab. No.	Description of sample	Number of determinations	Gold Content, ppm				Relative standard deviation percent
			Maximum	Minimum	Average	Standard deviation	
234557	Vein sample, Treasure Vault Mine----	9	1.00	0.60	0.81	0.13	16.1
224707	Chip sample, Ella No. 1, Lawson area----------	4	0.98	0.73	0.81	0.10	12.3
223181	Gold Anchor Mine, Alice Creek District----------	5	24.0	18.4	21.7	2.01	9.3

Table 3.--Comparison of data by TMK method with fire assay on gold ores from Clear Creek County, Colorado

Sample No.	Description and Location	Gold content, ppm	
		Average of duplicate analysis TMK method	Fire assay[1]
216092	Vein sample from unknown mine----------	[2]0.83	0.68
222893	Galena sphalerite breccia ore, Silver Creek area----------	1.57	1.37
229657	Mill heads, Goldridge Mill, Central City District[3]----------	1.16	1.37
222897	Quartz pyrite, copper, sphalerite ore, Silver Creek area----------	3.75	4.80
223184	Grab sample from dump Gold Anchor mine-------	6.42	6.84
223180	Channel sample Gold Anchor mine----------	14.3	10.3
224702	Quartz-pyrite-sphalerite, Lawson area--------	[2]24.4	26.5

[1]Parts per million calculated from oz/ton of Fire assay by D. W. Skinner, U. S. Geological Survey.

[2]Average of triplicate analysis

[3]Gilpin County, Colorado.

Modified procedure of gold method for field use

Sample solution.

(1) Place 1 g (or one 1-ml scoopful) of the finely powdered sample in a porcelain crucible and ignite for 10 minutes over a burner. (2) Transfer cool sample to a 50-ml Erlenmeyer flask and add one teflon covered magnet, 0.2 ml solid $NaBrO_3$ and 5 ml concentrated HBr. Warm slightly to start reaction. (3) Add, at once, 15 ml concentrated HBr and boil until the volume is reduced to 5 ml. Allow to cool.

Extraction

(1) Transfer entire contents of flask to a 22- x 175-mm rimless culture tube. Wash flask with 15 ml water and add to culture tube. Total volume in the tube should be approximately 20 ml. (2) Add 15 ml of ethyl ether to the contents of the culture tube, stopper the tube with a cork and shake for 1 minute. (3) Allow the phases to separate and, with an automatic pipet, transfer the ether phase to an 18- x 150-mm culture tube. The ether should be colorless. If the ether is colored, return it to a 22- x 175-mm culture tube containing 10 ml of 1.5N HBr, shake for 15 seconds and repeat the removal process. (4) Add 1 ml water and a teflon covered magnet to the ether. Evaporate the ether by placing the tube in a water bath on a magnetic stirring hot plate.

Estimation

(1) To the cool solution add 1 ml NTA solution, 4 ml water, and 1 ml TMK. Stopper tube and shake gently for 15 seconds. (2) Compare the sample solution with standards prepared at the same time.

Preparation of standards

Transfer appropriate aliquots of a gold solution corresponding to 0, 0.5, .1, .2, .5, 1.0, 1.5, 2, and 3 γ Au to 22- x 175-mm rimless culture tubes containing 20 ml of 3N HBr and 0.1 ml $FeBr_3$. Add 15 ml ethyl ether, stopper the tubes with corks and shake for 1 minute. Proceed from step 3 of extraction procedure.

Reagents and apparatus

Reagents

Same as for laboratory method except: Thio Michler's ketone (TMK): Dissolve 14.25 mg of 4,4'-bis(dimethylamino) thiobenzophenone in 400 ml isoamyl alcohol. Heat gently to hasten solution. Cool and dilute to 1000 ml with isoamyl alcohol. Keep cold and protect from light.

Apparatus

Electric hot plate with magnetic stirrer, 9-inch diameter.
Magnets, teflon covered bars, 0.5 inch long.
Erlenmeyer flasks, 50 ml.
Culture tubes, 18 x 150 mm; 22 x 175 mm. Corks to fit both sizes.
Water bath, to accommodate 18-mm culture tubes.
Test tube racks, to accommodate 18-mm and 22-mm culture tubes.
Porcelain crucibles, low form, capacity 17 ml.
Propane torch and support for porcelain crucibles.
Icebox for storage of ethyl ether.
2 Automatic pipets, 5 ml.
Pipets, measuring 10 ml, calibrated in 0.1 ml; measuring 1 ml, calibrated in .01 ml.
2 Scoops, 0.1-ml and 1-ml capacity.

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