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Determination of Gold in Geological Samples at Parts Per Milliard Levels by Flameless Atomic-Absorption Spectroscopy

By

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The determination of gold in geochemical samples presents some difficulties because of the low concentrations involved. Several methods have been proposed¹, most of them based on the use of atomic-absorption spectrometry after concentration of the gold by fire assay or solvent extraction techniques. With these methods, however, analytical sensitivity is rarely sufficiently high to permit Au determinations at the levels normally occurring in non-mineralized silicate rocks [about 0.5—5 ppM (parts per milliard)]. In order to assay these levels, large amounts (tens of grams) of sample must be employed^{2,3}. This, together with analytical problems (large amounts of interfering elements in the analytical solutions, general slowing down of analysis, etc.), prevents material not available in large amounts, such as certain minerals or meteorites, from being analysed.

This paper sets out a relatively rapid procedure for gold determination at low ppM levels in geochemical samples, starting from one gram of sample. Adequate analytical sensitivity is achieved by means of a flameless atomic-absorption (A. A.) procedure combined with a prior liquid-liquid extraction of the gold. The method is applied in the analysis of the silicate standards GSP-1, BCR-1, DTS-1, PCC-1 and Syenite-1. The source of these standards is given by Flanagan⁴.

Experimental

Control of Parameters for Gold Extraction

Quantitative extraction of gold as Au(III) from hydrobromic acid solutions by a number of organic solvents has been reported⁵. Ethyl ether, ethyl acetate and methyl isobutyl ketone (MIBK) are the solvents most often used to extract the bromoaurate complex over a large pH range. The choice of extractant may depend on several factors, of which the most important are basically the effectiveness of extraction required and the characteristics of the technique employed in the subsequent step of analysis. In our case, since only the flameless A. A. technique can provide a sufficiently high analytical sensitivity for the purpose of the work, the limiting conditions imposed by the use of the graphite furnace must be taken into account in the chemical extraction of gold. All the extractants cited above were tested, and MIBK was chosen because, besides ensuring an almost total extraction of gold, the ketone was found to ensure a sufficient production of atomic vapour when placed directly in the graphite tube. This avoids any further treatment of the gold in an aqueous phase that could lead to an appreciable loss of gold, essentially caused by adsorption on the glass containers. If the ketone phase is used directly for analysis, use of the minimum volume of MIBK provides the highest analytical sensitivity. The degree of extraction of gold at varying aqueous-organic volume ratios was checked on 5- and 50-ppM Au solutions against a second extraction (aqueous/organic volume = 1) to see how much gold remained in the 2.6M hydrobromic acid after the first extraction. This solution cannot be analysed directly because of the production of a large amount of smoke in the graphite tube. The data obtained (see Table 1) show that gold extraction both from 5- and 50-ppM solutions was effective (>80%) for aqueous-phase-ketone volume ratios up to 15. The use of very small volumes of extractant imposes a limitation, however, for the ketone is soluble in hydrobromic acid solutions. This solubility depends on the temperature and acid concentration⁶. An estimate of the solubility of MIBK in 2.6M hydrobromic acid was obtained by measuring the volume of ketone recovered after shaking 10 ml of it with 25, 50 and 100 ml of 2.6M HBr and allowing the layers to separate out without centrifugation. The volumes of organic phase required to saturate the HBr solutions were found to be 1, 2 and 4 ml, respectively i. e. approx. 4% of the volume of the aqueous phase (loss of MIBK due to evaporation during handling is negligible). On the basis of the results obtained, 3 ml of MIBK were used to extract

gold from 25 ml of analytical solution obtained by dissolving one gram of sample. Under these conditions, an almost total extraction of gold is ensured, even in the presence of other co-extracted elements (iron), as will be seen later, and the end volume of the

Table 1. Gold Fraction Found in the Second Extract after a First Extraction at Varying Aqueous-MIBK Volume Ratios

Aqueous-MIBK volume ratios	1	5	10	15	20
	Peak height**				
5 ppM Au	1 5*	1	1	1	1
50 ppM Au	5 51*	7	6	8	10

* First extract

** Relative to height for aqueous/organic volume ratio = 1

organic phase is, apart from loss due to handling, 2 ml, i. e., the gold is diluted by only a factor of 2 with respect to its concentration in the sample.

As the volume of MIBK discarded with the hydrobromic acid solution is not negligible with respect to the final ketone volume recovered, a fair amount of gold may also be lost. An estimate of this was obtained by heating the discarded solution to 80°C and analysing the liberated ketone phase. According to previous work⁶ the latter contains only minor amounts (<10%) of the gold. Besides gold and other rare elements (Sb, Mo, Sn), the separated ketone phase contains part of the iron present in the analytical solution. The possible effects of iron on the gold extraction rate were studied on 5- and 50-ppM Au solutions. It was found that the gold extraction is practically unaffected by the presence of iron up to 2000 ppm, but as iron may interfere with the atomization of gold during the subsequent analysis step, it is almost totally back-extracted from the MIBK phase by washing with dilute hydrobromic acid.

Equipment

Instrument. Perkin-Elmer Model 403 atomic-absorption spectrophotometer with a Model 56 recorder.

Light source. Perkin-Elmer Intensitron® gold lamp.

Graphite furnace. Model HGA-2000 equipped with a Deuterium Background Corrector.

Operating Conditions

Wavelength: 2428 Å.

Slit: 0.7 nm.

Graphite furnace: 20 sec drying at 100⁰ C; 20 sec ashing at 550⁰ C; 7 sec atomization at 2180⁰ C.

Purge gas: interrupted nitrogen flow, set at 3 divisions on the flowmeter.
Recording system: 0.5 mA full scale.

Sample volumes: normally 50 μ l. In the case of Au levels below 1 ppM in the MIBK phase, larger volumes (up to 200 μ l) may be used by adding separate 50- μ l aliquots.

For both standards and unknown samples, triplicate readings were made and the average values reported.

Reagent and standards: Superpure concentrated reagent grade chemicals were used.

Preparation of the Au standard solutions: Dissolve 0.100 g of gold foil in a few ml of aqua regia and evaporate the solution to dryness on a water-bath. Add 1—2 ml of conc. hydrochloric acid and evaporate to near-dryness. Dissolve the residue in 0.1M hydrochloric acid and make up to 100 ml. From this stock solution (100 ppm Au) prepare very dilute Au solutions (1, 2, 5, 10, 20 and 50 ppM) by dilution with 0.1M hydrochloric acid immediately before they are used for analysis. Evaporate 5 ml of each solution to near-dryness in the presence of a few milligrams of sodium chloride and convert the Au into bromoaurate by addition of enough hydrobromic acid to make the HBr concentration 2.6M. Extract the gold into 5 ml of MIBK in the same manner as for the unknown samples. Prepare a blank in the same manner.

Stability of gold solutions. The stability of gold solutions is known to be affected by exposure to bright sunlight and by base-exchange reactions and absorptions by glass containers. The optimum conditions to guarantee a good conservation of Au solutions have been described^{7,8}. Our findings show that very dilute aqueous Au solutions (less than 10—20 ppM) are unstable over a period of some hours, probably because of absorption phenomena on the part of the polyethylene containers and/or creeping effects, as previously suggested⁹. Au-MIBK solutions stored in a freezer are, however, stable for several weeks.

Decomposition Procedure

Decomposition of samples was performed in a cylindrical Teflon vessel (details reported by Sighinolfi¹⁰) placed on a hot-plate to obtain slow but complete evaporation of the analytical solution. One gram of sample is decomposed with 5 ml of hydrofluoric acid and 2 ml of aqua regia, the solution is evaporated to dryness and converted into bromide salts by the addition and evaporation of 2 ml of concentrated hydrobromic acid. The residue is dissolved in

10 ml of conc. hydrobromic acid and some water and the solution is transferred to a 25-ml volumetric flask. An alternative decomposition method consists of the use of only aqua regia, which was found⁷ at least 99% efficient in removing gold from siliceous materials. Here, a combined hydrofluoric acid-aqua regia reagent was preferred because it ensures higher analysis speed.

Extraction Procedure

Transfer the analytical solution to a 60-ml separating funnel, add 3 ml of MIBK and shake vigorously for 3–4 min to extract the gold. Allow the layers to separate and discard the aqueous layer. Wash the organic phase with 10 ml of 0.1M hydrobromic acid and shake for 1 min to back-extract the iron. Transfer the MIBK phase into a 10-ml borosilicate glass bottle.

Results and Discussion

The working curves obtained by pipetting 50 μ l of aqueous and organic solutions of gold are linear and reveal an apparent 30–40% loss of gold when the MIBK phase is directly used in the graphite tube. Since the extraction procedure has been proved to be effective, the decreased absorption signal may essentially be ascribed to (a) the nature of the solvent, as organic solutions wet graphite easily with dispersion of the solution components, and (b) lower production of gold atomic vapour from the Au complex present in the MIBK phase than from that in aqueous solutions.

The sensitivity of the method, under standard conditions, measured as concentration/1% absorption, is approx. 0.8 ppM in solution, which is equivalent to 40 pg absolute Au content and not far off the limit (30 pg) accepted for the use of the graphite furnace. Thus, the sensitivity limit for a 1-g sample is about 1.6 ppM when standard volumes (50 μ l) are pipetted, since in this case the blank signal is negligible. To improve this limit, larger volumes of solution may be introduced into the tube by adding separate 50- μ l aliquots, taking care to activate the charring stage for short periods (10 sec) between each addition. With the use of the standard graphite tube, a maximum volume of 200 μ l was found to give an absorption signal proportional to the concentration, provided the total concentration did not exceed about 2 ppM. The absolute sensitivity limit then becomes 0.4 ppM Au for a 1-g sample, but at the same time the blank signal (caused by impurities of the reagents and/or unresolved broad-band absorptions) is not negli-

gible. Thus, the detection limit (the concentration that produces a signal equal to twice that of the blank value), for 200 μ l, can be estimated to be about 0.6—0.8 ppM.

Matrix effects due to foreign elements, which are considered¹¹ to be the most limiting factor in the use of the graphite cell, can be discounted owing to the marked selectivity of the extraction procedure employed. Instrumental precision was checked by means of a series of replica readings on 2- and 50-ppM Au solutions. Aqueous solutions slightly acidified with nitric acid afford very good precision (2—4% coefficient of variation) over the whole concentration range. MIBK solutions afford adequate precision (5—10%) at the 50-ppM level while the error increases markedly at low Au levels (20—30% at 2 ppM; about 50% at 0.8 ppM). The error is strongly reduced when “grooved” graphite tubes are employed, but so too is the analytical sensitivity.

Since natural standards with appreciable Au contents are not available, in order to test the bulk reproducibility and accuracy of the method a 10-ppM Au rock standard was prepared by adding an adequate amount of gold to almost Au-free rock (PC-1) and analysing it in the usual manner. The results obtained (Table 2)

Table 2. Analytical Results (ppM)

Sample	Au found	Average	Literature data
PC-1 + 1 ppM Au	8.0—8.5 9.1—9.3 9.6—9.6 9.8—9.8	9.2	
GSP-1	1.4—1.6	1.5	1.6 average value, Flanagan ¹³
BCR-1	0.5—0.7	0.6	0.95 magnitude value, Flanagan ¹³ 0.58, Morgan <i>et al.</i> ¹⁴ 0.75, Morgan <i>et al.</i> ¹⁵
PCC-1	0.5	0.5	1.6 magnitude value, Flanagan ¹³
DTS-1	0.8—0.8	0.8	0.8 magnitude value, Flanagan ¹³
Syenite-1	36—42	39	1 ppm, Sine <i>et al.</i> ¹⁶

show that the reproducibility of the bulk analysis may be considered satisfactory (about 10—15% error) and that the mean Au content recovered is appreciably lower (by about 10%) than the gold added. The Au loss presumably occurred during the sample dissolution phase, as also observed by Moore and Wessman¹². Table 2 also reports the results for some silicate standards and some comparative data drawn from the literature. The data from the present work for most of the samples are comparable to these of

other authors. This, however, does not enable conclusions to be drawn as to the accuracy of the method, on account of the scarcity and spread of the values. Some largely discordant values may be ascribed not so much to analytical mistakes as to the possible heterogeneity of standard rock samples regarding elements in ppm ranges.

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Summary

Determination of Gold in Geological Samples at Parts Per Milliard Levels by Flameless Atomic-Absorption Spectroscopy

A method is described for the determination of gold at ppM levels in geological materials by the use of flameless A. A. spectroscopy. The gold is separated as bromoaurate from HBr solution by methyl isobutyl ketone (MIBK). The MIBK phase is pipetted directly into an HGA-2000 Graphite Furnace. Detection limits of about 0.6—0.8 ppM Au for a 1-g sample are achieved. The error of determination (relative standard deviation) varies in the range 5—50%, depending on the absolute gold level.

Zusammenfassung

Ein Verfahren zur Bestimmung von ppM-Mengen Gold in geologischem Material mit Hilfe der flammenlosen Atomarabsorption wurde beschrieben. Dabei wird das Gold als Bromoaurat aus bromwasserstoffsaurer Lösung mit Methylisobutylketon extrahiert. Die organische Phase wird unmittelbar in einen HGA-2000 Graphitofen pipettiert. Die Nachweisgrenze beträgt etwa 0,6—0,8 ppM Au in einer 1-g-Einwaage. Die relative Standardabweichung variiert je nach der absoluten Goldmenge zwischen 5 und 50%.

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