

A rapid field analytical method for gold in geochemical exploration

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Abstract

A rapid field method for gold analysis in geochemical exploration has been developed. Cold extraction of Au, at room temperature, using a mixture of sodium bromide, sulphuric acid, hydrogen peroxide is performed; the technique has the advantage of avoiding the irritating odour of commonly used aqua regia digestion. Polyurethane foam is used to concentrate gold from solution. After desorption of Au using mixed reagents (0.5% Na₂SO₃–NaCl solution at pH 8), two sequential procedures, depending on the concentration, are followed for the determination of gold. (1) A 1 mL portion of desorbed solution is used to form Au–TMK–DBS (Thio Micher's Ketone and dodecyl benzene sodium sulphonate) ternary complex. Concentrations below 20 ng/g Au are determined by visual colour comparison of the organic layer with a series of standards. (2) If the concentration is greater than 20 ng/g Au, a complexation reaction using the same reagents is followed by fibre-optic colorimetry. The method is rapid and simple, and the tiresome operation of ashing the foam is avoided. The limit of detection is 0.5 ng/g Au and eighty determinations can be made in one working day. The method could be used for rapid follow-up of rock sample or in situ drill core analyses. About 600 samples from 5 gold districts were tested by this method. The results are very satisfactory.

1. Introduction

Geochemical exploration for gold has achieved great success recently in China. During the implementation of China's national geochemical mapping project (Xie et al., 1989), thousands of significant regional gold anomalies were delineated. After the follow-up of detailed geochemical and geological surveys, more than 300 new gold occurrences were found, many of which are being developed into workable mines.

A variety of rapid field methods have been developed by Chinese workers for camp-site determination of gold in samples collected during follow-up of regional gold anomalies and detailed geochemical surveys. The methods developed by Jiang (1986) and Shi and Teng (1986) using hot aqua regia attack in closed vessels, followed by preconcentration using polyurethane foam

or sulphhydryl cotton, and TMK (Thio Micher's Ketone) colorimetry, can achieve a detection limit of 4 to 5 ng/g Au. The tedious operation of ashing the foam, and the irritating odour generated by aqua regia under field conditions could not be avoided even though closed vessels were used. Interference of As, Sb, Bi and Hg in complex samples from mineralized regions is also a problem.

The authors have developed an efficient cold extraction method to avoid using aqua regia in the field. A desorbing procedure has also been developed to avoid ashing the foam. The detection limit with the present method is 0.5 ng/g Au. The method is simple and robust, and can be used in detailed geochemical surveys, for follow-up of regional gold anomalies and as a rapid evaluation technique for gold prospects.

2. Experimental

2.1. Reagents

TMK(1) (Thio Micher's Ketone) — 0.02%: dissolve 20 mg of TMK in 100 mL of the mixed solvent (prepared by adding 10 mL n-octanol and 10 mL tributyl phosphate to 80 mL absolute alcohol, and shaking for 1 min). Pour the solution into a brown bottle wrapped with black paper and keep in a dark place. Dilute to 0.002% TMK with the above mixed solvent before use.

Standard gold solutions:

- (a) stock solution: 100 $\mu\text{g/mL}$ (10% aqua regia).
- (b) working solution: 0.1 $\mu\text{g/mL}$ (1% aqua regia).
- (c) working solution: 1 $\mu\text{g/mL}$ (1% HCl).
- (d) working solution: 10 $\mu\text{g/mL}$ (5% HCl).

Buffer solution: acetic acid–sodium acetate buffer at pH 3.5.

Mixed desorption reagents: dissolve 0.5 g of sodium sulphite and 0.5 g of sodium chloride in 50 mL of deionized water, adjust pH to 8 using diluted acid solution, dilute solution to 100 mL, mix well.

DBS solution (dodecyl benzene sodium sulphate): 100 g/L

TMK(2) (Thio Micher's Ketone) — 0.02%: dissolve 20 mg of TMK in 100 mL absolute alcohol.

2.2. Apparatus

The equipment used to perform the analyses consists of the following: (1) a water bath; (2) a fibre-optic colorimeter, model 250, manufactured by the No.3 Analytical Instrument Factory, Shanghai; (3) a digital scale measuring at ± 0.1 g; (4) a universal pulverizer made by Experimental Factory of the Institute of Geophysical and Geochemical Exploration, Langfang.

2.3. Pretreatment of polyurethane foam

The polyurethane foam is cut into pieces measuring $1.5 \times 1.5 \times 1.0$ cm³ (about 0.15 g each). After washing, the pieces are soaked in 0.5 M nitric acid for 12 hours, then washed with water and dried at room temperature. Afterwards, they are soaked with acetone and MIBK; this restores the foam to its original volume. Finally, the foam is once again washed with water and dried, ready for use.

2.4. Analytical procedure

Sample dissolution

Weigh 10 g of pulverized ($-74 \mu\text{m}$) sample into a 100-mL polyethylene bottle, wet the sample with a small amount of water, add 2 g of NaBr and 25 mL of 10% sulphuric acid. Shake the bottle to disperse the sample, add 3 mL of hydrogen peroxide (30%), and allow to stand for at least 3 hours; shake 2 to 3 times during that period. Stir with a glass rod if the sample adheres to the bottom of the bottle.

Preconcentration of gold using the foam

Dilute the solution with water to about 100 mL, add a piece of polyurethane foam and shake for 30 min. Remove the foam from the bottle, wash it with water and squeeze to dryness; transfer it into a 25-mL tube, add 5 to 10 mL of mixed desorption reagents, and heat the tube on a boiling water bath for about 25 min. Remove the foam and squeeze to dryness; discard the foam and retain the solution containing desorbed gold.

Measurement

Measurements are carried out in two steps. The first is used as a screening process and to determine Au concentrations below 20 ng/g. If the concentration is above 20 ng/g Au, the second step is carried out using fibre-optic colorimetry.

Step 1 — Transfer 1 mL of the desorbed gold solution into a porcelain crucible (5 mL), add 1 mL of 2 : 1 HCl, 3 drops of H₂O₂, 2 drops of 20% KCl and allow to stand for 3 to 5 min. Evaporate to dryness on a boiling water bath. Add 2 drops of 20% KCl, 3 drops of pH 3.5 buffer solution, and 2 drops of absolute alcohol. Shake well and allow to stand for 5 min; then add 0.02 mL of 0.002% TMK, 3 drops of water, and 2 drops of 10% DBS. Rotate the crucible carefully to make the tiny droplet of the organic layer grow into a well-separated longer bead. Compare visually the colour of the bead with a standard series. If the gold concentration is higher than 20 ng/g, proceed to Step 2.

Step 2 — Transfer 1 to 5 mL of desorbed solution into a 25 mL tube, add 3 mL of pH 3.5 buffer solution, 2 mL 10% DBS, and 1.5 mL of 0.02% TMK(2); mix well, heat the solution on 60°C water bath for 15 min, allow to cool, and measure the absorbance (or read the concentration directly) of Au with the fibre-optic colorimeter.

Preparation of the series of standards

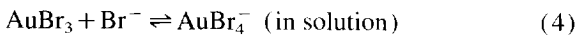
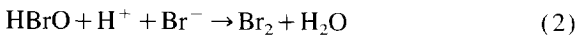
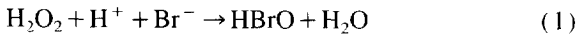
Standard Series 1: Place 0, 1, 2, 4, 6, 8, 10, 20 ng of gold into a porcelain crucible (5 mL), add 1 mL of HCl (2 : 1), 3 drops of H₂O₂, 2 drops of KCl, and allow to stand for 3 to 5 min. Evaporate the solution to dryness on a boiling water bath. Add 2 drops of 20% KCl, 3 drops of pH 3.5 buffer solution, 2 drops of absolute alcohol, shake well and allow to stand for 5 min. Add 0.02 mL of 0.002% TMK, 3 drops of water and 2 drops of 10% DBS; after the droplets of organic solvent appear, rotate the crucible carefully to make the fine droplets coalesce into a floating micro-bead.

Standard Series 2: Place 0.0, 0.25, 0.50, 1.0, 2.0, ..., 50 µg Au into a set of 25 mL tubes, add 1–5 mL of mixed desorption reagent, 3–5 mL of pH 3.5 buffer solution, 2 mL of 10% DBS, 1.5 mL of 0.02% TMK(2), mix well, heat the solution on a 60°C water bath for 15 min, and allow to cool. Measure the absorbance of the solution with the fibre-optic colorimeter at 560 nm, with reference to the blank solution. Construct the calibration curve using the data obtained.

3. Results and discussion

3.1. Mechanism for dissolution of gold

From our own experience, 5 to 20% H₂SO₄ is optimum for the extraction of gold by sodium bromide in an acidic solution. A possible mechanism for the dissolution of gold is as follows:



The bromo-anion complex, AuBr₄⁻, which is presumed to be the dissolved ionic form in aqueous medium, can be removed from solution according to reactions (5) and/or (6) where the equilibrium is shifted to the right by the high acid strength. This can explain the lower recoveries at high H₂SO₄ concentrations.

Table 1

Recovery of Au by acetone–MIBK loaded polyurethane foam using different solution media

Solution	Au added (ng)	Au found		Recovery (%)
		mean ^a (ng)	%RSD	
5% HCl	10	9.5	10.5	95.0
	100	97.7	2.6	97.7
10% HCl	10	9.9	4.2	99.0
	100	97.0	1.4	97.0
5% aqua regia	10	9.5	14.8	95.0
	100	99.0	2.2	99.0
10% aqua regia	10	9.3	2.5	93.0
	100	98.0	2.4	98.0
5% H ₂ SO ₄	10	9.6	0.49	96.0
	100	97.3	1.7	97.3
10% H ₂ SO ₄	10	9.57	1.7	95.7
	100	98.0	3.3	98.0
	500	493	1.7	98.7

^a Average of 3 determinations.

3.2. Adsorption efficiency of gold by the foam

Polyurethane foam has been used successfully for the preconcentration of gold as complex anions from aqua regia solutions (<20%). Incomplete AuBr₄⁻ adsorption can occur due to variable quality of foam from different manufacturers. However, impregnation of the polyurethane foam with acetone and MIBK can improve the percentage of recovery from different acid media to over 98%, as shown in Table 1.

3.3. Efficiency of desorption

Various desorption reagents have been tested for the desorption of gold from foam in acidic, weakly basic and neutral aqueous solutions. The efficiency of desorption of gold from weakly basic and neutral aqueous solutions of pH 7 to 8 is better than from more acidic or basic solutions. Table 2 shows the efficiency of the mixed desorption reagent for desorbing gold from the foam. The recovery of gold ranges from 93.2 to 98.0% for amounts of added Au ranging from 5 to 1000 ng.

Table 2
Efficiency of mixed reagents (0.5% Na₂SO₃-NaCl) for desorption of gold from the foam

Au added (ng)	Au found		Recovery (%)
	mean ^a (ng)	%RSD	
5	4.66	10.6	93.2
10	9.44	5.3	94.4
50	48.2	4.8	96.4
100	97.6	2.4	97.6
1000	980	2.0	98.0

^a Average of 5 determinations.

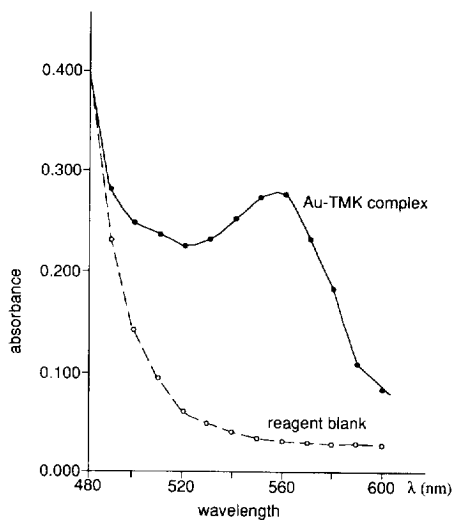


Fig. 1. Absorption spectrum of Au-TMK-DBS ternary complex.

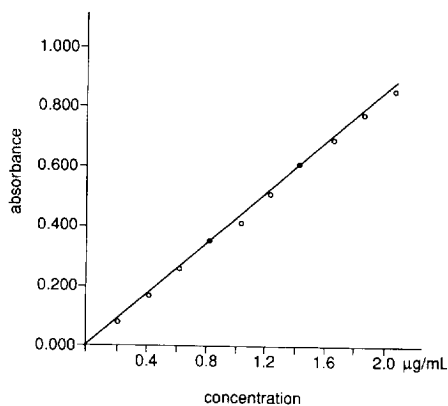


Fig. 2. Calibration curve for Au.

3.4. Measurements and interferences

To obtain a very low detection limit of gold by TMK colorimetry, a micro-analysis technique (Shen et al., 1988) was used with modifications for field conditions. In the modified procedure, the colour developing process is performed in a small crucible. Only 0.02 mL of 0.002% TMK is used. The floating tiny coloured droplet that forms is compared with a series of colour standards. If organic matter, As, S or Sb are present at high concentrations, the samples must be ignited prior to dissolution. The presence of 100 mg As or Bi, 20 mg Hg, or 50 mg Pb will produce a positive interference of 1 ng gold; 10 mg Sb will produce a blue tint to the tiny droplet formed. When the amount of gold is greater than 20 ng/g, the fibre-optic colorimeter can be used to measure absorbance of the solution for accurate quantitative measurements.

Table 3
Results of the determination of gold in standard reference materials

Sample	certified (μg/g)	this method	
		mean ^a (μg/g)	RSD%
GAu-2	0.00082	0.00086	17.4
GAu-3	0.0062	0.0055	23.2
GAu-7	0.087	0.084	7.8
GAu-17	3.14	3.26	3.9
GAu-18	10.3	10.0	1.4

^a Average of 11 determinations.

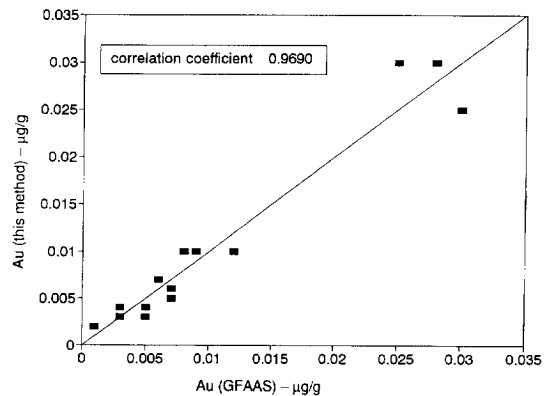


Fig. 3. Comparison between the field analytical method and GFAAS for the determination of Au in geochemical samples ($n = 16$).

3.5. Measurement of gold by fibre-optic colorimetry

Gold reacts with TMK at pH 3.5 to form a soluble violet–red ternary complex when surfactant is used. The absorption spectra of Au–TMK–DBS ternary complex shows an absorption maximum at 555 nm (Fig. 1). A wavelength of 560 nm was chosen as a compromise between the analyte and background absorption for the measurement of gold. Under the experimental conditions used in this research the Au–TMK–DBS ternary complex was found to be stable for over four hours.

Calibration standards were measured under the conditions described above. As shown in Fig. 2, the calibration graph was linear for the concentration range of 0 to 2 $\mu\text{g}/\text{mL}$.

Results of the determination of gold in geochemical reference materials (Yan and Wang, 1986) GAu-2, GAu-3, GAu-7, GAu-17 and GAu-18 by this method is shown in Table 3. The results are in good agreement with the certified gold values, with precision better than 8% RSD for concentrations above 1 $\mu\text{g}/\text{g}$, although somewhat poorer precision was obtained for lower concentrations. Over 600 samples were analyzed by this field method. Some samples were also analyzed by graphite furnace atomic absorption spectrometry for comparison purposes; this showed good agreement (correlation coefficient: 0.969) as shown in Fig. 3.

4. Conclusion

The field analytical method described is rapid and simple. The tedious operation of ashing the foam, and the exposure to irritating odour of aqua regia under field conditions is avoided. With the limit of detection of 0.5 ng/g, and the sample throughput of eighty determinations per working day, the method is a useful tool in field geochemical surveys for gold.

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