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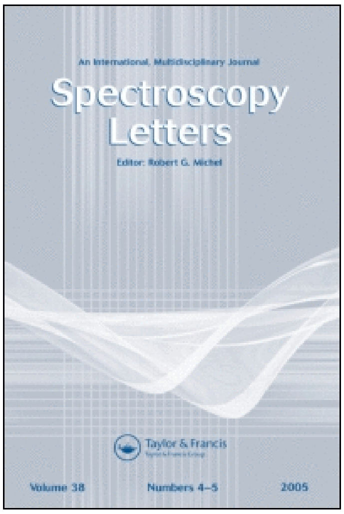

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Preconcentration and Separation of Gold(III) from Ore Samples by Solid-Phase Extraction Prior to Its Catalytic Fluorescent Determination

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ABSTRACT A new catalytic kinetic fluorescent quenching method for the determination of trace gold(III) was investigated. The method was based on the catalytic effect of gold on oxidation of 3-(3′-methylphenyl)-5-(2′-arsenoxylphenylazo) rhodanine by hydrogen peroxide in potassium hydrogen phthalate–hydrochloric acid ($pH = 3.4$). Under the optimum conditions, the great decrease of fluorescence intensity has a linear relationship against the concentration of gold in the range of 0 to $12.0\,\mu g \cdot L^{-1}$ with a detection limit of $6.0 \times 10^{-10} g \cdot L^{-1}$. The coexistent metal ions can be separated, and gold can be enriched by TBP resin of solid-phase extraction, which greatly improves the selectivity and sensitivity of the system. The method can be used to determine trace amounts of gold in ore samples successfully with satisfactory results.

KEYWORDS catalytic kinetic, fluorescent quenching method, gold(III), 3-(3′-methylphenyl)-5-(2′-arsenoxylphenylazo) rhodanine, solid-phase extraction

INTRODUCTION

As we can conclude from reports, there are many methods for determination of gold, including catalytic spectrophotometry,[1] atomic absorption method,[2–4] emission spectrometry, inductive coupling plasma–MS,[5] electrochemistry,[6,7] and so forth. However, they often suffer from a variety of limitations. Catalytic spectrophotometry is known as a sensitive method for determination whose indicator reaction is mainly based on oxidation–deoxidation, but interference from coexisting substances is too strong to be erased or the accuracy is low. The preparation for atomic absorption method is complex, and the matrix interference interfere of this method is difficult to be eliminated. Emission spectrometry may not be the choice if you want to determine polycomponent simultaneously. Inductive coupling plasma–MS calls for expensive instrument, and electrochemistry has poor repeatability.

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Catalytic dynamic spectrofluorimetry is a kind of sensitive determination method that has developed very widely and quickly in the determination of trace metals in recent years.[8–13] It also can be used for determination of simultaneous components. Having been combined with preconcentration and separation of solid-phase extraction, the selectivity of catalytic dynamic spectrofluorimetry has greatly improved to make it a powerful determination tool. Up to the present time, there are no published reports concerning gold determined by catalytic dynamic spectrofluorimetry method.

In this work, we propose a catalytic dynamic spectrofluorimetry method for the determination of gold with 3-(3′-methylphenyl)-5-(2′-arsenoxylphenylazo) rhodanine (3MRAAP) as a catalyst after preconcentration and separation of solid-phase extraction. The TBP extraction resin used in this procedure is very much selective to Au^{3+}, and Au^{3+} could be preconcentrated and separated under certain conditions while interference of the coexisting metal ions could be erased. There are many advantages of preconcentration and separation of solid-phase extraction, such as simplicity of operation, high adsorption capacity, quick adsorption speed, and facility of elution and preparation of adsorbent. The method is proved to be more sensitive and more selective and has been successfully applied to determination of trace gold in ore samples with a satisfactory result.

MATERIALS AND METHODS

Synthesis of New Type of Rhodanine

The new type 3-*m*-methylphenyl-5-(2′-arsenoxylphenylazo) rhodanine has been synthesized for the first time by the authors.[14,15]

In a 250 mL conical flask, 60 mL ammonia (1.0 moL) and 34 mL carbon disulfide (0.45 moL) were added, and 43 mL *m*-methylaniline (0.4 moL) was added in later while stirring. The above mixture was kept stired for 10 h, and then with pump filtrations, the dithio-*m*-methylbenzene amine formate ammonium, which was (a), was obtained. Thirty grams of chloroacetic acid was neutralized to pH 7.0 with sodium hydroxide in 40 mL water. Afterward, (a) was put in the neutralized solution, and 100 mL concentrated hydrochloric acid was added, which was heated to boiling and at once was filtrated, then a straw-yellow solid was obtained, which was called 3-*m*-methylphenyl rhodanine, (b).

The diazonium salt was obtained by mixing 0.025 moL *p*-toluidine arsenate with 14 mL hydrochloric acid and adding 1.87 g sodium nitrite in the mixture in an ice bath.

In the ice bath, 0.025 moL (b) was added in 20 mL ammonia, afterward the diazonium salt was injected in 20 mL of $0.1\,mol \cdot L^{-1}$ ammonium chloride and 6 mL concentrated ammonia. After 1 h of stiring, the mixture was filtrated, and the filtrate was acidized with concentrated hydrochloric acid (at room temperature), and precipitate was found. The 3-*m*-methylphenyl-5-(2′-arsenoxylphenylazo) rhodanine was obtained by filtrating and drying. The synthetic route is shown in Fig. 1.

Physical Measurement

Data from infrared spectrogram (KCl disks, cm^{-1}) is as follows: v OH = 3371; ν N=N = 1240; ν C=S, Ar–C–N=1240; ν Ortho-disubstituted = 764; ν As = O = 900; ν $C–CH_3$ = 3141; ν benzene ring (C=C) = 1522, 1589, 1643.

The elemental analysis of 3MRAAP gave a composition (%) of C (42.43%), H (3.26%), N (9.08%), S (14.43%), which is in good agreement with the theoretical composition of 3MRAAP: C (42.58%), H (3.13%), N (9.31%), S (14.21%).

Apparatus

A Perkin-Elmer LS55 fluorescence spectrophotometer was used with a 1-cm quartz cell (Perkin-Elmer). An AL204 precision electronic autobalance (Mettler Toledo, Shanghai, China) was taken to measure chemicals used in this work. A 601 ermostatic

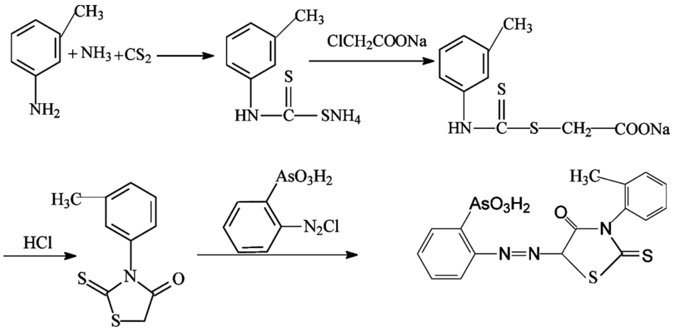

FIGURE 1 Synthesis route of the reagent 3MRAAP.

water-circulator bath (Jiang Su Jin Tan, Jiang Su, China) was used for the water bath of catalyzed and uncatalyzed solutions. The pH measurements were made by using a home-made PHS-3C digital pH meter (Shang Hai Lei Ci Device Works, Shanghai, China) with a combined glass-calomel electrode.

Reagents

All chemicals were of analytical reagent grade or above. Doubly distilled demineralized water used throughout was obtained by SYZ-550 quartz sub-boil high-purified water distiller (Jiang Su Jin Tan, Jiang Su, China).

Preparation of the TBP extraction resin:[16] 3.0 g of polytetrafluoroethylene (grain size: 30 μm) was soaked in 3.0 mL TBP–ethyl ether solution (ν_{TBP}:$\nu_{\text{ethyl ether}} = 4{:}6$) while being mixed and then dried in the water bath for use. This procedure was repeated three times.

Preparation of the solid-phase extraction pole (shown in Fig. 2): the prepared TBP was filled and compacted in a glass tube with inner diameter 7.0 mm and length 30 mm, and both tube ports were slipped with sieve plates. Then two column covers were tightly capped on top of the sieve plates to make sure the TBP extraction resin did not leak out from the extraction pole.

A stock solution of gold ($1.0\,\text{mg}\cdot\text{mL}^{-1}$) was prepared by dissolving 0.2092 g of spectrographically $HAUCl_4 \cdot 4H_2O$ (Tianjinshi Delan Jingxi Huagongchang, Tianjin, China, A.R.) in 20 mL $2.0\,\text{mol}\cdot\text{L}^{-1}$ HCl solution and diluted to 100 mL with water. A $0.1\,\mu\text{g}\cdot\text{mL}^{-1}$ standard solution of gold was prepared by dilution of this stock solution with water. A stock solution containing $1.0 \times 10^{-4}\,\text{mol}\cdot\text{L}^{-1}$ 3-(3′-methylphenyl)-5-(2′-arsenoxylphenylazo) rhodanine (3MRAAP) was prepared by dissolving 4.5 mg of 3MRAAP with 50 mL water. A $2.0 \times 10^{-5}\,\text{mol}\cdot\text{L}^{-1}$ standard solution of 3MRAAP was obtained by diluting the stock solution with water. A potassium acid phthalate–HCl buffer solution was obtained by dissolving 4.08 g potassium acid phthalate (Shanghai Chemical Reagent Company, Shanghai, China) in water and adjusting the pH with $0.2\,\text{mol}\cdot\text{L}^{-1}$ hydrochloric acid solution to give a final total volume of 250 mL. An 0.03% solution of hydrogen peroxide was prepared by mixing 0.5 mL hydrogen peroxide in 500 mL water in a volumetric flask protected from light.

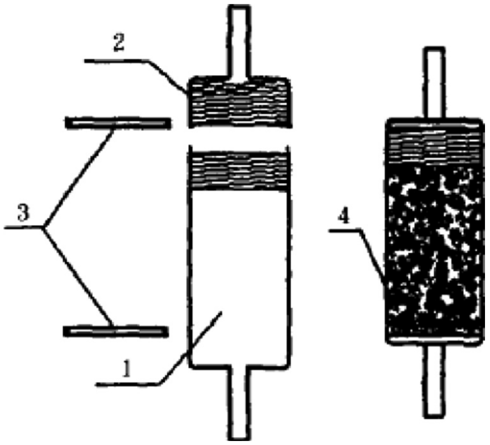

FIGURE 2 Solid-phase extraction pole: 1, filling resin; 2, column cover; 3, sieve plate; 4, TBP extraction resin.

Procedure

Certain volume of Au(III) standard solution (or ore sample solution) was measured into a 10 mL color comparison tube with cover, and 1.2 mL $2 \times 10^{-5}\,\text{mol}\cdot\text{L}^{-1}$ 3MRAAP, 1.8 mL potassium hydrogen phthalate–HCl buffer solution (pH = 3.4), and 2.0 mL 0.03% hydrogen peroxide were added in turn, which was diluted to the standard volume. The color comparison tube was heated in boiling water bath for 20 min, cooled with running water quickly as soon as it came out of the water bath. This is what is called catalyzed solution. The uncatalysed solution is obtained in the same way except addition of standard solution of gold (or ore sample solution). The fluorescence intensity of uncatalyzed solution (F_0) and catalyzed solution (F_1) were measured at an emission wavelength of 404 nm and at excitation wavelength of 310 nm (slit = 10/10). The enhanced fluorescence intensity (ΔF) was obtained by subtracting the uncatalyzed fluorescence intensity (F_0) from that of the catalyzed sample or antimony standard solution (F_1).

RESULTS AND DISCUSSION

Fluorescence Spectrum

It can be found in the excitation spectra and emission spectra (Fig. 3) that the fluorescence intensity of 3MRAAP itself is very strong (curve 1′), but it quenches minorly when hydrogen peroxide is added in (curve 2′). Also, we can see from the graph that

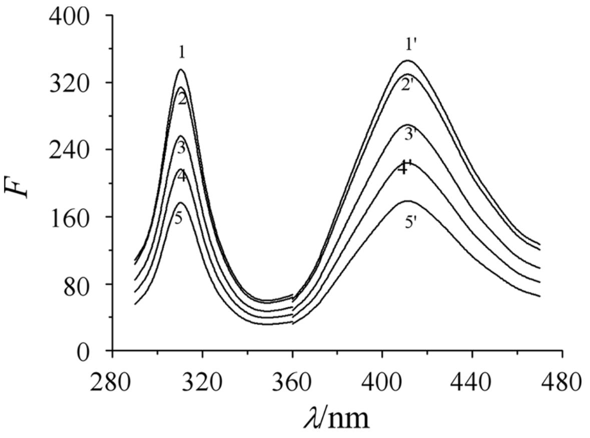

FIGURE 3 Excitation spectra and emission spectra of system. (1) 1′ 3MRAAP, (2) 2′ 3MRAAP-H_2O_2, (3) 3′ 3MRAAP-H_2O_2-Au^{3+} (4.6 μg · L^{-1}, (4) 4′ 3MRAAP-H_2O_2-Au^{3+} (7.0 μg · L^{-1}, (5) 5′ 3MRAAP-H_2O_2-Au^{3+} (10.0 μg · L^{-1}

the fluorescence intensity of the catalyzed system 3MRAAP–H_2O_2–Au(III) is blatantly quenched than the uncatalyzed system 3MARAAP–H_2O_2 (curve 3′), and it is the catalytic action of trace gold that makes this work. The quenched fluorescence intensity has a linear relationship against the amount of gold in certain range of concentration of Au(III). According to what is shown in Fig. 3, 310 nm and 404 nm have been chosen to be the wavelength of excitation peak and emission peak at which determination for trace gold by 3MRAAP was carried out.

Mechanism of the Catalytic Kinetic Reaction

It is known that there is a transformation between the group carbonyl and the enol form in 3MRAAP at pH 3.4 (Fig. 4), which ensured 3MRAAP coplanar and conjugated so that it can give the strong fluorescence emission. Neither lower pH nor higher pH would make it. In the proposed method, all solutions were in the buffer solution of pH 3.4, which ensured 3MRAAP could emit strong and steady.

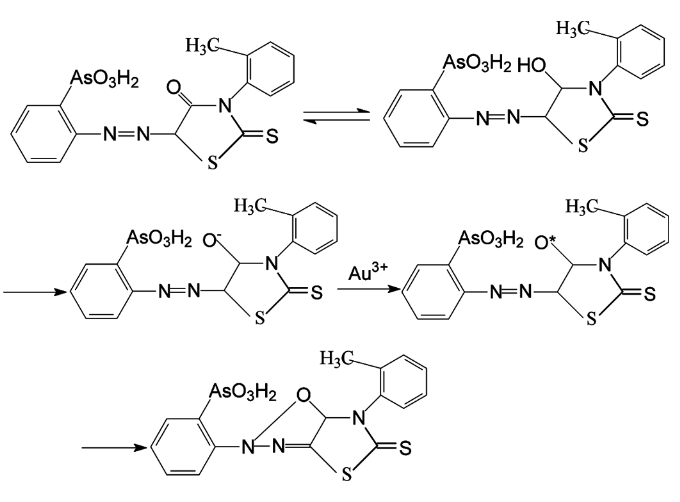

FIGURE 4 Possible mechanism.

Under the buffer solution of pH 3.4, H_2O_2 has the ability to oxidize Au^+ into Au^{3+} while the hydroxyl oxygen deprotonated into oxygen ion. Energy transferred between 3MRAAP and Au^{3+}, which made the Au^{3+} be reduced to Au^+ and caused the transition from oxygen ion to oxygen free radical. The oxygen free radical of high level returned to the ground state and at the same time formed ring, conjugated and coplanar structure so that the fluorescence emission could be measured.

The mechanism can be expressed simply as:

$$\begin{aligned} Au^{3+} - 3MTAAP &\longrightarrow 3MRAAP^* + Au^- + E \\ 3MRAAP^* &\longrightarrow 3MRAAP + h\nu \\ Au^+ + H_2O_2 &\longrightarrow Au^{3+} \end{aligned}$$

Optimal Conditions

The following conditions were optimum in order to obtain the greatest sensitivity. The optimal conditions are shown in Table 1.

Optimal pH

Initially, the fluorescence intensity of gold with oxidant and 3MRAAP in different mediums was tested; these were potassium hydrogen phthalate–HCl buffer solution, acetic acid–sodium acetic acid buffer solution, disodium hydrogen phosphate–citric acid buffer solution, and tartaric acid–sodium tartaric acid buffer solution. It was found that the gold solution quenched the most in the potassium hydrogen phthalate–HCl buffer solution. The proper pH range was found to be 3.2∼3.6, and the proper amount of buffer solution was 1.6∼2.4 mL. Hence, 1.8 mL potassium hydrogen phthalate–HCl buffer solution at pH 3.4 was chosen as the pH conditions for further study.

Optimum of Other Chemicals

The influence of other chemicals (oxidant and the amount of 3MRAAP) was studied at pH 3.4. H_2O_2, KIO_4, and $KBrO_3$ have been tested as oxidants, and

TABLE 1 Optimization of the Proposed Spectrofluorimetry for Antimony Determination

Variable	Studied range	Optimal conditions
pH	3.2~3.6	3.4
Buffer solution	Potassium hydrogen phthalate–HCl; acetic acid–sodium acetic acid; disodium hydrogen phosphate–citric acid; tartaric acid–sodium tartaric acid	Potassium hydrogen phthalate–HCl
Buffer solution amount (mL)	1.6~2.4	1.8
Oxidant	H_2O_2; KIO_4; $KBrO_3$	H_2O
Oxidant amount (mL)	1.8~2.4	2.0
3MRAAP amount (mL)	1.0~1.4	1.2
Temperature (°C)	70~100	100
Heating time (min)	18~21	20

it was found that the fluorescence intensity quenched the most and stayed steadiest with H_2O_2 as oxidant. The proper amount of H_2O_2 is 1.8~2.4 mL as tested, hence 2.0 mL $2 \times 10^{-3}\,mol \cdot L^{-1}$ H_2O_2 was selected as oxidant. The proper amount of 3MRAAP was found to be 1.0~1.4 mL, during which the fluorescence intensity of 3MRAAP–H_2O_2–Au(III) system quenched the most. Therefore, 1.2 mL $2 \times 10^{-5}\,mol \cdot L^{-1}$ 3MRAAP was chosen for further study.

Effect of Heating Parameters

The influence of temperature was studied in the range 70~100°C. It came to a conclusion that the reaction speeds up in the temperature range 80~100°C, in which ΔF was quenched, and the ΔF has a linear relationship against temperature. The regression equation of the system is calculated to be $-\ln\Delta F = 8.31 \times 10^3/T - 27.53$ according to the formula of Arrhenius and temperature curve with the relative coefficient r of 0.9844, and the active energy is $69.09\,kJ \cdot moL^{-1}$.

The proposed method was tested at 100°C every 5 min the range 5~30 min, respectively. It was found that the quenched fluorescence intensity ΔF is directly proportional to heating time t when heated for 3~16 min, from which it can be investigated that at the initial state, the reaction of 3MRAAP–H_2O_2–Au(III) is zero order, whose regression equation is $\Delta F = 5.15t(\text{min}) + 26.99$ with relative coefficient $r = 0.9987$. The reaction rate constant k is $8.6 \times 10^{-2}\,s^{-1}$. The fluorescence intensity was found to stay steady when heated from 18 min to 21 min, and finally the reaction was made to be heated for 20 min.

The quenched fluorescence intensity of 3MRAAP–H_2O_2–Au(III) ΔF could stay invariable for more than 24 h.

Solid-Phase Extraction of Gold

The extraction pole was soaked in $4\,mol \cdot L^{-1}$ HCl for 20 min; after being rinsed out by 10 mL of $4\,mol \cdot L^{-1}$ HCl, it can be used for the concentration of gold. HCl is mostly used to flow through when the samples are concentrated in the pole. The experimental result showed that gold concentrated better on the resin when the concentration of HCl was at the range $2.0{\sim}8.0\,mol \cdot L^{-1}$. Eventually, $4\,mol \cdot L^{-1}$ HCl was chosen to flow through the pole with sample being concentrated.

After the sample was completely concentrated, it would be eluted from the resin. Sodium sulfite was usually used to elute gold from the extraction resin. Gold could be eluted well with the concentration of sodium sulfite in the range $0.02{\sim}0.1\,mol \cdot L^{-1}$, and $0.05\,mol \cdot L^{-1}$ sodium sulfite was chosen as the eluent for further study.

It called for more than 12 mL of eluent to make sure the gold could be clearly eluted in the positive direction if the amount of gold concentrated on the extraction pole reached up to 10 mg. On the contrary, if the pole was eluted in the negative direction, at least 5 mL of eluent would be necessary. In this work, the pole was put in the negative direction after concentration, and 6 mL of sodium sulfite was taken to elute gold from the resin. Considering the real amount of gold determined in this work is in the range of certain amount of some micrograms, the eluent used is sufficient to make sure there is no gold remaining on the extraction resin after the elution.

TABLE 2 **Determination Results of Samples**

Samples	Recommend ($\mu g \cdot g^{-1}$)	Found ($\mu g \cdot g^{-1}$)	RSD (%)	Added (μg)	Recovery (%)	ICP-AES ($\mu g \cdot g^{-1}$)
Platinum mine	0.4	0.44	3.21	0.50	102.8	0.43
Copper mine	0.40	0.41	1.59	0.50	104.2	0.41
Chalcocite mine	0.58	0.55	3.82	0.50	97.5	0.60
GBW07209	0.421	0.43	1.09	0.50	101.4	0.42

Adsorption mechanism of TBP resin[16] can be expressed simply as:

$$\mathrm{HCl} + \mathrm{TBP} \longrightarrow \mathrm{HCl} \cdot (\mathrm{TBP})_3$$

$$\mathrm{Au}^{3+} + \mathrm{HCl} \cdot (\mathrm{TBP})_3 \longrightarrow \mathrm{HAuCl}_4 \cdot (\mathrm{TBP})_3$$

$$\mathrm{HAuCl}_{-4} \cdot (\mathrm{TBP})_3 + \mathrm{SO}_3^{2-} \longrightarrow \mathrm{H}_2\mathrm{SO}_3 \cdot (\mathrm{TBP})_3 + \mathrm{Cl}^- + \mathrm{Au}^{3+}$$

Effect of Coexisting Species

It is known that the intensity of fluorescence is affected by the coexistence of other chemicals. The tolerable concentration ratios of foreign species on the determination of 0.1 μg of Au(III) in 10 mL 3MRAAP–H_2O_2–Au(III) system are (the relative error is under ±5%; fold) Mg^{2+} (1000), Mn^{2+} (500), Al^{3+} (1000), V^{5+} (1000), Zn^{2+} (500), Mo^{6+} (500), Ni^{2+} (300), Co^{2+} (200), W(VI) (100), Cr^{3+} (500), Ti^{4+} (500), Cd^{2+} (50), Sn^{4+} (50), Cu^{2+} (100), Ag^{+} (20), Hg^{2+} (10), Pb^{2+} (10), Pt^{4+} (5), Pd^{2+} (2); NO_3^-, Cl^-, F^-, K^+, Na^+, and NH_4^+ do not interfere with determination of gold. It can be seen from the data that Ag^+, Hg^{2+}, Pb^{2+}, Pt(IV), and Pd^{2+} interfered greatly in the determination of gold, but after the solid-phase extraction of gold, they would be separated away and would no longer interfere until the fold reached up to 200.

Analytical Characteristics

The proposed catalytic dynamic spectrofluorimetry method was studied for linearity, precision, and sensitivity. Under the optimal conditions, a linear relationship between gold concentration and quenched fluorescence intensity was obtained over the range $0 \sim 12\,\mu g \cdot L^{-1}$, with a regression equation of $\Delta F = 59.16 + 0.92\rho$ ($\mu g \cdot L^{-1}$) and correlation coefficient (r) of 0.9986. The detection limit of gold was found to be $6.0 \times 10^{-10}\,g \cdot L^{-1}$ according to 11 times parallel determination for the uncatalyzed solution.

APPLICATION

Certain amount of ore sample that was dried for 1.5 h at 110°C was accurately weighed, then it was dissolved in aqua regia by heating for 1.0 h. After that, 100~150 mL water was added in when the solution was cooled, then the sample solution was obtained.

The sample solution was adsorped and eluted according to the preconcentration and separation of solid-phase extraction method mentioned above and then determined with the proposed catalytic dynamic spectrofluorimetry method. The determination results are shown in Table 2. It can be shown that the results were in agreement with that obtained by the official ICP-AES. We can conclude from Table 2 that the recoveries of added gold in the eluent after treatment can be quantitive, and *t*-tests assume there were no significant differences between recovery efficiency and 100% at confidence level of 95%.

CONCLUSIONS

A novel spectrofluorimetry method for the determination of trace gold was established with 3MRAAP as the fluorescent reagent, and the method was satisfactorily applied to the determination of gold in ore samples.

Catalytic dynamic spectrofluorimetry has been used rarely for determination of trace gold, and like the development of fluorescent reagents and the combination of other methods of sample treatments, the proposed method will surely develop further and further and will become a powerful tool for determination of trace metal.

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