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Determination of Gold by Graphite Furnace Atomic Absorption Spectrometry after Coprecipitation with Nickel Diethyldithiocarbamate

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The coprecipitation method is widely used for the concentration of trace metal ions prior to their graphite furnace atomic absorption spectrometric determination, and a variety of coprecipitants have been studied. For the preconcentration and separation of gold prior to a graphite furnace atomic absorption spectrometric determination, tellurium¹⁻⁶ and mercury⁷⁻⁹ have until now been proposed as coprecipitants. However, the use of tellurium¹⁻⁶ is disadvantageous, because it is necessary to heat a sample solution to complete reductive coprecipitation and for the resultant precipitate to dissolve only slowly. The use of mercury⁷⁻⁹ is also undesirable because of its toxicity.

In a previous paper,¹⁰ the authors proposed nickel diethyldithiocarbamate (nickel DDTC) as a coprecipitant for cadmium, because of its good collecting ability, ease of dissolution in nitric acid (1+1) and acetone, and selectivity; nickel DDTC hardly coprecipitates alkali and alkaline earth metals. We have found that this coprecipitant is also an excellent collector of trace amounts of gold, and overcomes the weak points of the coprecipitants mentioned above.¹⁻⁹ The use of nickel DDTC also does not cause interference in the graphite furnace atomic absorption spectrometric determination of gold. The method proposed here is simple and reproducible and applicable to the analysis of river, tap or sea-water samples which contains down to 30 pg cm⁻³ of gold.

This paper describes the fundamental conditions for the coprecipitation of trace amounts of gold in water with nickel DDTC and for the graphite furnace atomic absorption spectrometric determination of gold.

Experimental

Apparatus

All of the apparatus employed in this work were described previously.¹⁰

Reagents

The reagents were the same as those described previously,¹⁰ except for that mentioned below.

A solution containing about 1 mg cm⁻³ of gold was prepared by dissolving chloroauric acid tetrahydrate in distilled water. The concentration of gold was determined by complexometric back-titration with a standard manganese(II) solution using Eriochrome Black T as an indicator.

Recommended procedure

An aqueous solution containing 3 mg of nickel and 2 cm³ of

2% DDTC solution is added with stirring to a sample solution (up to 1000 cm³) containing 30 - 1100 ng of gold; the pH is adjusted to about 9 with aqueous ammonia (1+3). To settle the produced nickel DDTC, the solution is allowed to stand for a few min, subsequently, the precipitate is collected on a 3G4 sintered-glass filter. After the precipitate is washed with a small amount of distilled water, 1 cm³ nitric acid (1+1) is poured onto the precipitate. Within a few min, the precipitate is considerably dissolved, turning in color from yellowish-green to brown. Then, 1 cm³ of acetone is added to completely dissolve the precipitate and the solution is diluted to 10 cm³ with distilled water. If turbidity appears in the final solution, the use of 2 cm³ of acetone is recommended. The atomic absorbance of gold is measured under the operating conditions given in Table 1. A blank is also run using distilled water as a sample solution.

Results and Discussion

Optimum conditions for coprecipitation

Effect of the amount of coprecipitant. The necessary amount of nickel DDTC for coprecipitation was studied with a sample solution (50 - 1000 cm³) containing 500 ng of gold. For the quantitative recovery of gold, the complexation of 2 mg of nickel with DDTC was necessary for up to 1000 cm³ of a sample solution. Since the use of up to at least 10 mg of nickel did not affect the determination of gold, 3 mg of nickel was selected in this study. The use of up to 10 cm³ of a 2% DDTC solution also did not influence the gold determination. Thus, 2 cm³ of it, corresponding to about 3-times (as a mole ratio) 3 mg

Table 1 Recommended operating conditions for the atomic absorption spectrometer

Analytical wavelength	242.8 nm
Lamp current	10 mA
Slit width	No. 2 (1.1 nm)
Argon gas flow rate	
Sheath gas	3 dm ³ min ⁻¹
Carrier gas	0 dm ³ min ⁻¹
Injection volume	10 mm ³
Cuvette	uncoated tube type graphite furnace
Drying conditions	21 A (ca. 150°C), 45 s
Ashing conditions	80 A (ca. 700°C), 90 s
Atomizing conditions	280 A (ca. 2700°C), 5 s

Table 2 Effect of diverse ions on the determination of 500 ng of gold

Mass ratio ^a [Ion]/[Au]	Ion
3700000	Cl ⁻
2400000	Na ⁺
1000000	K ⁺
500000	Mg ²⁺ , Ca ²⁺
200000	Br ⁻ , I ⁻ , SO ₄ ²⁻
20000	F ⁻
4000	PO ₄ ³⁻
2000	Li ⁺ , Be ²⁺ , Sr ²⁺ , Ba ²⁺ , Al ³⁺ , Ga ³⁺ , Pb ²⁺ , Sb ³⁺ , Bi ³⁺ , Cu ²⁺ , Ag ⁺ , Zn ²⁺ , Cd ²⁺ , La ³⁺ , Ce ³⁺ , Zr ⁴⁺ , Th ⁴⁺ , Mo ^{VI} , W ^{VI} , Cr ³⁺ , Mn ²⁺ , Fe ³⁺ , Co ²⁺
200	Rh ³⁺ , Ir ⁴⁺ , Pd ²⁺ , Pt ^{IV} In ³⁺ , Sn ⁴⁺

The coprecipitation was carried out from about 80 cm³ of the sample solution at a pH of about 9.

a. The errors are within ±5%.

of nickel, was used for coprecipitation, because the mole ratio of nickel to DDTC in the complex was confirmed to be 1:2 by elemental analysis. The time required to filter nickel DDTC from 1000 cm³ of the sample solution was about 10 min. In the case of using a volume of more than 1000 cm³ of sample solution, however, nickel DDTC gradually became a finely dispersed precipitate, and more than 60 min was required for its filtration from 2000 cm³ of the sample solution. Thus, an upper limit of 1000 cm³ of the sample volume was taken in this experiment.

Effect of the pH on coprecipitation. Nickel DDTC coprecipitated gold quantitatively over a wide pH range from 2.4 to 10.5. A pH of about 9 was used for the coprecipitation of gold in further experiments, because nickel DDTC obtained above a pH of about 8 was bulky, and hence easy to handle. The recovery of gold reached almost 100% about 2 min after the formation of nickel DDTC, and the recovery remained almost unchanged upon standing for at least 3 h. Thus, the precipitate was filtered after some settlement had occurred.

Dissolution of nickel DDTC. It is difficult to dissolve the precipitate of nickel DDTC in common mineral acids at room temperature. However, it can be easily dissolved with nitric acid (1+1) and acetone without any digestion or heating.¹⁰ In this experiment, 1 cm³ each of nitric acid (1+1) and acetone was used to dissolve the precipitate, since the addition of 0.5–3 cm³ of nitric acid (1+1) and 0.5–4 cm³ of acetone did not affect the gold absorption. If the final obtained solution becomes turbid, the use of 2 cm³ of acetone is recommended.

Calibration curve

A linear relationship, passing through the origin, between the peak height and the concentration was obtained from 30 to 1100 ng of gold in the final solution (10 cm³). This calibration curve was almost the same as that which was prepared without the coprecipitation procedure, using a standard solution containing various amounts of gold, 3 mg of nickel, 2 cm³ of 2% DDTC solution, 1 cm³ of nitric acid, and 1 cm³ of acetone in 10 cm³. The reproducibility of this method (relative standard deviation)

Table 3 Recovery of gold from spiked water samples

Sample volume/cm ³	Au added/ ng	Au found/ ng	RSD, %
River water ^a			
1000	30	30.1	3.9
Tap water ^a			
1000	30	30.8	2.2
Seawater			
1000	30	30.9 ^b	2.2
1000	500	498.9 ^b	1.5

The obtained recoveries are the average of three replicate determinations.

a. The amounts of gold in river and tap water were less than the detection limit of the proposed method.

b. The recoveries of gold were calculated by subtracting the peak height due to seawater alone from that due to seawater spiked with gold.

for the peak heights obtained from five repeated determinations was 2.4% for 500 ng of gold in about 300 cm³ of the sample solution. The detection limit (signal to noise=2) was 6 pg cm⁻³ of gold in 1000 cm³ of the initial sample solution.

Interferences

The influence of each of 39 diverse ions on the determination of gold in about 80 cm³ of a sample solution was examined according to the recommended procedure (Table 2). Gold could be determined within a ±5% error in the presence of large amounts of sodium, potassium, magnesium, calcium, fluoride, chloride, bromide, iodide, sulfate, and phosphate, as well as 100 µg of indium and tin(IV). No other ions tested produced any serious interference effect, even at a concentration 2000-times the mass of the gold present.

Recovery of gold from some spiked water samples

To evaluate the potential of this method, the recoveries of gold from river, tap, and sea-water samples spiked with gold were examined. The results obtained by the calibration method were satisfactory, which indicates that the proposed method is applicable to analyses of these water samples which contain down to 30 pg cm⁻³ of gold (Table 3).

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