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Synthesis of silica gel immobilized thiourea and its application to the on-line preconcentration and separation of silver, gold and palladium

Peng Liu, Qiaosheng Pu and Zhixing Su*

Department of Chemistry, Lanzhou University, Lanzhou, Gansu 730000, China

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A new silica gel based chelating sorbent with thiourea as a functional group was used for the flow injection (FI) on-line preconcentration and separation of trace levels of silver, gold and palladium. Its sorption characteristics were evaluated by FI-FAAS. The selected metal ions were adsorbed on a column packed with thiourea modified silica gel (TuSG) with a sampling flow rate of 5.0 ml min^{-1}, eluted with 5% thiourea with a flow rate of 2.5 ml min^{-1} and determined by FAAS. Common co-existing ions did not interfere with the preconcentration and determination. The detection limits, defined as three times of the standard deviation of the blank (3σ), of Ag, Au and Pd are 1.3, 14 and 21 ng ml^{-1}, respectively, with a 1 min sample loading time. The RSD is not more than 3.0% for 0.040 μg ml^{-1} of Ag, 0.20 μg ml^{-1} of Au and 0.30 μg ml^{-1} of Pd. With 40 min of the sample loading time, 1.0 ng ml^{-1} of Ag, 5.0 ng ml^{-1} of Au and 7.5 ng ml^{-1} of Pd were successfully preconcentrated. The total dynamic capacity of TuSG was 24.5, 50.9 and 30.3 mg g^{-1} for Ag, Au and Pd, respectively. The sorbent exhibited excellent stability. Its sorption properties did not change after 1000 cycles of use. The selected metals in a secondary nickel alloy, an anode slime, an electrolytic solution and three national certified ore samples were determined satisfactorily using the proposed method.

Introduction

In spite of the improvements in the sensitivity of analytical systems, preconcentration and separation of analytes from the sample matrices are still necessary to obtain reliable results. Flow injection (FI) on-line preconcentration and separation with microcolumns has been proved to be a suitable method and has been widely used in trace element analysis owing to its simple automated operation and high reproducibility.[1] Numerous chelating adsorbents have been prepared for selectively adsorbing metal ions from aqueous solution,[2] but only a few of them have been applied to FI on-line preconcentration and separation. This is perhaps due to the requirements that an adsorbent must meet when it is used in an FI on-line system, *i.e.*, the sorption and desorption of analytes must be rapid enough. Hence the selection of sorbents suitable for FI on-line preconcentration and separation is necessary.

The determination of noble metals in various materials usually requires their preconcentration and separation from sample matrices. There are some excellent reports on the use of FI on-line preconcentration and separation for the FAAS determination of Ag,[3,4] Au[5–7] and Pd.[8,9] However, KCN or warm thiourea had to be used for the desorption of Ag[3,4] and Au,[5,6] or the tolerance of co-existing Ag in the determination of Au was limited.[7] Further, Pd could only be quantitatively adsorbed at relatively low acidity (pH > 0).[8,9] In most of these studies, organic material based adsorbents were adopted. Chemically modified silica gel has been widely used as a column packing for liquid chromatography owing to its porous structure, large surface area and low swelling. Silica gel immobilised chelating groups are gaining increasing importance for the preconcentration and separation of metal ions from aqueous solution.[10] In our previous work, 2-mercaptobenzothiazole bonded silica gel was used for the on-line preconcentration of silver,[11] but a large amount of Cl^- interfered with the preconcentration of silver. In the present work, another chemically modified silica gel sorbent with thiourea as functional group (TuSG) was prepared and it was more suitable for the FI on-line preconcentration and separation of Ag, Au and Pd because it can adsorb these ions over a wide range of strong acid concentrations and exhibits excellent tolerance for co-existing ions.

Experimental

Reagents

A stock standard solution of Ag(I) (500 mg l^{-1}) was prepared by dissolving $AgNO_3$ in dilute HNO_3 and those of Au(III) and Pd(II) (1000 mg l^{-1}) were prepared by dissolving spectrometrically pure Au and Pd powders in *aqua regia*. All other reagents were of analytical-reagent grade. Distilled water was used throughout.

Synthesis of adsorbent

Aminopropylsilica gel (APSG) was prepared with chromatographic grade silica gel (60–80 mesh, surface area 250 m^2 g^{-1}) (Institute of Inorganic Chemistry and Engineering of Shanghai, Shanghai, China) and γ-aminopropyltriethoxysilane as described previously.[12]

TuSG was prepared by the following procedure: 5 g of APSG, 5 g amount of pre-milled fine NH_4SCN powder and about 30 ml of dry xylene were combined in a three-necked 100 ml flask equipped with a refluxing condenser, a thermometer and an agitator. The mixture was refluxed with gentle agitation for 6 h. The contents were cooled to room temperature and the resulting product was filtered and washed with ethanol several times. The adsorbent was then washed repeatedly with water until no SCN^- was detected with 1 g l^{-1} Fe^{3+} solution. The adsorbent (yellow) was dried under infrared irradiation for later use.

Instrumentation

A Hitachi (Tokyo, Japan) Model 180-80 polarized Zeeman-effect background corrected atomic absorption spectrometer was used with the following conditions: absorption line: Ag 328.1 nm, Au 242.8 nm, Pd 276.3 nm; slit widths, Ag 2.6 nm, Au 1.3 nm, Pd 0.4 nm; and lamp currents, Ag 7.5 mA, Au 10 mA, Pd 15 mA. The flow rates of air and acetylene were set as recommended by the manufacturer. All results were evaluated using peak area absorbance owing to its higher precision compared with the peak height mode.

The FI system was composed of two LP-1 peristaltic pumps (KYKY Eastern Instrument Corp., China), a 16-way rotary injection valve and a microcolumn (3 cm × 3 mm id) (Zhaofa Institute for Laboratory Automation, Shenyang, China).

FI procedures

The manifolds were set up as described previously.[11] With the injection valve in the Fill position, sample solution was loaded on to the column at a flow rate of 5.0 ml min^{-1} for 60 s, then the blank solution (1 M HNO_3 or 0.5 M HCl) was pumped through the column for 30 s to wash off the residing sample matrix on the column. The valve was turned to the Inject position, the eluent was pumped through the column in the reverse direction to FAAS at a flow rate of 2.5 ml min^{-1} for 30 s and the peak area absorbance was read. Subsequently, the valve was turned to the Fill position again and the blank solution was pumped through the column for another 30 s to eliminate the eluent before the next sample was loaded.

Sample pre-treatment

A 0.5 g accurately weighed amount of national certified ore samples (GBW07204, GBW07205 and GBW07206) in a nickel crucible was roasted in an electric muffle furnace at 650 °C for 30 min and dissolved in 20 ml of *aqua regia* with heating on an electric hot-plate. The solution was filtered into a 25 ml calibrated flask. The filter-paper and residue were washed with dilute *aqua regia* several times and the washings were added to the same flask. The volume of the filtrate was adjusted to the mark with water.

A 0.5 g amount of secondary nickel alloy was fused with 2 g of Na_2CO_3–Na_2O_2 in a porcelain crucible at 700 °C for 10 min, dissolved in 0.5 M HCl and the solution was filtered into a 25 ml calibrated flask.

The anode slime was treated in the same way as ore samples without the roasting procedure.

$CoCl_2$ electrolyte was used directly for preconcentration and determination without any pre-treatment.

Results and discussion

Influence of acidity

The influence of the concentration of HNO_3 on the absorbance of silver and of that of HCl on the absorbance of gold and palladium was examined. The results showed that the concentration of acids had very little influence on the preconcentration of these metals. The deviation of the peak area was not more than 5% when the HNO_3 concentration varied from 0.2 to 3 M and the HCl concentration from 0.1 to 6 M. This is a very important advantage of TuSG because the acidity of the sample solution decomposed with strong acids need not be adjusted. Although HNO_3 was used as the sample medium for silver to evaluate the effect of acid concentration, the presence of HCl actually did not affect the preconcentration of silver. The excellent tolerance to Cl^- was confirmed in the interference study. In subsequent experiments, 1 M HNO_3 was used as the sample medium for silver and 0.5 M HCl as that for gold and palladium.

Desorption

Thiourea solution could efficiently elute the adsorbed Ag, Au and Pd, although the functional group of TuSG was thiourea. The influence of the concentration of thiourea on the absorbance of Ag, Au and Pd was studied. When the thiourea concentration was < 0.5% for Ag, 1.0% for Au and 2.0% for Pd, the peaks obtained were so broad that the selected elution period (30 s) could not encompass the whole peak. The peaks became sharper as the concentration of thiourea increased. The peak areas of Au and Pd increased slightly until a 5% thiourea concentration. No evident improvement in the sensitivity was observed with further increase in thiourea concentration. Hence 5% thiourea was used as the eluent. Although the total dissolved solids of 5% thiourea was higher than for the normal sampling procedures of FAAS, no blockage of the nebulizer or the burner was observed, because water was sucked into the nebulizer continuously to wash it off in the sample loading and column washing steps.

Interference study

The effect of metal ions and anions, Cl^-, NO^-, SO_4^{2-}, PO_4^{3-} and ClO_4^-, either co-existing with noble metals or introduced into the sample solution during the sample pre-treatment, was investigated (Table 1). The amount of anions, such as Cl^- and NO_3^-, was always large owing to the use of HCl and HNO_3 in the sample decomposition. When the alkali fusion method was used, the amount of these anions was especially high. High concentrations of these ions may cause a problem in the direct FAAS determination of Ag, Au and Pd. However, it was obvious that their influence was negligible using the present procedure. Even when the sample matrix was saturated NaCl solution, the recovery of silver was satisfactory (98.5%). This is an advantage of TuSG because Cl^- interferes with the determination of silver when using some other sorbents.[3,11] Heavy metal ions could not be adsorbed by TuSG in the acidic medium used in the present study. The residual sample matrix in the column could hardly enter the nebulizer owing to the effect of the washing procedure after sample loading. Hence these ions did not interfere with the preconcentration and determination of selected noble metals. It is worth mentioning that the concentration of co-existing ions given in Table 1 was not the upper tolerance limit. For example, Pd in 20–30% $CoCl_2$ solution was also determined successfully by the proposed procedure although the concentration of Co^{2+} in Table 1 is 1000 μg ml^{-1}. The presence of other noble metals at reasonably high concentration did not interfere with the preconcentration and determination of Ag, Au and Pd. This demonstrates that TuSG is suitable for the preconcentration and separation of selected metals from complicated sample matrices.

Effect of concentration

In order to examine the adsorption properties of TuSG for lower concentrations of selected metal ions, a longer preconcentration time must be used to acquire a sufficiently high absorbance. For comparing the results conveniently, the lower the concentration, the longer was the sample loading time used so as to maintain the amount of metal ions loaded on to the column constant. The results in Table 2 demonstrate that the adsorption of lower concentrations of Ag, Au and Pd was satisfactory. In fact, the

peak area absorbance with lower concentrations and longer loading times was larger than that with higher concentrations and shorter loading times. This was probably because the time (30 s) used to remove the residual thiourea from the column before sample loading was not long enough so that the initial portion of sample solution could not be adsorbed efficiently. Hence the adsorption efficiency for longer samples loading times was higher. However, a 30 s washing period was adopted in the present work as a compromise between sensitivity and sampling frequency because a further increase in washing time might decrease the sampling frequency. In the preconcentration and determination of lower concentrations of selected metal ions with longer sample loading times, a coefficient should be used to correct for the difference in adsorption efficiency if calibration curves with a 60 s loading time are adopted.

Adsorption capacity and stability

The total dynamic capacity of TuSG for Ag, Au and Pd with the selected sample medium was 24.5, 50.9 and 30.3 mg g^{-1}, respectively. The functional group content evaluated according to the sulfur content of the adsorbent was 0.268 mmol g^{-1}. The ratio of functional groups to the metal ions was 1 : 0.85, 1 : 0.97 and 1 : 1.07 for Ag, Au and Pd, respectively, when they were adsorbed at saturation. The stability of TuSG was excellent; its adsorption properties did not change after 1000 cycles of sorption and desorption.

Calibration graphs and detection limit

The graphs of peak area absorbance *versus* metal ion concentration were linear up to 0.8 μg ml^{-1} for Ag and 3.0 μg ml^{-1} for Au and Pd with a preconcentration time of 60 s. The equations of the calibration curves are:

$$A = 1.662C_{Ag} + 0.0007 \quad (r = 0.9999)$$

$$A = 0.509C_{Au} + 0.0142 \quad (r = 0.9998)$$

$$A = 0.358C_{Pd} + 0.0128 \quad (r = 0.9996)$$

where A is peak area absorbance and C is the concentration of the respective metal in μg ml^{-1}. The detection limits, defined as three times the standard deviation of the blank (3σ, $n = 21$) are 1.3 ng ml^{-1} for Ag, 14 ng ml^{-1} for Au and 21 ng ml^{-1} for Pd. The slope of the calibration curves increased proportionally with increase in preconcentration time and the standard deviation of the blanks showed no evident change when the preconcentration time increased. Hence lower detection limits could be achieved when a longer preconcentration time was used. As mentioned above, 1.0 ng ml^{-1} of Ag, 5.0 ng ml^{-1} of Au and 7.5 ng ml^{-1} of Pd were successfully preconcentrated and determined with a sample loading time of 40 min. The enrichment factor (EF) could not be evaluated directly by peak area. If peak height was used, EF was 15–20 for Ag, Au and Pd with a 60 s sample loading time.

Analytical application

Three national certified reference ore samples for Ag and Au, a secondary nickel alloy, an anode slime and a $CoCl_2$ electrolytic solution for Pd were selected for evaluation of the suitability of TuSG as the sorbent for FI on-line preconcentration and separation. In the determination of these metals, separation of the sample matrices is necessary to obtain reliable results even when the concentration of the analytes is high enough to be directly determined. The results (Tables 3 and 4) obtained using the proposed procedure showed good agreement with the certified values and demonstrated the potential of TuSG as a sorbent for the FI on-line preconcentration and separation of Ag, Au and Pd. It was expected that with a more sensitive AAS

Table 1 Effects of co-existing ions on the determination of Ag, Au and Pd

Species	Amount added/ μg ml^{-1}	Relative error (%)			Species	Amount added/ μg ml^{-1}	Relative error (%)		
		Ag	Au	Pd			Ag	Au	Pd
Ca^{2+}	2 000	−1.0	+0.6	−2.5	SO_4^{2-}[a]	2 000	—	+0.6	+0.2
Mg^{2+}	2 000	−0.2	0	−1.7		20 000	−0.2	—	−0.4
Cu^{2+}	2 000	+0.2	−2.9	+0.5	ClO_4^-[a]	2 000	0	+0.7	+0.9
Fe^{3+}	2 000	+0.5	−0.8	−1.5		20 000	−0.3	+2.0	+0.7
Al^{3+}	2 000	+0.7	+2.5	−0.7	NO_3^-[a]	2 000	—	+1.8	−0.5
Ni^{2+}	2 000	+0.5	+1.7	−1.1		20 000	—	0	−1.4
Pb^{2+}	2 000	−1.6	+1.4	−2.2	Ag^+	15	—	−1.6	+0.5
Co^{2+}	1 000	−1.3	+0.9	−1.0		30	—	−0.8	+1.4
Mn^{2+}	2 000	−1.0	−2.2	−0.4	Au(III)	15	−0.7	—	+1.6
Zn^{2+}	2 000	+0.3	−2.7	−0.8		30	−0.5	—	+0.9
Cr^{3+}	2 000	0	+0.7	+0.6	Pd(II)	15	−0.3	+0.1	—
Cd^{2+}	1 000	+0.6	+1.2	−1.1		30	−0.2	+0.6	—
PO_4^{3-}[a]	4 000	—	−1.0	+0.7	Pt(IV)	30	−1.5	+1.6	+0.2
	16 000	+0.8	−1.6	−0.2	Ir(IV)	30	−0.8	−0.1	−0.6
Cl^-[a]	2 000	−1.0	+1.5	+1.7	Ru(III)	30	−0.8	+0.8	−2.0
	20 000	−2.0	+1.1	−0.1	Rh(III)	30	−0.7	+1.4	−2.5
	Sat[b]	−1.5	—	—					

[a] Added as sodium salts. [b] Saturated NaCl solution.

Table 2 Preconcentration of Ag, Au and Pd at different concentrations

Parameter	Preconcentration time/min					
	40.0	20.0	10.0	5.0	2.0	1.0
Concentration of Ag/ng ml^{-1}	1.0	2.0	4.0	8.0	20.0	40.0
Relative peak area (%)	125.3	119.1	115.7	111.2	107.5	100.0
Concentration of Au/ng ml^{-1}	5.0	10.0	20.0	40.0	100.0	200.0
Relative peak area (%)	124.7	118.1	113.2	110.0	106.9	100.0
Concentration of Pd (ng ml^{-1})	7.5	15.0	30.0	60.0	150.0	300.0
Relative peak area (%)	118.1	115.1	112.3	110.8	105.0	100.0

Table 3 Determination of Ag and Au in national certified ore samples (n = 3)

	Ag			Au		
Sample	Found/g t^{-1}	RSD (%)	Certified/g t^{-1}	Found/g t^{-1}	RSD (%)	Certified/g t^{-1}
GBW07204	3.35	1.1	3.34	7.08	1.5	7.16
GBW07205	19.4	2.6	19.4	14.4	1.4	14.0
GBW07206	24.4	3.5	24.6	19.5	2.4	19.4

Table 4 Determination of Pd in samples (n = 3)

Sample	Found/g t^{-1} or μg ml^{-1}	RSD (%)	Certified/g t^{-1} or μg ml^{-1}
Nickel alloy	162.7	1.7	161.0
Anode slime	89.1	2.3	91.0
$CoCl_2$ solution	0.149	2.1	0.150

instrument and a more efficient FI system, better performance could be achieved using this adsorbent.

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