

Application of 2-mercaptobenzothiazole-modified silica gel to on-line preconcentration and separation of silver for its atomic absorption spectrometric determination

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2-Mercaptobenzothiazole-modified silica gel was used for the flow injection on-line preconcentration–separation and determination of silver by flame atomic absorption spectrometry. Two types of manifold, with one or two columns, were adopted. The results showed that Ag^+ was selectively adsorbed from 0.05 to 6 M HNO_3 solution and was readily desorbed by thiourea solution. The ions co-existing with Ag^+ exhibit virtually no interference in the determination with the exception of Cl^- . An Ag^+ concentration as low as 1 ppb could be determined reliably if a long preconcentration time was used. The sample throughput was 60 h^{-1} using the two-column manifold with a preconcentration time of 60 s. Silver in a geological sample, a copper metal sample and a lead nitrate sample was determined satisfactorily.

Keywords: Adsorbent; on-line preconcentration; silver; flow-injection; flame atomic absorption spectrometry

The flow injection on-line column preconcentration technique is becoming important owing to its characteristics of high preconcentration efficiency and great savings of time and sample consumption. Much work on its use for the determination of heavy and noble metals has been published.^{1–8} Fang and co-workers have made a detailed study on flow injection systems involving on-line separation–preconcentration with a microcolumn⁹ and proposed a mathematical model for evaluating the sensitivity enhancement effects.¹⁰ However, the adsorbents used for this purpose are limited and the most widely used adsorbents, such as Chelex-100 and quinolin-8-ol treated controlled pore glass (CPG), have only moderate selectivity. Hence, the search for suitable adsorbents that have high selectivity and good dynamic properties is important for the technique to be applied more widely.

Silver is a useful element in many respects and the determination of low levels of silver is needed because it is often present as an impurity in Cu, Zn, As and Sb ores and their compounds. FAAS is a simple and readily available technique but its sensitivity is not sufficiently high; therefore, preconcentration and separation of silver from the matrix is necessary for the determination of this metal in many samples. Electrothermal AAS is a suitable technique owing to its high sensitivity, but matrix effects are more serious than with FAAS. ICP-AES, ICP-MS and NAA are also suitable but their application for this purpose requires complicated and expensive instrumentation. Many reports of the use of chelating resins to preconcentrate and separate silver by off-line methods have been published.^{11–13} Pei and Fang¹⁴ determined silver in geological materials using FAAS coupled with on-line flow injection preconcentration by coprecipitation with diethyl dithiocarbamate. Gomez *et al.*¹⁵ and Gong *et al.*¹⁶ described on-line preconcentration methods for the determination of silver by flow injection FAAS using sulfhydryl cotton and rhodanine fibres, respectively, but KCN and warm thiourea must be used as eluents.

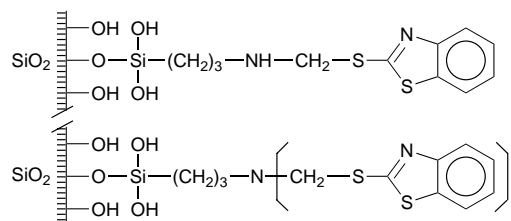
Su *et al.*¹⁷ synthesised 2-mercaptobenzothiazole-bonded silica gel (MBTSG) and applied it to the preconcentration and separation of Au, Pt and Pd for their determination by ICP-OES. In the present paper, MBTSG was used as a selective adsorbent for the on-line flow injection preconcentration and separation of silver for its determination by FAAS. The influence of the experimental conditions was also studied.

Experimental

Reagents

A stock standard silver solution (500 mg l^{-1}) was prepared by dissolving AgNO_3 in dilute HNO_3 . Standard silver solutions were prepared daily by dilution of the stock solution. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, ZnO and $\text{Pb}(\text{NO}_3)_2$ were spectroscopically pure. All other reagents used were of analytical-reagent grade. Distilled water was used for preparing sample solutions.

MBTSG, which has the structure given below, was prepared by the Mannich reaction between 2-mercaptobenzothiazole and γ -aminopropyl silica gel.



Apparatus

A Hitachi 180-80 polarized Zeeman-effect background corrected atomic absorption spectrometer equipped with a Hitachi Model 056 recorder was employed. The instrument settings were: absorption line, 328.1 nm; lamp current, 7.5 mA; monochromator spectral bandpass, 2.6 nm; burner position, adjusted by normal nebulization of $5 \mu\text{g ml}^{-1}$ silver; air pressure, 1.6 kg cm^{-2} (9.4 l min^{-1}); and acetylene pressure, 0.1 kg cm^{-2} (1.4 l min^{-1}). All data were read from the 180-0205 data processing unit of the spectrometer. The signal recorded by the chart recorder was only used for monitoring the peak shape. The sensitivity, defined as the concentration for acquiring 1% absorption (0.00436 A), was $0.11 \mu\text{g ml}^{-1}$ under the optimum conditions.

The flow injection system was composed of peristaltic pumps (pump tubing from Tector), a 10-way rotary valve (laboratory-made), a 16-way rotary injection valve and one or two microcolumns ($3 \text{ cm} \times 3 \text{ mm id}$, from Flow-Injection Analysis Research Centre, Shenyang).

Procedures

The manifolds were set up as shown in Figs. 1 and 2 with the flow rates of sample, washing solution and eluent as shown;

MBTSG was packed into the microcolumn by the normal procedure. The pumps and valves were controlled manually as given in Figs. 1 and 2 and Tables 1 and 2.

When using manifold 1, switches between sample and wash solution were performed manually. The pump 1 was stopped when changing solution or the valve position to avoid aspirating air into the column. Water was aspirated by the nebulizer of the AA spectrometer to stabilize the flame and wash the nebulizer. To avoid cross-contamination, it was necessary to run a blank solution for one or two cycles before the analysis of the next sample. Re-set zero should be avoided during analysis as it may lead to deviation of results.

A solution of the geological sample (GBW 07204) was prepared by two methods: 1. A 0.5 g amount of sample was dissolved in 20 ml of 1 + 1 HNO₃ with several drops of HClO₄. After the acids had been evaporated, the moist residue was dissolved in 0.5 M HNO₃ and the solution was filtered. The filter-paper was washed several times with 0.5 M HNO₃ and the washings were added to the filtrate. The volume of the filtrate was then adjusted to 25 ml. 2. A 0.5 g amount of sample was placed in a nickel crucible and fused with 2 g of Na₂CO₃-Na₂O₂ in an electric muffle furnace at 700 °C for 10 min, then carefully dissolved in 0.5 M HNO₃ and filtered into a 25 ml calibrated flask. The copper metal sample was dissolved in concentrated HNO₃. The Pb(NO₃)₂ sample was dissolved in 0.5 M HNO₃.

Results and discussion

Manifolds

In order to facilitate analysis, a washing process is generally considered to be unnecessary in flow injection on-line column preconcentration. However, when dealing with complex samples such as geological samples and alloys, the effects of a high matrix concentration should not be ignored. A small amount of the matrix inevitably remains in the column after adsorption and will affect the elution if a washing process is not conducted. For example, some metal ions may form complexes with the eluent when a chelating reagent is used as the eluent. This increases the consumption of the eluent and gives rise to the possibility of

these matrices interfering with the determination of the analyte. If the complex formed by the eluent and matrices is insoluble, it will block the pores of the adsorbent and affect the preconcentration seriously. On the other hand, there is eluent in the column after elution; if the sample is loaded immediately without washing, the initial portion of the sample will not be adsorbed but used to wash away the eluent and re-establish the appropriate acidity. This will decrease the sensitivity. Thus,

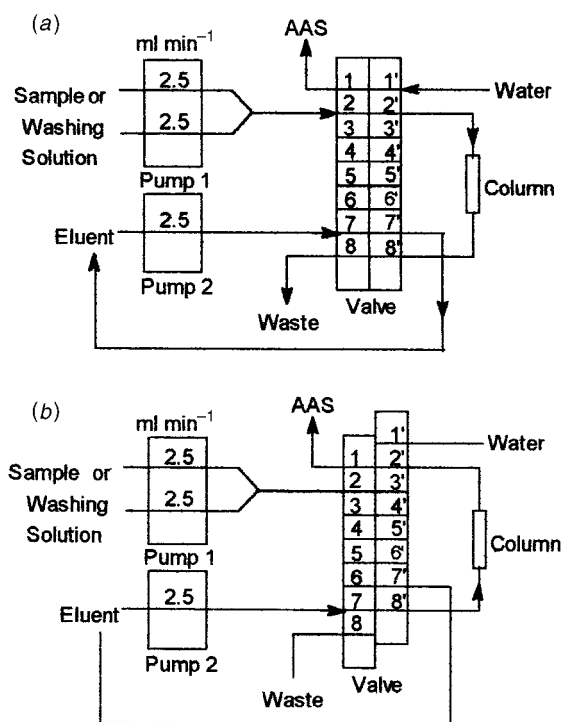


Fig. 1 Manifold 1. (a) Wash and load sample; (b) elution.

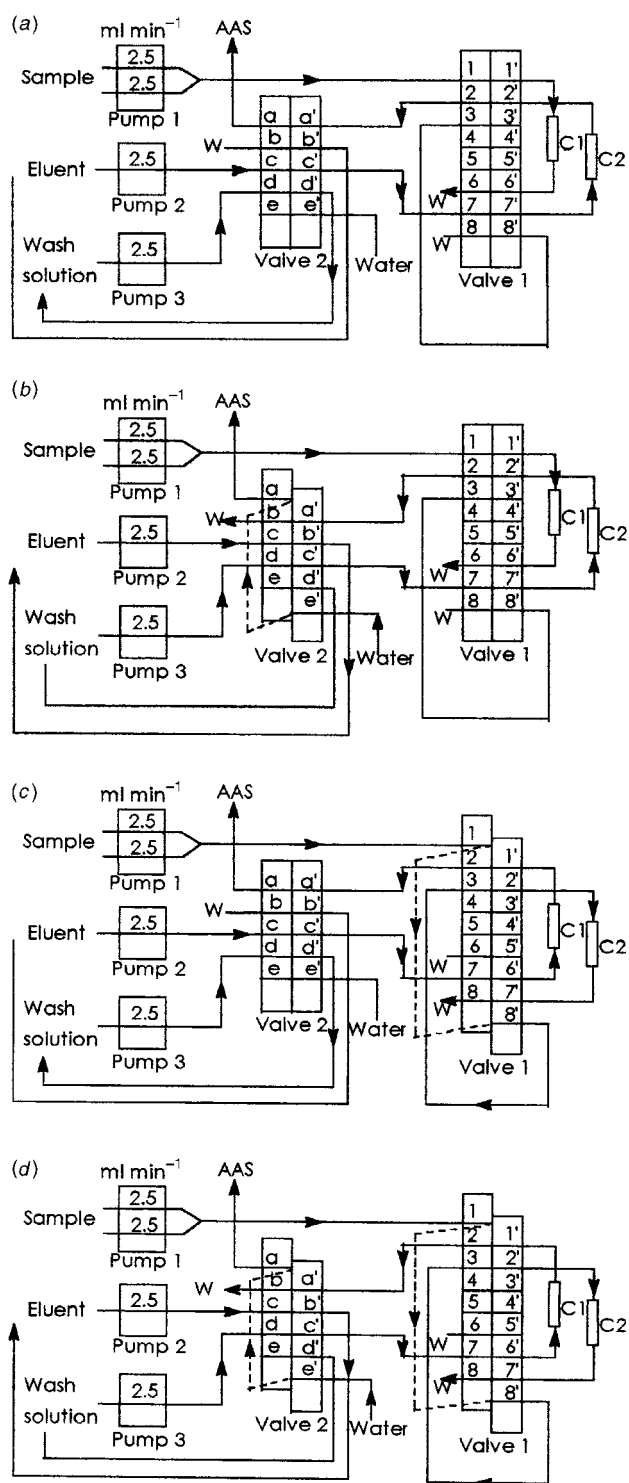


Fig. 2 Manifold 2. (a) Eluting column 2 and preconcentration on column 1; (b) wash column 2 and preconcentration on column 1; (c) eluting column 1 and preconcentration on column 2; and (d) wash column 1 and preconcentration on column 2.

these two washing processes should not be omitted when dealing with complicated samples. In this work, a manifold containing two columns with two washing processes was used (Fig. 2). Considering that the preconcentration time is usually longer than the elution time, when one of the columns was used for preconcentration, washing and elution could be performed on the other column. Hence, if the preconcentration time is longer than or equal to the time needed for two washing processes and elution, the sampling frequency is not affected by adding a washing process. In the determination of silver in real samples, the preconcentration time was 60 s, the elution time 30 s and the washing time 15 s. The sampling frequency was dependent on the preconcentration and was 60 h⁻¹ under the selected conditions.

However, the purpose of this work was to test the possibility of the application of MBTSG to the on-line preconcentration and separation of silver; hence, one column was used (manifold 1) even though only 20–23 injections can be performed per hour. When two columns are used, the difference between them might lead to a slight difference in peak shape and give rise to some difficulties in comparing the results. Manifold 2 was only used for sample analysis. As the rotation rate of the pumps is fixed, the influence of flow rate on adsorption and elution was not studied. The way to increase the flow rate is to add pump tubing. Although using a higher flow rate in loading the sample leads to a higher concentration factor, the flow rate is not stable when more tubing is used. Hence, a parallel connection of two tubes was adopted. A sharp peak and high peak height were obtained when two tubes were used in the elution; the peak area remained constant on changing the elution flow rate. In addition, the precision of peak areas (RSD 1–2%) is much better than that of peak height (RSD 5%); hence, one pump tube was used in the elution and peak area absorbance was measured with a 12 s integration time. All data given below are the average of three or five determinations.

Table 1 Operation of the valve and pumps using the single-column manifold (Fig. 1)

	Washing 1	Preconcentration	Washing 2	Elution
Valve position*	A	A	A	B
Pump 1	On	On	On	Off
Pump 2	On	On	On	On
Time/s	30	Given period	30	30

*A and B are the positions of the valve illustrated in Fig. 1(a) and (b), respectively.

Table 2 Operation of the valves using the two-column manifold (Fig. 2)

Valve position*	Washing and eluting column 2			Washing and eluting column 1		
	Preconcentration on column 1			Preconcentration on column 2		
	B	A	B	D	C	D
Time/s	15	30	15	15	30	15

* A, B, C and D are the positions of the valve illustrated in Fig. 2 (a)–(d), respectively.

Table 4 Peak area absorbance with different eluents.* TU = Thiourea

Eluent	0.05% TU	0.5% TU	5% TU	0.5% TU in 0.5 M HNO ₃	0.5% TU in 2 M HNO ₃	0.5% TU in 0.5 M HCl	0.5% TU in 3 M HCl
A	0.0750	0.0788	0.0809	0.0783	0.0785	0.0774	0.0753

* [Ag⁺] = 40.0 ppb, preconcentration time = 60 s, [HNO₃] = 0.5 M.

Influence of acidity

The influence of the concentration of HNO₃ is shown in Table 3. From 0.05 to 6 M HNO₃, there is no evident difference, and hence the concentration of HNO₃ need not be adjusted precisely when preparing the sample. Compared with the sulfhydryl cotton fibre used by Gomez *et al.*,¹⁵ MBTSG seems more suitable for silver because high concentrations of HNO₃ oxidize the sulfhydryl group and make it inactive. However, the absorbance acquired by using MBTSG when no HNO₃ was added (acidity is about pH 4) was lower.

Desorption

A 0.05% thiourea solution can quantitatively desorb Ag⁺ from the MBTSG. Because thiourea can enhance the sensitivity of silver, the absorbance increased with increasing thiourea concentration. Dilute HNO₃ has no influence on the desorption, but high concentrations of HNO₃ (>3 M) oxidise thiourea seriously. High concentrations of HCl decrease the absorbance slightly (Table 4). A warm eluent usually exhibits a high desorption efficiency and is essential for some adsorbents. In this work, when the thiourea solution was warmed to 70 °C, the peak became sharp and the peak height increased by about 20%; however, the connecting plastic tube softened owing to the temperature, which gave rise to difficulties in operation. However, a 0.05% thiourea solution is probably too dilute if there are metal ions that can be adsorbed by MBTSG, such as Au³⁺ and Pd²⁺, in a real sample. On the other hand, some metal ions retained on the column, such as TiO₂⁺, will hydrolyse and form a precipitate when a neutral thiourea solution is used. Thus, 0.5% thiourea in 0.5 M HNO₃ was used as the eluent.

Influence of Cl⁻

Cl⁻ can form a chloro complex with Ag⁺ and the presence of Cl⁻ gives rise to an apparent interference in the determination (Table 5). By using the formation constant of the chloro complex, the fraction of each chloro–silver species can be evaluated.¹⁸ When the concentration of Cl⁻ is less than 0.001 M, the main species is Ag⁺. When C_{Cl} is 0.05–0.1 M, the main species are AgCl and AgCl₂⁻ and the adsorption efficiency decreases by about 7%. When C_{Cl} > 0.1 M, the concentrations of AgCl₃²⁻ and AgCl₄³⁻ increase and the absorbance decreases by 20, 36 and 64% when 30, 54 and 99%, respectively, of the silver exists as AgCl₃²⁻ and AgCl₄³⁻. Thus only 40–50% of AgCl₃²⁻ and AgCl₄³⁻ is adsorbed by MBTSG. However, silver can be determined accurately by the on-line procedure if the concentration of Cl⁻ is the same in the standard and the sample, as the standard and sample experience the same procedure in the system.

Table 3 Influence of HNO₃ concentration on the peak area absorbance*

C _{HNO₃} /M	0 [†]	0.05	0.1	0.5	1	2	3	6
A	0.0523	0.0779	0.0792	0.0786	0.0780	0.0787	0.0810	0.0820

* [Ag⁺] = 40.0 ppb, preconcentration time = 60 s, elution with 0.5% thiourea in 0.5 M HNO₃. † pH 4.

Table 5 Influence of concentration of Cl^- on the absorbance*

C_{NaCl}/M	0	0.01	0.03	0.1	0.3	1	3
A	0.0790	0.0742	0.0740	0.0731	0.0627	0.0505	0.0280

* $[\text{Ag}^+] = 40.0$ ppb, preconcentration time = 60 s, $[\text{HNO}_3] = 0.5$ M, elution with 0.5% thiourea in 0.5 M HNO_3 .

Table 6 Effect of co-existing species on the determination of silver*

Species	Added/ mg ml^{-1}	Relative error (%)	Species	Added/ mg ml^{-1}	Relative error (%)
Ca^{2+}	2.0	+1	Pb^{2+}	2.0	0 [†]
Mg^{2+}	2.0	0	Cd^{2+}	2.0	+3 [†]
Cr^{3+}	2.0	+2	Al^{3+}	2.0	+3
Mn^{2+}	2.0	+2	SO_4^{2-}	1.6	+2
Fe^{3+}	2.0	-1		16	+3
Co^{2+}	1.0	+1	PO_4^{3-}	1.6	+2
Ni^{2+}	2.0	-3		16	0
Cu^{2+}	2.0	+1 [†]	ClO_4^-	2.0	-1
Zn^{2+}	2.0	-1 [†]		20	+1

* Conditions as in Table 5. [†] Calculated from recovery of added Ag^+ .

Table 7 Effect of concentration of Ag^+ *

Concentration of Ag^+ (ppb)	40.0	4.0	1.0
Preconcentration time/min	1.0	10.0	40.0
A	0.0799	0.0805	0.0858

* Conditions in Table 5 except for preconcentration time and $[\text{Ag}^+]$.

Influence of accompanying ions

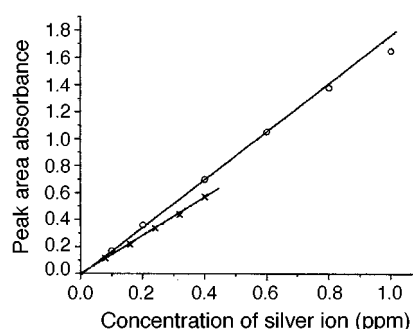
The anions SO_4^{2-} , PO_4^{3-} and ClO_4^- and 12 metal ions were tested when Ag^+ was determined at 40 ppb (Table 6). Because silver is one of the impurities in Cu, Zn, Pb and Cd, the peak area absorbance obtained from these ions as the matrix is higher than that obtained when these ions are not present. Because these metals do not cause pseudo-absorbance under the present instrumental conditions, the influence of these metal ions on the determination can be evaluated by the recovery of added Ag^+ . Hence, the relative errors given in Table 6 for these metal ions were obtained from the recovery of added Ag^+ . The results indicated that all these ions exhibited virtually no interference in the determination of silver.

Influence of Ag^+ concentration

Different concentrations of silver were preconcentrated by the same procedure. In order to compare them conveniently, the lower was the concentration of silver, the longer was the preconcentration time used so as to maintain the total amount of silver passed through the column constant (Table 7). The results show that from 40 to 1 ppb, the efficiency of adsorption is the same, but the peak broadens with increasing preconcentration time. This is due to a portion of Ag^+ diffusing into the inner pores of the adsorbent; desorption from such sites is more difficult than from the outer surface. Although 40 min is too long for practical analysis, it does prove that MBTSG can efficiently adsorb very low concentrations of Ag^+ .

Calibration graphs, precision and detection limit

The graph of peak area absorbance versus silver concentration is linear up to 800 ppb for a preconcentration time of 60 s (Fig. 3). The equation of the calibration is: $A = 1.76C_{\text{Ag}^+} - 0.0037$ ($r = 0.999$). The slope increases proportionally with increasing preconcentration time. The RSD at the 40 ppb level

**Fig. 3** Calibration graphs of silver(I) for (O) no Cl^- and (X) 0.3 M Cl^- .**Table 8** Determination of silver in real samples ($\mu\text{g g}^{-1}$) ($n = 5$)

Sample	Found	RSD (%)	Certi- fied	Added	Total found	RSD (%)	Re- covery (%)
GBW07204	3.34*	0.9	3.34	—	—	—	—
	3.26 [†]	2.0	—	—	—	—	—
Copper metal	21.5	1.6	—	20.0	40.2	0.9	93.5
Lead nitrate	9.1	1.2	—	20.0	29.3	1.6	101.0

* Acid decomposition. [†]Alkali fusion.

with a sampling time of 60 s is 1% ($n = 5$). The detection limit, defined as three times the standard deviation of the blank ($n = 21$), is 0.66 ppb with the same sampling time. The graph of peak area absorbance versus silver concentration when 0.3 M NaCl is present is also linear (Fig. 3); its equation is: $A = 1.41C_{\text{Ag}^+} - 0.0019$ ($r = 0.999$). The stability of MBTSG is very good; after using 200 times its adsorption properties were unchanged.

Determination of silver in real samples

Silver in a geological sample (GBW07204), an analytically pure copper metal sample and a lead nitrate sample was determined using manifold 2 under the recommended conditions. Two types of method, viz., acid decomposition and alkali fusion, were used for preparing the geological sample solution, because it was uncertain whether $\text{HNO}_3 + \text{HClO}_4$ was able to decompose the sample efficiently. The results show that both methods are successful. For copper metal and lead nitrate samples, the reliability was confirmed by the standard additions method (Table 8). The results demonstrate that the proposed method is potentially suitable for the determination of trace amounts of silver in geological samples and high-purity materials.

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