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SEPARATION OF ANTIMONY FROM ARSENIC AND COPPER BY EXTRACTION CHROMATOGRAPHY

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Arsenic and copper can be rapidly and quantitatively separated from antimony by extraction chromatography using silica-gel impregnated with tribenzylamine /TBA/ as a stationary phase and hydrochloric acid solutions of As/V/, Cu and Sb/V/ as mobile phase. Antimony is retained in the silica-gel column while copper and arsenic are collected in the effluent. A separation run takes about 30 minutes.

INTRODUCTION

The separation of ^{76}As from ^{122}Sb is an important problem in radiochemistry and activation analysis, since the γ-ray energies of the main photopeaks for those radioisotopes are to close apart for a simultaneous detection and counting with NaI/Tl/ scintillators. Depending on the relative amounts of ^{76}As and ^{122}Sb, as in certain tin-lead base alloy with high proportion of antimony as compared to arsenic, even the use of Ge-Li detectors may not resolve the corresponding main photopeaks sufficiently well /559 keV for ^{76}As and 564 keV for ^{122}Sb/. In general the activities corresponding to the lower intensities of the photopeaks for ^{76}As and $^{122-124}Sb$ are too weak for the precise quantitative determination, unless a very long counting time is used.

The extraction with the organic solutions of tribenzylamine /TBA/ has been successfully applied by Qureshi et al[1] to separate antimony from arsenic and copper.

The reversed phase chromatography enables the use of the selectivity inherent to the solvent extraction and the multi-stage steps of a chromatographic process. For this reason studies have been undertaken to develop a chromatographic method in which solvent extraction procedure of Qureshi et al[1] could be used in a continuous separation process using silica-gel, impregnated with TBA, as a stationary phase and hydrochloric acid solution as the mobile phase.

The process described in this paper is rapid and allows the separation of antimony from arsenic and copper in less than half an hour and it combines the selectivity of solvent extraction with the simplicity of chromatography and advantages of a multi-stage separation process.

EXPERIMENTAL

The following C.P. grade reagents were used:

Silica-gel /0.05 to 0.2 mm granulometry/

Hydrochloric acid, 9N

Nitric acid, concentrate

Chloroform

Polystyrene granules, soluble in chloroform

Arsenic trioxide

Metallic copper

Metallic antimony

Tribenzylamine

Glass columns, 6 cm length and 0.9 cm in diameter, provided with sintered glass at the bottom were used. Two columns were used in the series joined by a ground-glass joint.

Silica-gel was first washed with 0.9N hydrochloric acid water and dried for two hours a 110°C. After cooling, 10 g of silica-gel was treated with 2 ml of a 10 mg/ml solution of polystyrene in chloroform and the chloroform was removed by vacuum evaporation, at room temperature. Then 10 ml of a solution of TBA in chloroform, at a concentration of 150 mg/ml, was added to the silica-gel impregnated with polystyrene. The chloroform was again removed by vacuum evaporation and the TBA-polystyrene-silica-gel was transferred to the chromatographic columns. Each column was filled with silica-gel up to three centimeters height.

Siliconized silica-gel can also be used but the polystyrene impregnated silica-gel has proved to be an excellent substitute[2].

Radioisotopes of arsenic, antimony and copper were prepared by the irradiation of 15 mg of As_2O_3, 25 mg of metallic copper and 37 mg of metallic antimony, at a thermal neutron flux of about 10^{12} n cm^{-2} sec^{-1} for 30 min., followed by one hour cooling period. The labelled solution of copper was prepared by dissolving the irradiated material with a small volume of conc. nitric acid and diluting with 9N hydrochloric acid to a final concentration of about 0.5 mg Cu/ml. The irradiated antimony was dissolved with some drops of aqua-regia and diluted with 9N hydrochloric acid to the concentration of 0.74 mg Sb/ml. As_2O_3 was dissolved in 40 % sodium hydroxide solution and diluted with 9N hydrochloric acid, giving a solution with

a concentration of 0.22 mg As/ml. About 1 ml of concentrated nitric acid was used in order to oxidize arsenic to its higher oxidation state. Nonirradiated copper ions were added to the arsenic and antimony solutions in order to check when to start collecting the effluent of the columns. The copper concentration of these solutions was equal to 0.5 mg Cu/ml.

One ml of each solution labelled with ^{64}Cu, ^{76}As and $^{122-124}Sb$, respectively, was passed over a different double-column of TBA-polystyrene-silica-gel. When the green colour of copper ions disappeared at the end of the first column, the columns were washed with 3 ml of 9N HCl solution, while the effluent of the second column was collected. Collection of the effluent continued until all copper disappeared from the bottom of the second column.

The γ-ray spectra of the effluents of the copper and arsenic columns and the silica-gel of the antimony column, were measured with a NaI/Tl/ well-type scintillation detector coupled to a 400-channel analyser. The areas under the 511 keV annihilation radiation of ^{64}Cu, and 559 keV and 561 keV photopeaks of ^{76}As and ^{122}Sb, respectively, were determined.

In seven runs the mean value for the retention of antimony was equal to 99.9 % ± 0.1. The recovery of arsenic and of copper in the effluents of the two other columns was equal to 99.6 % ± 0.2 and 99.8 % ± 0.4, respectively.

To study the separation of a mixture of arsenic, copper and antimony, one ml of a labelled solution of the three radioisotopes of known activity of the same concentration as in the individual tests was prepared. The solution was percolated

through the TBA-polystyrene-silica-gel double column using controlled vacuum suction.The flow rate was equal to about 0.5 ml/min. When the green colour of the copper solution disappeared from the bottom of the first column, the columns were washed out with 3 ml of 9N HCl.The first effluent, before copper entered the second column was discarded, and the collection of effluent started when copper ions entered the second column. After all of the green colour from copper ions came off the bottom of the second column, the columns were washed again with 3 ml of 9N HCl, the columns were separated and the first one was used to count $^{122-124}Sb$. The effluent contains copper and arsenic, which can be separated by deposition of copper on iron-wire.

To check the purity and the recovery of each fraction, the γ-ray spectrum corresponding to each one measured using

TABLE 1

Separation of ^{122}Sb from ^{76}As and ^{64}Cu

Run	Effluent				Column	
	^{64}Cu*		^{76}As*		^{122}Sb*	
	CPM	%	CPM	%	CPM	%
1	23623	99.5	12139	99.1	37921	101.9
2	24194	101.9	12227	99.8	36953	99.3
3	24029	101.2	12031	98.2	38185	102.6

* Added ^{64}Cu : 23753 cpm
^{76}As : 12247 cpm
^{122}Sb : 37200 cpm

a Ge-Li detector coupled to a 4096-channel analyser. Again the areas under the 511-keV annihilation radiation of ^{64}Cu, and 559-keV and 561-keV photopeaks of ^{76}As and ^{122}Sb, respectively, were determined and compared with the respective areas for standards of the same radioisotopes.

Table 1 presents the results for the three separation runs.

REFERENCES

1. I.H.Qureshi, F.I.Nagi, M.Naera, M.N.Cheema, J.Radioanal. Chem., 7 /1971/ 221.

2. G.A.de Jesus, Master's Dissertation, Institute of Chemistry, University of São Paulo, 1974.