

Preconcentration of Pb(II), Cd(II), Cu(II) and Hg(II) with 2-mercapto-5-phenylamino-1,3,4-thiadiazole impregnated on silica gel¹

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Abstract

Silica gel modified by the addition of 2-mercapto-5-phenylamino-1,3,4-thiadiazole (MPATD) was developed for the preconcentration of Pb(II), Cd(II), Cu(II) and Hg(II) at trace levels. A "series" experimental procedure permitted the determination of the optimal working conditions (time and pH) and an "on-column" experimental method permitted the determination of the quantity of MPATD retained on silica gel, the uptake capacity, the most suitable eluent and the minimum volume of eluent for which the maximum quantity of metal cations is recovered. The maximal retention capacity on the impregnated silica gel columns was obtained at pH 7.5–8 and was $1500 \mu\text{g g}^{-1}$ for Pb(II) and about $1000 \mu\text{g g}^{-1}$ for Cd(II), Cu(II) and Hg(II). The effect of preconcentration is relevant; on passing 1 l of solution containing $1 \mu\text{g ml}^{-1}$ of cation through a column containing 5 g of impregnated silicagel, after elution with 30–50 ml of the appropriate eluent the cation concentration increased about 15–20-fold. The determination of cations by flame AAS was statistically evaluated and showed recoveries higher than 96% for Pb(II), 98.5% for Cd(II) and 97.95% for Cu(II) after elution with 4 M HNO₃ and about 99.15% for Hg(II) after elution with thiourea.

Keywords: Flame AAS; Heavy metals; 2-Mercapto-5-phenylamino-1,3,4-thiadiazole-impregnated; silica gel; Preconcentration

1. Introduction

The concentration of metallic ions in different types of waters (rivers, ponds, lakes, drinking, sea, waste and industrial) is often below the detection

limits attainable with the most sensitive reactions. In order to detect and determine trace levels of metals (especially for toxic metals such as lead, cadmium, copper and mercury), it is necessary to enrich them preliminarily by coprecipitation, extraction and especially by preconcentration on an ion-exchange chromatographic column or with reagents on solid supports such as silica gel or microcrystalline cellulose [1–12].

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This paper proposes the use of 2-mercapto-5-phenylamino-1,3,4-thiadiazole (MPATD) impregnated on silica gel for the preconcentrating traces of lead, cadmium, copper and mercury. The conditions for obtaining the absorbant material (SiO_2 -MPATD), the preconcentration conditions and the retention capacity of this support for the above metallic ions, the eluent composition to separate the ions, their determination after preconcentration, the calculation of the recovery and the statistical evaluation of the results are discussed.

The bivalent cations M(II) together with MPATD form chelated complexes, in a 1:2 ratio, established by elemental analysis by means of Job's isomolar series method, by studying the IR spectra, etc. The probable structure of the complex is given in Fig. 1.

The ions preconcentrated in this way were determined by flame atomic absorption spectrometry (AAS).

2. Experimental and results

2.1. Apparatus

An Ultrospec III spectrophotometer (Pharmacia LKB, Bromma, Sweden), a flame AAS instrument (Karl Zeiss, Jena, Germany), an MV-84 pH-meter (Clamann and Granert, Dresden, Germany) and glass and plastic columns (50 mm \times 10 mm i.d. and 70 mm \times 18 mm i.d.) were used.

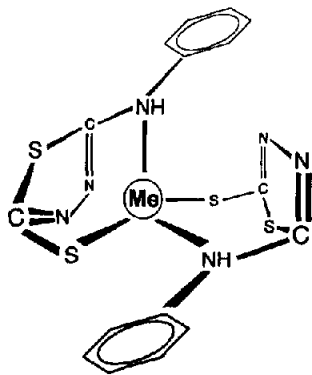


Fig. 1. Probable structure of the metal cation (Me)-MPATD complex.

2.2. Reagents

The following were used: silica gel 60 (Merck), 60–80 mesh granules; 2-mercapto-5-phenylamino-1,3,4-thiadiazole, prepared from reagents from Merck and purified in the laboratory (m.p. 215–218°C); lead nitrate (Merck); cadmium acetate (Merck); copper nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Reactivul București); mercury nitrate, 60% solution (Reactivul București); thiourea (Fluka); $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (Merck); HCl and HNO_3 (Merck); ethanol, 96% (Reactivul București); and absolute ethanol (Merck).

2.3. Preparation of immobilized reagent

In order to purify the silica gel (that contains traces of iron), it was washed with 1:1 (v/v) HCl, then with distilled water and subsequently with doubly distilled water until it was free of chloride; washing was continued with 1:2 (v/v) HNO_3 and then again with distilled and doubly distilled water until it was completely free of nitrate. It was then dried in a drying oven at 120°C for 24–72 h.

The purified silica gel, washed with 2.5×10^{-3} M ammonia in order to neutralize the residual acids, was introduced into 2% MPATD solution in ethanol, stirred for 5 min and kept in a refrigerator (at 4°C) for 24 h, after which it was filtered and dried in vacuum. In order to determine the amount of reagent (MPATD) fixed on the silica gel, SiO_2 -MPATD was introduced into a 50 mm \times 10 mm i.d. column (the height of the layer was 15 mm) and over this was passed 20 ml of absolute ethanol with a constant flow-rate of 1 ml min^{-1} . The effluent was collected in a 50 ml volumetric flask and made up to volume with absolute ethanol. The amount of reagent (MPATD) was determined by UV spectrophotometry, measuring the absorbance at 320 nm. The amount of MPATD fixed on silica gel was about 2%.

2.4. Preconcentration of lead, cadmium, copper and mercury

There were two experimental procedures for preconcentration, using the same SiO_2 -MPATD reagent material, “in series” by stirring and “on-column”.

The first procedure consisted in stirring a series of 20 ml dilute sample solutions containing 5 mg l⁻¹ of M(II) (M = Pb, Cd, Cu, Hg) with 0.5 g of SiO₂-MPATD in conical flasks with polished stoppers for 5–300 s, after which the solutions were filtered through dry filters into 25 ml calibrated flasks, and diluted to volume with doubly distilled water.

The quantity of unretained ions on the SiO₂-MPATD was determined in the filtered solution from the volumetric flask by flame AAS. The quantity of cations retained on the support was calculated by difference.

In the on-column procedure, 1 g of SiO₂-MPATD was introduced into a plastic chromatographic column of 50 mm × 10 mm i.d., ammonia solution was passed through it until the effluent had pH = 8.0 and then 20 ml of M(II) solution containing 5 mg l⁻¹ M(II) was passed through at a flow-rate of 1 ml min⁻¹.

In order to determine the quantity of ions retained, a 20 ml volume of eluent, consisting of HCl, 1, 2, 4, 6 and 9 M HNO₃, 10⁻² Na₂EDTA solution or 1% thiourea in 0.1 M HCl, was passed through the column in 2 ml portions; in each effluent portion the metallic ions were determined by flame AAS at 283.3 nm (Pb), 228 nm (Cd), 324.7nm (Cu) or 256 nm (Hg). The concentrations were calculated using the equation

$$c_p = \frac{A_p C_e}{A_e}$$

where c_p = M(II) concentration found in the sample, A_p = sample absorbance, c_e = standard concentration and A_e = standard absorbance.

The recoveries were calculated; for the lead, the highest recovery (96.94%) was obtained by elution with 6 ml of 4 M HNO₃; for cadmium, the highest recovery (100.6%) was obtained by elution with 10 ml of 1 M HCl, but a high recovery (98.54%) was also obtained with 4M HNO₃; for copper, the highest recoveries were obtained by elution with 20 ml of 1 M HNO₃ (99.63%) and 4 M HNO₃ (97.95%); finally, for mercury, the highest recovery was obtained by elution with 20 ml of 1% thiourea solution in 0.1 M HCl. The experimental results are given in Table 1.

The maximum uptake capacity of the column

Table 1
Optimum eluents and recoveries percentages of M(II) preconcentrated on SiO₂-MPATD

M(II)	Eluent (ml)	Recovery (%)
Pb ²⁺	6 ml of 4 M HNO ₃	96.94
Cd ²⁺	10 ml of 1 M HCl	100.60
Cu ²⁺	20 ml of 1 M HNO ₃	99.63
Hg ²⁺	20 ml of 1% thiourea in 0.1 M HCl	99.16

for the studied cations retained on SiO₂-MPATD, expressed in ppm per gram of support, was determined and was 1500 ppm for Pb and 1000 ppm for Cd, Cu and Hg.

Finally, the repeatability of the preconcentration procedure with SiO₂-MPATD for a series of six samples for each cation was determined. In each case good recoveries were obtained, the RSD varying between 1.39% for Hg and 7% for Pb.

3. Conclusions

A new reagent support consisting of 2-mercapto-5-phenylamino-1,3,4-thiadiazole on silica gel, is proposed for preconcentrating very small quantities of Pb, Cd, Cu and Hg, with application to the detection of polluting and toxic cations in natural and waste waters. This procedure could also be used for preconcentration of other heavy metal cations (Ag, Co, Ni, Pd, Bi, etc.). For the determination of the preconcentrated ions, they were eluted with 1 and 4 M HNO₃ (Pb, Cd, Cu), 1 M HCl (Cd) and 1% thiourea in 0.1 M HCl (Hg), and were determined in the effluents by flame AAS; the recoveries were of 96.94% for Pb, 98.54% for Cd, 99.63% for Cu and 99.16% for Hg.

This procedure should also be useful for the determination of trace levels of Pb in drinking water and pharmaceutical solutions and for compendial heavy metal assays.

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