SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF Sn(IV) AFTER PRECONCENTRATION ON A CHELATE FORMING RESIN

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Abstract

A method for the preconcentration of trace amounts of Sn(IV), using a chelate forming resin, is proposed. The sulphonated derivative of an aromatic complexing agent-Pyrocatechol Violet (PV)-is adsorbed by a strong-base anion-exchange resin (Dowex 2x4) by simple ion-exchange. The resin containing the dye behaves like a chelating resin, able to adsorb Sn(IV) from aqueous solutions, the optimum adsorption pH being 4. A high preconcentration factor for Sn(IV) was obtained.

The PV-resin was used for the preconcentration of Sn(IV) in a zinc sample. After desorption with a small volume of 1M HNO_3, the pH of the analyte was adjusted at pH 4 and then Sn(IV) was determined spectrophotometrically as Sn(IV):PV complex, at 555 nm.

Introduction

In trace metal analysis, preconcentration or separation of the analyte from the matrix is frequently a necessity. Various methods and materials are recommended for preconcentration and separation. Different solid sorbents (namely polymers, anion exchangers, reversed-phase octadecylsilica, controlled pore glass) have extensively been used for the immobilization of organic ligands.[1,2] It is well known that the chelating resins were recognized as being potentially useful for the selective retention of the specific metal ions. Chelating resins were prepared by the immobilization of chelating agents on various supports.[3-5]

A very efficient system is provided by immobilization of the sulphonic acid derivative of an aromatic complexing agent on an anion-exchange resin.[6,7]

Recently, we have examined such a chelating resin for preconcentrating Sn(IV) from a nickel sample prior to its determination by DCP-AES.[8]

In a continuation of this study we have examined the same anion-exchange resin (Dowex 2x4). As sulphonic acid derivative we selected Pyrocatechol Violet (PV) and have used the system with the aim of obtaining a higher preconcentration factor for Sn(IV). Also, in this paper we demonstrated the efficiency of the PV-resin as a preconcentrator for spectrophotometric determination of Sn(IV).

Experimental

Reagents

All the chemicals used were of analytical grade quality, and aqueous reagents were prepared with distilled water.

The anionic resin Dowex 2x4 in the chloride form (Dow) and having a bead size of 100-200 mesh, was used as polymer surface. The exchange capacity of the resin was found to be 3.98 mEq per g of air-dried resin.

Pyrocatechol Violet (3,3',4'-trihydroxyfuchsone-2-sulfonic acid) (Merck) was used as chelating reagent for preparation of the complexing resin.

A 10^{-2}M stock solution of tin(IV) was prepared by dissolving an appropriate amount of 99.99% pure metal in a few cubic centimeters of HNO_3 and diluting to an appropriate volume with distilled water.

Appropriate standard solutions of Sn(IV) were prepared daily by dilution with 0.1M HNO_3. The other metal ion solutions were prepared by diluting a 1000 $\mu g\ mL^{-1}$ atomic absorption standard metal ion solution (Merck) with distilled water.

The pH adjustment was made with NaOH and/or acetate buffer (pH 4).

A 1M nitric acid solution was used for desorption of Sn(IV) from the chelate forming resin.

Instruments

A Specord M40 UV-VIS spectrophotometer equipped with a pair of 1-cm length quartz cuvettes was used for the absorbance measurements. The determination of Sn(IV):PV complex was performed at λ=555 nm. pH measurements were made with an Orion EA 920 pH meter equipped with a combined glass-calomel electrode.

Preparation of the PV-resin

An aqueous solution of 10^{-3}M PV was prepared and used to modify the Dowex 2x4 resin (Cl^-) as described previously.[9] Thus, the anion-exchange resin Dowex 2x4(Cl^-) (200 mg) was stirred with 25 mL

of PV 10^{-3}M. After equilibration for 3h by a mechanical shaker, the resin was filtered and washed with water to remove the excess reagent. The supernatant solution and the rinsing water were collected in a 50 mL volumetric flask. The amount of PV in the supernatant solution was determined spectrophotometrically at 450 nm. The sorption capacity was found to be 0.1 mmoles PV per gram of dry resin.

Calibration curve

Mixtures of standard solutions containing suitable amounts of Sn(IV) were placed into 25 mL calibrated flasks and after addition of 2 mL of PV (10^{-3}M) and 7 mL of buffer solution (pH 4) further diluted to the mark with water and mixed. After allowing the flasks to stand for 15 min., the absorbances of the solutions were measured vs. a blank containing all reagents except metal ion.

Procedure for preconcentration of Sn(IV)

A mixture containing 0.2 g of PV-modified resin was treated with 100 mL of acetate buffer (pH 4) and equilibrated with a mechanical shaker for about 1h. To this mixture an aliquot of Sn(IV) solution with a concentration of 0.01 μg/mL was added and the obtained solution was shaken for about 3h. Then, the resin was separated from the supernatant solution by filtration in a fritted-glass funnel and washed with distilled water. After that, the resin was treated with 10 mL of 1M nitric acid and the mixture was shaken for 2h to desorb Sn(IV) ions. The resin was filtered and washed with a small volume of distilled water. A previous study[8] showed the desorption of Sn(IV) from the chelating resin was quantitative when using 1M HNO_3.

The acid solution containing desorbed Sn(IV) was collected into a 25 mL volumetric flask and treated with 2 mL of 2M NaOH and 7 mL of acetate buffer to adjust the pH to 4. To this mixture 2 mL of 10^{-3}M PV was added, diluted to the mark with water and mixed.

Results and Discussion

Conformance to Beer(s law for the Sn(IV):PV complex

Ross and White studied the complexation reaction between Sn(IV) and PV.[10] They found that the wavelength of maximum absorption is located at 555 nm and that the complex absorbing at that wavelength had a Sn(IV)/PV = 1/1 stoichiometry, at pH 4 in the presence of an acetate buffer. We obtained similar results, using the Job method.[11]

In a continuation of this study and in order to establish the detection limit of Sn(IV) by spectrophotometry, a series of solutions was prepared: with a fixed concentration of PV and a gradually increasing concentration of Sn(IV). From the graph of absorbance versus Sn(IV) concentration it was found that the lower limit for quantitative determination of Sn(IV) is 0.2 μg/mL. There is a linear correlation between the concentration of Sn(IV) and the absorbance of the Sn(IV):PV complex over the concentration range from 0.2 to 1.6 μg/mL of Sn(IV).

Determination of the preconcentration factor

Pyrocatechol Violet is one of the most versatile chelating agents used for the spectrophotometric determination of Sn(IV). It was demonstrated that the fixation of this metal ion on the Dowex 2x4 anion exchanger loaded with PV takes place by the same mechanism as the formation of the PV:Sn(IV) complex in solution. Thus, the higher stability of the Sn(IV):PV complex in solution at pH 4 predicted the higher retention of Sn(IV) on the resin modified with PV at the same pH.[8]

On the basis of these results previously reported a determination of the preconcentration factor of Sn(IV) using the PV-resin was performed.

The experiments were carried out as follows: for the first experiment, a weighed amount (0.2 g) of PV-modified resin was shaken with a 200 cm^3 aliquot of a Sn(IV) solution at a concentration of 0.01 μg/mL Sn(IV), and having the pH 4 (adjusted with an acetate buffer). After retention in the complexing resin, Sn(IV) was desorbed using 10 mL of IM HNO_3. Thus, Sn(IV) was preconcentrated by a factor of 20. The desorbed metal ion was collected into a 25 mL volumetric flask and determined spectrophotometrically according to the procedure described above. The data in Table 1 show that this first test of concentration is not sufficient to determine Sn(IV) spectrophotometrically.

Therefore, a second experiment was performed as follows: after the resin was shaken with a first portion of Sn (IV) solution (200 cm^3), it was separated from the supernatant solution by filtration and then treated with another 200 cm^3 aliquot of water sample. The metal ion retained in the PV-resin was released with 10 mL of IM HNO_3. Thus, the initial amount of Sn(IV), available in 2x200 mL of solution, was preconcentrated to a volume of 10 mL. A preconcentration factor of 40 was obtained in this way. Like in the first experiment, the released metal ion was collected into a 25 mL volumetric flask and determined spectrophotometrically as described for the recommended procedure. As it can be seen on Table 1, the relative error in the Sn(IV) concentration determined after this second test of preconcentration was at a level of –69%.

In order to find the Sn(IV) concentration factor required by the spectrophotometric determination of this metal ion, the third and fourth experiment were performed. Thus, the resin was treated successively resp. with three and four 200 cm^3 aliquots of the Sn(IV) solution (0.01 μg/mL). After the last portion of the supernatant solution was eliminated, the metal ion was recovered in a similar manner as described above and it resulted in a Sn(IV) preconcentration respectively by 60 and 80 fold. In the third and fourth

experiment the amount of Sn(IV), recovered after preconcentration in 10 mL of 1M HNO_3 and collected in 25 mL volumetric flask, could be determined spectrophotometrically with good results. As it shown on Table 1 (experiments 3 and 4) after preconcentration, there is a good correlation between the calculated and determined concentration of Sn(IV).

From the experimental results it comes out that for the spectrophotometric determination of Sn(IV) in a dilute solution, it is necessary this to be preconcentrated so that the amount of metalic ion retained in the resin and then eluted with a minimum volume of 1M HNO_3 (in this experiment 10 mL), should be enough to reach the lower limit for quantitative determination of Sn(IV) by the spectrophotometric method. In this case, for the first and the second experiment, the resin was treated respectively with 200 and 400 mL aliquot of Sn(IV) solution (0.01 μg/mL).

After desorption, the concentration of metal ion collected in a 25 mL volumetric flask was under the sensitivity of the spectrophotometric method (0.08 and 0.16 μg/mL respectively). Hence the error of the spectrophotometric determination. When the complexing resin was stirred successively with three and resp. four 200 mL aliquots of 0.01 μg/mL solution, the total amount of Sn(IV) retained in the chelating sorbent and then released with 10 mL of 1M HNO_3 was enough to reach and even to exceed the lower limit for quantitative determination of Sn(IV) by the spectrophotometric method (here 0.2 μg/mL)

Table 1 Results of the Sn(IV) preconcentration

Experiment No.	Volume of solution, mL		Concentration of Sn(IV), μg/mL			
			before preconc.		after preconc.	
	initial	final	calculated	determined[a]	calculated	determined[a]
1.	1[b]x200	25	0.01	-	0.08	-
2.	2[b]x200	25	0.01	-	0.16	0.05
3.	3[b]x200	25	0.01	-	0.24	0.22
4.	4[b]x200	25	0.01	-	0.32	0.30

Note: a. concentration of Sn(IV) was determined spectrophotometrically as Sn(IV):PV complex, at 555 nm.

b. 1-4 represents the number of 200 cm^3 aliquots of the water sample containing Sn(IV), added successively to the PV-resin.

Application

In order to determine the usefulness of the described preconcentration procedure, a method for determination of Sn(IV) in a zinc sample supplied by The Institute of Rare and Nonferrous Metals, Bucharest was proposed. 2 g of zinc was completely dissolved in a minimum volume of concentrated hydrochloric acid (about 10 mL) by heating on a water bath. The solution was evaporated to about 5 mL. To this a small volume of water was added. The solution was cooled, filtered and diluted to 50 mL in a calibrated flask. An aliquot (40 mL) of the sample was adjusted to pH 4 with 1M NaOH and added to a mixture of 0.2 g of PV-resin and 10 mL of acetate buffer (pH 4). The mixture was shaken for about 2h. The supernatant solution was eliminated and the resin was then washed with distilled water. The retained Sn(IV) was then eluted with 10 mL of 1M HNO_3 and determined spectrophotometrically as described in the general procedure. The results were compared with those obtained by the ICP-AES technique (Table 2). It can be seen that the results of Sn(IV) determination after preconcentration are in good agreement with those obtained by ICP-AES.

We mention that Ba(II), Sr(II), Ca(II), Mg(II), Zn(II), Co(II) and Ni(II) were not retained up to a level of 50 mg/mL; Cu(II), Cd(II),and Pb(II) were not retained up to a level of 10 μg/mL while only 1 μg/mL of Fe(III), Al(III), Ti(IV), Cr(III) and 0.5 μg/mL of Zr(IV), V(V) and Sb(III) were not retained by the PV-resin, as we found previously.[8]

Conclusion

The method described can be regarded as an alternative to the determination of Sn(IV) by a more sensitive method. Thus, Sn(IV) could be determined by ICP-AES or ICP-AES combined with standard addition method from a solution with a tin concentration under 0.2 μg/mL. In order to check the result obtained by ICP-AES, in this paper we propose the preconcentration of Sn(IV) followed by its determination by an accessible method such as spectrophotometry. Moreover, the proposed method allowed an improvement of the sensitivity in the spectrophotometric determination of Sn(IV) as Sn(IV):PV complex, from 0.2 μg/mL to 0.01 μg/mL Sn(IV).

Table 2 Analysis of a sample for Sn (IV)[a]

	Composition	Sn(IV), μg/g		
Sample	Metal, μg/g	certified value	without preconc.[b]	proposed method
zinc	Cd, 3.75; Cr, 0.20; Cu, 2.50; Fe, 14.75; Mg, 0.025; Mn, 0.65; Ni, 2.75; P, 0.025; Pb, 33.75; Sb, 0.025; Si, 163,75; Ti, 0.10; Zr, 0.025; Al, 8.75.	3.50	3.48±0.03	3.47±0.03

Note: a. Average of three experiments.
b. The ICP-AES technique was combined with standard addition method.

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