

Ion exchange separation of thallium(I) from lead(II)

The separation of thallium(I) and lead(II) is an interesting analytical problem in the analysis of thallium-lead alloys. Since these metals have similar properties they are difficult to separate and a number of procedures have been suggested to achieve this. In recent years the use of ion exchange resins in the presence of a suitable ligand such as tartaric acid or sodium pyrophosphate has been proposed¹.

In the course of a polarographic investigation on the use of glycerol as a ligand it was found that thallium(I) is not complexed, whereas lead(II) and other elements form negatively charged complexes in strongly alkaline solution. The polarographic behaviour of thallium(I) in acid and in basic media is almost the same and its wave is not affected by the presence of glycerol. Since thallium(I) is always cationic, it seemed likely that it could be separated from elements that form negatively charged complexes with glycerol in a strongly alkaline medium by making use of ion exchange chromatography. Electrophoresis on Whatman and glass fibre paper shows that the lead(II)-glycerol complex migrates towards the anode, while thallium(I) ion moves towards the cathode. The separation can be performed in two different ways either by fixing the glycerol-lead(II) complex on an anionic resin, or the thallium(I) on a cationic resin. In the former method elution of the lead(II) complex with nitric acid and regeneration of the anionic resin is a lengthy procedure; in the latter thallium(I) is adsorbed on a strongly acid cation exchanger and is displaced with calcium ions. It is necessary to employ calcium(II) as eluent since thallium(I) is strongly adsorbed by a cation resin².

Experimental

Stock solutions of thallium(I) and lead(II) were prepared from Tl_2CO_3 (C. Erba) and $Pb(NO_3)_2$ (C. Erba), respectively. Thallium(I) was standardized gravimetrically as iodide³ and chromate⁴, and lead(II) as sulphate, according to WINKLER⁵. Working solutions 0.5-1 M in NaOH and 1 M in glycerol were made by diluting sodium hydroxide and glycerol. Solutions of other elements were prepared by dissolving their salts in alkaline solutions of glycerol.

A column of Dowex 50, 16-40 mesh (about 20 g), was prepared and converted to the sodium form with a concentrated solution of sodium chloride. After washing with distilled water until the chloride ions had been removed, the resin was eluted with an alkaline solution of glycerol. This step is necessary to prevent local precipitation on the resin bed of insoluble hydroxo complexes at the beginning of the next step. The solution, containing Tl(I) and Pb(II) (about 100 ml) was passed through the column, whereby thallium ions were adsorbed, and anionic glyceric complexes passed into the eluate. The resin was washed with an alkaline solution of glycerol, and the eluate, combined with the washings (total volume about 250 ml), was concentrated for the determination of lead(II) as sulphate.

The resin was rinsed with distilled water until neutral, and thallium(I) was eluted with 1 M $Ca(NO_3)_2$. About 400-500 ml of this solution were needed to elute all the thallium. The solution was concentrated to about 100-150 ml and thallium was determined gravimetrically as iodide.

The resin was finally regenerated with a 2 M sodium chloride solution, until the calcium ions had been completely removed; this was the slowest step of the entire cycle.

TABLE I

SEPARATION OF Tl(I) AND Pb(II) BY ION EXCHANGE ON DOWEX 50 FROM ALKALINE SOLUTIONS OF GLYCEROL

Dowex 50: about 20 g; alkaline glycerol solution: 0.5-1 M NaOH, 1 M glycerol; 100 ml eluted.

Tl(I)			Pb(II)		
Amount taken (g)	Amount found (g)	Difference (mg)	Amount taken (g)	Amount found (g)	Difference (mg)
0.0775	0.0769	-0.6	0.5356	0.5336	-2.0
0.1512	0.1512	0.0	0.2142	0.2121	-2.1
0.1590	0.1583	-0.7	0.4285	0.4279	-0.6
0.2238	0.2235	-0.3	0.3214	0.3207	-0.7
0.2349	0.2349	0.0	0.2142	0.2148	+0.6
0.2495	0.2478	-1.7	—	—	—
0.2919	0.2928	+0.9	0.1071	0.1066	+0.5
0.5117	0.5100	-1.7	—	—	—
—	—	—	0.6427	0.6439	+1.2

Results

Some results of thallium(I)-lead(II) separations by ion exchange from alkaline solutions of glycerol are given in Table I.

The separation is quantitative and the experimental errors are small, although thallium was precipitated as iodide (its solubility is not negligible), and from concentrated calcium solution.

Complex formation with polyols in alkaline medium is quite general. It takes place with several elements, such as Pb(II), Al(III), Sn(II), Zn(II), Sb(III) which form anionic hydroxo complexes in strongly alkaline solution, the only effect of glycerol being to increase their solubility. For other cations, which are precipitated in alkaline medium as insoluble hydroxides, such as Cu(II), Fe(III), Bi(III), the glycerol yields solutions of these elements as anionic complexes; this was proved by electrophoretic measurements. Their solubility is not very great, but sufficient for analytical separations.

Thallium(I) can be separated from these elements by the same procedure as

TABLE II

SEPARATION OF Tl(I) FROM Pb, Cu, Sn, Zn, Bi, As, Sb, Se, Te, Fe AND Al BY ION EXCHANGE ON DOWEX 50 FROM ALKALINE SOLUTIONS OF GLYCEROL

Dowex 50: about 20 g; alkaline glycerol solution: 1 M NaOH, 1 M glycerol; amount of other element added: up to 0.1 g of each; 100 ml eluted.

Tl taken (g)	Tl found (g)	Difference (mg)	Other elements present
0.0910	0.0911	+0.1	Pb, Cu, Bi, Sb, Al
0.1739	0.1732	-0.7	Pb, Cu, Bi, Sb
0.0770	0.0764	-0.6	Fe
0.1943	0.1930	-1.3	Al
0.1595	0.1593	-0.2	Pb, Cu, Bi, Sb, Al, Zn, Sn
0.1708	0.1683	-2.5	Pb, Cu, Bi, Sb, Al, Zn, Sn
0.1307	0.1296	-0.9	As, Se, Te

that used to separate it from lead(II). In Table II some results are shown of the separation of thallium in the presence of about 100 mg of each of the following elements: Pb(II), Al(III), Sn(II), Zn(II), Sb(III), Cu(II), Fe(III), Bi(III), As(III), Se(IV), Te(IV).

Ag(I), Cd(II), Hg(II), and the alkaline earths are insoluble in alkaline solutions containing glycerol, and therefore cannot be separated from thallium(I) by ion exchange. Elements, such as Cr(III), which is easily oxidized to chromate in alkaline solutions, or V(V) and U(VI), which form insoluble thallos vanadate and uranate, respectively, in alkaline solution, interfere with the described procedure.

*Istituto di Chimica Analitica,
Università di Napoli (Italy)*

GIOVANNI CAROBENE
MARIO VICEDOMINI

- 1 O. SAMUELSON, *Ion Exchange Separations in Analytical Chemistry*, Wiley, New York, 1963, p. 403.
- 2 W. K. LOWEN, R. W. STOENNER, W. J. ARGERSINGER, Jr., A. W. DAVIDSON AND D. N. HUME, *J. Am. Chem. Soc.*, 73 (1951) 2666.
- 3 L. ERDEY, *Gravimetric Analysis*, Part II, Pergamon Press, Oxford, 1965, p. 584.
- 4 L. MOSER AND A. BRUKL, *Monatsh. Chem.*, 47 (1927) 709.
- 5 E. SCHULEK AND J. BOLDIZSAR, *Z. Anal. Chem.*, 120 (1940) 410.

Received October 9th, 1967

J. Chromatog., 33 (1968) 566-568