

S.a.c.5. LUCY JOSEPH.—Studies on Chelating Ion-Exchange resins—1988—Dr. V.N. Sivasankara Pillai

During the last fifty years ion-exchange method has evolved as a major technique in analytical chemistry as well as in process technology. This is mainly due to the operational convenience and versatility of the technique in achieving preconcentration and separation of anions and cations. The quest for achieving better selectivity for ion-exchange resins led to the development of resins bearing chelating functional groups. The ultimate aim was to synthesize resins specific for each kind of metal ion. In spite of the extensive investigations, chelating exchangers are still insufficiently used in the practice of analytical chemistry due to the complexity of their synthesis and high cost.

Our study outlined in this thesis, was concentrated on preparing chelating resins with improved selectivity. Starting from polystyrene a new chelating resin, ST-3, was synthesized. It is a sulfur and nitrogen containing resin prepared by a simple three-step procedure. The thiol group is protected from oxidation by a prosthetic group. The resin is stable in 2M HCl, 0.1M NaOH and 0.1M HNO₃. Sorption studies of metal ions on the resin revealed its high selectivity towards mercury (II) ($K_c = 1500$) and silver (I) ($K_c = 4600$). The resin is very effective in the enrichment and recovery of mercury at ppb levels prior to determination. Results of mercury stripping studies from chlor-alkali effluents on the analytical scale are given. The resin shows promising properties in this application and reduces mercury in the effluent to an environmentally acceptable level of < 5 g/l. Investigation on the scale up aspects of the resin is being carried out. The resin is capable of competing with chloride ions present in high concentration in the brine effluent and the sorbed mercury can be eluted using thiourea in dil. HCl, thus effecting the recovery of the resin.

The commercially available sulfur-bearing resins are also capable of removing mercury from aqueous effluents after pretreatment to the environmentally acceptable level. Of these resins IMAC TMR and Duolite ES 465 (Diamond Shamrock) are stable in acid medium, but are sensitive to oxidants. MISSO ALM-525 (Nippon Soda) and Sumichelate Q-10R (Sumitomo) are also capable of stripping mercury at trace levels. These being dithiocarbamates deteriorate in acid medium and are sensitive to oxidation even by mild oxidizing agents. ST-3 resin has similar sorption characteristics to IMAC TMR and Duolite ES 465 resins. It has a definite advantage that it is prepared by simple procedure and has a higher stability due to the thiol group being protected from oxidation (by mild oxidants) by an additional functional group.

Another chelating resin was prepared by electrostatically anchoring pyrogallol disulfonic acid to the commercially available strong base anion-exchange resin, Seralite SRA 400. The reagent loaded resin, R-PGC, is stable towards Fe (III), Mo (VI) and V(V). Exchange behaviour of several metal ions were studied and a comparison of K_D values for various metal ions showed that R-PGS is an excellent medium for the preconcentration and separation of a number of metal ions. Thus separations of Fe(III)-Mn(II), Fe(III)-Cu(II), Fe(III)-Ni(II), Fe(III)-Mo(VI), V(V)-Mn(II), V(V)-Mo(VI) and Mn(II)-Cu(II)-Fe(III) were carried out successfully and recovery and standard deviations are reported. Elution of Cu(II), Ni(II) and Mn(II) were possible with very dil. HCl. Fe(II) and V(V) could be eluted with ascorbic acid in dil. HCl. Elution of Mo(VI) from the column was achieved using 1M HClO₄. The reagent loaded resin can be prepared by running the reagent solution through the anion exchange column. This is a definite practical advantage of R-PGS over chelating resins with covalently-bound functional group. Preconcentration and recovery of Mo(VI) from lean sources are also reported.