Accomplishment of difficult chemical separations using solid phase extraction

R.M. Izatt,[1] J.S. Bradshaw,[1] and R.L. Bruening[2]

[1]Department of Chemistry, Brigham Young University, Provo, UT, 84602, U.S.A.
[2]IBC Advanced Technologies, Inc., American Fork, UT, 84003, U.S.A.

Abstract

A solid phase extraction (SPE) system is described which is capable of highly selective removal of trace amounts of metal ions from solutions containing matrices which normally make separations difficult. Highly acidic or basic solutions and concentrated salt mixtures are included in the matrices. Significant volume reductions can be achieved with SPE. Separations using SPE have been commercialized in both industrial and analytical applications.

INTRODUCTION

There is a growing need for novel separation methods which are more effective than conventional procedures (ref. 1). Driving forces to develop these methods include the need for greater selectivities; the requirement in many cases to separate ppb and ppt levels of metals from solutions even if present in difficult matrices; the need for rapid and effective removal of trace levels of metals from large volumes of solution on a continuous basis; the need for large concentration factors in element separations; and the need for improved methods for analytical determinations involving elements present at ppb/ppt levels.

These needs are found in a large number of industrial and environmental operations. Many of them are a result of increased awareness of the detrimental effect of metals such as lead, mercury, bismuth, and cadmium on the environment and on the production of other pure metals. These and other elements are found in trace amounts in sulfide ore bodies. As the ore moves through the refining process, these trace elements may accumulate and affect the purity or production of the desired product and/or move as waste into the environment. If sufficient trace element remains in the product, and this product is used to manufacture containers for food products, the trace element may reach the ultimate consumer with potential negative health effects.

There is widespread pollution of our environment by various undesireable elements. Heavy metals, radioactive ions, and other chemical species are often found either free in the environment or in specific waste sites, such as the Berkeley Pit in Montana, U.S.A. (ref. 2). It is common to find trace amounts of these contaminants in aqueous solutions of variable pH ranging from highly acidic to highly basic solutions and containing high salt concentrations. The need is to separate the desired ion(s) from other ions of similar chemical properties which may be present in one million to one billion times the concentration of the desired ion(s) and to do this rapidly and efficiently. In addition, it is desirable to effect a large reduction in the volume of the original solution by the separation process. All of this should be accomplished without adding replacement ions, other contaminating species, or solvents. Similar needs exist in the preparation of samples for analysis when the ions of interest are at the ppb/ppt levels.

Conventional separation procedures do not handle these problems well. Generally, solution volumes are increased or remain about the same. Kinetics are usually slow. Selectivity, in many cases, is poor being a few orders of magnitude at best. In most cases, replacement ions are introduced or large solvent volumes must be handled. Generally, performance by these procedures decreases as trace element concentration decreases to low ppb/ppt levels.

In this paper, the basis for use of solid phase extraction (SPE) will be presented together with the advantages of this method over other separation procedures. Examples will be given of metal and Cl⁻ separations by SPE from a variety of aqueous solutions of industrial interest.

SOLID PHASE EXTRACTION

Our approach to these separations problems has been to use an SPE device. This device consists of three parts, a macrocycle or other ligand, a connecting spacer, and a solid polymeric support such as silica gel. Each of these components is essential to the success of the separation. For analytical separations, the device is termed AnaLig™ while for industrial separations, it is termed SuperLig®.

Ligand

The macrocyclic ligand incorporates into the system the known high selectivites of these ligands for metal ions (ref. 3-5). Using proper design principles, one can obtain ligands which have orders of magnitude greater selectivites in the cases of separations involving similar cations. Macrocycles have been found to be effective in the selective separation of cations in liquid membrane systems (ref. 6,7). One disadvantage of such liquid membrane systems from a commercial standpoint is the cost to purchase or synthesize extremely water insoluble macrocycles which are continuously being lost to the aqueous phase. However, these model systems demonstrate well the remarkable cation selectivites of macrocycles in separations. The achievement of high binding strength between the ligand and the cation together with high selectivity over similar cations is of prime importance in the SPE procedure.

Connecting Spacer

The connecting spacer serves the useful purpose of separating the macrocycle from the solid phase thus allowing it to be immersed in the aqueous phase. The spacer is bound by a stable covalent attachment to the silica gel. Since the ligand is attached by a covalent bond to the spacer, all bonds have high stability (ref. 8).

Solid Phase

The solid phase in the SPE system must be compatible with the solution from which the separation is to be made. It should not react with or dissolve in the medium used. Effective and rapid separations require that the supports used in aqueous solution be hydrophilic in nature. We have used a variety of support materials allowing effective separations to be made in highly acidic, highly basic, and HF-containing solutions. In a recent review (ref. 9), solid organic and inorganic materials including silica gel bearing organic functional groups are discussed. The review includes syntheses of the materials, properties of solid supporting surfaces, and uses of the bonded complexing agents for various chemical reactions including separations.

Silica gel is one of the most effective solid phase materials for use in SPE separations (ref. 9,10). It can be obtained in pure form, is hydrophilic, has a high concentration of active sites for chemical bonding, and is easy to convert to an SPE material by chemical synthesis (ref. 9). However, silica gel has one serious drawback in SPE separations. It has a small solubility in water which increases markedly in the presence of either F⁻ or OH⁻. Industrial processes with major separation needs, such as electronics and steam generation, cannot have even small quantities of silica in their systems. In order to address these concerns, we have developed a proprietary support material which can be used without reaction in solutions of HF or F⁻. The use of zirconia or titania along with other materials allows separations to be carried out in strongly basic solutions.

We have employed SPE in two modes, fixed bed columns and Empore™ disks. Both modes allow one to make use of the unique characteristics of the SPE technology. However, use of the Empore™ disk mode has resulted in marked improvement in separation efficiency in many cases. Empore™-encased materials have several advantages over columns for ion separations. The mesh size of the SuperLig® or AnaLig™ material is markedly reduced from greater than 100 μm to less than 10 μm

in diameter. This allows a greater concentration of active sites to be present. The Empore™ disk may be considered to be a short column which is much more compact than a normal column. The combination of these effects results in a system capable of much more rapid separations than is possible with the fixed bed column mode or ion exchange. For example, flow rates in the Empore™ system can be up to 400 times those of a column system and 4000 times those of ion exchange. Furthermore, the selectivity and removal ability of the ligands employed in the SPE systems are maintained at these flow rates making separations of trace amounts of metal ions from large volumes of solution feasible. The high flow rates which are possible in the membrane system can be appreciated better by realizing that a 200 mL•min^{-1}•g^{-1} flow in the column mode is equivalent to a 200 L•min^{-1} flow through a kilogram membrane system. The residence time in each system is about 0.3 second per increment volume (ref. 11). Even with this small residence time, essentially complete separation of the target ion(s) is achieved. It is apparent that Empore™-based systems have advantages in situations where speed of operation is important and where large volumes of solution are involved. IBC and 3M have entered into a joint agreement for marketing these Empore™-based separations materials (ref. 12).

APPLICATIONS OF SPE TECHNOLOGY

Separations of industrial interest involving removal of trace amounts of elements from various matrices have been itemized (ref. 13). SPE technology has been used commercially for precious metal (Pd, Pt, Rh) separations and purification (ref. 13-16) and for removal of base metal impurities (Bi, Sb, Fe, Pb, Bi, Cu, Hg) from refinery streams, electrogalvanizing baths, and plating baths (ref. 11, 13, 17). The base metals involved include copper, tin, and zinc.

One important industrial pollutant is mercury. SPE technology has been successful in removing mercury from a commercial sulfuric acid stream (ref. 14). Streams with initial mercury feed concentrations ranging from < 100 ppb to 200 ppm were treated successfully. Analytical applications developed by IBC using SPE principles have been described (ref. 18). These applications include the removal at the ppb/ppm levels and concentration for subsequent AA analysis of the following: Pb^{2+} from simulated potable water and seawater matrices, Sr^{2+} from a simulated seawater matrix, Pb^{2+} from Benadryl (Parke Davis Co.) tablet extracts and Robitussin CF (A.H. Robins Co.) cough medicine, Ni^{2+} and Cu^{2+} from Benadryl tablet extracts, iron and nickel from petroleum oil, Hg spikes from aqueous solution, simultaneous removal of spikes of a variety of transition and post-transition bivalent metal ions and Ag^+ from aqueous solutions, and Cl^- from aqueous solution.

The effectiveness of SPE can be illustrated by the use of this technology to effect separations of metal ions from a nuclear waste matrix. One of the most challenging separations problems today is the removal of radionuclides from stored nuclear waste. Over the past half-century, U.S. nuclear defense activities have produced enormous volumes of nuclear waste that now require long term disposal. The radionuclides ^{137}Cs and ^{90}Sr contribute 98% of the thermal energy and 97% of the penetrating radiation during the first 30 years after nuclear waste is formed. It is highly desireable to remove these isotopes and, in so doing, to decrease the volume of the waste. In this way, the volume of the material sent on to geological disposal would be greatly reduced. The need for this treatment is found at many sites in the U.S.A. and abroad.

In collaboration with 3M and Pacific Northwest Laboratory a project has been initiated to test SPE Empore™ membrane techniques for separation of Cs^+ and Sr^{2+} from simulated nuclear waste solutions (ref. 14, 19). A typical Cs^+ separation from a highly basic solution using a polymer-bound SuperLig® material is given in Table 1. The composition of the simulated nuclear waste solution from which Cs^+ is removed is as follows (molar concentration in parentheses): Al^{3+} (0.43), Na^+ (5.00), K^+ (0.12), Rb^+ (5 x 10^{-5}), Cs^+ (5 x 10^{-4}), NO_3^- (1.67), NO_2^- (0.43), F^- (0.089), PO_4^{3-} (0.025), SO_4^{2-} (0.025), CO_3^{2-} (0.23), OH^- free (1.68), OH^- total (3.40). It is seen that the separation of Cs^+ must be accomplished in the presence of molar quantities of NaOH and NaNO$_3$ and of 0.1 M KNO$_3$. Both Na^+ and K^+ are normally strong competitors with Cs^+ for ligands. The SuperLig® material

Table 1. Separation of Cs^+ from a highly Alkaline plus NO_3^- Containing Stream also Containing 5 M Na^+, 0.12 M K^+, and Several Other Inorganic Species (see text) Using a Polymer Bound pH Sensitive SuperLig® Material

Sample Description	Cs^+ Concentration (ppm or mg/l)
Original Feed Solution	70
0 - 10 l Feed Effluent[a]	<1
10 - 20 l Feed Effluent[a]	21
20 - 30 l Feed Effluent[a]	46
0 - 100 mL 0.5 M HNO_3 Elution[b]	12,000
100 - 200 mL 0.5 M HNO_3 Elution[b]	2,660
200 - 300 mL 0.5 M HNO_3 Elution[b]	133
300 - 400 mL 0.5 M HNO_3 Elution[b]	1

[a]   30 mL/min. flowrate.
[b]   Flow rate of 3.33 mL/min. start of elution measurement after previous column void volume has exited the column.

used in the separation must have the ability to bind Cs^+ at least four orders of magnitude greater than Na^+ or K^+ which are present at much higher concentrations than Cs^+. The Cs^+ binding must also be large enough to permit complexation and removal by SPE at the low level of Cs^+ present. The data in Table 1 show that Cs^+ is separated quantitatively from Na^+ and K^+ in one pass through the SuperLig® column.

In Table 2, the removal of $^{90}Sr^{2+}$ and Pb^{2+} from an acid waste tank farm at Idaho Nuclear Energy Laboratory (INEL) is presented. This project was carried out in collaboration with INEL and 3M. Different SuperLig® systems are used for separation of the two metal ions. The SuperLig® systems have negligible interactions with cations other than Sr^{2+} and Pb^{2+}. As indicated, selectivity for either of these two cations in the presence of the other is achieved by the SuperLig® systems used.

Table 2. Removal of $^{90}Sr^{2+}$ and Pb^{2+} using two Different SuperLig® Materials (0.2 g each) in Empore™ from an Acid Waste Tank Farm[a] at Idaho Nuclear Energy Laboratory.[b]

Sample Description	^{90}Sr Concentration (ppm)[c]	Sample Description	$Pb(NO_3)_2$ Conc. (ppb)[d]
Feed solution	269	Feed solution	1044
25 Bed volumes	< 1	10 Bed volumes	0.11
50 Bed volumes	< 1	20 Bed volumes	0.54
75 Bed volumes	85	30 Bed volumes	36
100 Bed volumes	168	40 Bed volumes	462
125 Bed volumes	239	50 Bed volumes	1044
150 Bed volumes	265		

[a]   Chemical make-up of tank WM-185 used for "hot" feed: total $Sr(NO_3)_2$ in feed, 5.22 ppm (~20% $^{90}Sr^{2+}$); 269 ppm $Pb(NO_3)_2$; 0.19 M KNO_3; 0.62 M $Al(NO_3)_3$; 0.41 M $NaNO_2$, 0.81 M $NaNO_3$, 0.033 M NaF, 1.62 M HNO_3.
[b]   Flowrate = 2.2 mL•min-1. Empore disk diameter = 0.22 mm.
[c] ^{90}Sr concentration calculated at INEL from the ^{90}Sr activity, disintegrations • s^{-1}• mL.
[d] Pb^{2+} concentration determined at INEL by ICP analysis.

CONCLUSIONS

The reactive SPE polymer system has been shown to be effective in separations of a wide variety of trace elements from difficult matrices. Encasement of the SPE material in Empore™ greatly enhances its effectiveness in chemical separations. The resulting system is capable of removing trace quantities of metal ions from large volumes of solution at high flow rates. The nature of the SPE system allows large volume reductions to be made during separations. SPE systems can be used effectively in both industrial and analytical applications.

REFERENCES

1. G.J. King, ed., *Separation and Purification*, National Academy of Sciences, U.S., **1987**.
2. Baum, D.; Knox, M.L., *Smithsonian* **1992**, *23*, 46.
3. Izatt, R.M.; Bradshaw, J.S.; Nielsen, S.A.; Lamb, J.D.; Christensen, J.J.; Sen, D., *Chem. Rev.*, **1985**, *85*, 271.
4. Izatt, R.M.; Pawlak, K.; Bradshaw, J.S.; Bruening, R.L., *Chem. Rev.* , **1991**, *91*, 1721.
5. Izatt, R.M.; Pawlak, K.; Bradshaw, J.S.; Bruening, R.L.; *Chem. Rev.* **1995**, *95*, 0000.
6. Izatt, R.M.; Clark, G.A.; Bradshaw, J.S.; Lamb, J.D.; Christensen, J.J., *Sep. Purif. Methods* **1986**, *15*, 21.
7. Izatt, R.M.; Bradshaw, J.S.; Lamb, J.D.; Bruening, R.L., In *Liquid Membranes: Chemical Applications*; Araki, T.; Tsukube, H., Eds.; CRC Press: Boca Raton, FL, **1990**; Chapter 7.1, pp 123.
8. Bradshaw, J.S., Krakowiak, K.E., Tarbet, B.J., Bruening, R.L., Griffin, L.D., Cash, D.E., Rasmussen, T.D., Izatt, R.M., *Solvent Extr. Ion Exch.* **1989**, *7*, 855.
9. Biernat, J.F., Konieczka, P., Tarbet, B.J., Bradshaw, J.S., Izatt, R.M., *Sep. Purif. Methods*. **1994**, *23*, 77.
10. Bradshaw, J.S.; Bruening, R.L.; Krakowiak, K.E.; Tarbet, B.J.; Bruening, M.L.; Izatt, R.M.; (the late) Christensen, J.J. , *J. Chem. Soc., Chem. Commun.* **1988**, 812.
11. R.L. Bruening, J.B. Dale, W.R. Holbrook, N.E. Izatt, M.H. Rytting, B.J. Tarbet, J.S. Bradshaw and R.M. Izatt, in 'Proceedings of the 24th Annual CIM Hydrometallurgical Meeting' B. Harris and E. Krause (eds.), CIM Publications, Montreal, Canada, **1994**.
12. *C&EN* , 29 August **1994**, p 10.
13. Izatt, R.M.; Bradshaw, J.S.; Bruening, R.L.; Tarbet, B.J.; Krakowiak, K.E. "Novel Metal Separations Using SuperLig® Materials Involving Macrocyclic Chemistry"; *Emerging Separation Technologies for Metals and Fuels,* V.I. Lakshmanan, R.G. Bautistia, and P. Somasundaran, Eds., Warrendale, PA, TMS, **1993**.
14. Izatt, R.M.; Bradshaw, J.S.; Bruening, R.L.; Tarbet, B.J.; and Bruening, M.L.; "Selective Separations Using Supported Devices", in Vol. 10, *Supramolecular Technology and Applications*, J.M. Lehn, Ed., Oxford, Pergamon Press, In press.
15. M. Bargeron, M. Beaumier, A. Herbert, *Analyst*, **1991**, *116*, 1019.
16. C. Wright and R.L. Bruening, in *Precious Metals Recovery and Refining*, L. Manziek, ed., Historical Publications, Austin, TX, **1990**, 95.
17. Izatt, N.E.; Bruening, R.L.; Anthian, L.; Griffin,L. D.; Tarbet, B.J.; "Novel Applications of SuperLig® Materials To Separations of Metallurgical Interest"; *Proceedings: Metallurgical Processes for Early 21st Century*, H.Y. Sohn, Ed., Warrendale, PA, TMS **1994.**
18. Izatt, R.M., Bradshaw, J.S., Bruening, R.L., and Bruening, M.L. *Am. Lab.*, **1994**, *26*, , 28c.
19. G. Goken, R. Bruening, L. Bray, "Solid Phase Extraction Membranes for Selective Radionuclide Separation," presented at the AIChE Summer National Meeting, Denver, CO, 14-17 August 1994.