

## Solid phase extraction of ions using molecular recognition technology

R.M. Izatt,<sup>1</sup> J.S. Bradshaw,<sup>1</sup> R.L. Bruening,<sup>2</sup> B.J. Tarbet,<sup>2</sup> and M.L. Bruening<sup>2</sup>

<sup>1</sup>Department of Chemistry, Brigham Young University, Provo, UT, 84602, U.S.A.

<sup>2</sup>IBC Advanced Technologies, Inc., Provo, UT, 84606, U.S.A.

### *Abstract:*

Solid phase extraction (SPE) materials are described that are capable of highly selective separations of trace levels of cations and anions from aqueous solutions. The extraction kinetics are rapid, either small or large volumes of solution can be treated, and large volume reductions can be achieved. By varying the SPE system, the separations are effective even in the presence of large concentrations of acid, base, or salt. A review is given of the application of SPE technology to a variety of industrial and analytical separations.

### INTRODUCTION

A major interest in our research program at Brigham Young University during the past three decades has been the identification and investigation of factors affecting the cation selectivities shown by complexing agents. This investigation resulted in the early identification of remarkable selectivities by certain macrocycles for uni and bivalent cations in single solvent systems (ref. 1-4). The high selectivities found by us and others (ref. 5-6) in macrocycle-cation systems led to an explosion of interest in the synthesis of new macrocycles with specific cation selectivities.

Our early work in separating cations from one another involved the use of simple bulk liquid membrane systems (ref. 7). Subsequent separations systems used by us (ref. 8-10) included liquid membranes of the emulsion, supported, hollow fiber, and dual module hollow fiber types. These membrane systems provided much useful information concerning cation selectivities in separation systems. However, several features of the systems limited their use in practical separations. First, the preparation of water-insoluble macrocycles was expensive. Second, loss of these expensive reagents to the aqueous phase over time would be prohibitive. Third, large scale and continuous separations appeared to be difficult to engineer with these devices with the possible exception of the hollow fiber systems. Fourth, the separation kinetics were slow. Separation rates were much more rapid for the emulsion and hollow fiber systems, but were still too slow for large scale commercial applications. Finally, all of these systems were subject to fouling which is a serious problem for membranes generally.

The problems with membrane systems were overcome by attachment of macrocycles to silica gel by a chemical bond (ref. 11,12). This accomplishment coincided with the receipt by us of a research grant from the State of Utah Centers of Excellence Program. The purpose of this Grant was to accelerate the development of promising technologies on university campuses in Utah. The ultimate objective was to commercialize the particular technology through creation of a small business. The role of the university was to act as an incubator in this process. This goal was accomplished by the organization of IBC Advanced Technologies, Inc. (IBC) in 1988. The focus of IBC is to develop and commercialize separations of interest in the metallurgical processing; nuclear, mixed, and toxic waste; analytical; ultrapure fluids; electronics; and biopharmaceutical areas. Emphasis is on separations usually of trace amounts of cations or anions, which are either difficult or impossible by conventional methods. These objectives are in line with the recommendations of a National Academy of Sciences (U.S.) report (ref. 13) which recommends the development of new separations systems capable of high selectivity and of use with very dilute solutions.

The material which follows presents difficulties encountered in separations of trace amounts of ions, the basis for the IBC separations procedures, and a review of separations either employed or under development for commercial use by IBC.

### DIFFICULTIES ENCOUNTERED IN TRACE ELEMENT SEPARATIONS

In real life situations, elements in trace amounts which require separation are usually found in matrices of other species which complicate their separation (ref. 14). An effective separation of such an element (or group of elements) requires first that there be sufficient specificity by the system used for that element over other closely related elements even if these elements are present in high concentration. A second requirement is that the affinity of the bound ligand for the ion of interest be sufficiently high that low levels of the ion can be efficiently removed from the solution. Third, new contaminants, such as replacement ions and solvents, should not be added to the system during the separation as is done with many conventional procedures. Fourth, the separations system is often required to remove trace amounts of ions from large volumes of solution, a process which is difficult using conventional procedures. Much of this difficulty arises from the need for rapid separation kinetics. Slow kinetics can arise from slow diffusion rates and slow metal-ligand association or dissociation rates. Fifth, if the separations involve solutions with nuclear radiation present, reasonable stability to this radiation is necessary. Sixth, it is desirable to concentrate the species separated by a large factor thus reducing system volume. Finally, since space is at a premium in most industrial operations, the entire separations system should occupy as small an area as possible.

Since many of these difficulties are present simultaneously in a given separation, effective separations are often difficult to carry out. Overcoming the difficulties mentioned requires novel approaches. For example, design and synthesis of new molecules of high binding strength and high selectivity for the ion(s) of interest may be needed. Classical separations methods usually lose their effectiveness as the concentration of the species to be separated decreases. Slow kinetics and large spatial requirements are found for most conventional separations systems. New approaches to chemical separations are needed.

### BASIS FOR IBC SEPARATIONS PROCEDURES

IBC has pioneered the use of solid supported ligand systems to extract trace amounts of ions selectively from solutions. These supported systems are termed SuperLig® when used in industrial applications and AnaLig™ when used in analytical applications. In either case, the separation process employed makes use of solid phase extraction (SPE) by the SuperLig® or AnaLig™ material to remove a target ion or other species by transferring it to a ligand attached by a covalent chemical bond to a solid which comes in contact with the solution (ref. 14). SPE is usually carried out in the form of packed beds or columns. However, a significant advance in SPE was the development and use of microporous particles. A technique has been developed by 3M for enmeshing small microporous particles into a microfibrinous matrix to form what has been described as an SPE membrane or an Empore™ membrane (ref. 15). The path of flow through the membrane is very tortuous but also uniform because of the controlled spacing of the particles. These membranes have many advantages over packed beds of equivalent particle size. The particle diameter of the SuperLig® or AnaLig™ Empore™-encased material is markedly reduced from greater than 100 µm to less than 10 µm. 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 column mode or ion exchange. For example, flow rates in the Empore™ system (ref. 14,15) 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 SuperLig® and AnaLig™ materials are maintained at these flow rates. Residence time per increment volume in a typical Empore™ system is about 0.15 second (ref. 15). In addition, channeling problems are

eliminated. Channeling is a recurring problem with packed bed procedures. It is apparent that Empore™-based systems have important 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 to develop markets for metal separation processes (ref. 16).

Different support materials have individual advantages and disadvantages in separations systems. For this reason, IBC has developed SuperLig® and AnaLig™ materials using a variety of support materials. For example, silica gel is advantageous in many applications because of its high hydrophilicity, large number of binding sites, inert character to a large number of reagents, and rapid separation kinetics. However, the solubility of silica gel increases markedly as pH increases above about 10. There are many separations needs in basic solution which require a more stable support material. Also, the small solubility of silica gel in water prevents its use in the electric power and electronics industries where pure water is a requirement. These problems can be overcome by using titania, zirconia, or other polymers as support materials. The capacity of these supports is somewhat lower than that of silica gel, but still adequate for ion removal from basic solutions. Supports have been developed and tested which are capable of operation in F/HF solutions, also. A review on the attachment of reactive molecules to silica and other supports and the use of these materials in chemical separations has been published (ref. 17).

## REVIEW OF COMMERCIAL AND ANALYTICAL SEPARATIONS

Separations of industrial interest using SuperLig® materials have been described including removal of unwanted metal ions from base metal refinery streams (ref. 18-20); separations and purification of platinum metals (ref. 18, 21-23); removal of Pd<sup>2+</sup> from AgNO<sub>3</sub> streams (ref. 21); and removal of Cs<sup>+</sup>, Sr<sup>2+</sup>, and Pb<sup>2+</sup> from nuclear waste streams (ref. 14,21).

Separations of analytical interest have also been described (ref. 24). These include the removal of Pb<sup>2+</sup> and Sr<sup>2+</sup> from simulated seawater; removal of Pb<sup>2+</sup> from simulated potable water; removal of Pb<sup>2+</sup> spikes from Benadryl (Parke Davis Co.) tablet extracts and Robitussin CF (A.H. Robins Co.) cough medicine; Ni<sup>2+</sup> and Cu<sup>2+</sup> removal from Benadryl tablets; removal of Fe and Ni from petroleum oil containing a matrix of other transition and heavy metal elements; transition metal ion removal from simulated potable water solutions; the extraction and concentration of low level Hg<sup>2+</sup>; and removal of Cl<sup>-</sup> from HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> solutions.

### Lead Separations

Several of these separations illustrate the ability of the SPE procedure to overcome the difficulties present in separations of trace amounts of cations and anions. Separations involving Pb<sup>2+</sup> are particularly instructive. The presence of lead in the environment presents a serious and well known health risk to animals and humans as well as being detrimental in the production of purified metals from metallurgical streams. The presence of trace amounts of Pb<sup>2+</sup> in industrial streams is undesirable for two reasons. First, there is danger that the Pb<sup>2+</sup> may eventually be passed on to a food or other product used or consumed by people. The removal of Pb<sup>2+</sup> in tin refining and electroplating (ref. 19,21) is an example of this application. Second, the presence of Pb<sup>2+</sup> may result in an inferior major product or accumulation of Pb<sup>2+</sup> may affect adversely the refining process. In this case, it is necessary to maintain the Pb<sup>2+</sup> level at concentrations below some threshold value. This application is also illustrated by Pb<sup>2+</sup> removal during tin refining. SPE procedures have been effective both in the separation and analysis of Pb<sup>2+</sup> present at ppb levels in difficult matrices and in the removal of trace amounts of Pb<sup>2+</sup> from industrial streams (ref. 19,21). The data in Table 1 illustrate the removal of Pb<sup>2+</sup> from a tin refinery stream using an appropriate SuperLig® material. It is seen that Pb<sup>2+</sup> can be removed from a matrix of salts including large concentrations of tin. This removal can be accomplished on a continuous basis and the Pb<sup>2+</sup> can be recovered in pure form.

As allowable levels of Pb<sup>2+</sup> in potable water have decreased to ~5ppb, the need for rapid and accurate procedures to concentrate Pb<sup>2+</sup> for subsequent analysis has increased. In potable water and other solutions, the concentration of Pb<sup>2+</sup> usually must be done in the presence of difficult matrix species.

Table 1. Removal of Pb<sup>2+</sup> from a Tin Refinery Stream Using an Appropriate SuperLig® Material.

Processing Stream	Volume (liters)	Concentration in mg/L (ppm)	
		Pb	Sn
Feed	500	150	~45000
Barren Feed After going through SuperLig®	500	≤5 <sup>a</sup>	~45000
Dilute Acid Was	5	≤5 <sup>a</sup>	~17000
EDTA Elution <sup>b</sup>	5	15000	≤1

<sup>a</sup> Analysis suggests Pb is ≤ 1 ppm. However, the high Sn concentration makes it difficult to confirm this analysis.

<sup>b</sup> In many cases a K<sup>+</sup> salt with an anion matching or similar to the acid in the bath can be used as effectively as EDTA.

The analysis of Pb<sup>2+</sup> present in simulated potable water and seawater matrices is shown in Table 2 (ref. 24). In these examples, Pb<sup>2+</sup> is first separated from the matrix ions listed in the footnote using the indicated AnaLig™ material in a column mode. Concentration of the Pb<sup>2+</sup> is accomplished using a small volume of eluent. The amount of Pb<sup>2+</sup> in the concentrated solution can be determined using conventional atomic absorption spectrophotometry (AA) and the result used to calculate the Pb<sup>2+</sup> concentration in the original solution. The results in Table 2 show that accurate Pb<sup>2+</sup> concentrations at the ppb or high ppt level can be obtained using this procedure. A wide range of matrix ions is present in both cases, but no interference is found.

Table 2. Concentration of Pb<sup>2+</sup> from Simulated Potable Water and Sea Water Solutions (ref. 24)

Potable Water Matrix <sup>a</sup>		Sea Water Matrix <sup>b</sup>	
Pb <sup>2+</sup> spike (ppb)	Pb <sup>2+</sup> recovery (ppb ± S.D.) <sup>c</sup>	Pb <sup>2+</sup> spike (ppb)	Pb <sup>2+</sup> recovery (ppb ± S.D.) <sup>c</sup>
5	5.5 ± 1.0	0	0.9 ± 0.1
10	9.0 ± 0.5	5	5.8 ± 0.1

<sup>a</sup> NaCl = 4.0 M, MgSO<sub>4</sub> = 0.4 M, Ca(HCO<sub>3</sub>)<sub>2</sub> = 0.9 M, KNO<sub>3</sub> = 0.1 M. AnaLig™ Pb-01 in fixed bed column mode.

<sup>b</sup> NaCl = 0.459 M, MgSO<sub>4</sub> = 0.029 M, MgCl<sub>2</sub> = 0.023 M, CaCl<sub>2</sub> = 0.010 M, KCl = 0.010 M, SrCl<sub>2</sub> = 1.5 × 10<sup>-4</sup> M, NaBr = 8.1 × 10<sup>-4</sup> M, Pb(NO<sub>3</sub>)<sub>2</sub> = 2.4 × 10<sup>-8</sup> M, Hg(NO<sub>3</sub>)<sub>2</sub> = 1.5 × 10<sup>-10</sup> M. AnaLig™ Pb-02 in fixed bed column mode.

<sup>c</sup> S.D. = standard deviation based on at least two samples.

Three AnaLig™ materials are available for the concentration of Pb<sup>2+</sup> (ref. 24). AnaLig™ Pb-01 is pH independent while AnaLig™ Pb-03 is pH dependent. Thus, Pb<sup>2+</sup> can be eluted from the latter material by acid. On the other hand Pb<sup>2+</sup> can be separated from highly acidic solutions using the former material. Elution from Pb-01 is accomplished using a strong complexing agent such as ethylenediaminetetraacetic acid. A third pH independent material is available, AnaLig™ Pb-02, which allows separation of Pb<sup>2+</sup> at ppt levels in highly acidic solutions while maintaining high levels of selectivity for Pb<sup>2+</sup>.

### Bismuth Separations

The removal of bismuth from copper refinery streams is necessary in cases where high bismuth levels are found in the copper ore (ref. 20). The build up of bismuth in these streams results in a reduction in the quality of the cathode copper used in the manufacture of wire. An appropriate SuperLig® material is effective in reducing tankhouse bismuth levels and maintaining them at or below 100 ppm on a continuous operation basis. The equipment used is contained in a 2x2x2 meter

space. Use of the SPE process for this application has the following advantages. First, the process requires relatively few steps and is simple. Second, the process is environmentally friendly, the eluent ( $\text{H}_2\text{SO}_4$ ) is compatible with the tankhouse electrolyte and can be recycled, and no impurities are added to the system. Third, the bismuth that is removed can be collected as pure bismuth sulfate and sold as a product.

### Cesium and Strontium Separations from Nuclear Waste

A major interest in the nuclear waste area is the effective removal of radioactive  $^{139}\text{Cs}$  and  $^{90}\text{Sr}$ . These isotopes constitute the majority of the radioactivity during the first few decades of the lifetime of this waste. Their removal allows the remaining waste to be treated and disposed of by much more economical means.

IBC has four high capacity SuperLig® materials capable of removing  $^{139}\text{Cs}$  and  $^{90}\text{Sr}$ , two for each of these metal ions. One pair is pH insensitive while the other pair is pH sensitive allowing elution with acid. These SuperLig® materials have been incorporated into Empore™ membranes. The resulting systems have been tested in a joint IBC-3M-Department of Energy (DOE) project involving mimics of Hanford, Washington nuclear wastes (ref. 15) and actual Idaho Nuclear Engineering Laboratory (INEL) radioactive wastes.

$\text{Cs}^+$  removal from a simulated Hanford waste solution resulted in nearly 100% recovery of the  $\text{Cs}^+$  (originally present at the 10 ppm level) (ref. 14). Two features of this system are noted. First, it was necessary to design a ligand with a  $\text{Cs}^+$  binding constant large enough to remove  $\text{Cs}^+$  to ppb levels. Second, efficient separation of trace amounts of  $\text{Cs}^+$  (ppm) from large amounts of  $\text{Na}^+$  and  $\text{K}^+$  was required. The  $\text{Na}^+$  was present at molar levels,  $10^4$  to  $10^5$  times the concentration of  $\text{Cs}^+$ , while the  $\text{K}^+$  was present at  $10^3$  times the  $\text{Cs}^+$  concentration. The accomplishment of these two tasks required sophisticated design and synthesis procedures and resulted in proprietary products capable of selectively removing trace amounts of  $\text{Cs}^+$  from large amounts of  $\text{Na}^+$  over a wide pH range from highly acidic to highly basic solutions.

The removal of  $\text{Sr}^{2+}$  and  $\text{Pb}^{2+}$  from radioactive INEL waste solutions has been described (ref. 14). These cations were effectively removed from the solutions using two SuperLig® materials, one being selective for  $\text{Sr}^{2+}$  and the other for  $\text{Pb}^{2+}$ .

To test the volume reduction possible with the SPE system, 2.26 g  $\text{Cs}^+$  at the 6 ppm level was removed from 360 L of simulated nuclear waste solution (ref. 14,15). A laboratory scale Empore™ cartridge system containing a SuperLig® material was used at a flow rate of  $8 \text{ L} \cdot \text{min}^{-1}$ . The  $\text{Cs}^+$  was eluted in 0.25 L giving a volume reduction of 99.93% in a single pass.

### Anion Separations

The selective removal of trace amounts of anions either from industrial streams or for analysis has not received the attention given to cations. An example of selective anion removal is provided by AnaLig™ HA-01 which is able to selectively remove  $\text{Cl}^-$  from solution (ref. 24). In a typical experiment,  $\text{Cl}^-$  at concentrations of either 1000 or 10 ppm in 0.015 M  $\text{H}_2\text{SO}_4$  was removed selectively at the 97-99 % level. Selective removal of 1000 ppm  $\text{Cl}^-$  in the presence of 0.15 M  $\text{HNO}_3$  was also accomplished at the 99.6% level. It is seen that  $\text{Cl}^-$  is removed quantitatively and selectively from the indicated matrix.

## CONCLUSIONS

Materials have been developed that are capable of highly selective separations of trace amounts of a variety of cations and anions from aqueous solutions. These solutions include those which are highly acidic, highly basic, and composed of high concentrations of potentially interfering salts. The materials, termed SuperLig® and AnaLig™ operate in either fixed bed column or Empore™ membrane modes. Kinetics of removal is rapid, large volumes of dilute solutions can be treated on industrial scales, and large volume reductions can be achieved. The AnaLig™ materials are used

in either mode for ion separations, concentration, and subsequent analysis. The procedure has its basis in the ability to design and synthesize ligands of high selectivity for the ion(s) of interest over other similar competing ions usually present in much higher concentrations. In addition, the ligand must have high enough affinity for the ion of interest to bind it at the ppb/ppt level.

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