



## A lead-selective extraction chromatographic resin and its application to the isolation of lead from geological samples

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### Abstract

A novel extraction chromatographic resin comprised of a 0.75 M solution of the macrocyclic polyether bis-4,4'(5')-[*tert.*-butylcyclohexano]-18-crown-6 in isodecanol supported on an inert, polymeric substrate for the separation and preconcentration of lead from acidic media is described. The material is shown to retain lead efficiently and selectively over a wide range of nitric acid concentrations. Sorbed lead is readily recovered using any of a variety of complexing agents. The resin is demonstrated to be sufficiently stable to handle large sample volumes or to permit reuse. Application of the resin to the isolation of lead from geological samples for subsequent mass spectrometric determination of isotopic ratios is described.

*Key words:* Chromatography; Mass spectrometry; Extraction resin; Geological samples; Lead

### 1. Introduction

The potential adverse human health effects associated with exposure to lead have long been recognized [1-3]. Accordingly, there has been considerable interest in the development of methods for its determination in various biological and environmental samples [4-6]. The determination of individual lead isotopes or of isotopic

ratios in various samples has also been of frequent interest. Lead-210 and its radioactive decay products (e.g., <sup>210</sup>Bi and <sup>210</sup>Po), for example, have served as valuable tracers for monitoring atmospheric, oceanic, and terrestrial processes [7]. Similarly, lead isotope ratio measurements (e.g., <sup>206</sup>Pb/<sup>207</sup>Pb) have permitted the identification of the source of lead contamination in a variety of samples, ranging from household dust to the blood of children [8,9], and are of great interest in isotope geology [10], ore prospecting [11], and archaeological science [12]. Although several extremely sensitive methods exist for lead quantitation (e.g., graphite furnace atomic absorption for total lead, thermal ionization mass spectrometry

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(TIMS) for individual isotopes), the complexity of many sample matrices can preclude their direct application. As a result, an important step in many lead determinations is an initial separation and/or preconcentration, both to free it from inert matrix constituents and to reduce the potential for interference.

A variety of methods have been proposed to effect this separation and preconcentration, among them solvent extraction [13], ion-exchange [14], extraction chromatography [15], precipitation [16] and combinations thereof [7]. In many instances, however, these methods suffer from one or more drawbacks which limit their utility. Solvent extraction, for example, is far too cumbersome for routine use on large numbers of samples. Similarly, the lack of selectivity of conventional ion exchange resins complicates separations. Moreover, these methods are typically ineffective for highly acidic samples.

Earlier work in this laboratory directed at the development of improved methods for the removal and recovery of strontium-89 and -90 from nuclear waste solutions has led to a novel extraction chromatographic material (Sr · Spec<sup>TM</sup>) for the separation and preconcentration of radiostrontium from aqueous solutions containing a wide range of nitric acid concentrations (1–8 M). Recently, this material, which is comprised of a solution of a macrocyclic polyether in 1-octanol, has also been shown to exhibit extremely strong retention of lead under a wide range of solution conditions [17], too strong, in some instances, for convenient stripping. In an effort to develop an extraction chromatographic resin which exhibits satisfactory lead retention from nitric acid-containing aqueous phases yet which permits ready removal of sorbed lead, we have examined lead uptake by a modified version of the Sr · Spec<sup>TM</sup> resin based upon a higher molecular weight alcohol. In this report, we present a systematic evaluation of the selectivity of this new material for lead over selected elements and of the effect of macro levels of several elements on lead retention. In addition, we examine the elution behaviour of a variety of common metal ions on a column of this material and compare the effectiveness of various stripping agents for the re-

moval of sorbed lead. Finally, we describe the application of this new material to the mass spectrometric determination of lead isotopes in geological samples.

## 2. Experimental

### 2.1. Reagents

The crown ether, bis-4,4'(5')-[*tert.*-butylcyclohexano]-18-crown-6 (abbreviated as DtBu-CH18C6), was obtained from Parish Chemical Co. (Orem, UT) and purified via recrystallization from methanol. Nitric acid was Ultrex II grade (J.T. Baker, Phillipsburg, NJ). All water was obtained from a Milli-Q2 system. Unless otherwise noted, all other reagents were A.C.S. reagent grade and were used as received.

### 2.2. Procedures

#### *Preparation of extraction chromatographic resin*

The extraction chromatographic material was prepared by impregnating Amberchrom<sup>TM</sup> CG-71md resin (Supelco, Bellefonte, PA) with a 0.75 M solution of DtBuCH18C6 in isodecanol using a procedure such as that described previously [18]. The resultant lead-selective chromatographic resin is now commercially available as Pb · Spec<sup>TM</sup> (for lead specific) from EICrom Industries (Darien, IL).

#### *Determination of weight distribution ratios and column characteristics*

Radiochemical experiments were performed using the tracers and methods described in a previous report [17]. The activity levels employed (typically  $10^4$  to  $10^6$  cpm total) were chosen both to simplify handling of the radiotracers involved and to yield acceptable counting statistics in a reasonable time (< 30 min per sample). A detailed description of the measurement of weight distribution ratios, column capacity factors, and matrix effects has been given previously [17]. Column preparation and characterization were performed as outlined in an earlier report [17].

*Elution behaviour of selected elements*

The elution behaviour of a number of cations on the Pb·Spec<sup>TM</sup> resin was evaluated by introducing to a column of the material (bed volume = 1.0 ml; bed height = 2.5 cm) a 600  $\mu$ l portion of a multi-element stock solution consisting of more than two dozen metal ions in 1 M nitric acid. (A detailed description of the solution composition can be found in Ref. 19.) The elements included were selected because of their presence in various environmental or biological samples or because of literature indicating their interaction with 18-crown-6-based macrocycles [20]. The sample was then eluted with 0.1 M nitric acid and the eluent collected in a series of 6.35 ml [ca. 10 free column volume (FCV)] aliquots until approximately 60 FCV had been gathered. The elutriant was then changed to 0.1 M ammonium oxalate and ca. 10 FCV were again collected. A portion of each of these fractions was then subjected to analysis by ICP-AES [21] or atomic absorption. The elution behaviour of various alkali and alkaline earth elements was similarly determined using a second stock solution containing only these elements. The composition of this solution was such as to permit ready detection of each element by ICP-AES or atomic absorption while not exceeding 5% of the column capacity (Table 1). Flow rates were maintained at 1–2 ml cm<sup>-2</sup> min<sup>-1</sup> throughout.

*Stripping of sorbed lead*

To compare the effectiveness of various stripping agents for the removal of lead from a Pb·Spec<sup>TM</sup> column, an aliquot of a <sup>210</sup>Pb tracer was applied to the column and the column rinsed with ca. 60 FCV of 0.1 M nitric acid to simulate removal of matrix constituents. The elutriant was then changed to any of a variety of stripping agents (e.g., 0.1 M ammonium oxalate solution) and a series of 0.5–1 FCV aliquots of column effluent were collected until either no appreciable lead was detected or 100 FCV had been reached.

*Resin stability*

To evaluate the stability of the Pb·Spec<sup>TM</sup> resin, the elution profile of a <sup>85</sup>Sr tracer (a conve-

Table 1  
Characteristics of lead-selective extraction chromatographic material and packed columns

|                                    |  |
|------------------------------------|--|
| <i>Bulk material</i>               |  |
| Stationary phase                   | 0.75 M DtBuCH18C6 in isodecanol ( $\rho = 0.917$ g/ml) |
| Support                            | Amberchrom <sup>TM</sup> CG-71                         |
| Particle size                      | 50–100 $\mu$ m   |
| Extractant loading                 | 40% (w/w)  |
| Density of extractant-loaded beads | 1.16 g/ml.   |
| <i>Packed columns</i>              |  |
| $V_s$ , ml/ml of bed               | 0.16   |
| Bed density (g/ml)                 | 0.37   |
| $V_m$ , ml/ml of bed (also FCV)    | 0.65 (Cs-137 breakthrough)                             |
|                                    | 0.68 ( $V_{bed} - V_{resin}$ )                         |
| $V_s / V_m$                        | 0.24   |
| Capacity                           |  |
| calculated, mg Pb/ml of bed        | 24.86  |
| experimental, mg Pb/ml of bed      | 20.5   |

nient gamma-emitting stand-in for lead) was measured on a new Pb·Spec<sup>TM</sup> column using 1 M nitric acid as the elutriant. After elution was complete, the column was rinsed with a large volume (1000–2000 FCV) of deionized water and reconditioned with 1 M acid. The strontium elution profile was then remeasured. Changes in the location of the peak maximum and in peak width were taken as indications of a change in the condition of the column.

*Blank minimization for geological samples*

To achieve the sub-nanogram blanks required in the isolation of lead from geological samples for thermal ionization mass spectrometry, all experiments involving such samples were performed in better than Class 100 chemical workstations located inside a suite of Class 1000 overpressured clean rooms. For the same reason, all chemistry was carried out using Teflon–FEP<sup>TM</sup> ion-exchange columns and Teflon–PFA<sup>TM</sup> vessels (Saville<sup>TM</sup>, Minnetonka, MN). Ammonium carbonate was chosen for the removal of sorbed lead from the Pb·Spec<sup>TM</sup> columns (vide infra). Because the purest available form of this reagent (Normatom<sup>TM</sup> aqueous ammonium carbonate) was found to contain unacceptable levels of lead, however, a preliminary purification was carried

Table 2  
Elution behaviour of various elements on the lead-selective resin <sup>a</sup>

| Element | Percent of element found in FCV number |       |       |       |                        |       |       |
|---------|--|-------|-------|-------|------------------------|-------|-------|
|         | 0.1 M HNO <sub>3</sub>                 |       |       |       | 0.1 M AOX <sup>b</sup> |       |       |
|         | 1–10                                   | 11–20 | 21–30 | 31–40 | 41–50                  | 51–60 | 61–70 |
| Li      | 100                                    |       |       |       |                        |       |       |
| Na      | 96                                     | < 1   | < 1   | 1     | < 1                    | < 1   | < 1   |
| K       | 100                                    | –     | –     | –     | –                      | –     | –     |
| Rb      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Cs      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Mg      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Ca      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Sr      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Ba      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Al      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Cr      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Mn      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Fe      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Co      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Ni      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Cu      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Zn      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Y       | 100                                    | –     | –     | –     | –                      | –     | –     |
| Zr      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Mo      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Ru      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Rh      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Pd      | 58                                     | –     | 24    | 18    | –                      | –     | –     |
| Ag      | 100                                    | –     | –     | –     | –                      | –     | –     |
| Cd      | 100                                    | –     | –     | –     | –                      | –     | –     |
| La–Eu   | 100                                    | –     | –     | –     | –                      | –     | –     |

<sup>a</sup> Column parameters: particle size = 50–100  $\mu\text{m}$ ; bed volume = 1.0 ml; height = 2.5 cm; 1 FCV = 0.66 ml; load solution volume = 0.60 ml; load solution contained 0.1 M oxalic acid to solubilize zirconium.

<sup>b</sup> AOX = ammonium oxalate.

out using Diphonix<sup>TM</sup> (EiChroM Industries, Darien, IL), a new chelating cation exchange resin capable of selectively removing a wide range of transition and post-transition elements [including Pb(II)] from solutions containing high salt concentrations [22,23]. Briefly, a rigorously pre-cleaned Teflon–FEP<sup>TM</sup> ion-exchange column (6 mm i.d.; 15 ml reservoir) was packed with Diphonix<sup>TM</sup> to a height of 27 cm (corresponding to a bed volume of  $\sim 7.63$  ml). Traces of lead were removed from the column by passing through 95 ml of a 1 M solution of Ionquest-201 (Albright and Wilson, Richmond, VA) at a rate of 0.5 ml/min. The last 10 ml of solution were left in the column overnight. The column was then eluted with 83 ml of 3 M hydrochloric acid and

rinsed with  $\sim 10$  ml of water to pH 5. The column was then preconditioned with 14 ml of 2 M ammonium chloride, followed by 36 ml of 2 M isothermally distilled ammonia. Next, 14 ml of 1 M ammonium carbonate (Normatom<sup>TM</sup>) were passed through the column and discarded. An additional 100 ml portion was then passed through and collected. From this purified material, a working solution of purified 0.2 M ammonium carbonate was prepared by dilution with Milli-Q water.

Purification of the Pb·Spec<sup>TM</sup> resin supplied by EiChroM (50–100  $\mu\text{m}$  “Pb Spec SPS”) to remove traces of lead was also found to be necessary to achieve the required blank levels. Advantage was taken of the ability of sulfuric acid to

strip lead from the resin (see Table 3), since this reagent can be obtained in a very pure state. Repeated batch cleaning of the resin was carried out with 0.2 M sulfuric acid (Romil/Seastar) in closed Teflon-PFA<sup>TM</sup> vessels, stirred with Teflon<sup>TM</sup>-enclosed stirrer bars on a magnetic stirrer plate.

#### Lead determination in ore samples by TIMS

For the analysis of ore samples by TIMS, complete sample dissolution was achieved by treating a 1 g portion of each ore with nitric and hydrochloric acids in succession in closed Teflon-PFA<sup>TM</sup> vessels in a microwave oven (CEM<sup>TM</sup> Ltd., Buckingham) [24]. The solute was converted to the nitrate form by two successive evaporations with 0.5 ml portions of 3 M nitric acid. The residue was then dissolved in 3–6 M nitric acid.

For the isolation of lead from the dissolved ore samples, batch-cleaned Pb·Spec SPS<sup>TM</sup> was packed into a 0.24 cm i.d. Teflon-FEP<sup>TM</sup> ion-exchange column having a porous polyethylene frit and a 3 ml reservoir to yield a 0.14 ml bed. The resin was further cleaned by passing through 20 column volumes of 0.2 M sulfuric acid, then leav-

ing the column to soak overnight in this reagent. The column was then washed with water (four 0.2 ml aliquots) to neutrality, then with 0.5 ml of 3 M nitric acid. The centrifuged sample solution (in 3–6 M nitric acid) was then loaded onto the column. The loaded resin was washed with five 0.5 ml aliquots of 3 M nitric acid to remove matrix constituents. This was followed by four water washes (0.2 ml each) to remove nitric acid and raise the pH of the column effluent to 4, thereby facilitating lead stripping. Sorbed lead was then removed from the column with three 1 ml portions of 0.2 M ammonium carbonate (~33 FCV) and the column effluent collected in a Teflon-PFA vessel. The strip solution was evaporated to dryness and the ammonium carbonate sublimed away by heating the vessel in a heating block maintained at 155°C. Upon completion of the sublimation, a drop of 8 M nitric acid was added to the vessel (still at 155°C) and the resultant solution taken to dryness to eliminate any trace of organic matter and to convert the sample to the nitrate form. If necessary, this treatment was repeated a second time. Finally, the sample was taken up in 4  $\mu$ l of 0.1 M nitric acid and loaded with 1  $\mu$ l of 1 M phosphoric acid and 2  $\mu$ l of silica gel [25] onto the center of a zone-refined rhenium filament for mass spectrometry.

The yield of this method was estimated using a synthetic ore sample containing 13% copper and 12% iron. Specifically, a 1 g sample of this synthetic mixture was spiked with 10  $\mu$ g of the NIST Pb Isotopic Standard Reference Material (SRM) 981 and subjected to the above-described dissolution/separation procedures. The recovery of lead was evaluated via isotope dilution mass spectrometry after spiking the eluate from the Pb·Spec<sup>TM</sup> column with highly enriched <sup>207</sup>Pb.

#### 2.3. Apparatus

For thermal ionization mass spectrometry, a modified VG Isotech (Middlewich) Isolab 54 computer-controlled three-stage (E–B–E) mass spectrometer equipped with seven Faraday collectors and a Daly ion counting detector system was used. The instrument was used in the static multicollector mode [26].

Table 3  
Efficiency of lead stripping from a Pb·Spec<sup>TM</sup> column by selected reagents

| Stripping agent <sup>a</sup>   | Peak maximum<br>(FCV) | Peak width <sup>b</sup><br>(FCV) | Total elution volume <sup>c</sup><br>(FCV) |
|--------------------------------|-----------------------|----------------------------------|--|
| Sulfuric acid                  | 4.0                   | 2.5                              | 8.5  |
| Ammonium oxalate<br>(pH 6.4)   | 1.7                   | 0.4                              | 2.7  |
| Ammonium sulfate<br>(pH 6.0)   | 6.0                   | 13                               | 30   |
| Ammonium tartrate<br>(pH 6.7)  | 2.0                   | broad                            | –  |
| Ammonium citrate<br>(pH 5.1)   | 2.0                   | 1.5                              | 3.5  |
| Ammonium carbonate<br>(pH 9.1) | 7.0                   | broad                            | –  |
| EDTA (pH 7.5)                  | 1.3                   | 0.3                              | 2.0  |
| Glycine (pH 9.5)               | 2.0                   | 0.5                              | 4.0  |
| DTPA (saturated; pH 7.5)       | 2.0                   | 0.5                              | 3.5  |

<sup>a</sup> 0.1 M solution unless otherwise noted.

<sup>b</sup> At 1/e of the peak maximum.

<sup>c</sup> At 1% of peak maximum.

### 3. Results and discussion

#### 3.1. Acid dependency of metal ion sorption / resin selectivity

In an earlier report [27], it was demonstrated that the extraction of strontium by dicyclohexano-18-crown-6 into any of a wide range of oxygenated, aliphatic solvents from nitric acid is directly related to the solubility of water in the solvent. For a given solvent family (e.g., alcohols), this solubility, in turn, was found to decrease with increasing solvent molecular weight. Thus, strontium extraction was found to decrease when, for example, *n*-hexanol was replaced by *n*-octanol as the organic solvent. If this correlation applies to the extraction of other metal ions by crown ethers, it would be expected that the sorption of lead by a crown ether-based extraction chromatographic resin could be reduced as desired simply by changing the solvent to one with a higher molecular weight. In fact, as anticipated, a resin pre-

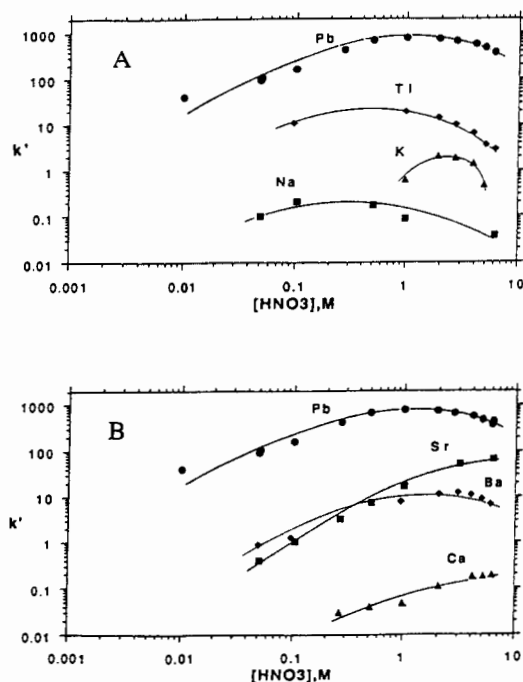


Fig. 1. Nitric acid dependency of  $k'$  for selected monovalent (A) and divalent (B) metal ions on Pb-Spec<sup>TM</sup> resin. ( $Cs^+$  retention is not measurable under the experimental conditions.)

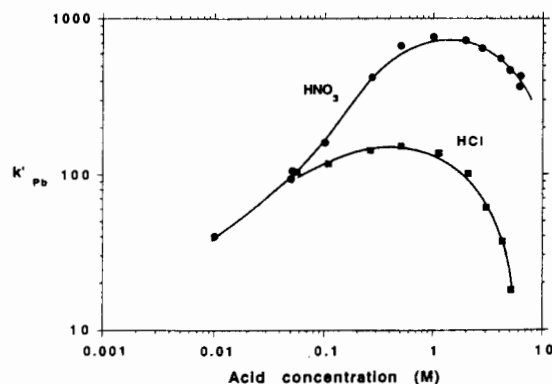


Fig. 2. Nitric acid and hydrochloric acid dependencies of  $k'$  for lead on Pb-Spec<sup>TM</sup> resin.

pared from a 0.75 M solution of DtBuCH18C6 in isodecanol yields  $D_w$  values for lead as much as four times lower than those obtained with Sr Spec<sup>TM</sup> [17], prepared using *n*-octanol as the diluent. Table 1 summarizes the essential features of this new resin.

Fig. 1 shows the nitric acid dependence of the capacity factor,  $k'$ , for selected metal ions on the Pb Spec<sup>TM</sup> resin. (These ions were chosen on the basis of literature data indicating the possibility of strong interaction with 18-crown-6-based macrocycles [20] or, as in the case of sodium, because of their presence in macro quantities in many biological and environmental samples.) As can be seen,  $k'_{Pb}$  exceeds that of each of the other metal ions by a wide margin over the entire range of acidities examined. In fact, in several instances, (e.g.,  $Cs^+$  and  $Na^+$ ), the ion is essentially unretained under typical column loading conditions (0.1–3 M  $HNO_3$ ). The excellent selectivity of the resin over sodium is especially significant given the ubiquitousness of this element. Also significant is the low capacity factor of the resin for calcium, an element present in substantial quantities in many biological and environmental samples.

Lead is also readily sorbed from hydrochloric acid solution (Fig. 2). Although the maximum  $k'_{Pb}$  observed is approximately a factor of five lower than that obtained from nitric acid, lead retention is still more than adequate for many purposes.

Table 2 summarizes the elution behaviour of a variety of different elements on a 1 cm<sup>3</sup> bed volume column packed with the Pb·Spec<sup>TM</sup> chromatographic resin. The data in this table indicate that the resin is quite selective for lead. In fact, under the load and rinse conditions, only lead exhibits significant retention. These results are consistent with the data presented in Fig. 1.

### 3.2. Matrix effects

It is well known that even elements which exhibit modest retention on an extraction chromatographic column may, if present in sufficiently large quantities (so as to approach the column capacity), reduce the sorption of a more strongly retained species. Sodium, potassium, calcium, iron, and aluminum are the major constituents of many environmental and biological samples [17]. The effect of increasing amounts of several of these matrix constituents on  $k'_{\text{Pb}}$  was therefore measured to establish the level of these constituents which could be tolerated without appreciably diminishing lead sorption. (Iron and aluminum were omitted because their extractability by DtBuCH18C6 has been shown to be less than that of sodium and calcium [28].) The results indicate that sodium and calcium concentrations of even 1 M produce no measurable effect upon  $k'_{\text{Pb}}$  from 1 M nitric acid. Concentrations of potassium ion exceeding 0.05 M, however, produce a significant decrease in lead sorption (Fig. 3). Nonetheless, even at 1 M K<sup>+</sup>, more than 80 FCV of 1 M nitric acid are required to reach the peak maximum in lead elution. Note that these results parallel those observed for strontium on the Sr·Spec<sup>TM</sup> resin [17]. This fact, along with the results of our earlier studies of the effect of macro levels of ammonium ion on Sr·Spec<sup>TM</sup> [17], suggests that high concentrations (> 0.1 M) of ammonium ion will also reduce lead sorption on the Pb·Spec<sup>TM</sup> resin, although not to the extent observed with potassium ion.

### 3.3. Stripping of sorbed lead

It is clear from the data presented in Fig. 1 that sorbed lead will not be efficiently stripped

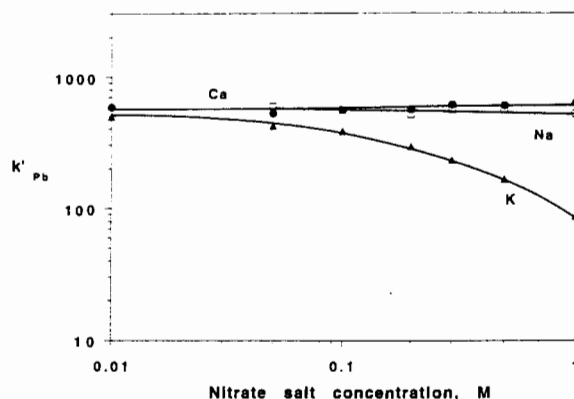


Fig. 3. Effect of matrix constituents on lead sorption by Pb·Spec<sup>TM</sup> resin.

from a Pb·Spec<sup>TM</sup> column simply by reducing the nitric acid concentration in the mobile phase, as lead is reasonably well retained from even 0.01 M nitric acid. A variety of reagents were therefore evaluated for possible use as stripping agents. Table 3 summarizes the results obtained with a number of these reagents, expressed as the number of free column volumes to the peak maximum ( $k'$ ) and the width of the peak at  $1/e$  of the peak maximum, both indicators of the efficiency of lead removal. The results show that satisfactory stripping of sorbed lead can be achieved with any of several of them, including 0.1 M solutions of ammonium oxalate, ammonium citrate, or glycine. Of these, ammonium oxalate solution is especially useful, as in addition to providing efficient stripping, it can be readily removed via sublimation once the column effluent has been evaporated to dryness. Note however, that this reagent is only suitable for use with trace amounts of lead because of the low solubility of lead oxalate [29]. Note also that under certain circumstances, the use of ammonium carbonate is preferred, despite its poor performance relative to other stripping agents (see below). Removal of macro concentrations of lead is probably best accomplished using a solution of DTPA or ammonium citrate.

### 3.4. Resin stability

Fig. 4 summarizes the results of studies of the stability of the resin to prolonged water washing

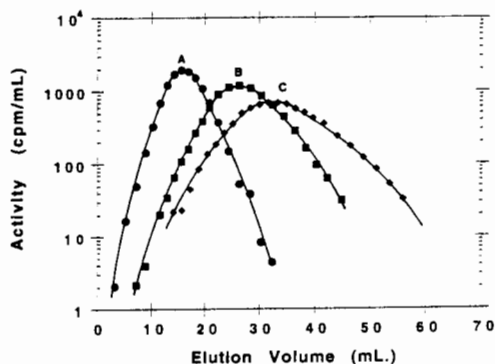


Fig. 4. Effect of column washing on strontium-85 elution on Pb-Spec<sup>TM</sup> resin.

(i.e., large sample volumes). Curve A depicts the elution profile for a <sup>85</sup>Sr tracer on a new Pb Spec<sup>TM</sup> column, while curves B and C show the profiles obtained on the same column after ca. 1000 and 2000 FCV of water washing, respectively. As can be seen, column washing is accompanied by a pronounced shift in the peak maximum to higher elution volumes, an observation consistent with loss of diluent (here, isodecanol) and a concomitant increase in the concentration of the crown ether in the stationary phase. This shift is accompanied by an increase in peak width (Table 4). The column efficiency, however, as reflected in the number of theoretical plates present [30], is unaffected by 1000 FCV of washing and is reduced only slightly by more extensive washing. It is worth noting here that ~ 1000 FCV

Table 4  
Effect of column washing on the elution behaviour of <sup>85</sup>Sr on Pb-Spec resin<sup>a</sup>

| Wash volume (FCV) | Peak maximum (ml) | Peak width <sup>b</sup> (ml) | <i>N</i> <sup>c</sup> |
|-------------------|-------------------|------------------------------|-----------------------|
| 0                 | 15.5              | 9.0                          | 23.5                  |
| 1000              | 26.4              | 15.4                         | 23.5                  |
| 2000              | 33.2              | 21.2                         | 19.6                  |

<sup>a</sup> Wash solution = deionized water; 1 FCV = 0.66 ml; <sup>85</sup>Sr tracer eluted with 1 M HNO<sub>3</sub>; *T* = 23°C; flow rate = 1–2 ml cm<sup>-2</sup> min<sup>-1</sup>.

<sup>b</sup> At 1/*e* of the peak maximum.

<sup>c</sup> Calculated from  $N = 8 (V_{mr} / W)^2$ , where  $V_{mr}$  is the elution volume to peak maximum and  $W$  is the peak width at 1/*e* of the peak maximum (from Ref. 30).

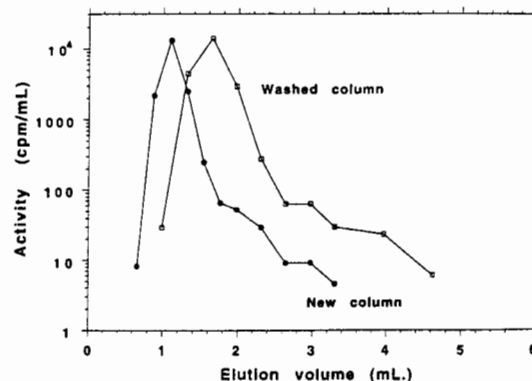


Fig. 5. Effect of column washing on lead stripping from Pb-Spec<sup>TM</sup> resin.

of washing leads to a significant (~ 33%) reduction in column efficiency for the analogous extraction chromatographic resin employing the more water-soluble 1-octanol as the diluent [31].

As a further check of the effect of column washing upon resin performance, the stripping of lead from a column of unused Pb Spec<sup>TM</sup> and from a column of the same resin washed with ~ 2000 FCV of water were compared. As shown in Fig. 5, stripping is only slightly more difficult from the washed column, with elution essentially complete by 5 ml. Taken together then, the results of these column washing studies demonstrate clearly that the Pb Spec<sup>TM</sup> resin possesses adequate stability to handle substantial sample volumes or to permit reuse of the column, provided of course, that the resin is washed carefully between runs to eliminate any possibility of cross-contamination.

### 3.5. Application of Pb Spec<sup>TM</sup> to the isolation of lead from geological samples for thermal ionization mass spectroscopy (TIMS)

Methods for the determination of either the concentration of lead or its precise isotopic composition in environmental, geological, or archaeological samples frequently require that a pure lead fraction (i.e., one free of interfering and extraneous matrix elements) be isolated from the sample for analysis. For example, in lead isotopic



analysis by thermal ionization mass spectrometry (including isotope dilution assays), chemical impurities must be removed from the lead because they may cause a severe reduction in ionization efficiency, variable isotope fractionation in the ion source, and instability in the measured ion beams. The isolation of lead from such samples can be particularly demanding because its concentration is frequently low (micrograms or less per gram of sample) and because the matrix composition is variable and often quite complex. Thus, an acceptable separation method must yield excellent decontamination from the macro constituents of typical samples and must perform satisfactorily despite variations in sample composition. The results presented in Fig. 1a and b and in Table 2 suggest that Pb·Spec<sup>TM</sup> should be well-suited to these demands.

The utility of Pb·Spec<sup>TM</sup> was evaluated by examining its performance in the isolation of lead from samples of one of the most difficult metallic ores we have encountered, a Cu–Ni–Fe–As–S ore containing tens of percent of each of these elements but only a few ppm lead. Although a number of procedures have been described for the isolation of lead from ordinary silicate rocks and minerals for TIMS, among them methods based on electrodeposition [32,33] or chromatography using conventional resins [34–36], these procedures yield unsatisfactory results (i.e., insufficient lead purity, low lead yields, and high blank values) for certain matrices, among them metal ores containing large amounts of iron, copper, arsenic and nickel. In contrast, application of the Pb·Spec<sup>TM</sup>-based procedure described above to the isolation of lead from these ore samples yielded a lead fraction free of any traces of organic matter and without detectable quantities of copper, nickel, iron, arsenic, or sulfur, the chief constituents of these ores. In addition, lead recoveries were both high and remarkably consistent, ranging from 90 to 95%.

The blank levels associated with the procedure were also well within acceptable limits. Table 5 summarizes the lead contents of the reagents employed in the ore preparation and analysis. From these results, the blank associated with the dissolution of a 1 g ore sample can be estimated

Table 5

Lead content of reagents used in the processing of geological samples

| Reagent   | Lead content (pg/g) <sup>a</sup> |
|---|----------------------------------|
| Water, Milli-Q  | 7.2                              |
| Water, doubly distilled in Teflon–FEP <sup>TM</sup>                 | 4.4                              |
| Water, Ultrex II  | 9.5                              |
| Nitric acid, 8 M, doubly distilled in Teflon–FEP <sup>TM</sup>      | 12.2                             |
| Hydrochloric acid, 6 M double distilled in Teflon–FEP <sup>TM</sup> | 12.7                             |
| Sulfuric acid, 97.5%, w/w (Romil/Seastar)                           | < 10                             |
| Ammonium carbonate, 1 M, Normatom <sup>TM</sup> , unpurified        | 4765                             |
| Ammonium carbonate, 1 M, Normatom <sup>TM</sup> , Diphonix treated  | 23                               |

<sup>a</sup> From these values, lead concentrations of 7.3 pg/g and 8.1 pg/g, respectively, can be calculated for the 3 M nitric acid and the 0.2 M ammonium carbonate solution actually employed in the isolation of lead from ore samples.

as 60–120 pg lead. The lead blank associated with the column separation step (including the final sublimation, evaporation, and TIMS filament loading steps) was measured using isotope dilution by substituting a small volume (6 ml) of <sup>207</sup>Pb-spiked 3 M nitric acid for the ore sample solution and following the procedure outlined above beginning with the loading of the sample onto the Pb·Spec<sup>TM</sup> column. The blank so obtained ranged from 240–380 pg lead. Of this, the acids, water, and strip solution used contribute, at most, 50 pg lead. (Some reduction in this contribution could, of course, be achieved by further purification of the acids and ammonium carbonate. A greater reduction, however, could probably be achieved by further purification of the Pb·Spec<sup>TM</sup> resin, perhaps by stripping the column with pre-purified EDTA, glycine, or ammonium oxalate. For smaller samples, lower blanks could be achieved simply by reducing the size of the column and the volumes of reagents used.) These results indicate that the total procedural blank for the method, as presently established, is less than 500 pg lead for a 1 g ore sample. If the sample actually contains 0.5 ppm

lead, a procedural blank of this magnitude represents only a 0.1% contribution to the total measured lead concentration. For such a sample, the lead contributed by the blank would not cause any measurable alteration in the experimentally determined sample composition as measured by TIMS.

It is important to note that ammonium carbonate solution was chosen for the removal of sorbed lead from the Pb · Spec<sup>TM</sup> column for these runs, despite its poor performance relative to several other reagents in our earlier stripping experiments (Table 3). This choice was prompted by the ease with which ammonium carbonate can be purified and by the comparatively low temperature required for its sublimation following stripping (150°C). In contrast, ammonium oxalate cannot be sublimed away at a temperature below the melting point of Teflon–PFA<sup>TM</sup> [37]. Similarly, sulfuric acid cannot be used since the temperature required to evaporate it is outside of the working range of these vessels (< 260°C).

#### 4. Conclusions

An extraction chromatographic resin comprised of a solution of bis-4,4'(5')-[*tert*-butylcyclohexano]-18-crown-6 in isodecanol supported on an inert polymeric substrate provides a simple and effective means for the separation and pre-concentration of lead from acidic aqueous solution. Lead is efficiently sorbed by the resin from a wide range of either nitric or hydrochloric acid concentrations and its removal from the resin can be effected using any of a variety of stripping agents. Although several other ions (e.g., Sr<sup>2+</sup>) are sorbed to varying degrees under certain conditions, the differences in the resin capacity factors for these ions are sufficient to permit isolation of only lead. Most commonly encountered cations (e.g., Ca<sup>2+</sup>, Fe<sup>3+</sup>, Na<sup>+</sup>) are essentially unretained by the resin, making it well suited to the isolation of lead from a variety of sample types. In particular, it has been demonstrated that this new resin is highly efficacious for the isolation of purified lead from difficult geological matrices for thermal ionization mass spectrometry.

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