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RADIUM SEPARATION THROUGH COMPLEXATION BY AQUEOUS CROWN ETHERS AND ION EXCHANGE OR SOLVENT EXTRACTION *

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by

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ABSTRACT

The effect of three water-soluble, unsubstituted crown ethers (15-crown-5 (15C5), 18-crown-6 (18C6) and 21-crown-7 (21C7)) on the uptake of Ca, Sr, Ba and Ra cations by a sulfonic acid cation exchange resin, and on the extraction of the same cations by xylene solutions of dinonylnaphthalenesulfonic acid (HDNNS) from aqueous hydrochloric acid solutions has been investigated. The crown ethers enhance the sorption of the larger cations by the ion exchange resin, thereby improving the resin selectivity over calcium, a result of a synergistic interaction between the crown ether and the ionic functional groups of the resin. Similarly, the extraction of the larger alkaline earth cations into xylene by HDNNS is strongly synergized by the presence of the crown ethers in the aqueous phase. Promising results for intra-Group IIa cation separations have been obtained using each of the three crown ethers as the aqueous ligands and the sulfonic acid cation exchange resin. Even greater separation factors for the radium - calcium couple have been measured with the crown-ethers and HDNNS solutions in the solvent extraction mode. The application of the uptake and extraction results to the development of radium separation schemes is discussed and a possible flowchart for the determination of ^{226}Ra/^{228}Ra in natural waters is presented.

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DISCLAIMER

INTRODUCTION

The naturally-occurring radium isotopes, ^{226}Ra ($t_{1/2}$ = 1622 y) and ^{228}Ra ($t_{1/2}$ = 6.7 y), products of the ^{238}U and ^{232}Th series, respectively, are of great environmental concern. ^{226}Ra is, in fact, among the most toxic long-lived alpha emitters present in environmental samples, as well as one of the most widespread (1). For this reason, there has been much interest in the development of improved methods for its determination, as well as for ^{228}Ra, in a variety of sample types (2).

The isolation of radium from complex matrices such as those found in environmental and biological samples generally involves a preconcentration step by repeated co-precipitation with insoluble sulfates, carbonates and phosphates (3). These methods are very time consuming because of the many chemical steps involved. Radium separation methods involving only the use of ion exchange or extraction chromatographic columns without the need of precipitation-based preconcentration steps would greatly simplify analytical procedures for radium determination.

A number of procedures using sulfonic acid-based ion exchangers to sorb alkaline earth cations have been described (3). The selectivity of these material is generally poor, however, and although individual cations can be sequentially eluted using solutions of organic complexants, careful pH control is required.

In our laboratory, we have focused our attention on the possible use of crown ethers for radium separation, taking advantage of the well known size-selective properties of these reagents (4). A similar initiative undertaken previously by us regarding the separation of strontium led to the development of a strontium-selective extraction chromatographic resin which has found wide acceptance in analyses of environmental, biological and nuclear waste samples (5-7).

Although little information on Ra complexation by crown ethers and related compounds is available in the literature (4), a number of works have been published by McDowell et al. on the use of crown ethers as solvent extraction reagents for alkali and alkaline earth cations (8-15), in some cases including Ra (9,15). In these studies, toluene solutions of substituted crown ethers, such as the dibenzo and dicyclohexano derivatives, were used. It was found in these studies that the usually poor extraction of alkaline earth cations by such macrocycles from media containing typical mineral acid anions (e.g., chloride, nitrate and sulfate) was strongly enhanced (synergized) by organophilic sulfonic, phosphoric and carboxylic acids in the organic phase. These organophilic acids act as cation exchangers and, by neutralizing the charge of the extracted cations, allow them to transfer to the organic phase without the mineral acid anion.

In alkaline earth cations separations, good extractability is not the only requirement; selectivity is also needed. In crown ether based systems, selectivity is usually provided by the ring size selection, that is, by matching the ring size with the size of the target cation (16). McDowell et al. (13) showed that the extraction of Sr and Ba by toluene solutions of didodecylnaphthalene sulfonic acid (HDDNS) is strongly synergized by substituted 18-crown-6 derivatives, while the Ca extraction is practically unaffected. Thus, the simultaneous presence in organic solution of a sulfonic acid and a crown ether with the appropriate cavity size can provide a means to both strongly increase the extraction of the larger alkaline earth cations and generate selectivity over calcium. The sulfonic acid alone is well known to exhibit very little selectivity among the alkaline earth cations. Although no data on Ra were reported, one would expect, based on the ionic diameters (17) and crown ether cavity sizes (8), that also extraction of Ra should be synergized by 18-crown-6 or 21-crown-7 derivatives.

The objective of our recent work has been to separate radium from the other Group IIa cations in a single step, using either ion exchange or extraction chromatography, by taking advantage of the synergism between crown ethers and either the sulfonic groups of a strong acid ion exchange resin or an organophilic sulfonic acid dissolved in an organic diluent. In the latter case, solvent extraction studies would be expected to provide the necessary basic data for the development of an extraction chromatographic resin for radium separation.

Some of our results for radium separation using either ion exchange resins or organic solutions of dinonylnaphthalenesulfonic acid (HDNNS) in combination with water-soluble unsubstituted crown ethers have been described in previous reports (18,19). In the present paper, we summarize the most important results of our investigations, with the aim of developing radium separation schemes. A possible flowchart for the determination of ^{226}Ra/^{228}Ra in natural waters is also presented.

It is important to note that a major difference exists between the present study and previous, related investigations (13,15). In previous works, *water-insoluble* benzo- or cyclohexano-substituted crown ethers were used as ligands. These compounds were dissolved in the organic phase along with the sulfonic acid. In the present study, in contrast, we have used only unsubstituted, *water-soluble* crown ethers in combination with organic solutions of the sulfonic acid or with a sulfonic type strong acid cation exchange resin. Our choice was based on the recognition that, because unsubstituted crown ethers are inexpensive and readily available, if synergism between them and the sulfonic acid groups present in the resin or in the organic solution were observed, the likelihood of practical application would be much higher.

EXPERIMENTAL

Materials

The sulfonic acid resin, Bio-Rad™ AG 50W-X8, was obtained in the H^+ form and 100-200 mesh size from Bio-Rad Laboratories (Hercules, CA). The resin was washed extensively, first with 1 M HCl and then with water, on a Büchner funnel and drained under low vacuum aspiration for about 10 minutes. The resin was then stored in a tightly closed bottle. For the determination of its solid content, an air-dried resin aliquot was weighed, dried overnight at 105 °C and weighed again.

The liquid ion-exchanger, dinonylnaphthalenesulfonic acid (HDNNS), was obtained from King Industries (Norwalk, CT) as a 50 % solution in heptane, and purified by ion exchange (20). The resulting material had a purity of 86 %, as measured by acid-base titration in ethanol. Solutions of HDNNS in o-xylene (Aldrich) were prepared based on its neutralization equivalent weight.

The 15-crown-5 and 18-crown-6 were obtained from the Aldrich Chemical Co. (Milwaukee,WI) and used without further purification. The 21-crown-7 was obtained from Pfaltz and Bauer (Waterbury, CT) and was used as received.

The isotopes ^{45}Ca, ^{85}Sr and ^{133}Ba were obtained from Isotope Products Laboratories (Burbank, CA). ^{223}Ra was milked from ^{227}Ac using an extraction chromatographic column containing bis(2-ethylhexyl) phosphoric acid (HDEHP).

All other reagents were of analytical grade and were used without further purification.

Distribution measurements

The measurements of the distribution of the alkaline earth cations between aqueous solutions containing the crown ethers and either the Bio-Rad resin or o-xylene solutions of HDNNS were performed following the procedures and counting techniques reported in detail previously (18,19). For the resin uptake experiments, dry weight distribution ratios, D (mL/g), were calculated as :

$$D = \left(\frac{A_o - A_f}{A_f}\right)\left(\frac{V}{w}\right) \qquad (1)$$

where A_o and A_f are the aqueous phase activity before and after equilibration, respectively, w is the weight of dry resin (g) and V is the volume of the solution (mL). The weight of the dry resin was calculated by correcting the weighed amount of resin used in the experiments with the solid percent values. Duplicate experiments showed that the reproducibility of the D measurements was generally within 5 %, although the uncertainty interval was somewhat higher for the highest D values ($D \geq 10^3$). For the solvent extraction experiments, the distribution ratio, D, was given by the ratio of the concentration of the metal species in the two phases. The reproducibility of these measurements was also within 5 %.

RESULTS AND DISCUSSION

Ion Exchange Experiments

Figure 1 reports the effect of increasing concentrations of 15-crown-5, 18-crown-6 and 21-crown-7 in the aqueous phase (0.5 M HCl) on the uptake of the alkaline earth cations by the sulfonic acid cation exchange resin. In several cases, the data show a remarkable enhancement of uptake, especially for the largest cations investigated. This effect is comparable to those reported previously for the extraction of cations by organic solutions of organophilic acids in the presence of substituted dibenzo and dicyclohexano crown ethers derivatives (8-15). Most likely, the uptake enhancements reported in Figure 1 have the same origin, that is, synergism between the sulfonic acid groups of the resin and crown ether molecules present inside the resin phase. Crown ethers, as neutral molecules, are not rejected by the Donnan potential of the resin.

In Figure 1, all ligands bring about at least some degree of uptake enhancement for the cations, except for Ca, whose uptake is slightly synergized only by 18C6. The effect of the crown ethers on the behavior of Sr, Ba and Ra seems to follow what would be expected based on the match between cavity size and ionic diameters. With 15C5, Sr, Ba and Ra are affected in an almost parallel way, so that their selectivity sequence in the absence of ligand remains practically unchanged, except for a limited crossover between Ba and Ra. The selectivity over calcium is substantially increased, however. Also, the Sr curve remains sufficiently separated from the Ba-Ra couple to make possible a separation of the Ba-Ra couple from Ca and Sr. 18C6 and 21C7 exhibit the strongest effect on the Ba-Ra uptake, as expected from the cavity and ionic size match. 18C6 also enhances the uptake of Sr to a higher degree than 21C7. This is not surprising, given that 18-

crown-6 macrocycles are traditionally the ligands of choice for strontium complexation (5-7).

From the above considerations, it can be deduced that the most promising crown ethers for intra Group IIa cation separations are 15C5 and 18C6. The 21C7 offers a good selectivity for Ra and Ba over Sr at very low crown ether concentration, but it is difficult to synthesize and hence very expensive. If one is interested in separating Ra and Ba from Sr, practically the same separation factor is offered by 15C5, which is more readily available and much less expensive than 21C7. For a relatively easy separation of Sr-Ba-Ra as a group from Ca, which is the single most important separation because of the abundance of Ca in water samples, the ligand of choice should be 18C6, because of its availability, relative low cost, and high efficiency in generating selectivity over calcium even at concentrations as low as 10^{-3} $\underline{M}$.

For purpose of comparison, the data of Figure 1 were obtained at a constant HCl concentration of 0.5 $\underline{M}$. At this acidity, all of the D values are too high for performing practical separations. If one wants to strip only Ca with 18C6, or Ca-Sr with 15C5, from a sulfonic resin with a few column bed volumes of elutriant, the D values must be much lower. Thus, solutions at a higher acidity should be used. It was important, therefore, to know if the resin - crown ether synergism shown in Figure 1 is maintained at higher acidities. Figures 2 and 3 report some uptake data in the form of acid dependencies at three 15C5 and 18C6 concentration levels (0, 0.001 and 0.01 $\underline{M}$). In all cases, the data follow a negative second power dependency, as expected assuming the displacement of two hydrogen ions from the resin by the sorbed cations. These results indicate that the synergism between sulfonic acid groups of the resin and the crown ethers is not affected by high acidities, at least in the investigated range of concentrations.

If the solution from which one wants to separate radium contains a high concentration of calcium ions, the sulfonic acid resin will eventually be saturated with calcium, and the uptake of radium might be negatively affected. To measure the effectiveness of the resin-crown ether system in the sorption of radium from solutions with a high calcium concentration, the uptake of strontium, barium and radium has been measured in the presence of 15C5 and 18C6 and three different HCl concentrations using the calcium form of the Bio-Rad resin. The results are reported in Figures 4 and 5. It appears from the figures that the increased calcium concentration in these systems has only a slight adverse impact on the sorption of the other cations. In fact, the data show that even with complete saturation of the resin with calcium, the uptake of radium and barium cations by the resin is still significant, and is sufficiently high to be of utility in an analytical scheme.

Solvent Extraction Experiments

The synergism between aqueous crown ethers and sulfonic acid groups might be even more pronounced when, instead of a sulfonic resin, an aqueous-immiscible solution of an organic sulfonic acid (a liquid ion exchanger), is used. In solution, the sulfonic groups are not immobilized in a polymer network and are therefore more able to interact with the positively charged metal - crown ether complex. If this hypothesis is correct, one might exploit the enhanced selectivity achieved by using extraction chromatographic resins prepared by impregnating a suitable inert support with a solution of the organic sulfonic acid. The extraction chromatographic resin could then be used for radium separations in the same way as the ion exchange resin.

The synergism between lipophilic sulfonic acids and lipophilic (i.e., substituted) crown ethers in the solvent extraction of alkali and alkaline earth cations has been discussed earlier. In the following, we will deal with synergism in the extraction of alkaline earth cations by o-xylene solutions of dinonylnaphthalenesulfonic acid (HDNNS) from aqueous solutions containing crown ethers. Note that water-soluble crown ethers in contact with a water-immiscible solvent will distribute between the two phases. Unsubstituted crown ethers are reported to transfer to some extent into the organic phase when contacted with toluene (9).

Figure 6 reports the extraction of the alkaline earth cations by a 0.01 F (concentration expressed in formula weight) HDNNS solution in o-xylene at 0.1 M HCl in the aqueous phase. As can be seen, in the presence of both HDNNS and a crown ether, the distribution ratios are at least two orders of magnitude higher than with HDNNS alone, and many orders of magnitude higher than with the crown ethers alone. (The distribution ratios measured with crown ethers alone, under the same experimental conditions are always in the 10^{-3} to 10^{-4} range). A comparison of Figure 6 to Figure 1 shows that the relative positions of the curves for the different cations in each crown ether system are practically the same, with a somewhat higher selectivity for the heavier cations over calcium measured in the case of solvent extraction. The comments made on the data of Figure 1 can, therefore, be extended to the data of Figure 6 as well.

Some of the experiments of Figure 6 were repeated at 1 M HCl and at 0.1 F HDNNS. The data (not reported here for brevity) confirmed the inverse second power dependency of the distribution ratios on the aqueous acidity, as in the resin uptake experiments, and the expected first power dependency on the extractant concentration, which is typical of highly aggregated systems such as HDNNS (21,22).

The results shown in Figure 6 demonstrate that the solvent extraction approach can also be used for intra-Group IIa cation separations. Practical considerations, however, such as the desirability of contacting a large volume of an aqueous sample with a much smaller volume of organic solution without significant solvent loss to the aqueous phase, suggest that it would be desirable to use the solvent extraction approach in an extraction chromatographic mode (23). In this case, the HDNNS would be impregnated into the pores of an inert solid support. The preparation of an HDNNS-based extraction chromatographic resin for radium separation has not yet been attempted. Difficulties that might be encountered in preparing such a resin have been discussed previously (19).

Analytical Procedure for Radium Separation

The data reported in the previous sections can be utilized to develop various procedures for the separation of $^{226}Ra/^{228}Ra$ from environmental samples prior to determination, one of which is schematically outlined in Figure 7. In this procedure, a sulfonic-type strong acid cation exchange resin is used. The procedure, however, can be easily adapted for use of an HDNNS-based extraction chromatographic resin, should this become available in the future. Also, the procedure is only outlined for radium isotopes determination. If strontium isotopes were also to be determined, the analytical scheme could be easily modified along the lines discussed previously (18).

In the procedure described in Figure 7, a 1 L sample of natural water (previously acidified to pH 1 - 2 with HNO_3 for sample preservation) is transferred into a large beaker or Erlenmeyer flask. The acidity of the sample is adjusted to 0.5 M by addition of concentrated HCl. Ammonium citrate and 18-crown-6 are added to the sample up to final concentrations of 0.001 M and 0.002 M, respectively. Ammonium citrate is added to the sample to chelate any thorium(IV) and uranium(VI) present in the sample so that they are not retained by the resin. Several thousand dpm of ^{133}Ba are also added to serve as a yield monitor. According to Figure 1, barium should follow radium throughout the separation scheme. Finally, 5 g of a strong acid cation exchange resin are added to the sample and the solution and the resin are stirred for at least 30 minutes with a magnetic bar. After settling of the resin, most of the solution is decanted to waste and the resin is transferred to a column of appropriate size, where it is rinsed with about 100 mL 0.5 M HCl. The Ra(Ba) is then eluted from the column with about 75 mL of 4 M HNO_3, completing the Ra(Ba) concentration/purification part of the procedure. If only the alpha-emitting ^{226}Ra is to be analyzed, source preparation would begin at this point.

If ^{228}Ra is to be determined as well, an additional column separation is required. The ^{228}Ra assay is performed by quantitative removal and subsequent counting of ^{228}Ac, the direct daughter of ^{228}Ra. This may be done by evaporating the 4 M HNO_3 solution containing the Ra(Ba) to dryness and taking up the residue in few mL of 2 M HNO_3. The sample is then loaded onto a small column packed with TRU Resin (Eichrom Industries, Darien, IL) preconditioned with 2 M HNO_3. Since Ra(Ba) isotopes are not retained on the TRU Resin (24), the sample load solution, along with a few mL of 2 M HNO_3 rinse solution, are collected and retained as the "Ra-226 fraction". This portion of the sample, now in about 10 mL 2 M HNO_3, is ready for source preparation and counting for α-emitting radium isotopes. This fraction may be analyzed in a variety of ways, including radon emanation, alpha spectromety or liquid scintillation counting (25). The ^{228}Ac is stripped from the TRU Resin with about 15 mL 1 M HCl, and the solution labeled as the "Ra-228 fraction". The separation time of ^{228}Ac from ^{228}Ra (taken as the time of the 2 M HNO_3 rinse) must be recorded, since the ^{228}Ac is now unsupported by ^{228}Ra. The ^{228}Ac is prepared for gas flow proportional counting by coprecipitation with CeF_3 and collection of the precipitate on a filter.

The procedure outlined in Figure 7 has been evaluated in a number of tests using as a sample a 0.5 M HCl solution spiked with ^{226}Ra and/or ^{133}Ba. In these experiments, which were performed in a column mode (a more efficient, although perhaps more inconvenient, alternative to the batch mode), no detectable loss of either isotope was observed. Also, the stripping of the two isotopes from the ion exchange column with 2 M HNO_3 was quantitative, and no significant separation of radium from barium occurred. However, during some of the test runs with known amounts of ^{226}Ra and ^{133}Ba, discrepancies between the final yields for the two nuclides were noticed. That is, in every case, the apparent recovery of radium was higher than that of barium. Tests using different amounts of 18-crown-6 and ammonium citrate revealed that some radium-barium separation was occurring during the source preparation for counting (micro-precipitation with $BaSO_4$ prior to alpha spectrometry). The interference was apparently due to small amounts of the 18C6 remaining in the sample after the column separation, which reduced the precipitation yield for barium. Work to correct this minor problem is now in progress.

CONCLUSIONS

The need exists for more efficient and rapid methods for the separation of radium from water samples. New separation procedures can be developed based on the size specific complexation ability of crown ethers for alkaline earth cations, coupled with ion exchange or extraction chromatography.

In this work, we have obtained basic data on the behavior of Group IIa cations with both sulfonic acid-based ion exchange resins and liquid extractants in the presence of water-soluble crown ethers. Our results indicate that the synergism between the water-soluble unsubstituted crown ethers 15-crown-5 (15C5), 18-crown-6 (18C6) and 21-crown-7 (21C7) and the sulfonic acid groups of either strong acid ion exchange resins or liquid ion exchangers such as dinonylnaphthalenesulfonic acid (HDNNS), generates strong enhancement of radium, barium and, in some cases, strontium uptake or extraction. Calcium extraction, on the other hand, is little affected. The enhanced uptake of the larger alkaline earth cations can provide the basis of improved separation and preconcentration procedures for radium analyses in natural water samples. Preliminary tests of one possible procedure have been performed and indicate that radium can be satisfactorily separated and preconcentrated. Work to apply this procedure to actual environmental samples is now underway.

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Figure Captions

Figure 1 : Effect of the concentration of 15-crown-5, 18-crown-6 and 21-crown-7 on calcium, strontium, barium and radium uptake by the Bio-Rad AG 50W-X8 resin from 0.5 M HCl.

Figure 2 : Acid dependencies of the calcium, strontium, barium and radium uptake by the Bio-Rad AG 50W-X8 resin at various concentrations of 15-crown-5.

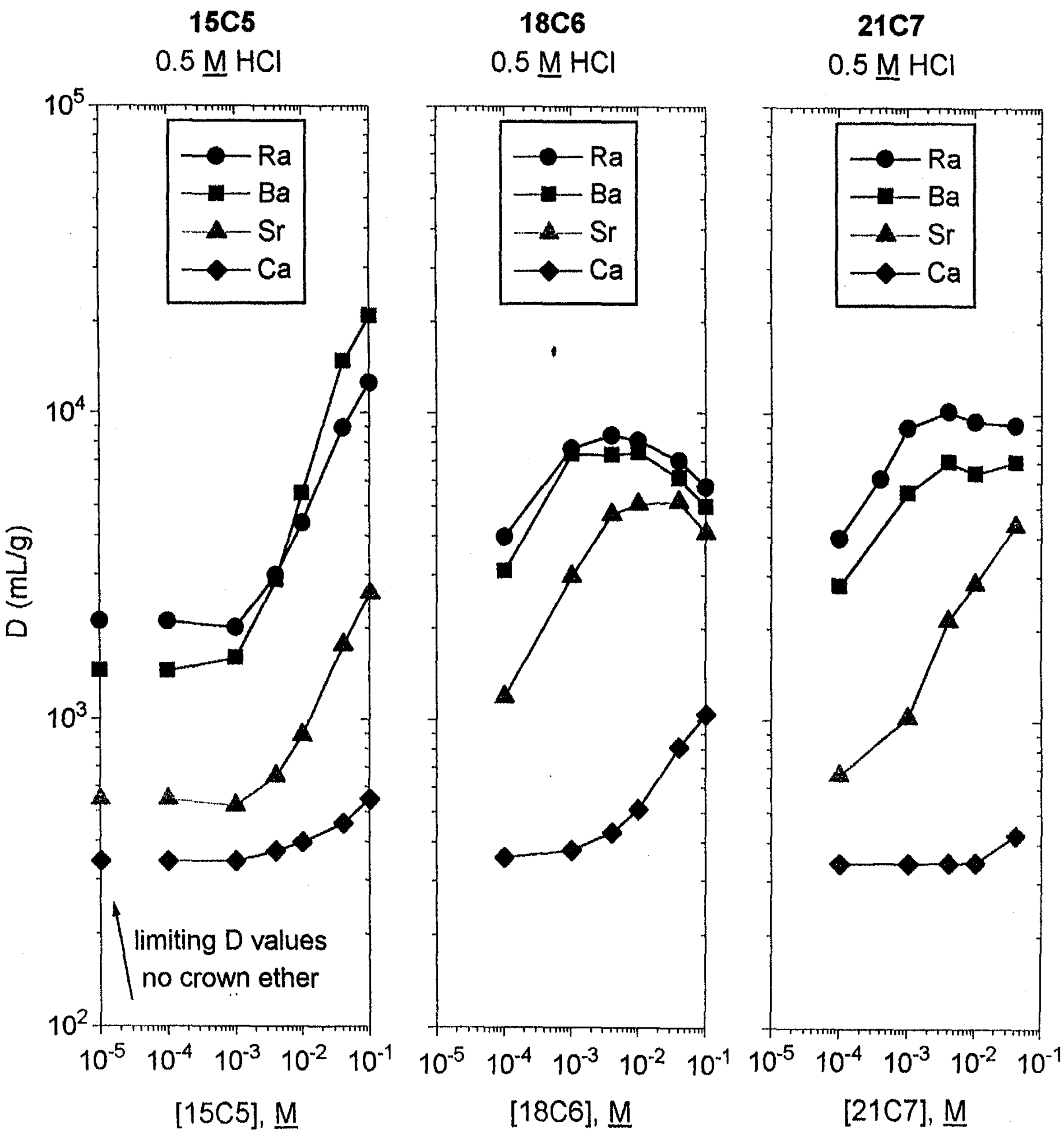
Figure 3 : Acid dependencies of the calcium, strontium, barium and radium uptake by the Bio-Rad AG 50W-X8 resin at various concentrations of 18-crown-6.

Figure 4 : Effect of the concentration of 15-crown-5 on strontium, barium and radium uptake by the calcium form of the Bio-Rad AG 50W-X8 resin from 0.5, 1 and 2 M HCl.

Figure 5 : Effect of the concentration of 18-crown-6 on strontium, barium and radium uptake by the calcium form of the Bio-Rad AG 50W-X8 resin from 0.5, 1 and 2 M HCl.

Figure 6 : Effect of the concentration of 15-crown-5, 18-crown-6 and 21-crown-7 on calcium, strontium, barium and radium extraction by 0.01 F HDNNS from 0.1 M HCl.

Figure 7 : Proposed separation and preconcentration procedure for assay of radium isotopes in natural waters.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18C6
0.5 M HCl
21C7
0.5 M HCl
Ra
Ba
Sr
Ca
D (mL/g)
10^5
10^4
10^3
10^2
limiting D values
no crown ether
10^{-5}
10^{-4}
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10^{-2}
10^{-1}
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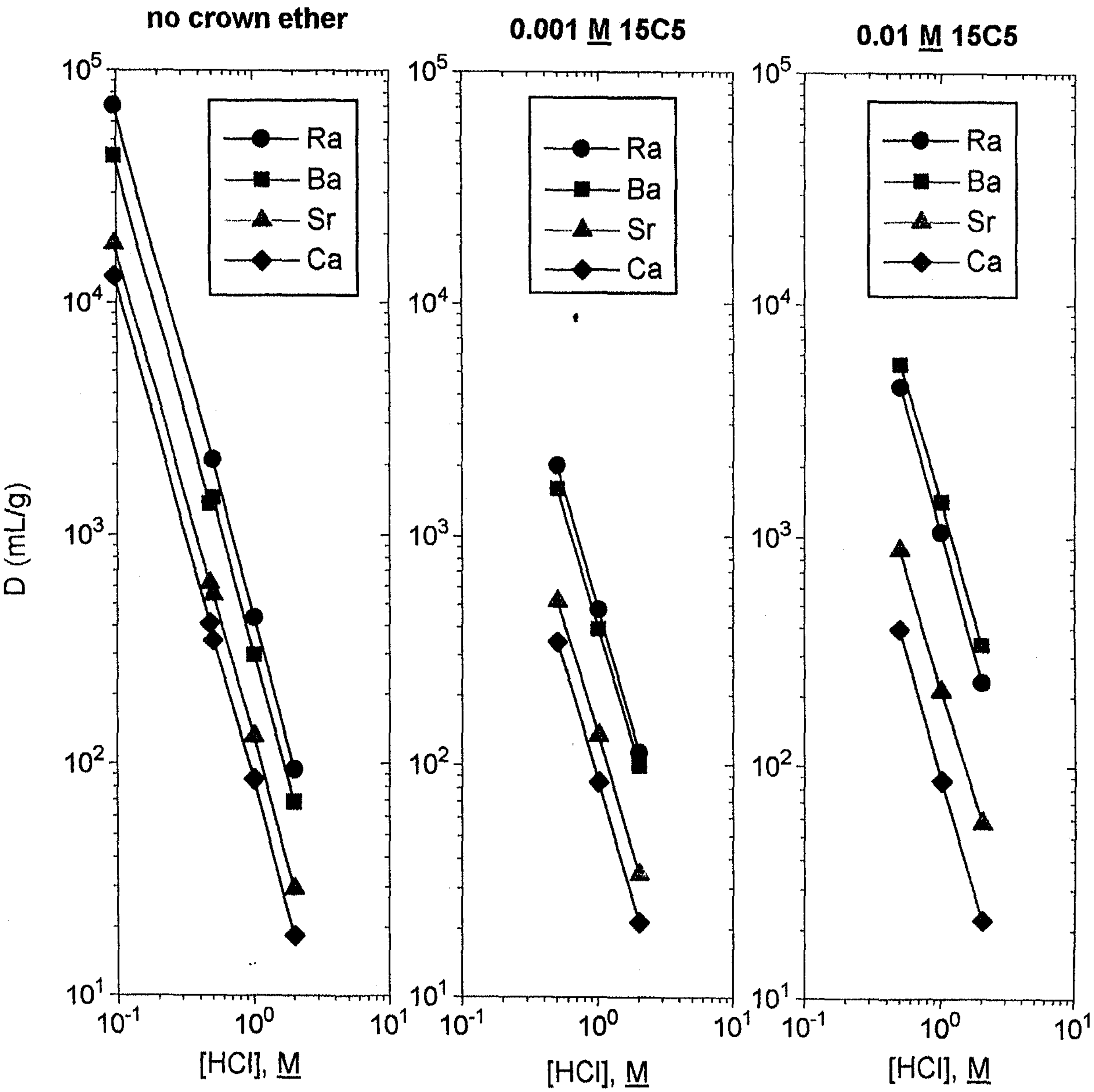
[18C6], M
[21C7], M

Fig. 1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0.001 M 15C5
0.01 M 15C5
D (mL/g)
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10^4
10^3
10^2
10^1
10^-1
10^0
10^1
[HCl], M
Ra
Ba
Sr
Ca

Fig. 2

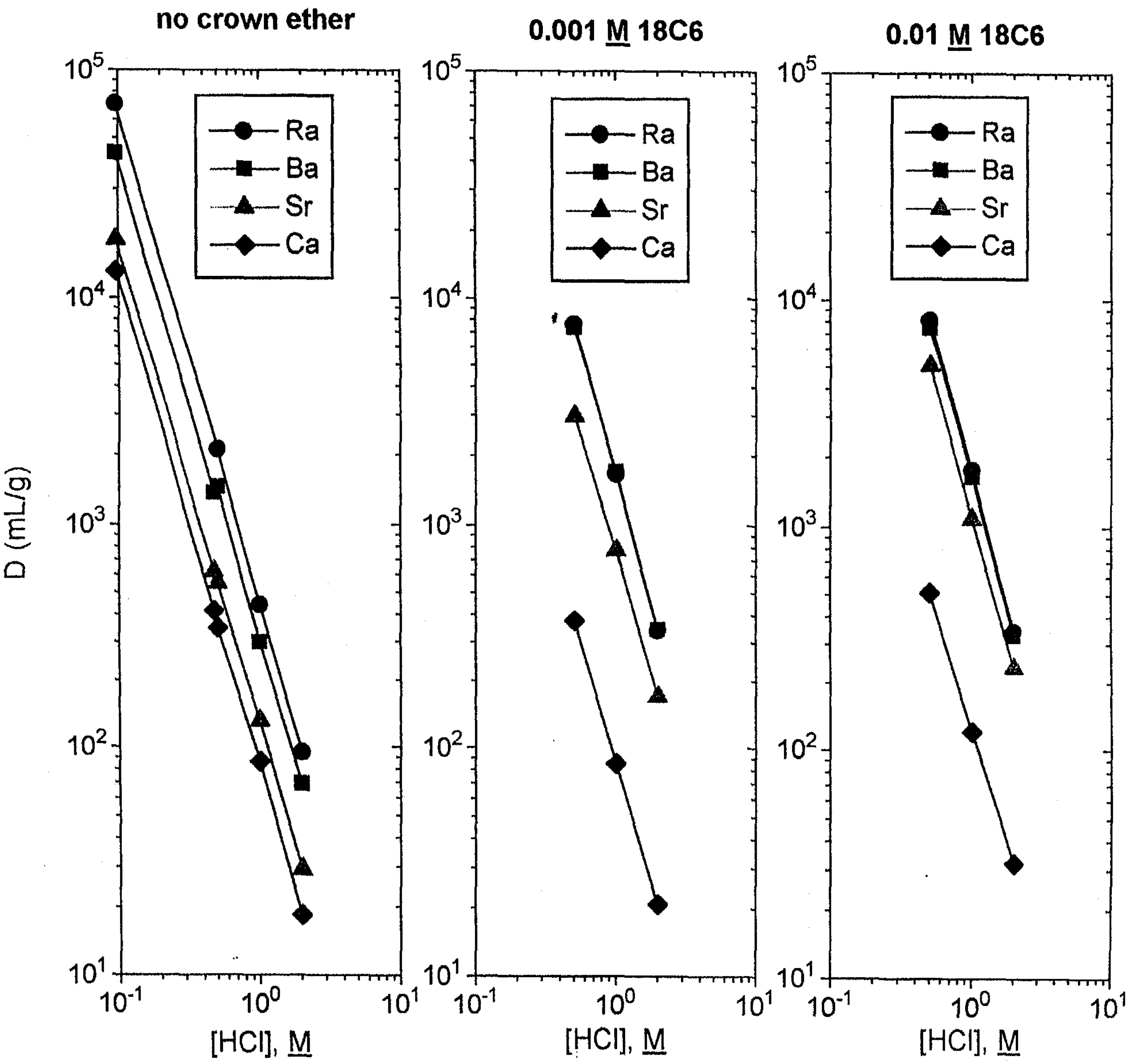
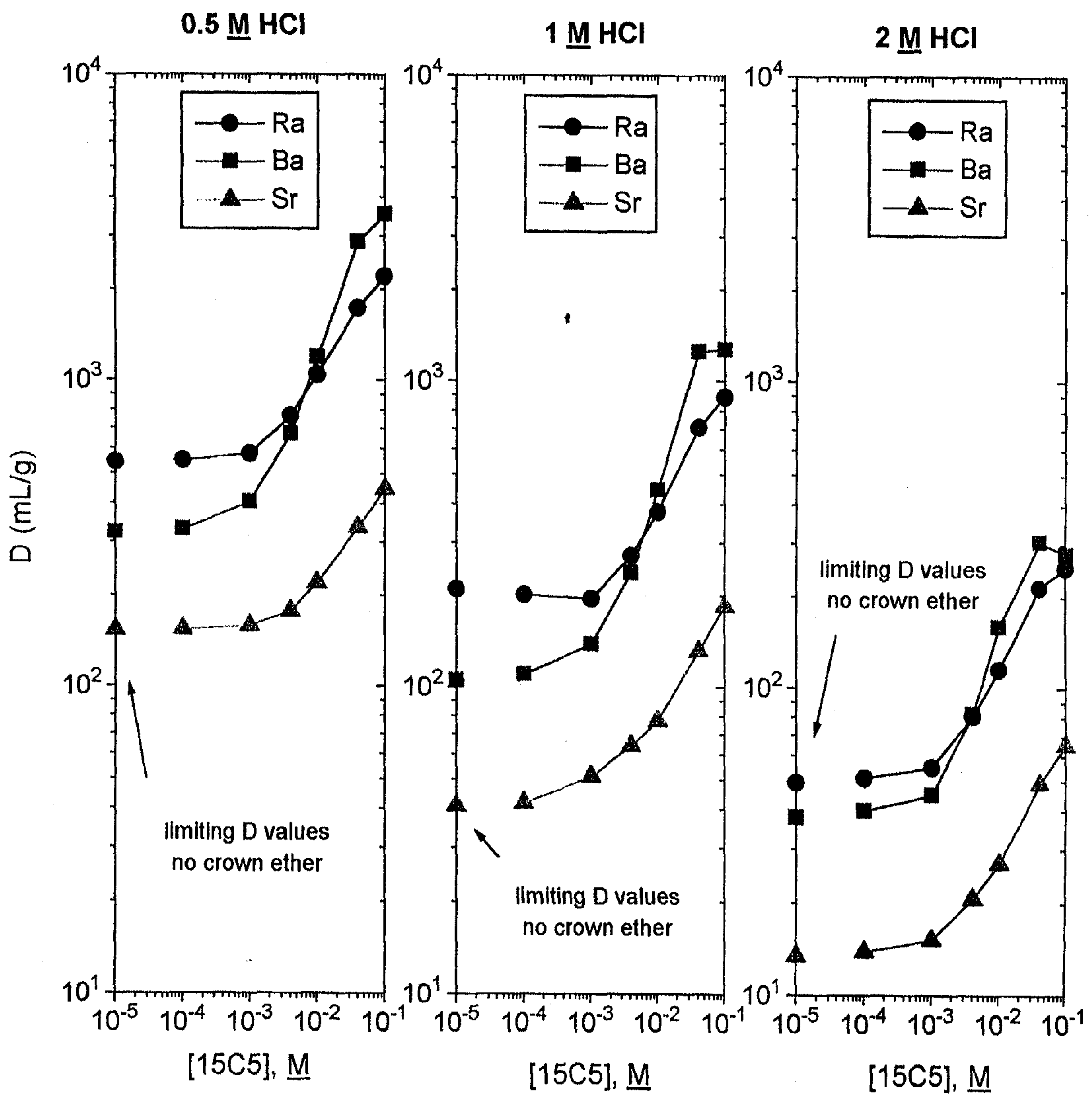

no crown ether
0.001 M 18C6
0.01 M 18C6
D (mL/g)
10^5
10^4
10^3
10^2
10^1
10^{-1}
10^0
10^1
[HCl], M
Ra
Ba
Sr
Ca

Fig 3


0.5 M HCl
1 M HCl
2 M HCl
D (mL/g)
10^1
10^2
10^3
10^4
10^-5
10^-4
10^-3
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Ra
Ba
Sr
limiting D values no crown ether

Fig.4

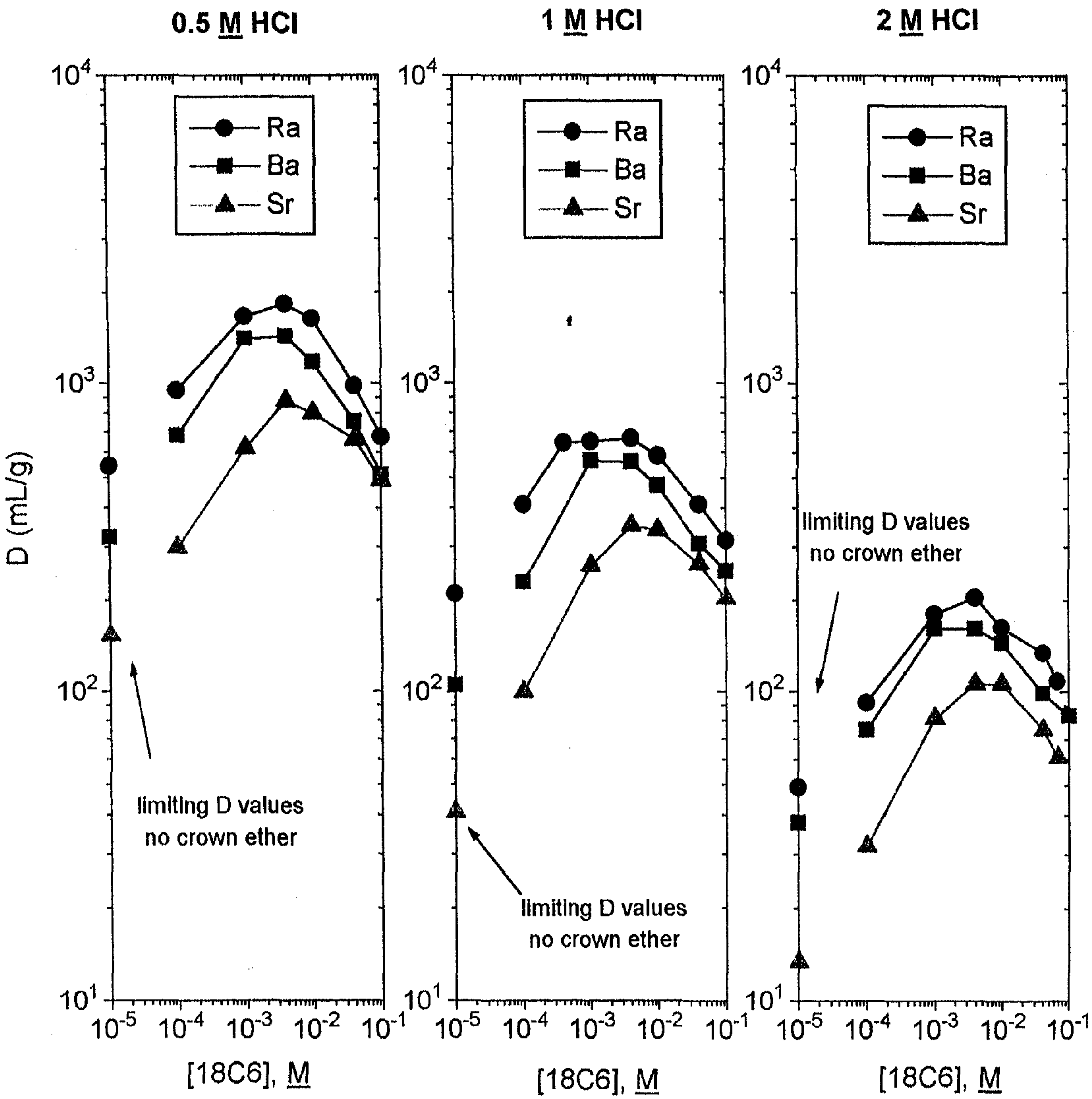
0.5 M HCl
1 M HCl
2 M HCl
Ra
Ba
Sr
D (mL/g)
10^1
10^2
10^3
10^4
10^-5
10^-4
10^-3
10^-2
10^-1
[18C6], M
limiting D values
no crown ether

Fig-5

0.01 F HDNNS in o-xylene - 0.1 M HCl

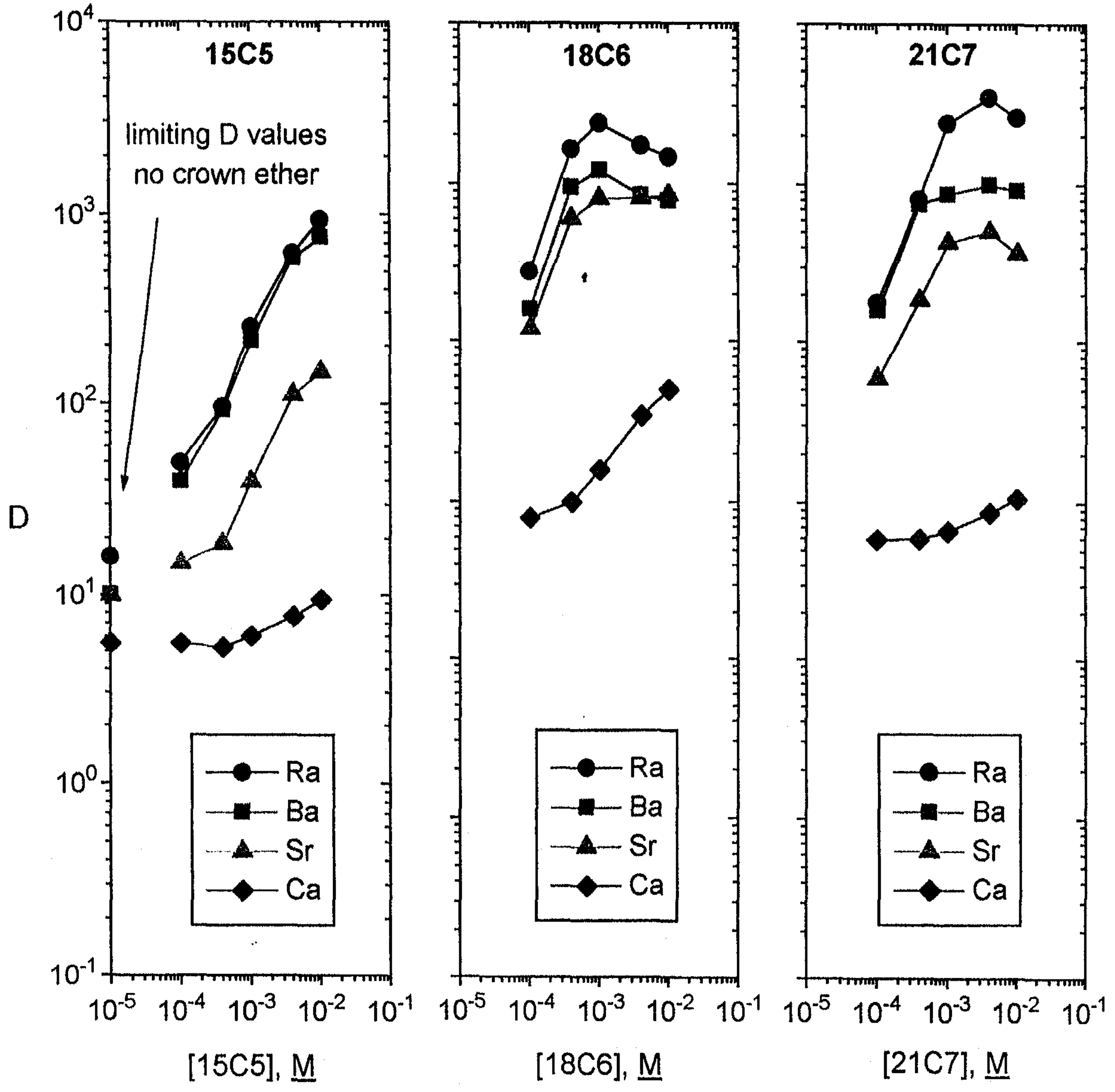

Fig. 6

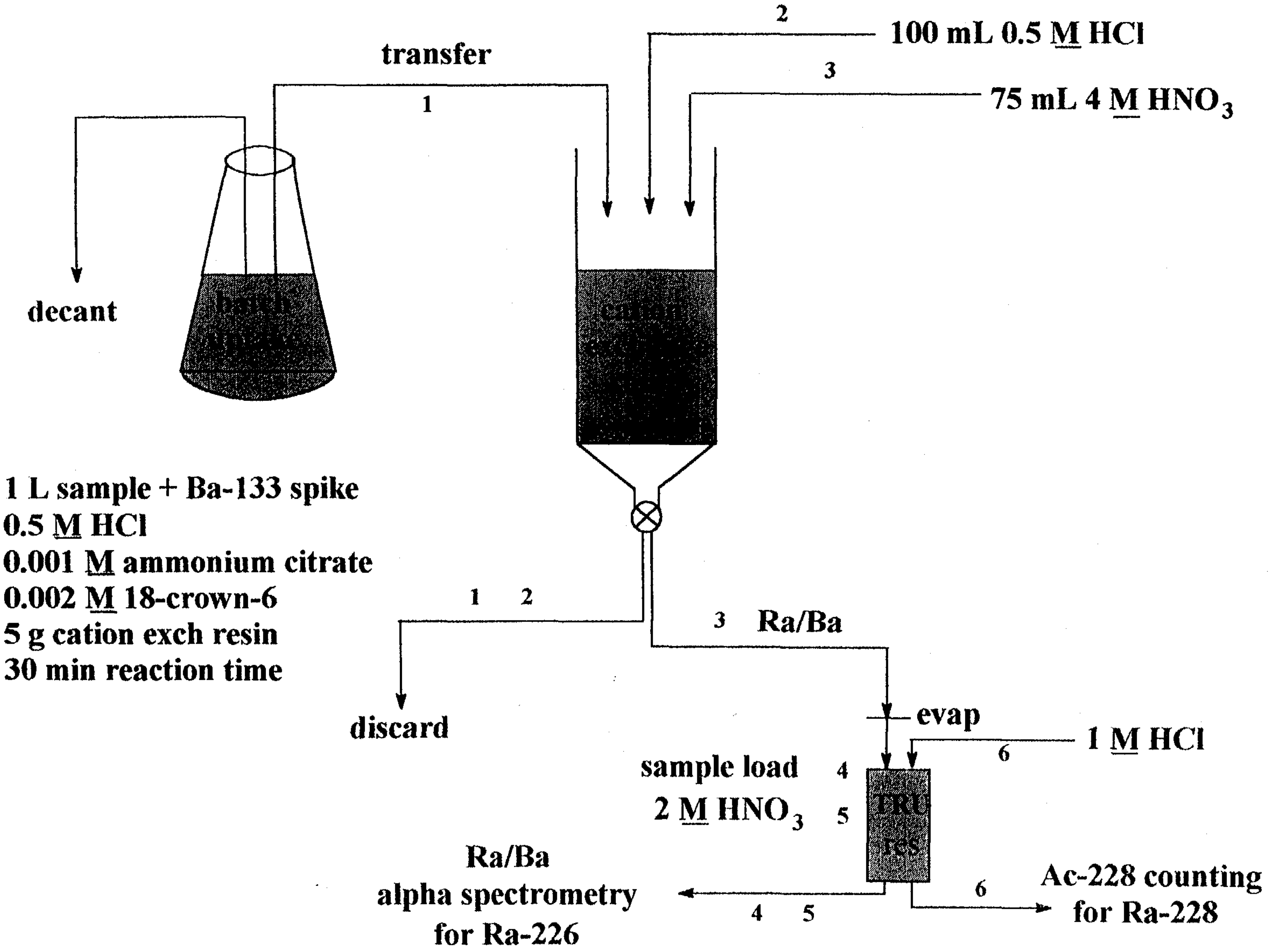
100 mL 0.5 M HCl
75 mL 4 M HNO_3
transfer
1
2
3
decant
batch uptake
cation exchange
1 L sample + Ba-133 spike
0.5 M HCl
0.001 M ammonium citrate
0.002 M 18-crown-6
5 g cation exch resin
30 min reaction time
1 2
discard
3 Ra/Ba
evap
1 M HCl
6
sample load 4
2 M HNO_3 5
TRU res
Ra/Ba
alpha spectrometry
for Ra-226
4 5
6
Ac-228 counting
for Ra-228

Fig 2