

CHROMSYM. 2337

Reversed-phase separation of transition metals, lanthanides and actinides by elution with mandelic acid^a

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(First received January 26th, 1991; revised manuscript received March 4th, 1991)

ABSTRACT

Mandelic acid was investigated as an eluent for the determination of inorganic cations via dynamic ion-exchange and 'hydrophobic interaction' chromatography. Mandelic acid displays similar complexation chemistry to α -hydroxyisobutyric acid, but it is a more hydrophobic ligand and thus the resultant metal-ligand complexes are retained more strongly by the reversed phase surface. The retention behaviour of transition metals, lanthanides and actinides was studied. Retention of the actinides depends on the concentration and pH of the mandelic acid eluent, the column temperature and the concentration of organic modifier. Increasing either the column temperature or the eluent pH above 3.5 altered the selectivity between the actinides. Near-baseline separation was achieved for U, Am, Pu, Np and Th with mandelic acid eluent using isocratic conditions.

INTRODUCTION

One of the key advantages of "dynamic ion-exchange chromatography" is the ability to rapidly alter the column ion-exchange capacity and selectivity. With α -hydroxyisobutyric acid (HIBA) as eluent, thorium and uranium can either be eluted amongst the lanthanides or well after them, depending on the concentration of the 1-octanesulphonate in the mobile phase [1]. This selectivity change results from differences in the complexation chemistries and the ion-exchange equilibria of the two classes of metal ions. Under typical HIBA eluent concentrations the lanthanides should be predominantly in the MI_2^+ form (based on stability constants) and are retained largely through ion-exchange reactions with the 1-octanesulphonate sorbed on the reversed-phase surface. Uranium and thorium are also retained by an ion-exchange mechanism. However, previous studies have shown that if HIBA is used as

^a Presented at the *International Ion Chromatography Symposium, San Diego, September 30–October 3, 1990*. The majority of the papers presented at this symposium have been published in *J. Chromatogr.*, Vol. 546 (1991).

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eluent with no 1-octanesulphonate present, Th(IV) and U(VI) are selectively sorbed onto the reversed-phase support [2]. Lanthanides and a number of transition metal ions [Cu(II), Zn(II), Fe(II), Fe(III), Mn(II), Co(II), Pb(II) and Ni(II)] are not significantly retained and virtually elute at the solvent front [2]. This selective sorption of U(VI) and Th(IV) apparently results from hydrophobic interaction of the metal-HIBA complex with the reversed-phase surface. The mechanism could be referred to as an "ion-pair" separation; however, this term would downplay the complexation chemistry which is integral to the system. Therefore, the more generic term "hydrophobic interaction" will be used to refer to the selective sorption. This interaction has been used to determine U and Th in samples from ore refineries [2], to selectively preconcentrate U from ground waters [3] and to determine uranium in mixed uranium-aluminium nuclear fuels [4].

Mandelic acid (phenylhydroxyacetic acid) complexes metals in a similar manner to HIBA. However, since it also contains a phenyl group, it is much more hydrophobic than HIBA. Thus, the interaction of the mandelic acid-metal complexes with the reversed phase would be expected to be much stronger than that for HIBA. Given the great utility of the reversed-phase effect in the HIBA system from metal separations, this paper reports on studies of the separation characteristics of mandelic acid.

EXPERIMENTAL

Apparatus

Isocratic elutions were performed with a M6000A pump (Waters Assoc., Milford, MA, USA), while gradient elutions were carried out on a Shimadzu LC610 solvent delivery system. The inlet tubing and column were thermostatted using a Haake G refrigerating water bath. Samples were injected using a 7125 valve (Rheodyne, Berkeley, CA, USA) equipped with a 100- μ l sample loop. The post-column reagent was delivered with a syringe pump (Model M314, ISCO, Lincoln, NE, USA) and mixed with the column effluent at a screen-tee mixer [5]. The metal complexes were monitored using a fixed-wavelength detector (Model 441, Waters Assoc.) at wavelengths of 546 nm for 4-(2-pyridylazo)resorcinol (PAR) and 658 nm for 2,7-bis(*o*-arsenophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid (Arsenazo III). The output from the detector was recorded on a Spectra Physics computing integrator (Model SP4100).

Initial studies performed with inactive standards (transition metals, lanthanides, U and Th) were performed using stainless-steel tubing for all connections. For studies of the actinides, the tubing in the sample flow path was replaced with poly(etherether)ketone tubing (Upchurch Scientific, Oak Harbor, WA, USA) to minimize losses of actinides to metal surfaces.

Reagents and materials

Water used for solutions and eluents was freshly distilled and purified in a Milli-Q deionizing unit (Millipore, Bedford, MA, USA). Acetonitrile was high-performance liquid chromatographic (HPLC) grade (Fisher). DL-Mandelic acid was obtained from Fluka and was used as received. Mandelic acid eluents were protected from light to prevent decomposition. Stock solutions of sodium 1-octanesulphonate

(0.1 mol l^{-1} , C_8SO_3^-) and $1.5 \cdot 10^{-3} \text{ mol l}^{-1}$ Arsenazo III were purified using a Dowex 50W-X8 cation exchanger in the NH_4^+ form. The Arsenazo III solution contained 0.1 mol l^{-1} urea to prevent oxidation, and was diluted to the desired concentration ($1.5 \cdot 10^{-4} \text{ mol l}^{-1}$) with 0.1 mol l^{-1} HNO_3 prior to use. The PAR post-column reagent ($2 \cdot 10^{-4} \text{ mol l}^{-1}$) also contained 2 mol l^{-1} ammonia and 1 mol l^{-1} acetic acid. All HPLC eluents were filtered through $0.45\text{-}\mu\text{m}$ filters. Other chemicals were reagent grade.

Transition metal and lanthanide standards were prepared from SPEX Industries (Metuchen, NJ, USA) standards. Plutonium, neptunium-237 and americium-241 standards were prepared in 8 mol l^{-1} HNO_3 and were obtained at the Chalk River Laboratories. Their concentrations were determined by α -spectrometry.

Preliminary studies were performed using a $150 \text{ mm} \times 4.6 \text{ mm}$ I.D. stainless-steel column packed with $5\text{-}\mu\text{m}$ Supelcosil C_{18} packing (Supelco, Oakville, Canada). A $100 \text{ m} \times 4 \text{ mm}$ glass-lined column packed with $3\text{-}\mu\text{m}$ Spherisorb was used for all other work. This latter column was slurry-packed at 5000 p.s.i. from a solvent mixture of methanol-isopropanol-cyclohexanol-cyclohexane-1,1,1-trichloroethane (10:5:10:5:70, v/v) [6].

RESULTS AND DISCUSSION

Lanthanides

Since HIBA is most commonly used for the separation of the lanthanides [7-9], this application of mandelic acid was studied. Using a mandelic acid gradient containing 0.01 mol l^{-1} C_8SO_3^- all fourteen lanthanides can be separated (Fig. 1). Unlike the comparable gradient using HIBA, Th(IV) and U(VI) are well separated from the lanthanides. The cause of the baseline shift evident in Fig. 1 is not known. Passage of the stock mandelic acid solution through a Dowex 50W \times 8 cation-exchange column did not affect the baseline.

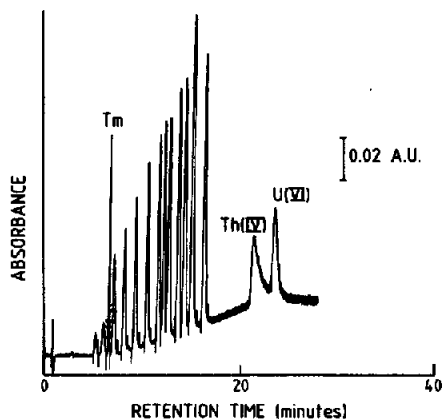


Fig. 1. Gradient separation of lanthanides, Th(IV) and U(VI) using mandelic acid and 1-octanesulphonate. Column $3\text{-}\mu\text{m}$ Spherisorb C_{18} , $100 \times 4.0 \text{ mm}$ I.D.; eluent 0.14 mol l^{-1} mandelic acid (pH 4.1) to 0.50 mol l^{-1} mandelic acid (pH 4.1) over 15 min, $[\text{C}_8\text{SO}_3^-]$ constant at 0.01 mol l^{-1} ; flow-rate, 1.0 ml min^{-1} ; Temperature, 23°C ; injection, $100 \mu\text{l}$ of 1 mg l^{-1} each of Lu, Yb, Tm, Er, Ho, Dy, Tb, Gd, Eu, Sm, Nd, Pr, Ce and La plus 2.5 mg l^{-1} U and Th; detection, post-column reaction with Arsenazo III.

While the separation shown in Fig. 1 is excellent, the chromatographic efficiencies ($H = 0.009$ mm for La) and the separation of the lanthanides are inferior to those obtained with HIBA [1,5]. With HIBA, the lanthanides are retained solely through ion exchange within the charged double layer which is formed when the hydrophobic 1-octanesulphonate modifier sorbs onto the reversed-phase surface. However, with mandelic acid, metal ions may be retained through either an ion-exchange or hydrophobic interaction mechanism. The degree to which the lanthanides retention is dictated by each mechanism is shown in Fig. 2 where the retention times under isocratic conditions are plotted *versus* eluent pH. As the pH is increased from pH 3.0 to 4.2, the proportion of mandelic acid which is ionized increases ($pK_a = 3.19$ [10]). For a pure ion-exchange mechanism, the retention times should decrease with increasing pH in proportion to the concentration of ionized mandelic acid present (about two-fold increase in ionized mandelic acid over the pH range 3.2 (pK_a) to 4.2). Alternatively, for the hydrophobic interaction mechanism retention should increase, as illustrated by U(VI) and Th(IV) in Fig. 2. The retention of La and Sm decreases with increasing pH indicating that the mandelic acid system lanthanide retention is largely due to ion exchange with the sorbed 1-octanesulphonate. Nonetheless, the change in retention time observed for La and Sm is smaller than would be expected for pure ion exchange, and Sm shows a small increase in retention at the higher pH values studied. Thus, some retention is believed to be due to the hydrophobic interaction of the lanthanide-mandelic acid complex with the surface, in addition to the dynamic ion exchange.

This conclusion is supported by the results obtained when mandelic acid alone is used as eluent (*i.e.*, no $C_8SO_3^-$ modifier in the eluent). A separation of the rare-earth elements is still possible (Fig. 3c). Interestingly, the order of elution of the lanthanides is the same as observed with the ion-exchange modifier; however, only the first seven heavy lanthanides are well separated; the lighter lanthanides essentially co-elute.

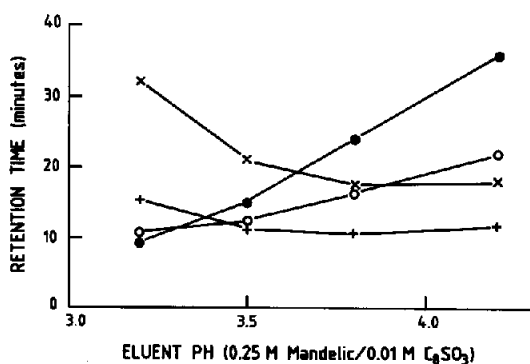


Fig. 2. Effect of pH of mandelic acid eluent on lanthanide and actinide separation in the presence of 1-octanesulphonate. Column, same as Fig. 1; eluent, 0.25 mol l^{-1} mandelic acid with $0.01 \text{ mol l}^{-1} C_8SO_3^-$; flow-rate, 0.8 ml min^{-1} ; column temperature, 23°C ; injection, $100 \mu\text{l}$ of 1.0 mg l^{-1} La and Sm and 2.5 mg l^{-1} U and Th; detection, post-column reaction with Arsenazo III. ● = U; ○ = Th; × = La; + = Sm.

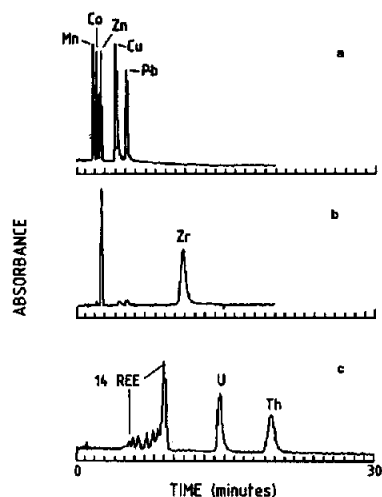


Fig. 3. Metal-ion separation with mandelic acid alone. (a) Transition metals; (b) zirconium; and (c) lanthanides, Th and U(VI). Column, 5- μm Supelcosil C₁₈, 150 \times 4.6 mm I.D.; Eluent, 0.5 mol l⁻¹ mandelic acid at pH 3.2; flow-rate, 1.0 ml min⁻¹; column temperature, room temperature; injection, 1–2.5 mg l⁻¹ of each metal; detection, post-column reaction with PAR for the transition metals and Zr and with Arsenazo III for the lanthanides, Th and U(VI).

Transition metals

If HIBA is used without an organic ion-exchange modifier, the transition metals are unretained and coelute [2]. Using mandelic acid alone, however, a number of transition metals can be separated, as shown in Fig. 3. The transition metals elute prior to the lanthanides and actinides, although there is some overlap with the heavier lanthanides. For Mn(II), Co(II), Ni(II) (not shown in figure), Zn(II) and Cu(II) the retention order is opposite to that observed using HIBA with an ion-exchange column [3], reflecting the opposite effect of complex formation in the two modes of chromatography. Pb(II), however, shows unexpected behaviour. Normally, Pb(II), elutes between Zn(II) and Ni(II) in the HIBA ion-exchange system and yet in the mandelic acid system it elutes later. Unfortunately, stability constants for the Pb(II)–mandelic acid system are not available, so it is not known whether the retention behaviour results from differences in complexation reactions of HIBA and mandelic acid towards Pb(II), or if the retention mechanism is different for this metal.

Cu(II) also displayed interesting behaviour in the mandelic acid system. The retention of Cu(II) relative to the other transition metals varied with eluent concentration and pH, while no other changes in selectivity for the other transition metal studied were observed. Increases in the concentration of the mandelic acid in the eluent improved the symmetry of the Cu(II) peak, but changes in eluent pH did not.

Fig. 3b shows the retention of Zr under the same chromatographic conditions as for the transition metal separation shown in Fig. 3a. In order to prevent hydrolysis of Zr prior to complexation with mandelic acid, it was necessary to react Zr directly from a strong acid (8 mol l⁻² HNO₃) solution with the mandelic acid. The pH was subsequently adjusted to match the eluent conditions. Standards were stable only at

concentrations less than 10 mg l^{-1} . More concentrated standards would precipitate upon standing. Hydrolyzed Zr eluted in the void volume. The Hf-mandelic acid peak could not be identified in this system. Subsequent test-tube experiments showed that the HF-PAR complex does form, but the kinetics of the complex formation is slow and so no significant colour formation occurred in the low dead-volume post-column reactor [5].

Fe(II) and Fe(III) were also separated using this system. Fe(III) eluted in the same time region as the heavy lanthanides, but the mandelic acid reduced Fe(III) *in situ*, resulting in Fe being distributed between the Fe(II) and Fe(III) peaks. Ca(II) was found to elute at a similar retention time to that of Mn(II).

Actinides

Previous studies have shown that HIBA, in the presence of 1-octanesulphonate, elutes the higher oxidation states of the actinides ahead of the lanthanides [1,11,12]. Significant retention of actinides such as Pu has only been achieved in the HIBA- C_8SO_3^- system by reducing the actinides to their +3 oxidation state [11]. Unfortunately, under these conditions the +3 state is not stable for either Pu or Np. In addition, Am(III) and Pu(III) elute in close proximity to one another (resolution, $R_s = 1.1$) leading to difficulties in their subsequent determination by α -spectrometry since Pu-238 and Am-241 emit α particles of very similar energy.

The use of HIBA alone (*i.e.*, no C_8SO_3^- present) has been shown to be a selective means of separating uranium from other metal ions [2-4]. Unfortunately, similar success is not possible for the other actinides using HIBA. Fig. 4 shows the separation of Th, U, Np, Pu and Am using HIBA alone. U(VI) and Th(IV) are strongly retained as has been reported previously [2-4]. However, Am(III) is only weakly retained and Pu(IV) co-elutes with Th(IV). The Np(IV) is separated from Th(IV), but some Np

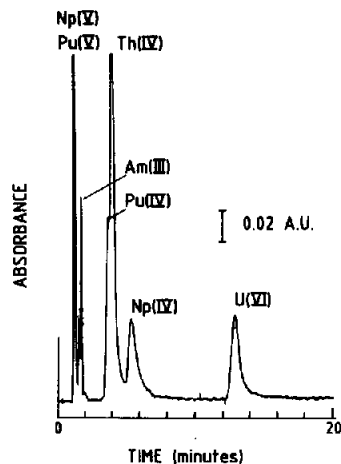


Fig. 4. Separation of actinides using HIBA in the absence of 1-octanesulphonate present. Column, $5\text{-}\mu\text{m}$ Supelcosil C_{18} , $150 \times 4.6 \text{ mm}$ I.D.; eluent, 0.16 mol l^{-1} HIBA (pH 4.5) with 4% methanol; flow-rate, 2.0 ml min^{-1} ; column temperature, room temperature; injection, 0.3 mg l^{-1} Am and 3.0 mg l^{-1} each U, Th, Pu and Np; detection: post-column reaction with Arsenazo III.

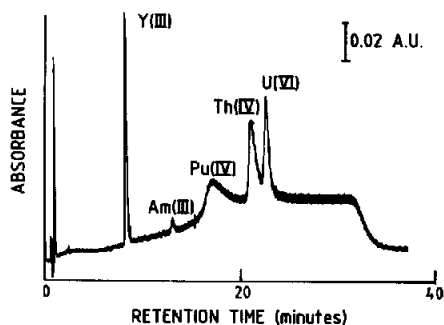


Fig. 5. Gradient elution of actinides using mandelic acid and 1-octanesulphonate. Column, 3- μm Spherisorb C_{18} , 100×4.0 mm I.D.; Eluent, 0.19 mol l^{-1} mandelic acid (pH 4.1) to 0.50 mol l^{-1} mandelic acid (pH 4.1) over 15 min, $[\text{C}_{18}\text{SO}_3^-]$ constant at 0.01 mol l^{-1} ; flow-rate, 1.0 ml min^{-1} ; temperature, 23°C ; injection, $100 \mu\text{l}$ of 1.0 mg l^{-1} Y, 2.5 mg l^{-1} of Th(IV) and U(VI), 0.3 mg l^{-1} Am and 2.5 mg l^{-1} Pu.

also exists as NpO_2^+ , and elutes at the solvent front. Furthermore, some changes in the Np and Pu oxidation states were observed when standards were allowed to stand in HIBA for a few days.

Use of mandelic acid–1-octanesulphonate as the mobile phase results in greater retention of the actinides than is possible with HIBA, as seen in Fig. 5. Under these conditions Am(III) elutes at the same retention time as would Sm, while Pu(IV) elutes as a broad peak just after the lanthanides (Fig. 1) and is followed by Th(IV) and U(VI). Interestingly, the elution order of Th(IV) and U(VI) reverses when 1-octanesulphonate is removed from the mandelic acid eluent. This differs from the behaviour observed with HIBA, where U(VI) is more strongly retained than Th(IV), regardless of the presence or absence of 1-octanesulphonate.

Unfortunately, the strong retention of mandelic acid on the reversed-phase support results in slow re-equilibration of the column to the initial gradient conditions, and thus limits the usefulness of mandelic acid to isocratic chromatography. Nevertheless, an excellent separation of the actinides can be achieved using mandelic acid alone under isocratic conditions (Fig. 6). Pu(IV) is stable for indefinite periods in mandelic acid solutions and can be quantitatively recovered from the system (Table I). Some tailing of the Pu-239 peak is evident in Table I, but this is believed to result from Pu retention on metal surfaces present in our fraction collection line. Am-241 was also quantitatively recovered (105% for a 84-ng injection), with 93% being present in the expected fraction. Np was recovered in two fractions, corresponding to the +4 and +5 oxidation states, with the latter eluting at the solvent front. Np can be reduced quantitatively to the +4 state by addition of Fe(II) to the sample; however, this also causes some reduction of the Pu(IV). The poor recovery of Np in Table I is believed to result from the increased background in the α -spectrum from Pu present in the Np fraction. Similar difficulties made the determination of Np-237 in the original mixed actinide standard impossible.

In order to achieve the separation shown in Fig. 6 a number of factors must be optimized or controlled. The temperature of the eluent strongly affected the selectivity, as can be seen in Fig. 7. While both enthalpic and entropic behaviour was observed upon altering the temperature, the most marked temperature dependence,

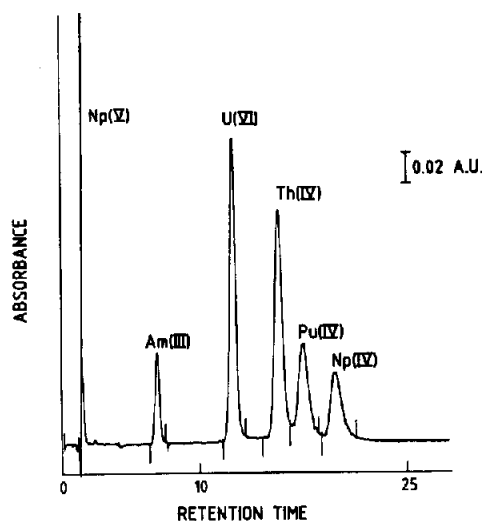


Fig. 6. Separation of actinides using mandelic acid alone. Column, 3- μ m Spherisorb C₁₈, 100 \times 4.0 mm I.D., eluent, 0.50 mol l⁻¹ mandelic acid (pH 3.2) with 5% acetonitrile; flow-rate, 0.8 ml min⁻¹; temperature, 23°C; injection, 100 μ l of 3.0 mg l⁻¹ of Th and U(VI), 0.3 mg l⁻¹ Am, 3.0 mg l⁻¹ Pu and 3.0 mg l⁻¹ Np; detection, post-column reaction with Arsenazo III.

TABLE I

DISTRIBUTION OF Pu, Np AND Am IN VARIOUS FRACTIONS COLLECTED DURING ISO-CRATIC ELUTION WITH MANDELIC ACID ALONE

Chromatographic conditions: column, 3- μ m Spherisorb C18, 100 \times 4.0 mm I.D.; eluent, 0.50 mol l⁻¹ mandelic acid (pH 3.2); flow-rate, 0.75 ml min⁻¹; temperature, 25°C; injection, 100 μ l of 2.5 mg l⁻¹ of Th, Y and U(VI), 100 mg l⁻¹ Sr and Ca and actinides as indicated in table; detection, fraction collection and subsequent α -spectrometry on 100 μ l of fraction (precision is \pm 10% due to variability in plate preparation).

Fraction collection times (min)	Weight of Pu-239 (ng)	Weight of Np-237 (ng)	Weight of Am-241 (ng)
0-4	0.8	69	0.02
4-8	1.0	—	0.02
8-12	—	—	82
12-18	—	—	5
18-22	—	—	0.9
22-27	20	—	—
27-32	710 ^a	—	—
32-36	75	360	—
36-40	13	—	—
40-44	9	—	—
44-48	7	—	—
48-52	4	—	—
Total mass recovered (ng)	840	429	88
Mass injected (ng)	860	830 ^b	84
Recovery (%)	97	52	105

^a Possibly Pu-240 present.

^b Np-237 was not detected in the mixed standard by α -spectrometry due to the presence of plutonium. Quantity indicated is from analysis of pure Np-237 standard used to prepare the solution injected.

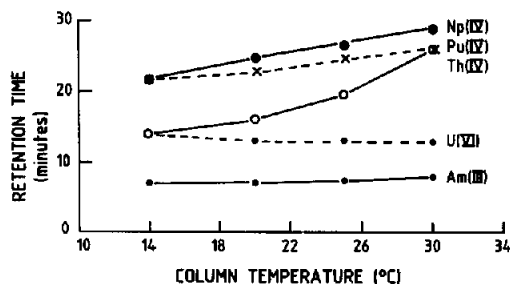


Fig. 7. Effect of temperature on separation of actinides using only mandelic acid. Conditions as in Fig. 6, except that the column temperature is varied.

and the only one which actually resulted in a selectivity change amongst the actinides was that for Th(IV). Above 27°C Th(IV) will overlap with the Pu(IV), so a temperature of 23°C was used for the actinide separations.

Increasing the pH of the eluent over the range 2.0–4.2 resulted in an increase in the actinide retention (Fig. 8), as would be expected from the increasing hydrophobicity of the metal ligand complexes. At low pH the actinides elute in two groups: the early-eluting group consisting of U(VI) and Am(III) and the later group of Pu(IV), Th(IV) and Np(IV). As the pH is increased up to a pH of 3.6 the order of elution is as shown in Fig. 6, but at pH 3.8 Pu(IV) elutes before Th(IV). Extension of this study to higher values of pH was precluded by the long retention times. Nevertheless, studies using lower mandelic acid concentrations have shown that at pH > 4 Pu(IV) will elute prior to U(VI). Unfortunately, Np(IV) also shows reduced retention relative to Th(IV) and U(IV) at pH > 4, resulting in poor separations between Th(IV) and Np(IV).

Increasing the mandelic acid concentration in the eluent showed an unexpected effect. Previously, it had been observed that increases in the HIBA concentration in the eluent results in small increases in the retention times of U(VI) and Th(IV) [2]. In the mandelic acid system (Fig. 9), increases in the concentration of mandelic acid (pH

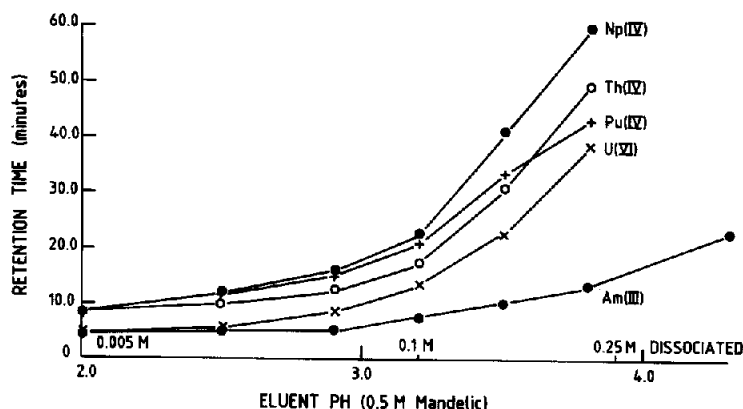


Fig. 8. Effect of eluent pH on separation of actinides using only mandelic acid. Conditions as in Fig. 6, except for eluent pH.

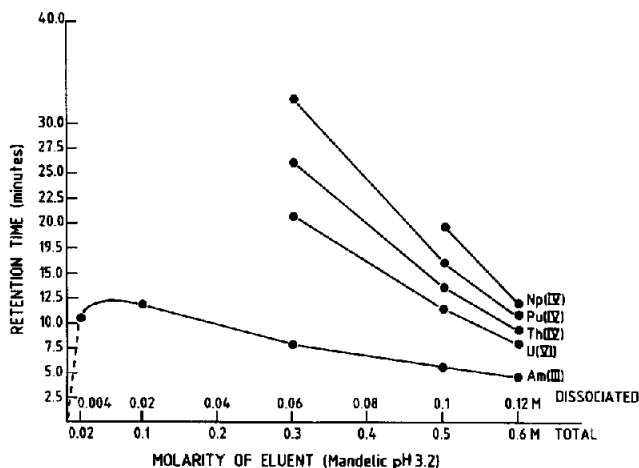


Fig. 9. Effect of mandelic acid concentration on retention of actinides. Conditions as in Fig. 6, except for the mandelic acid concentration.

3.2) from 0.3 to 0.6 mol l⁻¹ resulted in significant decreases in the retention time. Only the retention of Am(III) was studied below eluent concentrations of 0.3 mol l⁻¹ due to the long retention times under these conditions. Below a mandelic acid concentration of 0.1 mol l⁻¹ the retention of Am(III) was observed to decrease with decreasing concentration. However, under these conditions the Am(III) peak was extremely broad and displayed poor peak shape.

Two explanations are possible for the results in Fig. 9. First, increases in the mandelic acid concentration result in the formation of anionic metal–ligand complexes which have a lower retention than cation complexes. However, if this were the case, then a similar decrease in retention should be observed for increases in the eluent pH (Fig. 8) but the opposite was actually observed, *i.e.*, the retention increased with pH. Furthermore, if formation of anionic complexes were the cause of the decreased retention, then some selectivity changes should be observed as a result of the different formation constants for the metal–ligand complexes. Again this effect was not observed. Therefore the formation of anionic metal–ligand complexes is not believed to be responsible for the reduced retention observed for increased eluent concentration.

A second explanation is that the protonated mandelic acid is competing with the actinide–mandelate complex for adsorption onto the reversed-phase surface. Essentially, the protonated mandelic acid is believed to act like an organic modifier. Additions of a more conventional organic modifier, *e.g.*, acetonitrile, over the range 0–20% (v/v) also resulted in reduced retention of the actinides without alteration of the selectivities. This is analogous to the behaviour previously observed with the U(VI)–HIBA system [2]. Unlike the U(VI)–HIBA system, however, no significant improvements in peak shape were observed using methanol rather than acetonitrile [4]. Nevertheless, these results do suggest that the primary effect of increased mandelic acid concentration is to act as an organic modifier, resulting in more rapid elution of the actinides.

CONCLUSIONS

Mandelic acid is not as efficient an eluent for dynamic ion-exchange separations of transition metals and lanthanides as is HIBA. This is due to the more hydrophobic character of mandelic acid causing increased hydrophobic interaction with the stationary phase, resulting in poorer efficiencies than those obtained with the dynamic ion exchange.

Nevertheless, the hydrophobic interaction of the mandelic acid-metal ion complexes with reversed-phase surfaces displays useful selectivities for the separation of actinides, both from each other and from other metals. Use of mandelic acid alone as the eluent results in the separation of metal ions primarily based on the charge on the cation: +2 transition metals elute early, followed by +3 species such as the lanthanides, and finally the +4 species such as many of the actinides.

Actinide retention is enhanced by increasing the eluent pH or by decreasing the concentration of either the mandelic acid or the organic modifier (acetonitrile) in the mobile phase. Selectivity can be altered either by changing the eluent pH over the range 3.5–4.5 or by changing the column temperature.

Studies are now underway to investigate the suitability of this system for the determination of actinides in low-level radioactive waste, and of lanthanides in uranium fuels.

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