UPTAKE OF METAL IONS BY A NEW CHELATING ION-EXCHANGE RESIN. PART 2: ACID DEPENDENCIES OF TRANSITION AND POST-TRANSITION METAL IONS

by

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ABSTRACT

Diphonix™ is a new dual-mechanism polyfunctional resin containing sulfonic and gem-diphosphonic acid groups. In Part 1 of this series the effectiveness of Diphonix in removing actinide ions from very acidic solutions was demonstrated. In this paper we report on the uptake of various transition and post-transition metal ions with Diphonix and two other resins for comparison. The results show that Diphonix has a very high affinity for Fe(III) and Cr(III) in very acidic solutions. From neutral solutions Diphonix exhibits a high selectivity for lead and transition metals over calcium. Conditions for efficient stripping of the investigated ions have been found.

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INTRODUCTION

Diphonix™ is a styrene-divinylbenzene sulfonated ion exchange resin containing chemically bonded gem-diphosphonic acid groups. The rational leading to the formulation of this dual-mechanism polyfunctional polymer and its synthesis have been described in (1,2). The resin is now commercially available from Eichrom Industries, Inc., Darien, Illinois. In (2) distribution studies were reported comparing the behavior of actinide ions with Diphonix, the commercial sulfonic-type strong acid cation exchanger Bio-Rad™ AG MP-50, and a sulfonated monophosphonic resin prepared in the same way as Diphonix but containing monophosphonic instead of gem-diphosphonic acid groups. It was found that Diphonix is much more effective than the other two resins in removing actinide ions from very acidic solutions and uranium from near-neutral solutions. The remarkable performance of Diphonix was attributed to the relatively high acidity of the gem-diphosphonic acid and to its capacity to chelate to actinide ions through either ionized or neutral diphosphonic acid ligands, leading to metal complexes of high stability.

By analogy with the behavior of the methane substituted gem-diphosphonic acids in solution, one would expect Diphonix to show a high affinity also with those metal ions that form stable complexes with the aqueous soluble ligands (3). The aim of this work was to measure the distribution of several transition and post-transition metal ions between Diphonix and acid or neutral solutions, comparing the behavior of Diphonix with the monophosphonic and a sulfonic-acid resin, and to find suitable stripping agents for the sorbed metal species.

EXPERIMENTAL

The materials and procedures used throughout this work were the same as reported in (2). The properties of the Diphonix, monophosphonic and Bio-Rad AG MP-50 resins have been reported in Table 1 of ref. (2). The uptake experiments were performed using the following radioisotopes: $^{152\text{-}154}Eu$, ^{45}Ca, ^{51}Cr, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{63}Ni, ^{65}Zn, ^{109}Cd, ^{110}Ag, ^{113}Sn, ^{125}Sb, ^{203}Hg and ^{212}Pb. They were obtained from either Amersham (Arlington Heights, Illinois) or Isotope Products Laboratories (Burbank,California), with the exception of ^{212}Pb, which was separated from ^{224}Ra (which in turn came from ^{228}Th) according to the procedure reported in (4). In the experiments involving Al(III), Cu(II) and Bi(III), analyses of the metals were performed by ICP-AES. Fe(II) was obtained from Fe(III) by making the test solutions 0.1 $\underline{M}$ in ascorbic acid and awaiting about two hours before running the uptake measurements.

As described in (2), a two hours stirring time of the resin-solution system was generally employed. This time is more than sufficient for equilibrium attainment with all the investigated cations, except Cr(III). In the case of Al(III) and Fe(III), however, the test-tubes containing the resin and the solution were stirred overnight. With Cr(III), owing to its slow uptake kinetics, distribution measurements were made after 48 hours of contact under constant stirring of the resins and aqueous phases. The kinetics of metal uptake by Diphonix will be reported in Part 4 of this series.

RESULTS AND DISCUSSION

Uptake of Metal Species from Acid Solutions

Nitric acid dependencies of the dry weight distribution ratio, D, as defined in (2), of Fe(III), Cr(III), Al(III), Eu(III) and Bi(III) with Diphonix are reported in Fig. 1. Figure 2 reports the nitric acid dependencies of D for some divalent cations (Ca(II), Zn(II), Co(II), Hg(II)), of Sb(III) and of Ag(I). Acid dependencies of D for selected cations (Fe(III), Fe(II), Al(III), Eu(III) and Bi(III)) have also been measured in hydrochloric acid because it is very likely that analytical procedures using Diphonix for the separation and concentration of actinide ions from nuclear waste solutions and biological or environmental complex matrices would be performed in this medium. Fe(III) and lanthanide ions are present in significant concentrations in rad-waste solution, Fe(III) and Al(III) are always present in dissolved soil samples, and Bi(III) may be present in fecal samples. All these cations may interfere with the uptake of actinide ions by Diphonix. It was important, therefore, to investigate their behavior with Diphonix in hydrochloric acid solutions. The results of the measurements are reported in Fig. 3. Figure 4 shows a comparison of the data obtained with the Diphonix, monophosphonic and sulfonic resins for some selected cations for which the different behavior of the three resins is more evident. A more complete set of the nitric acid dependency data with the three resins is reported in Table 1.

The most noteworthy feature of the data of Fig. 1 is the behavior of Fe(III). It strongly resembles the curve reported in (2) for Pu(IV) and Np(IV), with a plateau in the intermediate acidity range and D values declining for lower acidities. The latter feature of the Fe(III) data might be due to the competition of the OH^- ions for the highly hydrolyzable Fe^{+3} ion (5). The same explanation was given in (2) for the Pu(IV) and Np(IV) data.

By comparing the curves of Ca(II) (see Fig. 2) and Fe(III), based on the slope analysis equation

$$\frac{\partial \log D_w}{\partial \log [H^+]} = -n \tag{1}$$

derived in (2), it appears evident that Ca(II) is exchanged with a pure ion- exchange mechanism (with saline invasion affecting the data in the 5 to 10 $\underline{M}$ HNO$_3$ range) as indicated by the slope value of about minus two, while Fe(III) is extracted predominantly through coordination to the phosphoryl groups of the diphosphonic acid, without release of H$^+$ ions by the resin, thus explaining the near-zero slope up to very high acidities (2).

The behavior of the other trivalent cations of Fig. 1 also shows an unusual feature, that is, a complete reversal of selectivity over the acidity range from dilute to concentrated acid. The data in Fig. 1 also show that the higher the distribution ratio at low acidity, (for example, 0.2 $\underline{M}$), the lower the distribution ratio at high acid concentration.

The behavior of Cr(III) deserves special attention. As previously mentioned, the Cr(III) data were obtained after 48 hours of equilibration. This time is sufficient for attainment of equilibrium at low acidities but not for [HNO$_3$] > 1 $\underline{M}$ (more details will be given in Part 4 of this series). However, the distribution ratios at high acidities are not very far from the value they would have at equilibrium. Consequently, the general shape of the curve would not change significantly, with very high D values for Cr(III) at high acidities, indicating also in this case the predominating coordination to the resin ligand, leading to the formation of protonated complexes.

The Eu(III) data confirm the expected similar behavior of lanthanides and trivalent actinides. The acid dependency of Eu(III) closely follows the one reported in (2) for Am(III), with slightly higher D values for the former. At 1 $\underline{M}$ HNO$_3$, for example, a Eu/Am separation factor of about 3 is observed.

In Fig. 2 the divalent ions Ca(II), Co(II) and Zn(II) share a very similar behavior, completely different from that of Fe(III) and Cr(III), indicating the

displacement of H^+ in the metal uptake process with a D vs. acid concentration slope of about minus two. The data of Sb(III) and Hg(II) roughly parallel the curve of Ag(I), although with lower D values. Because this behavior is also exhibited with the other two resins (see Table 1), it is evidently due to the chemistry of the ions in solution and not to a particular type of interaction with Diphonix. It is known that Sb(III) exists as $Sb(OH)_2^+$ even at high acidities (5). For Hg(II), the higher than minus one slope is most likely due to the small amount of Cl^- ions introduced in the test solutions with the radioisotope spike (the ^{203}Hg stock solution was 0.1 $\underline{M}$ in HCl). Cl^- forms strong complexes with Hg(II). Consequently, the metal was present in the test solutions mostly as $HgCl^+$ and $HgCl_2$ (6).

The HCl acid dependencies of Fig. 3 require some comments. With Al(III) practically the same D values are measured in both HCl and HNO_3. They are quite high in the range 0.1 to 1 $\underline{M}$ acid. From a practical standpoint, this means that aluminum can significantly interfere with the uptake of trivalent actinides in both nitric or a hydrochloric medium. The same can be said for lanthanides. The uptake of europium from HCl is slightly higher than from HNO_3, again paralleling the behavior of americium (2). The change of medium from nitric to hydrochloric acid strongly affects the Fe(III) data, which exhibit a steep decline for high HCl concentrations, due to the formation of Fe(III)-chloride complexes (6). The strong interference of Fe(III) with the uptake of all other cations, including tetravalent actinides, can thus be somewhat reduced in high HCl concentrations. A better way to eliminate or, at least, to substantially reduce the Fe(III) interference is shown in Fig. 3, where the acid dependency of Fe(II) has been reported for comparison. Although the D values of Fe(II) seem to be somewhat too high as compared to the Ds of other divalent cations (see Fig. 2), indicating a possibly incomplete reduction of Fe(III), the use of suitable reducing agents should eliminate the otherwise significant interference of Fe(III).

The HCl medium is also very effective in depressing the uptake of bismuth, which is also strongly complexed by the Cl^- anions (6). At about 1 $\underline{M}$ HCl, the uptake of Bi(III) by Diphonix is very low.

The different behavior of the three investigated resins with respect to Fe(III) and Cr(III) is very evident in Fig. 4, which clearly shows the superiority of the Diphonix resin in removing these ions from very acidic solutions. At 5 $\underline{M}$ HNO$_3$, for example, Fe(III) and Cr(III) show distribution ratios which are about 10^3 and 10^2 times, respectively, higher with Diphonix than with Bio-Rad AG MP-50. The difference is evidently due to the diphosphonic acid group of Diphonix, because the monophosphonic resin behaves in a manner not very different from the sulfonic resin. With Ag(I), however, the sulfonic type commercial resin shows a more efficient metal uptake, except in the 7 to 10 $\underline{M}$ HNO$_3$ range. The reason for this behavior is not clear. In the case of Sb(III), Zn(II), Co(II) and Hg(II) the three resins exhibit almost the same acid depencencies, with the sulfonic resin having slightly higher distribution ratios than the other two resins. With these cations, evidently, the presence on the Diphonix resin of the diphosphonic acid groups does not provide any improvement of the uptake from acidic solutions, indicating that the coordination of the metal species to the phosphoryl has a negligible overall effect. Unexpected, but important, is the different behavior of calcium ions with the Diphonix and the Bio-Rad AG MP-50 resins. The latter shows distribution ratios about ten times higher than the former. It follows that in ion-exchange procedures to remove heavy metals from acidic solutions, the competition between calcium ions and the other metal species for the resin sites should be less of a problem with Diphonix than with strong acid cation-exchange resins. A summary of the selectivity orders observed with the three investigated resins at 0.1 and 5 $\underline{M}$ HNO$_3$ is reported in Table 2.

Uptake of Metal Species from Near-Neutral Solutions

Figures 5 and 6 report the distribution ratios of all the investigated cations with the calcium salts of Diphonix and the Bio-Rad AG MP-50 resin in the pH interval 5 - 8. The data for U(VI), discussed in (2), are inserted for comparison. The data of Figs. 5 and 6 have been determined using as the aqueous solution a 0.1 $\underline{M}$ ammonium acetate buffer whose pH had been adjusted to 5, 6 or 8 by adding acetic acid or ammonia. The possible effect of NH$_4^+$ ions on the measured distribution ratios has been discussed in (2). It should be small with Diphonix, but

somewhat more significant with the sulfonic acid resin. The data are also affected by the presence of the acetate anions, which exhibit at least some complexing power toward several of the cations studied (6). The effect of acetate ions, however, is the same for both resins and, therefore, should have no consequence on the comparison.

With the previous considerations in mind, and within the approximations mentioned above, the distribution ratios of Figs. 5 and 6 can be considered to give an approximate idea of the selectivity of Diphonix and the Bio-Rad AG MP-50 resin for the different ions relative to calcium from neutral and near-neutral solutions. It appears from the data that Diphonix shows a much higher preference for most metal ions over calcium than the sulfonic acid resin shows. Al(III), Hg(II), Sn(II), Sb(III), and Ag(I) are exceptions.

Table 3 reports a comparison of the selectivities relative to calcium for several metal species of Diphonix and of a commercial iminodiacetic acid chelating resin (7,8). Although keeping in mind that the Diphonix data are probably somewhat affected by the presence of the NH_4^+ and CH_3COO^- ions in solution, and that the two sets of data refer to pH values differing by one unit (4 vs. 5), it still appears that the selectivity of Diphonix for Mn, Co, Ni, Zn, Cd and U is significantly higher.

Stripping Agents

The data of Fig. 1 show that it should be possible to easily strip the transition metal ions [except Fe(III)] from Diphonix with solutions of strong acids and especially of H_2SO_4 , because of the complexing power of the sulfate anions towards transition metal cations (6). Table 4 reports the distribution ratios of Fe(III), Co(II), Zn(II) and Cr(III) between Diphonix and solutions of H_2SO_4 at different concentrations. It appears that a 1 to 3 $\underline{M}$ acid solutions (HCl, HNO₃, H_2SO_4) generates very low D values, except for Fe(III). It should be noted, however, that the Cr(III) data refer to uptake experiments where the metal was initially in the aqueous solution. Other experiments where Cr(III) had been previously loaded on Diphonix, showed that a 1 $\underline{M}$ H_2SO_4 solution was completely

ineffective for metal strip, even after several days of contact with the resin. This behavior of Cr(III) has a kinetic origin and is most probably due to the well-known inertness of inner-sphere complexes of Cr(III). Also a 2 $\underline{M}$ NaCN solution proved to be completely ineffective for Cr(III) strip from a previously metal loaded Diphonix.

Other potential strip solutions were tried for Fe(III). The results are summarized in Table 5 and show that only 1-hydroxyethane-1,1- diphosphonic acid (HEDPA) at a relatively high concentration (1 $\underline{M}$) can prevent Fe(III) from being extracted by Diphonix and is, therefore, capable of stripping the ion from the loaded resin. A similar result was reported in (2) for actinide ions, and the reason for this behavior was given. Of special interest is the capability of Diphonix to extract Fe(III) even in the presence of EDTA at pH values as high as 4. This property can be exploited in analytical procedures. With Cr(III), however, even a 1 $\underline{M}$ HEDPA solution fails to remove the metal from a loaded Diphonix resin, again because of kinetic factors. A more detailed investigation of the Cr(III) stripping from Diphonix will be described in Part 4 of this series and the most effective ways to actually strip chromium from the resin will be discussed.

CONCLUSIONS

Diphonix is a new dual-mechanism chelating resin containing gem-diphosphonic acid and sulfonic groups. In the first part of this series (2), we showed that Diphonix exhibitis an extremely high affinity for actinide ions, even at acidities as high as 10 $\underline{M}$ HNO$_3$ and HCl. In this work we have examined the distribution behavior of a number of transition and post-transition metals ions, comparing Diphonix with a monophosphonic resin and a commercial sulfonic-type ion exchange resin. Our data have allowed us to conclude that Diphonix shows an affinity for Fe(III) in acidic solutions comparable to that for tetravalent actinides. Also Cr(III) is extracted very effectively, although slowly, by Diphonix at high acid concentrations.

Very high selectivities relative to calcium for several transition elements and lead have been measured with Diphonix in neutral and near-neutral solutions. Conditions for a very efficient strip of the investigated metal ions from Diphonix have been found: 1 $\underline{M}$ H_2SO_4 is generally effective for divalent metals, while a 1 $\underline{M}$ HEDPA solution is required to strip Fe(III). Diphonix and its salts could have application in all those cases where removal of metals from acidic or neutral waste effluents is desired.

AKNOWLEDGMENTS

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Table 1

Nitric acid dependencies of several metal ions with the Diphonix, the Monophosphonic and the Bio-Rad AG-MP 50 resins

D (ml g^{-1})

[HNO$_3$] M	Fe(III)	Cr(III)*	Sb(III)	Ca(II)	Zn(II)	Co(II)	Hg(II)	Ag(I)
				Diphonix				
0.01	-	-	-	2.2×10^5	4.6×10^4	9.5×10^3	4.6×10	-
0.02	3.0×10^4	-	2.2×10^2	-	2.5×10^4	-	-	4.0×10^3
0.04	5.0×10^4	6.1×10^3	1.1×10^2	1.7×10^4	-	3.0×10^3	1.8×10	2.2×10^3
0.1	1.2×10^5	2.8×10^3	6.1×10	2.6×10^3	1.1×10^3	7.0×10^2	1.05×10	7.3×10^2
0.27	2.7×10^5	6.2×10^2	3.8×10	2.7×10^2	1.4×10^2	1.0×10^2	8.5	3.2×10^2
0.51	2.3×10^5	2.0×10^2	2.5×10	7.5×10	4.1×10	3.4×10	5.6	1.8×10^2
1	2.4×10^5	8.2×10	2.3×10	1.9×10	1.3×10	9.5	4.4	8.9×10
2.4	1.9×10^5	7.0×10	1.6×10	2.7	3.0	4.9	4.5	4.4×10
5	1.0×10^5	1.9×10^2	9.1	6.5×10^{-1}	2.5	2.8	2.5	3.4×10
7.3	5.6×10^4	6.0×10^2	7.6	5.9×10^{-1}	2.6	2.0	3.1	7.7×10
10	2.4×10^4	3.6×10^3	1.5×10	1.4	4.0	2.0	1.8	1.8×10^2
				Monophosphonic				
0.1	6.6×10^4	2.5×10^3	3.4×10	1.0×10^3	6.9×10^2	5.8×10^2	9.7	6.1×10^2
0.51	1.3×10^4	1.2×10^2	7.9	3.5×10	2.9×10	2.4×10	6.1	1.2×10^2
1	2.3×10^3	1.6×10	6.0	1.1×10	8.6	7.4	5.7	7.3×10
5	3.0×10^2	1.7	3.0	1.5	2.4	2.1	3.6	3.6×10
10	1.1×10^3	1.15×10	7.5	5.6	3.5	1.8	3.6	3.1×10^2

Table 1 (Cont.)

Nitric acid dependencies of several metal ions with the Diphonix, the Monophosphonic and the Bio-Rad AG-MP 50 resins

				Bio-Rad AG-MP 50				
0.1	5.0×10^4	2.3×10^3	4.6×10	2.5×10^4	3.9×10^3	1.6×10^3	1.6×10	7.4×10^3
0.27	2.3×10^4	-	-	2.8×10^3	-	-	-	-
0.51	7.4×10^3	6.8×10^2	9.7	1.0×10^3	1.3×10^2	1.0×10^2	8.7	1.7×10^3
1	1.3×10^3	1.9×10^2	7.8	2.3×10^2	3.4×10	3.2×10	5.1	7.7×10^2
2.4	1.9×10^2	-	-	3.6×10	-	-	-	-
5	4.0×10	3.1	1.2	9.1	2.8	2.9	3.2	8.9×10
7.3	4.6×10	-	-	6.3	-	-	-	-
10	1.2×10^2	6.4	4.6	9.7	3.7	2.3	1.5	5.8×10

* Cr(III) data obtained after 24 hours stirring

Table 2

Selectivity order for the Diphonix, Monophosphonic and Bio-Rad AG MP-50 resins

0.1 M HNO₃

Diphonix :   Fe >>Ca ≅Cr >Zn >Ag >Co >>Sb >Hg

Monophosphonic :   Fe >Cr   >Ca ≅Zn ≅Ag ≅Co >>Sb >Hg

Bio-Rad AG MP-50:   Fe >Ca   >Ag >Zn >Cr >Co >>Sb >Hg

5 M HNO₃

Diphonix :   Fe >Cr   >Ag >Sb >Co ≅Zn ≅Hg >Ca

Monophosphonic :   Fe >Ag   >Hg ≅Sb ≅Zn ≅Co ≅Cr ≅Ca

Bio-Rad AG MP-50:   Ag >Fe   >Ca >Hg ≅Cr ≅Co ≅Zn ≅Sb

Table 3

Comparison of the relative selectivities of Diphonix and the
iminodiacetic chelating resin Amberlite IRC -718

	Amberlite IRC - 718[a]	Diphonix[c]
	pH $= 4$	pH $= 5$
Ca	1.0	1.0
Mn	1.2	4.1×10^3
Co	6.7	4.5×10^2
Ni	5.7×10	2.7×10^2
Cu	2.3×10^3	$> 10^3$
Zn	1.7×10	1.4×10^4
Cd	1.5×10	1.2×10^3
Hg	2.8×10^3	3.5×10^3
Pb	1.2×10^3	9.9×10^3
U	4.4×10^2 (b)	1.3×10^4

a) from ref. 7
b) from ref. 8
c) this work

Table 4

Distribution ratio of some metal ions between Diphonix and H_2SO_4 solutions

[H_2SO_4], $\underline{M}$	Fe(III)	Co(II)	Zn(II)	Cr(III)
		D		
0.5	4.8×10^4	1.9×10	2.3×10	3.8×10
1	1.8×10^4	4.8	7.3	4.8
2.5	4.7×10^3	2.7	1.9	1.3

Table 5

Distribution ratio of Fe(III) between Diphonix and possible stripping solutions

Solution	D_{Fe}
1 $\underline{M}$ $H_2C_2O_4$	5.5×10^1
0.1 $\underline{M}$ $NH_4HC_2O_4$	5.7×10^2
0.1 $\underline{M}$ $NH_4HCitrate$	1.0×10^4
0.1 $\underline{M}$ Ascorbic Acid	2.7×10^4
0.1 $\underline{M}$ Na_2EDTA at pH 4	1.2×10^2
0.1 $\underline{M}$ HCl saturated in Na_2EDTA	1.3×10^4
1 $\underline{M}$ HEDPA*	2.7

* 1-hydroxyethane-1,1-diphosphonic acid

Figure Captions

Fig. 1. Nitric acid depencency of the uptake of Fe(III) (●), Al(III) (■), Cr(III) (▼), Eu(III) (▲) and Bi(III) (□) by Diphonix.

Fig. 2. Nitric acid dependency of the uptake of Ca(II) (●), Zn(II) (■), Co(II) (▲), Ag(I) (▼), Hg(II) (○) and Sb(III) (□) by Diphonix.

Fig. 3. Hydrochloric acid dependency of the uptake of Fe(III) (●), Fe(II) (○), Eu(III) (▲), Al(III) (■) and Bi(III) (▼) by Diphonix.

Fig. 4. Comparison of the nitric acid dependencies of Fe(III), Cr(III), Ca(II) and Ag(I) uptake by the Diphonix (●), Monophosphonic (▲) and Bio-Rad AG MP-50 (■) resins.

Fig. 5. Comparison of the uptake of various metal ions by the calcium salts of the Diphonix (●)and Bio-Rad AG-MP 50 (■) resins in the pH range 5 to 8.

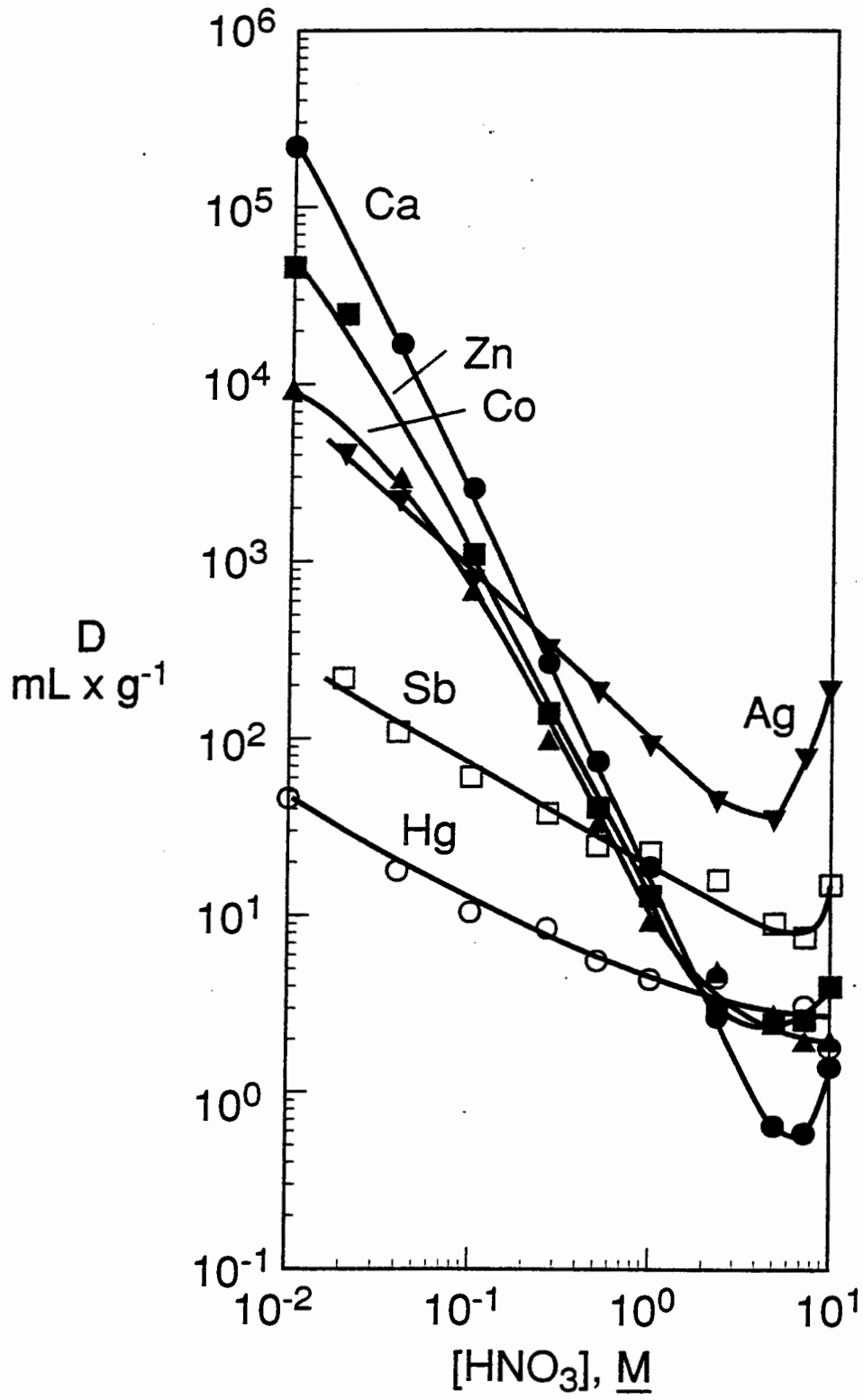Fig. 6. Comparison of the uptake of various metal ions by the calcium salts of the Diphonix (●)and Bio-Rad AG MP-50 (■) resins in the pH range 5 to 8.
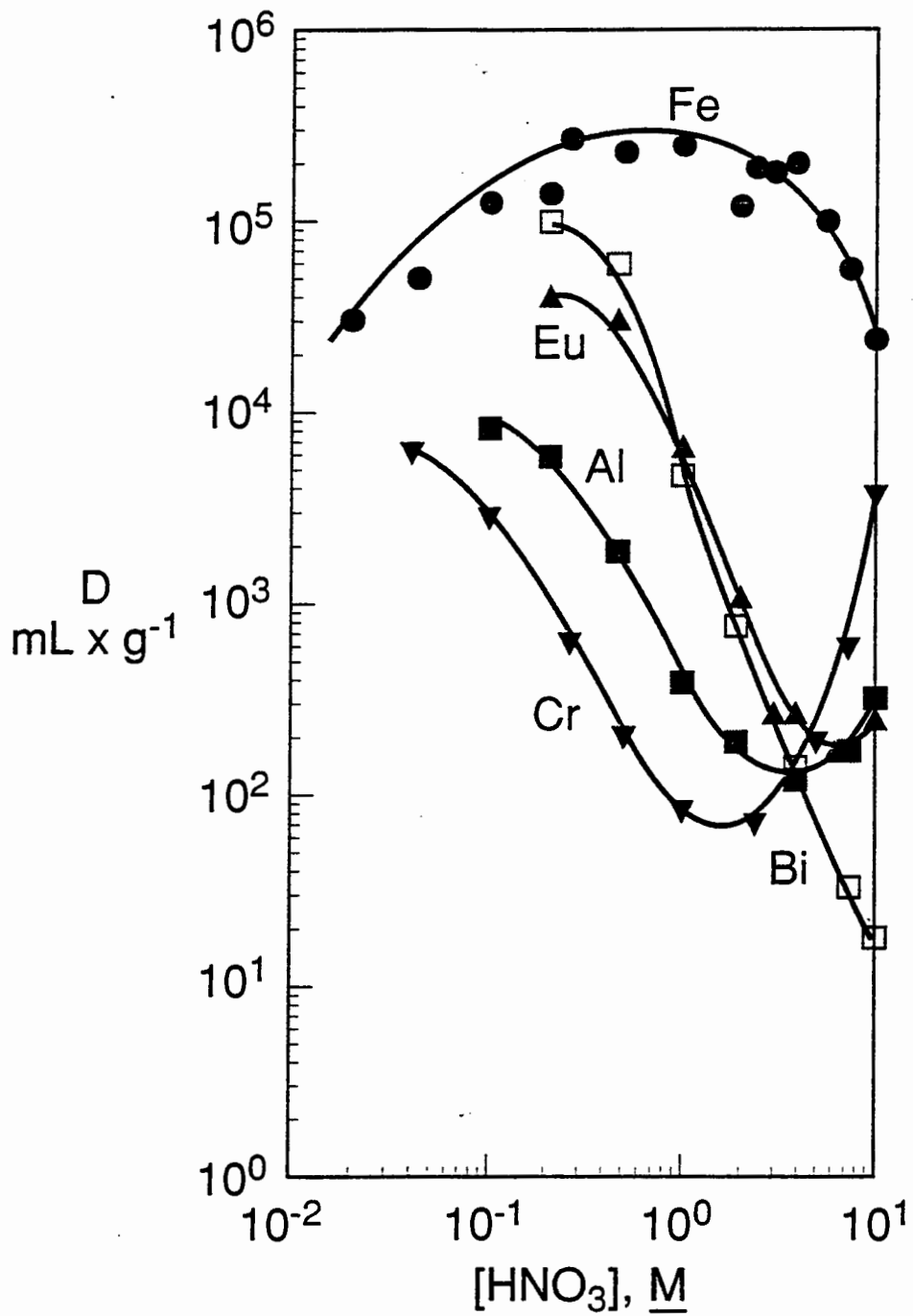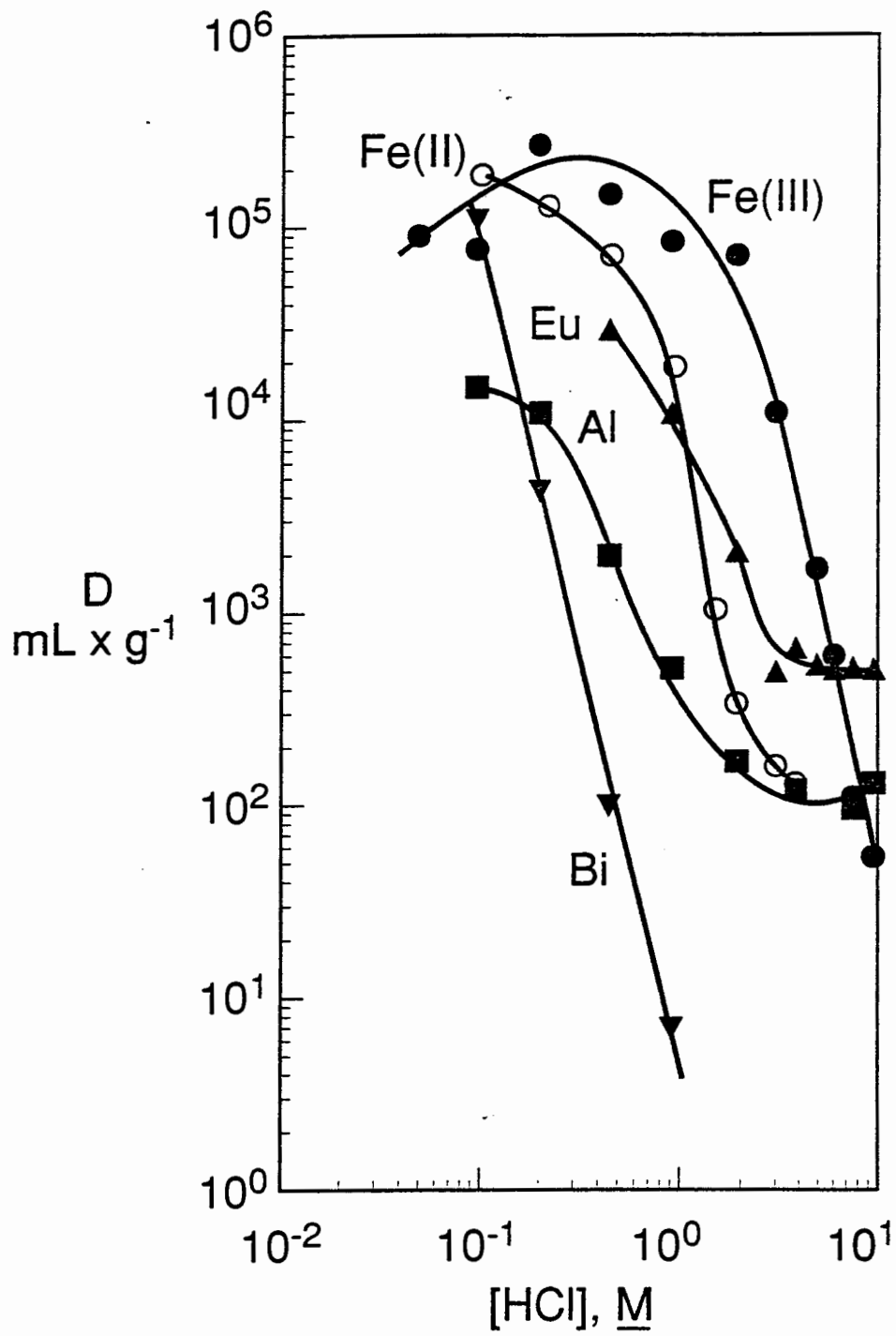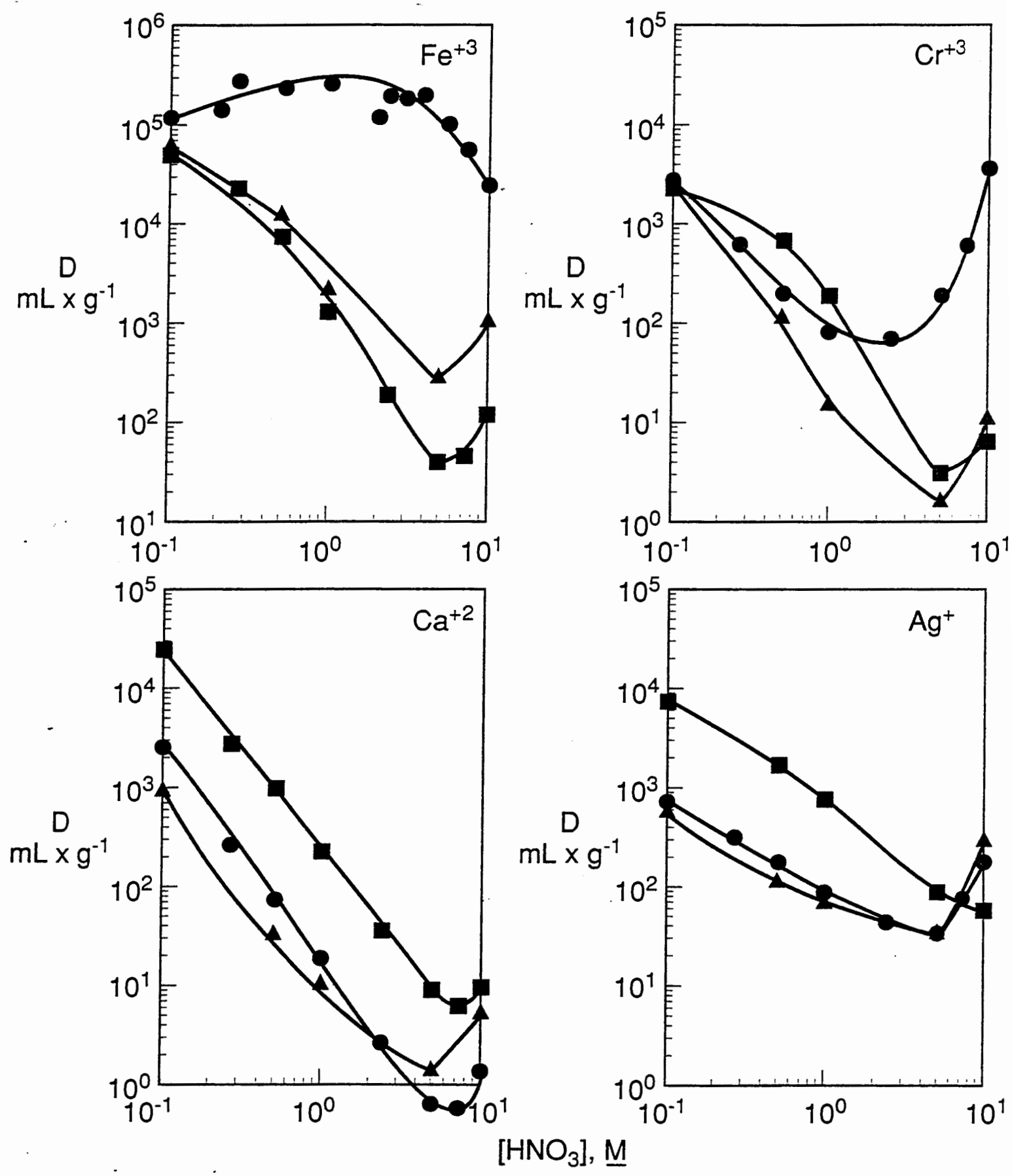
Fig. 1

Fig. 2

Fig. 3

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