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DIPHONIX™ RESIN : A REVIEW OF ITS PROPERTIES AND APPLICATIONS*

by

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ABSTRACT

The recently developed Diphonix™ resin is a new multifunctional chelating ion exchange resin containing geminally substituted diphosphonic acid ligands chemically bonded to a styrene-based polymeric matrix. Diphonix can be regarded as a dual mechanism polymer, with a sulfonic acid cation exchange group allowing for rapid access, mostly non-specific, of ions into the polymeric network, and the diphosphonic acid group responsible for specificity (recognition) for a number of metal cations.

The Diphonix resin exhibits an extraordinarily strong affinity for actinides, especially in the tetra- and hexavalent oxidation states. Therefore the resin has potential for applications in TRU and mixed waste treatment and characterization, and in the development of new procedures for rapid actinide preconcentration and separation from environmental samples. Metal uptake studies have been extended to alkaline earth cations, to transition and post-transition metal species, and to metal sorption from neutral or near neutral solutions. Also the kinetic behavior of the resin has been investigated in detail. In view of the above applications the influence of the most commonly occurring matrix constituents (Na, Ca, Al, Fe, hydrofluoric, sulfuric, oxalic and phosphoric acids) on the uptake of actinide ions has been measured.

This review paper summarizes the most important results obtained in the studies on the properties of the Diphonix resin and gives an overview of the applications already in existence or under development in the fields of mixed waste treatment, actinide separation procedures, treatment of radwaste from nuclear power plants, and removal of iron from copper electrowinning solutions.

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INTRODUCTION

The novel Diphonix™ ion exchange resin has been developed by members of the Separation Chemistry Group of the Chemistry Division of Argonne National Laboratory (ANL) together with members of the University of Tennessee, Department of Chemistry.

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The resin contains geminally substituted diphosphonic acid groups chemically bonded to a styrenic-based polymer matrix. The Diphonix resin also contains the strongly hydrophilic sulfonic acid group in the same polymeric network together with the diphosphonic acid group, to provide the polymer with the required high hydrophilicity for fast kinetics of metal species uptake. Because of the presence of both diphosphonic and sulfonic acid groups, the Diphonix resin can be considered a dual-mechanism polymer, characterized by a hydrophilic cation exchange group allowing for access (mostly non-specific) of ions into the polymeric network, and by another ligand group responsible for the resin specificity (recognition) toward target metal ions (1).

The development of the Diphonix resin can be seen as a spin-off of the studies performed at Argonne National Laboratory on the TUCS (Thermally Unstable Complexants) compounds (1). One of the TUCS families is based on the substituted methane diphosphonic acids, which are powerful complexing agents in acidic solutions (2). Their ability to complex actinides and lanthanides is mainly attributed to the high acidity of the diphosphonic acid group. Vinylidene-1,1-diphosphonic acid, VDPA, for example has a $pK_{a,1} = 1.4$ and a $pK_{a,2} = 2.1$ (3). The strong acidity of the diphosphonic acid group and its tendency to chelate actinides through either ionized or neutral diphosphonic acid ligands, thanks to the remarkable coordinating properties of the P=O groups, makes possible the formation of metal complexes of high stability under conditions too acidic for appreciable complexations by other acidic ligands such as carboxylic and monophosphonic acids to occur. We thought that, if successful, the attempt of synthesizing a polymeric chelating resin containing the diphosphonic acid ligand would provide the separation chemist with a new and powerful tool capable of combining the well established tecnique of ion exchange with the superior complexing ability of the diphosphonic acid group.

The synthesis of the Diphonix resin, whose structure is shown in Figure 1, was successfully achieved and is reported in detail in (4). Two United States Patents were issued in January 1994 and in September 1995 (5). The Diphonix resin received a 1994 R&D 100 Award as one of the 100 most technologically significant new products of the year. The resin is now commercially available in a variety of mesh sizes from Eichrom Industries, Inc., Darien, Illinois.

The behavior of the new resin with respect to the uptake of actinide ions was investigated in (6). As expected, the resin showed a most remarkable affinity for actinides, especially in the tetra- and hexavalent oxidation states.

A study of the uptake of transition and post-transition metal ions from acidic and near neutral solutions was reported in (7). This study demonstrated that the resin is also effective in sorbing other multivalent ions, such as Al(III), Cr(III) and especially Fe(III). For applications in the field of actinides separations, the last finding was considered a drawback, as it limits the selectivity of the resin for actinides, particularly for americium. But, while the limitations regarding the selectivity for actinides can be easily overcome through appropriate redox and complexation chemistry, the high affinity of the Diphonix resin for Fe(III) has made possible even more important applications in non-nuclear fields, such as in the electrowinning of copper.

The acid-base properties of the Diphonix resin were investigated in (8) and the kinetic behavior of the resin in the uptake of metal ions at tracer level concentration has been reported in (9). The study of the effect of high concentrations of matrix constituents (sodium, calcium, aluminum and iron, among cationic species; and fluorides, oxalates, sulfates and phosphates, among complexing anionic species) was performed in (10-11). The uptake of the alkaline earth cations was studied in (12). The behavior of a Diphonix resin containing also anion exchanging groups has been recently investigated and is reported in (13).

This review is divided in two parts. In the first part the most important properties of the Diphonix resin will be summarized especially in relation to the applications which have been proposed up to now for the resin; in the second part the most significant applications will be discussed.

PART 1 : PROPERTIES OF THE DIPHONIX RESIN

1. Uptake of Metal Ions

Figure 2 shows the nitric acid dependencies of the dry weight distribution ratio, D (mL/g), defined as the ratio between the metal concentrations in the resin phase and in the solution in equilibrium with the resin, for some representative actinide species. The most striking feature of the data of Figure 2 is the extremely high retention of hexavalent uranium and tetravalent actinides by the Diphonix resin in the whole acidity range even up to 10 M HNO_3. The uptake of Am(III) shows a strong negative dependence on the acid concentration, typical of the cation exchange behavior exhibited by strong acid sulfonic type resins. However, it has been shown in (6) that D_{Am} values measured with the Diphonix resin are substantially higher than those measured with sulfonic resins, especially in the high acidity range.

Figure 3 shows the behavior of the Diphonix resin with respect to non-actinide trivalent cations. The most noteworthy feature of the data of Figure 3 is the behavior of Fe(III). It strongly resembles the curve reported in Figure 2 for Pu(IV) and Np(IV), with a plateau in the intermediate acidity range. In all three cases the plateau region in the acid dependency curves is probably due to the competition of the OH^- ions for the highly hydrolyzable cations. The lack of a strong acid dependency in the uptake data of Fe(III) as well as of the tetravalent actinides and to some extent of U(VI), clearly indicates that the above species are sorbed at the higher acidities predominantly through coordination to the phosphoryl groups of the diphosphonic acid, without release of H^+ ions by the resin. Also noteworthy is the behavior of Al(III) and Cr(III), which show a pronounced minimum in their acid dependencies, with D values increasing substantially, especially in the case of Cr(III), at the highest acidities. Also in this case, the behavior of the uptake data seems to indicate a shift of the coordination reaction toward predominant formation of protonated complexes. From a practical standpoint, the data of Figure 3 clearly indicate that in the uptake of actinide ions by the Diphonix resin, a strong interference would be expected by Al(III) and especially by Fe(III), if these ions are present in solution at concentrations much higher that the actinides.

The acid dependencies of the uptake data for some representative transition elements are shown in Figure 4. The Zn(II), Cu(II) and Co(II) data are all clustered together along lines of slope approximately equal to minus 2, indicating that the ions are essentially sorbed through an ion exchange reaction involving the release of two hydrogens per atom of divalent metal. The same conclusion applies to the Ag(I) data, where the slope is of course close to minus 1. The figure also reports some uptake data obtained using a Fe(III) tracer in the presence of 0.1 M ascorbic acid. The data show that the D values for iron are strongly reduced in the presence of reducing agent capable of reducing Fe(III) to Fe(II), although the higher D values than for the other divalent transition metals show that the Fe(III) reduction was not quantitative in the conditions of the experiments. The possibility of strongly reducing the uptake of iron by the Diphonix resin through redox chemistry makes possible the achievement of selectivity for actinides over iron and also has important consequences on the non-nuclear application of the resin which will be discussed in the second part of this review.

Figure 4 also shows some uptake data obtained with Tc(VII). This element exists in solution mostly as pertechnetate anion TcO_4^-. The fact that TcO_4^- is sorbed by the Diphonix resin, although with relatively low distribution ratios, indicates the possibility of hydrogen bonding of $HTcO_4$ to the phosphoryl groups of the diphosphonic acid ligand. A more detailed discussion of Tc(VII) uptake by the Diphonix resin, a modified Diphonix resin containing also quaternary ammonium groups (the latter resin is called Diphonix A, for anion exchanger Diphonix resin), and conventional anion exchange resins can be found in (13).

The uptake of selected elements from neutral or near neutral solutions by the calcium salts of the Diphonix resin and of a sulfonic resin for comparison is shown in Figure 5. Among the selected elements are uranium and some of the fission products that contribute to the radioactivity of effluents of nuclear power plants. The much better performance of the Diphonix resin as compared to a conventional sulfonic resin in sorbing the selected elements suggests the possible use of the former resin in nuclear power plants radwaste treatment. This application will be discussed in detail later. The Pb(II) data of Figure 5 also suggest that the Diphonix resin might be successfully employed to reduce the lead content of drinking water.

The uptake behavior of the Diphonix resin toward the alkaline earth elements has been investigated in (12). Figure 6 reports a comparison between the Diphonix resin and the sulfonic resin Bio-Rad™ AG MP-50 (the latter data are taken from (14)). Although the values of the distribution ratios of the investigated elements do not show any major difference between the two resins, the different selectivity order shows that the type of interaction between the two resins and the alkaline earth cations is different. With the conventional sulfonic type resin the selectivity order is dictated by the size of the hydrated cation, as expected based on the simplified Gregor's theory (12), without any specific chemical interaction of the charged and hydrated cations with the fixed negatively charged sites of the resin. On the other hand, the almost complete lack of selectivity in the case of the Diphonix resin strongly indicates that the uptake of the Group IIa cations is mainly due to the chelation by the diphosphonic acid ligands. The data of Figure 6 may find application in analytical procedures where a group separation of the alkaline earth cations from other species is desired.

Another example of different behavior of the Diphonix resin as compared to other resins is shown in Figure 7, where acid dependencies are given for the U(VI), Pu(IV) and Fe(III) uptake by the Diphonix resin, by the sulfonic resin Bio-Rad AG MP-50, and by a monophosphonic resin prepared in the same way as Diphonix, but with monophosphonic instead of diphosphonic ligands (6). The different chemistry involved in the case of the Diphonix resin appears clearly from the comparison. In particular, the behavior of the monophosphonic resin appears to be always intermediate between the other two resins, indicating that the metals are extracted to some extent by the monophosphonic resin also through coordination with the phosphoryl group of the phosphonic acid, possibly with the formation of protonated complexes. With the Diphonix resin, on the other hand, the much higher uptake values and the strongly reduced acid dependencies indicate that the chelation of the metal ions by the diphosphonic ligands is the main factor for metal uptake, and that protonated complexes predominate at least at the highest acidities.

All the data discussed above have been obtained in nitric acid solutions. It is important, however, to know the behavior of the resin in other media, because, for example, analytical procedures for actinides determination in environmental samples are often run in hydrochloric acid and hydrometallurgical process generally employ sulfuric acid. Some representative data on the uptake of metal ions by the Diphonix resin from solutions of the above acids are shown in Figure 8. From HCl, the uptake of Fe(III), U(VI) and especially Bi(III) exhibits a much steeper acid dependency than it does from HNO_3, because of the strong tendency of these cations to form chloride complexes. Bismuth has been included in the figure because it is a troublesome elements in actinides analyses of fecal samples. The data of the figure show that Bi(III) can be easily removed from a Diphonix resin column by a 1 M HCl rinse. In spite of the steep acid dependency, the U(VI) D values are still high enough to be useful up to about 10 M HCl. The uptake of trivalent and tetravalent actinides is little affected by the presence of Cl^- ions, unlike that of Fe(III). As a consequence, a better selectivity for actinides over Fe(III) can be achieved in strong HCl media.

The data of Figure 8 reporting the behavior of some first row transition elements in the uptake from sulfuric acid are here reported for the first time. The selectivity of the resin for Fe(III) over Co(II) (and presumably over Cu(II) as well) is the basis for the application of the Diphonix resin in the electrowinning of copper.

2. Kinetics of Metal Uptake

As previously mentioned, the sulfonic groups of the the Diphonix polymer are needed to improve the kinetics of metal uptake. Figure 9 shows the kinetics of Am(III) uptake, expressed as fractional attainment of equilibrium vs. time data (see (9) for details), from 1 M HNO_3 by the Diphonix resin and by an unsulfonated sample of the same resin. The data show a dramatically faster metal uptake for the sulfonated resin, with 99.9 % of the equilibrium metal distribution achieved in about 10 minutes. With the unsulfonated resin, on the other hand, equilibrium is achieved only after a few days contact between resin and solution. This result fully demonstrates that the addition to the chelating resin of the highly polar sulfonic groups imparts to the resin the hydrophilicity required for fast uptake kinetics.

Figure 9 also shows a comparison of Diphonix with two commercial sulfonic-type, strong cation-exchangers, the macroporous resin Bio-Rad AG MP-50, and the gel resin Dowex™ 50W-X8, all with the same particle size (75-150 microns). Again, the chemical system taken as reference is the uptake of Am(III) from 1 M HNO_3. The data show that the kinetic behavior of the three resins is practically identical for up to more than 90 % of the course of the reaction. Beyond this value, the gel sulfonic-type resin is somewhat faster in reaching equilibrium. However, the kinetics of metal uptake by Diphonix, at least from 1 M HNO_3 and at very low metal concentration, appears to be fully satisfactory for practical applications, being comparable with that exhibited by non chelating sulfonic-type resins.

The uptake kinetics of a variety of metal species at tracer level concentration by the Diphonix resin has been measured (9). A few data are collected in Figure 10, showing the uptake kinetics of three representative actinides from various concentrations of HNO_3 or HCl. Under all conditions the uptake is sufficiently rapid for practical applications. The different kinetics measured for the actinides at different acid concentrations probably reflect the well-known effect of the selectivity on the kinetics of uptake (15-16) and is discussed in detail in (9). Figure 10 also reports some data on the uptake of Cr(III), whose hydrated cation $Cr(H_2O)_6^{3+}$ is known to be extremely inert. This is reflected in the very low uptake kinetics by the Diphonix resin at high acidity. However, if the acid concentration is lowered to the 0.1 M level, the mononuclear hydrolysis species $Cr(H_2O)_5OH^{2+}$ starts to form. The hydrolysis species is much more labile than the hexaaquo ion and reacts much more rapidly with the ligand in the resin. As a consequence, even the uptake of Cr(III) by the Diphonix resin becomes very fast at a pH value around 1, as the data in Figure 10 show.

3. Effect of Matrix Constituents on Actinides Uptake

As previously mentioned, the uptake of actinides by the Diphonix resin is expected to be affected by the presence in solutions of other cationic species exhibiting affinity for the resin. Two such species are Al(III) and Fe(III). Al(III) is normally present in soil samples and Fe(III) is generally present in all samples because of its ubiquitous nature. Figure 11 shows the effect of increasing Al(III) concentrations in 1 M HNO_3 on the uptake of three representative actinides. Tetra- and hexavalent actinides have such a strong retention by the Diphonix resin, that even in the presence of Al(III) concentrations above 0.1 M their D values are well above 10^3, that is, the effect of Al(III) on their uptake is practically negligible. The situation is different for the trivalent actinides, which are the least sorbed by the resin among the actinides. Fortunately, as will be shown later, Al(III) forms very strong complexes with fluoride ions while the Am(III) uptake by the resin in the presence of, for example, 1 M HF is little affected. Thus, the addition of HF to the sample solution largely removes the interference of Al(III) on the uptake of trivalent actinides.

Much more important is the interference on actinides uptake brought about by the presence of Fe(III), as already mentioned before. The effect of increasing Fe(III) concentrations on actinide uptake from 1 M HNO_3 is reported in the right hand side plot of Figure 11. The data show that even the uptake of Th(IV) and U(VI) is indeed strongly diminished when the Fe(III) in solution is above the 0.01 M concentration level. The detrimental effect of Fe(III) on actinides uptake, however, can be eliminated or at least controlled, by adding to the solution a reducing agent capable of reducing Fe(III) to Fe(II) (see also Figure 4 discussed previously). The data of Figure 11 show that in the presence of ascorbic acid the uptake of Am(III) is much less affected by the presence of iron species in solution, and that useful D_{Am} values can still be obtained even in the presence of 0.1 M iron.

The separation and preconcentration of actinides from soils, mixed-wastes, biological samples and other contaminated liquid or solid media involve matrices in which complexing anions may be present in significant concentrations. Commonly encountered complexing anions are fluorides (in dissolved siliceous materials, e.g. soil samples), oxalates (in many nuclear waste types), sulfates and phosphates (in analytical nuclear wastes). Figure 12 shows the effect of increasing concentrations of the respective acids on the uptake of three representative actinides by the Diphonix resin from 1 M HNO_3. The data show that in almost all cases concentrations of the complexing acids as high as 1 M or even higher can be tolerated in the sample solution without the actinides D values dropping below the limit of 10^3. The effect of the investigated acids on the actinides uptake will be, of course, a function of the initial nitric acid concentration, being, for example, much stronger at 0.1 M instead of 1 M HNO_3. A more detailed account of this effect can be found in (10). It is important however to mention here that the affinity of the Diphonix resin for the actinide ions is strong enough to overcome under most conditions the complexing power of fluoride, oxalate, sulfate and phosphate anions. This consideration is very important for some mixed wastes that contain high concentrations of sulfuric and phosphoric acids, such as the Davies-Gray waste whose treatment will be mentioned in the section on the applications of the Diphonix resin. The possibility of adding HF to aluminum bearing solutions in order to minimize the uptake of aluminum has been mentioned previously. The same approach can be used to suppress the uptake of titanium and zirconium relative to Am(III) (10).

The inability of oxalic acid to strongly depress the uptake of tetravalent and hexavalent actinides by the Diphonix resin, even at a concentration corresponding to the saturated solution, led the authors of (11) to attempt a quantitative interpretation of the data of Figure 12 and of the other data reported in (10) on the effect of anionic matrix constituents. Some results of the calculations, based on the literature values of the complex formation constants between actinide ions and the investigated anions, are shown in Figure 13 for a few exemplificative cases. In the Am(III) - $H_2C_2O_4$ case at 0.1 $\underline{M}$ HNO_3, the experimental points are well described by curve 1, calculated assuming that only the uncomplexed cation Am^{+3} is sorbed by the resin, while curve 2 assumes also the sorption of $AmC_2O_4^+$. The situation is completely different in the other two cases illustrated in Figure 13, that is Th(IV) - oxalic or phosphoric acids in 0.1 $\underline{M}$ HNO_3. In both cases, curves 1, calculated assuming that only Th^{+4} is sorbed by the resin, are several orders of magnitude away from the experimental data. The uptake data can only be reproduced by the curves 2, calculated assuming that all cationic and neutral complexes formed in solution between Th(IV) and the oxalate or the phosphoric ligands are sorbed by the resin. This is compelling evidence of the involvement of neutral complexes of tetravalent actinides in the metal uptake by the resin, as suggested by the previously discussed lack of acid dependency.

4. Strip of Metal Species from the Resin

For a convenient application of the ion exchange technique in metal species separation procedures, easy stripping of the sorbed species is required. The simplest stripping procedures with cation exchange resins is based on the acid dependency of the separated species. It is obvious that this is not possible with the Diphonix resin, at least for those species like the tetra- and hexavalent actinides and Fe(III) which show little if any acid dependencies. These metal species are so strongly retained by the resin that the only effective stripping agents are compounds belonging to the family of aqueous soluble diphosphonic acids, which contain the same ligand group as the resin. The stripping chemistry is in this case based on the mass action of an excess of ligand in the aqueous phase.

Figure 14 reports the uptake data of some actinides and Fe(III) by the Diphonix resin from solutions of 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), which is an inexpensive and commercially available reagent. Some of the data in Figure 14 have not been published before. As expected, the D values drop precipitously with an increase in the aqueous ligand concentration. Also, the effectiveness of the HEDPA ligand in suppressing the uptake by the Diphonix resin follows the order of complexation strength of actinides, that is, Th(IV) ≈ Pu(IV) > U(VI) > Am(III) (2). The data of Figure 14 indicate that HEDPA at a concentration between 0.1 and 0.5 M should be capable of stripping the actinides from a column of Diphonix resin in few column volumes.

The next question, however, is how to proceed further, if the separation of the single actinides is required. In this case, after stripping, the aqueous diphosphonic acid has to be thermally degraded for further processing of the actinides. This leads to solutions containing high concentrations of phosphoric acid, which, in turn, can generate problems in the successive separation steps. Also, the thermal degradation of the aqueous diphosphonic acid is not straightforward, requiring a catalyst and accurately controlled conditions. It seems, then, that there exists a trade-off between the extremely effective uptake of the actinides in most conditions and the relatively complicated procedure for their stripping. An alternative procedure is to avoid stripping the metals and to destroy through wet oxidation the whole resin bed used to sorb the actinides. The wet oxidation of several grams of resin is feasible but is time and reagent consuming, because the resin's polymeric backbone must also be destroyed. Whenever possible and when a further separation of the actinides is not necessary, the easiest solution is to leave the actinides on the resin which becomes a solid waste form, with the resin itself being the first confinement module for long term storage of the actinides.

5. New Developments

Modified Diphonix resins have been developed or are currently under development for more specific purposes. Examples of modified Diphonix resins are the already mentioned Diphonix A resins containing the same geminally substituted diphosphonic acid groups bonded to a styrenic-based polymer matrix as the regular Diphonix resin, plus strong base anion exchange groups such as the tetraalkylammonium (Diphonix A - Type 1 resins) or the quaternized pyridinium (Diphonix A - Type 2 resins) groups. The uptake measurements reported in (13) have shown that the Type 2 Diphonix A resins are as effective as the regular Diphonix resin in the rapid uptake of actinides from acidic solutions, while at the same time sorbing pertechnetate anions in a manner comparable to existing commercial anion exchange resins. A typical set of data is shown in Figure 15, where uptake data of representative actinides and of pertechnetate anions by a particular Type 2 Diphonix A resin are compared with the data obtained with the regular Diphonix resin.

Another modified Diphonix resin has been prepared, where the chelating diphosphonic acid groups are grafted to a silica support. The new material, which behaves in a very similar manner to the regular Diphonix resin should be more acceptable as a solid waste form for actinides, as it is made of about 90 % of inorganic material. A detailed account of the new material will be published shortly (17).

PART 2 : APPLICATIONS OF THE DIPHONIX RESIN

1. Analytical Procedures for Actinide Determinations

Traditional methods for actinides determination in environmental samples are time consuming and generate large quantities of wastes. Because of its high selectivity for actinides, the Diphonix resin has been included in the development of new efficient analytical procedures for concentrating and separating the actinide elements, with the specific goal of reducing the manpower and waste disposal costs associated with laboratory analyses of actinides. One of these procedures is reported here as an example of application of the Diphonix resin to soil samples analysis. Similar procedures, with appropriate modifications, can be used for most of the other environmental samples (surface and groundwaters, fecal and urine samples, etc.)

In this procedure, whose complete details can be found in (18), about five grams of soil sample are treated according to the following scheme :

- ash the sample to destroy organics;
- NaOH fusion to breakdown samples;
- after dissolution of the sample in water, a $Fe(OH)_3$ precipitation is used as a preliminary preconcentration step;
- dissolve the precipitate in HCl of appropriate strength;
- add ascorbic acid to reduce Fe(III) and flocculate the colloidal silica which is present in solution by adding polyethylene glycol; this step is needed to prevent plugging of the Diphonix resin column used in the following step;
- make the centrifuged solution 0.3 M in HF and pass it through a 10 mL Diphonix resin column;
- rinse the column with HCl - HF (to remove interfering matrix constituents) and water.

At this point a choice has to be made between the two alternative routes discussed in the section on stripping actinides from the Diphonix resin, that is, between stripping the actinides with HEDPA followed by HEDPA destruction, or destroying the whole resin bed without prior stripping the actinides. The first route is reported in detail in (18). It consists of the following steps :

- strip the actinides (and lanthanides) with few bed volumes of 0.5 M HEDPA;
- add $NaVO_3$ and H_2O_2 to oxidize the HEDPA at 80 °C;
- perform a second oxidation step by adding Cu^{+2}/Ag^{+} and $(NH_4)_2S_2O_8$ at 50 °C (this step should ensure the completeness of HEDPA destruction);
- add Ca^{+2} to coprecipitate lanthanides and actinides with the calcium phosphate (the phosphate ions are provided by the destroyed HEDPA);

- dissolve the precipitate in 2 M HNO_3 - 0.5 M $Al(NO_3)_3$;
- transfer to analytical cromatographic resin columns for separation of individual actinides.

By following the above procedure in the analyses of several references soils, chemical recoveries, based on alpha spectrometry results, ranged from 30 to 70 %, with the average recovery of approximately 50 % (18).

The alternative route, that is, complete destruction of the whole resin bed, was tested and the data reported in (19). The resin decomposition was achieved by wet oxidation with $NaVO_3$ and H_2O_2 at 95 °C for one hour, followed by several evaporations to dryness and additions of fresh aliquots of H_2O_2. At that point the residue was dissolved in nitric acid - aluminum nitrate and the same analytical columns as before were used for the individual separations. The chemical recoveries in the analyses of several soils were in the following ranges : 52-75 % for Th, 58-95 % for U, 38-81 % for Pu and 78-89 % for Am. Similar results were obtained with a wide range of fecal samples, for which a slightly modified procedure was developed (19).

In the above procedures the use of the Diphonix resin offers several advantages over traditional procedures. The resin, as amply demonstrated in the first part of this review, is highly selective for the actinides in very acidic solutions, even in the presence of complexing anions such as sulfates, phosphates and fluorides. Additionally, because the resin remains effective in the presence of relatively high concentrations of HF, the silica, which is generally present in soil samples, can be handled more effectively. Finally, an important waste minimization consideration : the silica is kept in solution rather than volatilized as SiF_4, as in more traditional methods.

2. Treatment of Mixed Wastes

The disposal of mixed waste solutions can be facilitated by removing activity below prescribed levels, and treating the residue as non-radioactive. Such separations can result in substantial saving in the disposal of laboratory waste and may be considered for applications on a larger scale. For this purpose, a facility has been built in the Chemistry Division of ANL to develop and test new processes for the removal of actinides from liquid mixed waste.

The pilot facility is shown schematically in Figure 16. It comprises a waste tank from which the solution is pumped through filters in a mixing tank where desired chemical adjustment can be made, a system of two ion exchange columns in series, a container for the decontaminated effluent, a strip reagent tank, a TRU product tank, and intermediate receivers, where effluents can be collected for subsequent sampling and analysis. Complete details of the facility are given in (20). The two columns have a total volume of about 1 L and have generally been used with the Diphonix resin. Several batches of locally generated mixed waste solutions have been tested successfully in this facility. When the recovery of the actinides was required, the resin was stripped with HEDPA followed by oxidation of the reagent as described in the previous section. In some other cases, when there was no interest in actinides recovery, the resin was removed from the first column, dried and discarded as solid radioactive waste. The second column then became the first column of the next batch.

A particularly interesting case of mixed waste treatment is discussed here, because it represents a good example of the potential of the Diphonix resin in this field. A mixed waste particularly difficult to treat is generated by the Davies-Gray analytical procedure for uranium determinations. The difficulty is due to the high concentration of phosphoric acid (about 2.8 M) which is present in the waste together with other acids and metallic species, including 0.024 M Fe(III). The strong complexation of uranium by phosphoric acid and the interference of the matrix cations, especially iron, make the uranium removal from this solution practically impossible with conventional ion exchange resins.

By using the Diphonix resin, a 5 gallon batch of Davies-Gray waste was treated in the above facility and the uranium concentration in the decontaminated effluent was reduced to well below that of drinking water. The details of the operation are reported in (20-21). We would like to emphasize here that the key to success is in the data reported in the previously discussed Figure 12, showing a steep dependency of the uranium uptake on the phosphoric acid concentration in experimental conditions close to those met with the Davies-Gray waste. From the waste solution as such, even the Diphonix resin would fail in efficiently sorbing the uranium. However, a two-fold dilution with water and the addition of ascorbic acid reduced the matrix interference of phosphoric acid and Fe(III) to a point where the uranium was retained by the resin columns without breaking through. The columns were subsequently stripped with 2 L of 0.5 M HEDPA. After destruction of HEDPA as described in the previous section, the uranium was reduced and precipitated as a phosphate, and, after further treatment, >99.8 % of the initial uranium was obtained pure in 1 L of diluted nitric acid.

3. Liquid Radwaste Processing

The operation of nuclear power plants involves collection, treatment and disposal of a variety of waste solutions collectively identified as radwaste. The composition of the radwaste depends on the type of nuclear reactor. Typically, PWR radwaste contain ^{58}Co, ^{60}Co, ^{51}Cr and ^{54}Mn, besides cesium isotopes, while in the case of BWR radwaste ^{65}Zn is is a major component of the radwaste along with cobalt and cesium isotopes. At least 50 % of the activity discharged from each power plant is due to the cobalt isotopes (22). The treatment and disposal of radwaste is needed to minimize radiation exposure to the plant workers and to the general public. The commonly used treatment of radwaste includes filtration and ion exchange with a mixed bed of conventional strong cationic and strong anionic resins. This treatment is not very efficient, because the affinity of the resin for the target cations is limited and because of the interference of inactive matrix constituents, such as sodium and calcium, which are present in the radwaste at concentrations about 10^9 times higher than the target cations and compete for the resin sites. As a consequence, the decontamination factors for radioactive cobalt are quite low, typically in the range from 1 to 50.

Because of the increasingly important cost of handling and disposal of low level radioactive waste, and the restrictions imposed by the ALARA (As Low As Reasonable Achievable) regulations, any change in the treatment technology which brings about a larger volume of liquid radwaste processed for unit spent waste generated, and also reduces the exposure dose for the personnel and the activity discharged to the environment, is highly welcome by the nuclear power industry. The data of Figure 5, showing a much higher uptake of Co(II), Mn(II) and Zn(II) from neutral solutions by the Diphonix resin as opposed to a conventional cation exchange resin, clearly show that the Diphonix resin is an ideal candidate for improvements in radwaste processing.

The Diphonix resin was tested in the treatment of the radwaste generated by the three Units of the Northeast Utilities, Millstone Station, Waterford, CT (21-22). Some data are shown in Figure 17, where the decontamination factor (DF) achieved with the Diphonix resin versus a conventional cationic resin is plotted as function of the volume of Unit 1 radwaste treated per cubic foot of resin. Typically, conventional resins process between 5,000 and 10,000 gallons of Unit 1 waste per cubic foot of resin before breathrough of the transition elements occurs. At the time when the communication (22) was presented, the Diphonix column had treated 35,000 gallons of radwaste per cubic foot of resin without activity breakthrough and the test was continuing.

The remarkable improvement in radwaste treatment shown in Figure 17, however, did require some optimization work. Unlike the data of Figure 5, obtained with pure synthetic solutions, laboratory tests conducted with real radwaste showed that only DF values lower than 20 could be reached. After several attempts to improve the DF through use of various techniques (22), the conclusion was reached that about 5 % of the total cobalt was present in the radwaste in an anionic form, obviously rejected by the Diphonix resin. To remove all detectable Co (cationic + anionic) from the radwaste, it was sufficient to pass the solution through a column of a strong base anion exchange resin in the hydroxide form in series with the Diphonix resin column.

This particular aspect of the cobalt removal from the radwaste is reported here to emphasize again that the uptake data discussed in the first part of the review are only a general guide for the applications of the Diphonix resin to real-world separation problems. Each application will very likely require a careful investigation of the behavior of the resin in the relevant non-ideal conditions, for appropriate solutions for each specific case to be worked out.

Another successful application of the Diphonix resin to radwaste treatment is reported in (23). Federal regulations required a southeastern U.S. nuclear fuel processor to achieve considerable reductions in its discharge of uranium. The new limit for discharge of alpha-emitting species was lowered from 30 pCi/mL to 0.3 pCi/mL. The existing technology at the plant was not capable of achieving this new limit. The data shown in Figure 5 clearly indicate that the Diphonix resin would probably resolve this problem, because of its superiority over conventional ion exchange resins in sorbing uranium from near - neutral solutions (the target pH range was in this case from 6 to 9). A number of tests were performed using a 914 x 15.2 cm Diphonix column. The same resin was used for eight different runs involving samples of wastewater from the plant neutralization tank. In all cases the alpha content of the column effluent was 0.07 pCi/mL or lower, that is 23% (or lower) of the discharge limit.

4. Copper electrowinning process

About 700,000 tons of copper are now produced worldwide via a solvent extraction (SX) route. In the USA alone, the SX produced copper amounts to 370,000 tons, equal to about 25% of the total USA copper production (24). The SX process is based on the selective extraction of copper from a leach solution by one of many organic reagents developed for this purpose, belonging in general to the families of extractants commercially known as LIX™ and ACORGA™ (24). The initial pregnant aqueous phase is normally a dilute impure sulfuric acid leach liquor at pH values between 1 and 3. The metal is then back extracted by a stripping solution at high acidity (about 1.5 M H_2SO_4). The SX procedure provides both concentration and purification of copper, such that pure metal can be obtained by electrolysis of the strip solution.

Because of the limited selectivity of the SX reagents and of mechanical entrainment, however, a small amount of iron and other impurities follow the copper into the strip solutions and hence in the electrolysis cells. By reducing to Fe(II) at the cathode and reoxidizing to Fe(III) at the anode, the iron reduces the electrochemical efficiency of the copper electrowinning. The iron concentration in the electrowinning solution is controlled by a "bleeding", which transfers copper and acid back to the primary leach circuit along with iron. To protect the Pb based anodes from corrosion due to oxidized manganese, which is also present as an impurity, cobalt(II) is added to the electrowinning solution. The bleeding operation causes the irreversible loss of the valuable added cobalt. Any process improvement capable of removing the iron from the electrowinning solution without loss of electrolyte and cobalt, would bring about considerable savings in terms of cobalt metal value and current efficiency.

From the data of Figure 8 discussed previously, it appears that the Diphonix resin exhibits the required high selectivity for Fe(III) over divalent transition elements from sulfuric acid solutions at the concentrations used in copper electrowinning. The resin has been therefore selected for a number of tests performed by Eichrom Industries on a laboratory scale and in pilot plants installed at the Magma Copper, San Manuel, AZ, plant (25-26) and at Mexicana de Cananea, Sonora, Mexico. Some results from the laboratory tests are reported in Figure 18, showing how the Diphonix resin retains Fe(III) from a copper electrowinning solution. It is interesting to notice how the resin discriminates between the Fe(II) (about 10 - 20 % of the total iron) which follows the Cu and Co breakthrough, and the much larger amount of Fe(III) which is much more strongly retained by the resin.

The copper electrowinnig plant modification based on the Diphonix resin consists in passing part of the solution through a column of appropriate size where the iron is retained while the Cu, Co and sulfuric acid are recycled to the electrolysis cell. For the modified process to be economically valid, it is imperative that the Diphonix resin is reused many times. For this purpose an efficient stripping technique of the Fe(III) from the resin has been developed by Eichrom based on a redox chemistry fully compatible with the rest of the process, without generating supplemental wastes (25-26). The pilot plant tests have been extremely successful. The Diphonix resin columns installed at the Magma plant have been continuously operated for eight weeks, through 230 cycles of iron loading and stripping without any sign of reduced performance. Further testing of the copper electrowinning Diphonix modified process is under way at the above mentioned Mexican copper plant, where the same batch of Diphonix resin previously used in the Magma plant is currently being used. A total of more than 400 cycles of iron loading and stripping has been successfully reached so far and the test is continuing.

CONCLUSIONS

The recently developed Diphonix™ resin is a new multifunctional chelating ion exchange polymer containing geminally substituted diphosphonic acid ligands chemically bonded to a styrene-based polymeric matrix.

In the first part of this review we focused our attention on the properties of the resin concerning the uptake of metal cations from a number of aqueous solutions. The account of the resin's properties given in this review is by no means exhaustive, however, because the physico-chemical behavior of the resin is still under intense investigations. Furthermore, as new modifications of the resin are synthesized and characterized, it is probably more appropriate to refer to the Diphonix resin as to a family of resins. We are confident that members of the Diphonix resin family will exhibit new and interesting properties which will need to be investigated both from a basic standpoint and in view of possible applications.

In the second part of the review a brief account of the major applications of the Diphonix resin was given. Although the resin was invented having in mind applications in the actinides separation field, it is now realized that the single most important application, both for its technological impact and for the scale of application, is in the copper electrowinning process. The initial disappointment in finding out that the resin has a strong affinity for Fe(III), which somewhat limits its applicability to actinides separation, has thus turned into exhilaration after we became aware of the number of opportunities existing in non-nuclear fields.

Other areas where the unique selectivity of the Diphonix resin may (and probably will) find applications, besides the ones discussed in this review, are in the potable water purification (for example from lead), in the preparation of special purity reagents for high tech applications (for example in the semiconductors industry), and in the hydrometallurgy and/or electrowinning processes used for other metals beside copper.

In the first of the areas mentioned above, that is control of lead in drinking water, for example, laboratory tests conducted at Eichrom Industries (27) have been very incouraging. Synthetic water samples of varying lead content (45-120 ppb), varying pH (6-8), and varying hardness (as calcium carbonate, 51-136 ppm) were treated with the Diphonix resin both in the hydrogen and calcium form. In all cases the concentration of lead was reduced to below the detection limit (< 5 ppb). Additional studies in a dynamic system are planned with the goal of designing a simple cartridge-type system for point-of-use application in the home.

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Figure Captions

Figure 1. Structure of the Diphonix resin.

Figure 2. Uptake of various actinides by the Diphonix resin (adapted from reference 6).

Figure 3. Uptake of trivalent ions by the Diphonix resin (adapted from reference 7).

Figure 4. Uptake of some transition elements by the Diphonix resin (adapted from references 7 and 13).

Figure 5. Uptake of some elements by the Diphonix resin and by a sulfonic resin from neutral solutions (adapted from reference 7).

Figure 6. Uptake of alkaline earth cations by the Diphonix resin and by a sulfonic resin (adapted from references 12 and 14).

Figure 7. Uptake of selected ions : Diphonix vs other resins (adapted from references 6 and 7).

Figure 8. Uptake of selected ions by the Diphonix resin from HCl and H_2SO_4 (the data in HCl are taken from references 6 and 7).

Figure 9. Kinetics of Am(III) uptake by selected resins (adapted from reference 9).

Figure 10. Uptake kinetics of selected ions by the Diphonix resin (adapted from reference 9).

Figure 11. Effect of some matrix cations on the uptake of actinides by the Diphonix resin (adapted from reference 10).

Figure 12. Effect of complexing anions on actinides uptake by the Diphonix resin. Data at 1 M HNO_3.(Adapted from reference 10).

Figure 13. Effect of complexing anions on actinides uptake by the Diphonix resin. Experimental points vs calculated curves (adapted from reference 11).

Figure 14. Uptake of selected ions from 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) solutions.

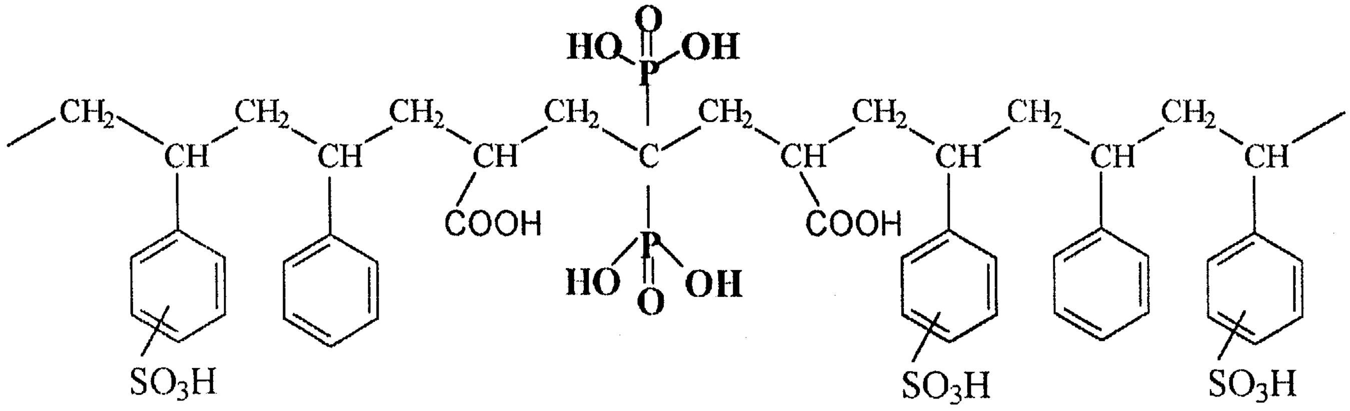
Figure 15. Uptake of selected actinides and Tc(VII) : Diphonix vs Diphonix A resins (adapted from reference 13)

Figure 16. Schematics of the Argonne National Laboratory pilot facility for mixed waste treatment (adapted from reference 20).

Figure 17. Millstone Unit 1 side stream test. Effective capacity for Co, Zn and other selected metals (adapted from reference 22).

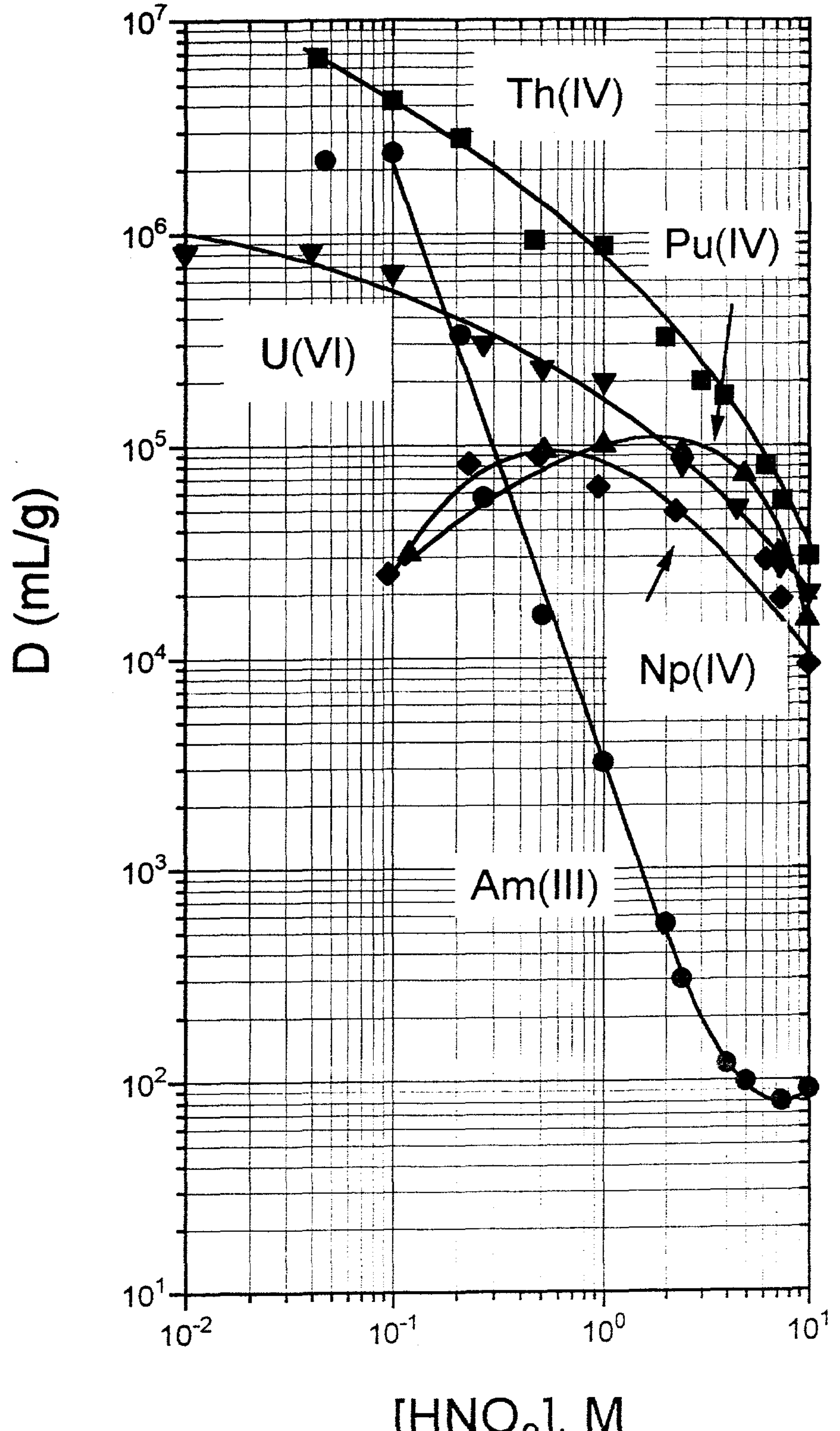
Figure 18. Iron control in copper electrowinning. Electrolyte loading studies (adapted from reference 26).

DIPHONIX RESIN



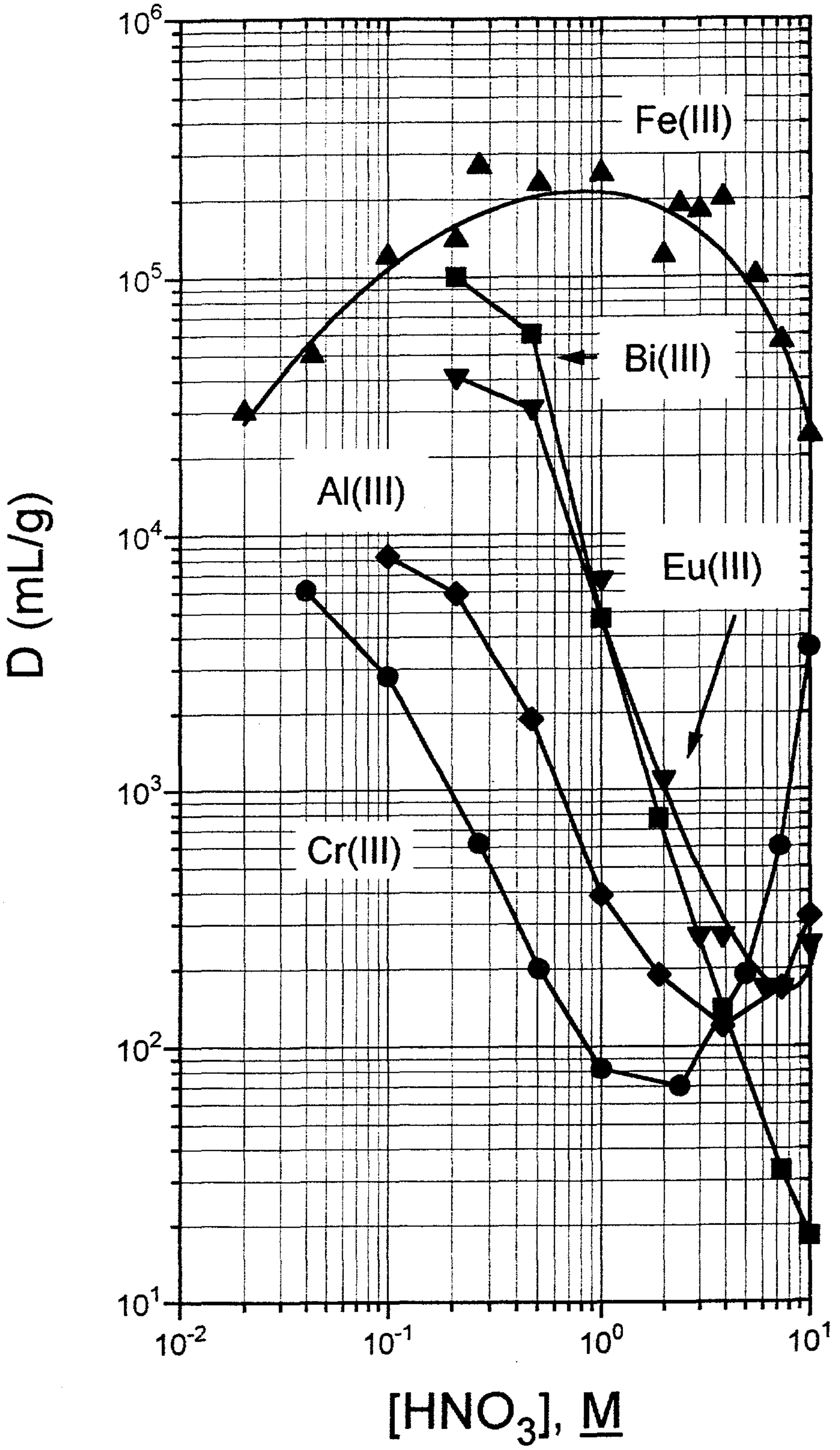
$pK_1 = 1.5$, $pK_2 = 2.5$, $pK_3 = 7.2$, $pK_4 = 10.5$

Fig. 1



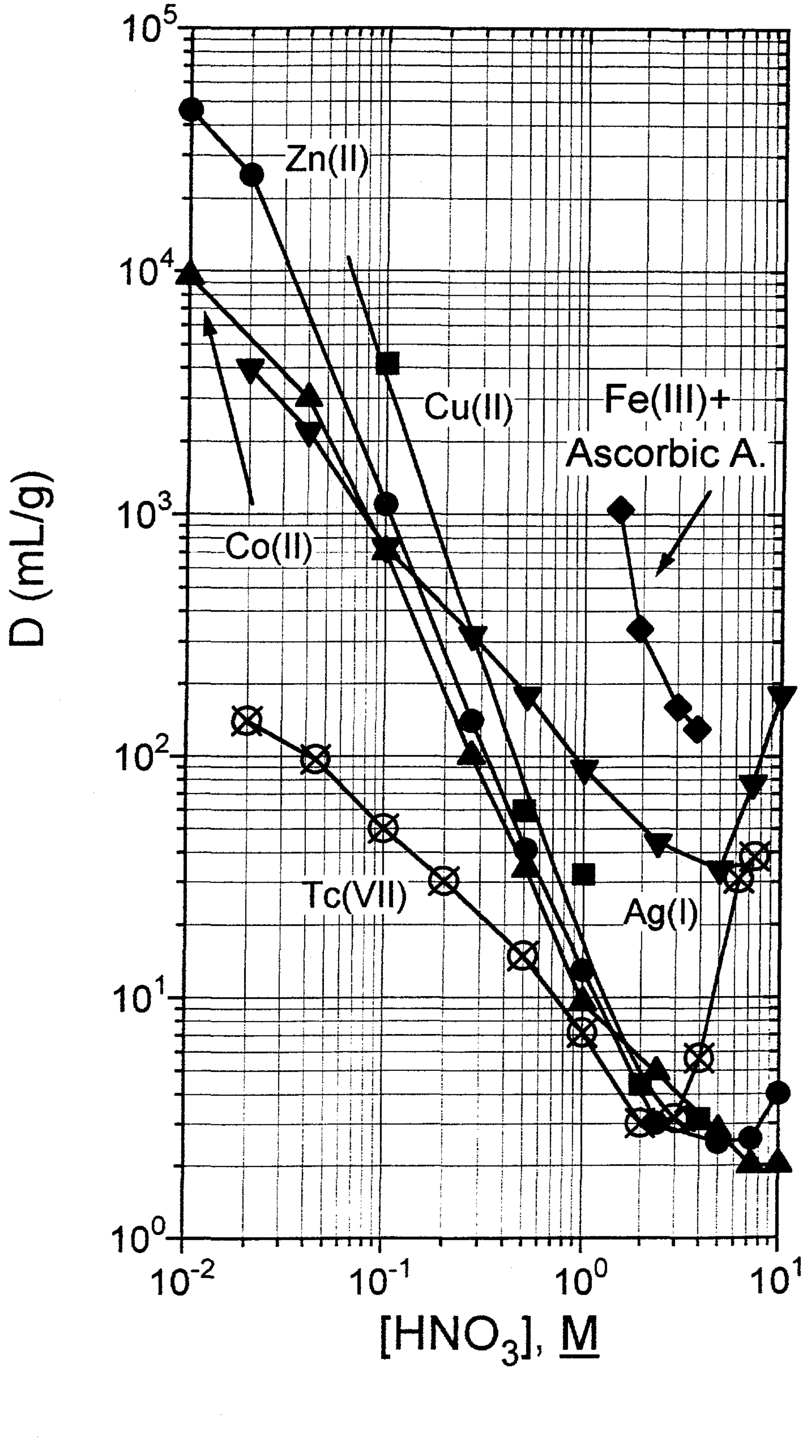
Th(IV)
Pu(IV)
U(VI)
Np(IV)
Am(III)
D (mL/g)
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^{-2}
10^{-1}
10^0
10^1
[HNO$_3$], M

Fig. 2



10^6
10^5
10^4
10^3
10^2
10^1
10^{-2}
10^{-1}
10^0
10^1
D (mL/g)
$[HNO_3]$, M
Fe(III)
Bi(III)
Al(III)
Eu(III)
Cr(III)

Fig. 3



D (mL/g)
10^5
10^4
10^3
10^2
10^1
10^0
10^{-2}
10^{-1}
10^0
10^1
[HNO$_3$], M
Zn(II)
Cu(II)
Fe(III)+
Ascorbic A.
Co(II)
Tc(VII)
Ag(I)

Fig

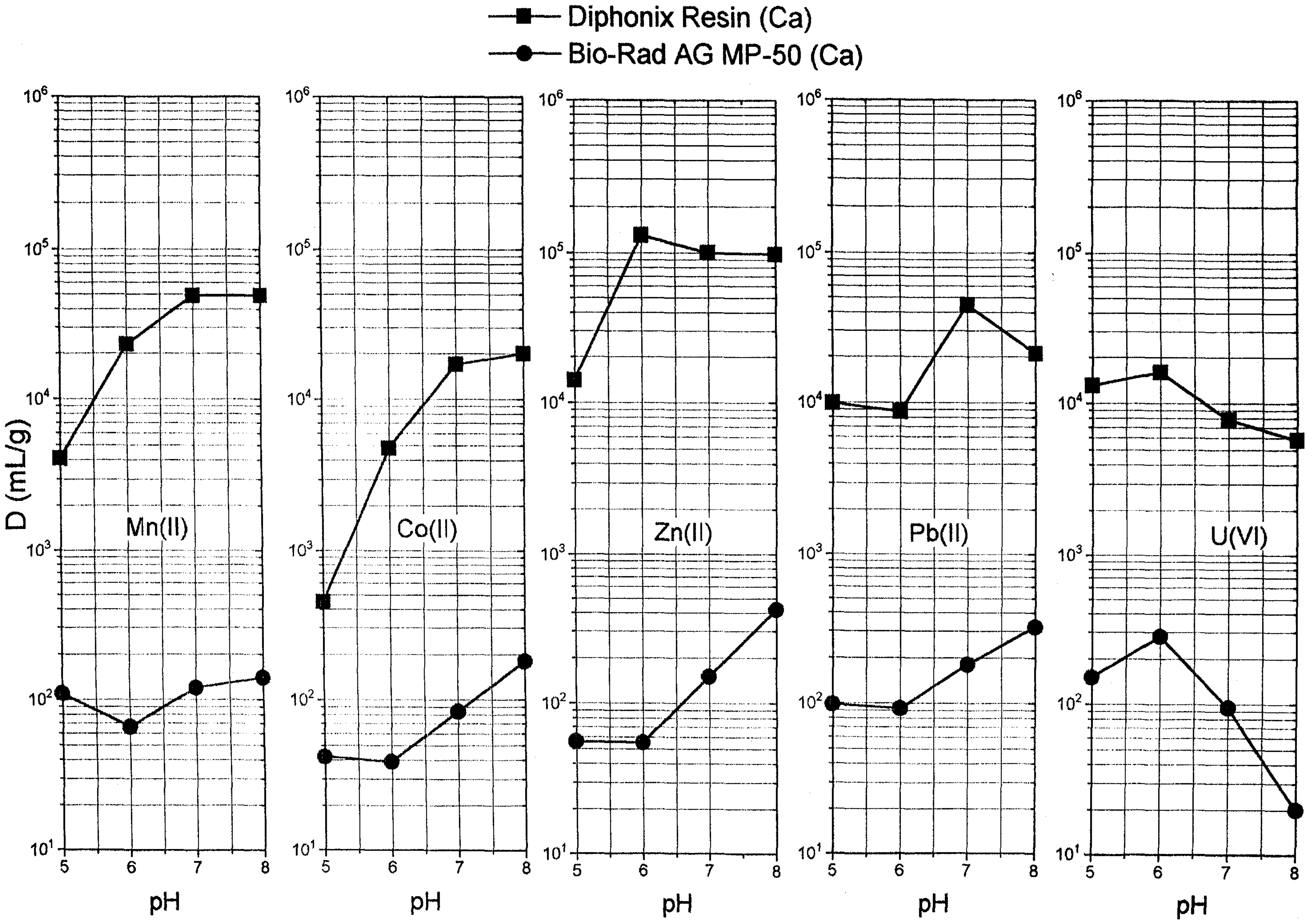
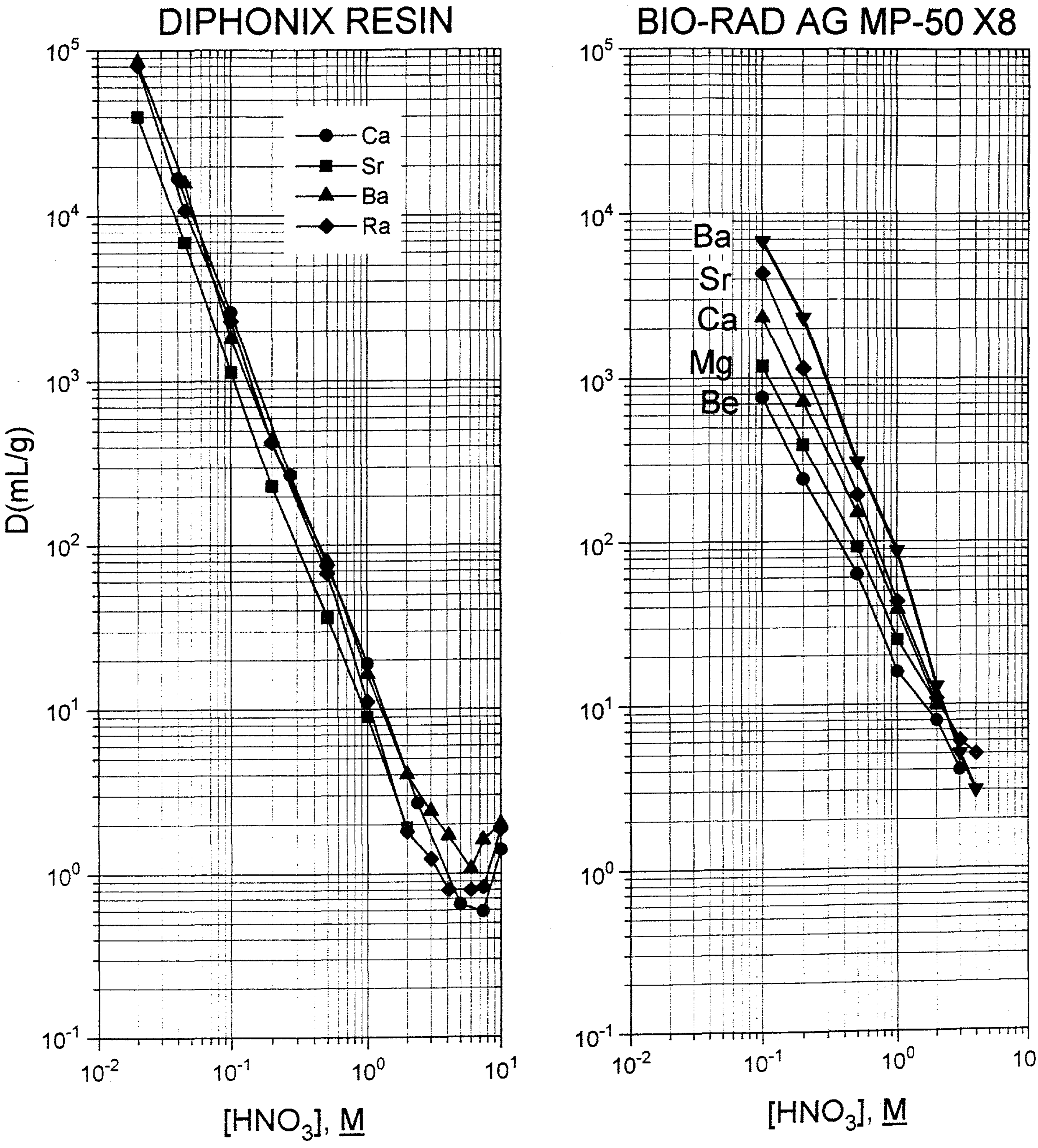
Diphonix Resin (Ca)
Bio-Rad AG MP-50 (Ca)
D (mL/g)
10^6
10^5
10^4
10^3
10^2
10^1
Mn(II)
Co(II)
Zn(II)
Pb(II)
U(VI)
5
6
7
8
pH

Fig. 5



DIPHONIX RESIN
BIO-RAD AG MP-50 X8
D(mL/g)
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
$[HNO_3]$, M
Ca
Sr
Ba
Ra
Ba
Sr
Ca
Mg
Be

Fig. 6

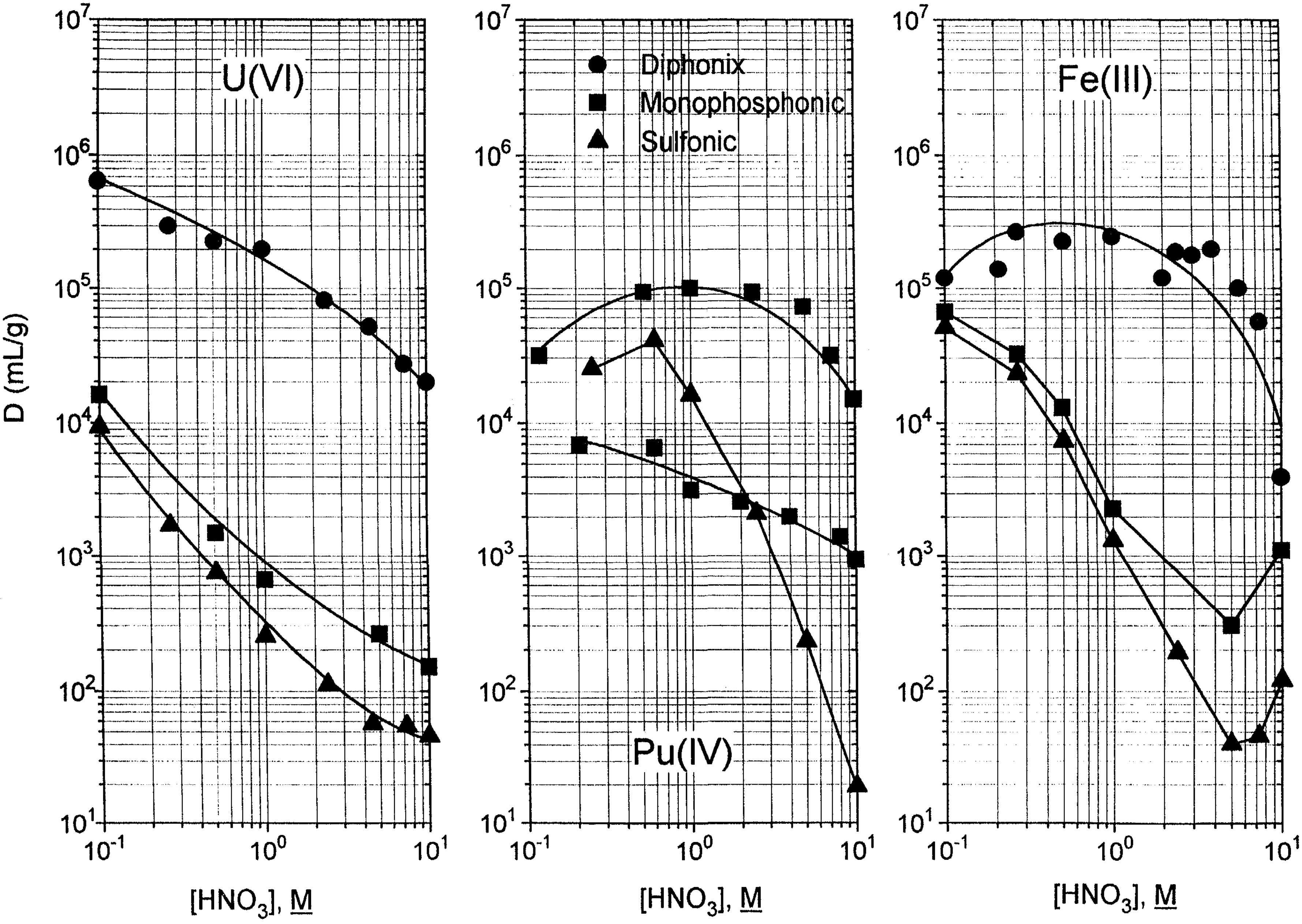
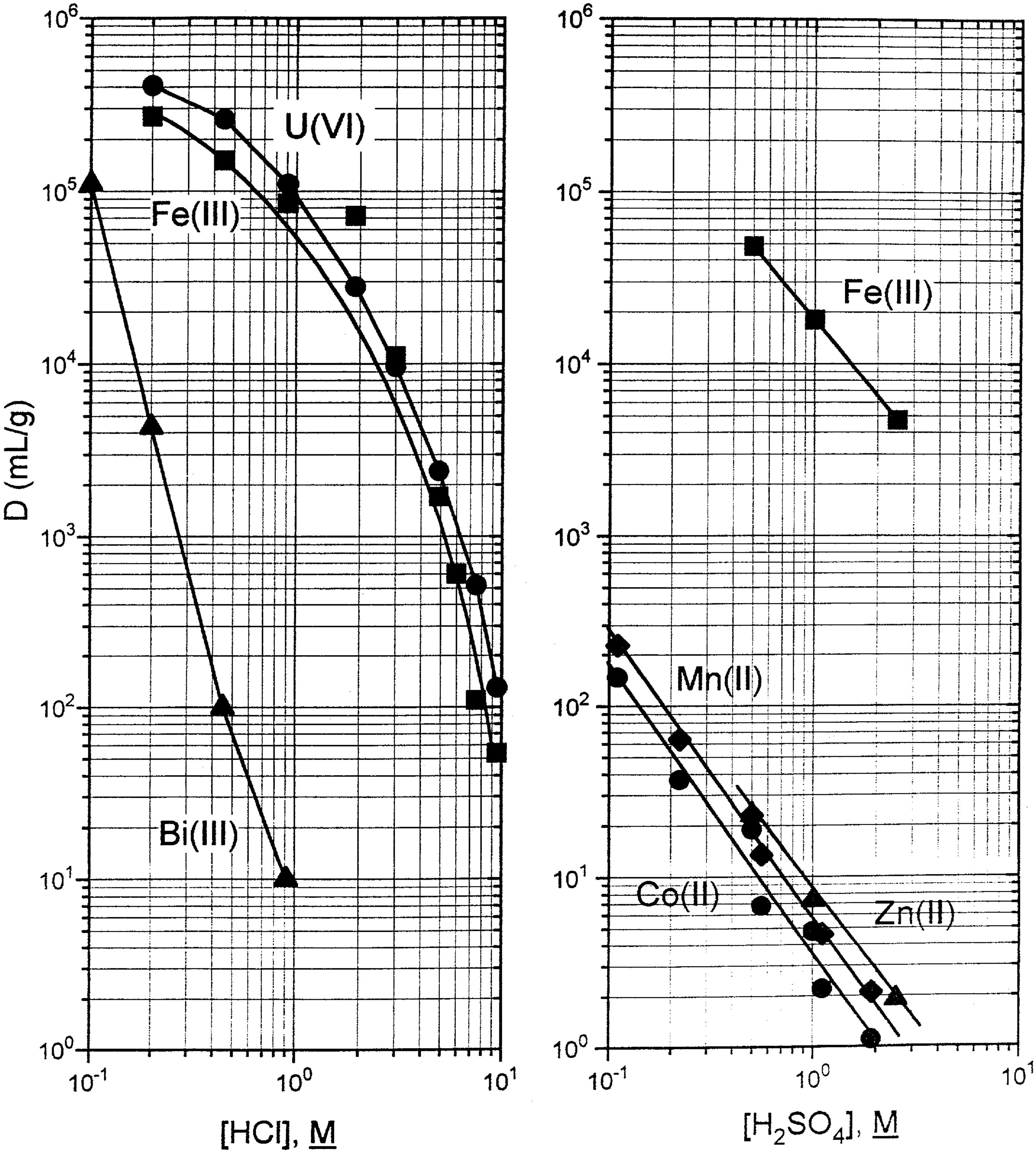
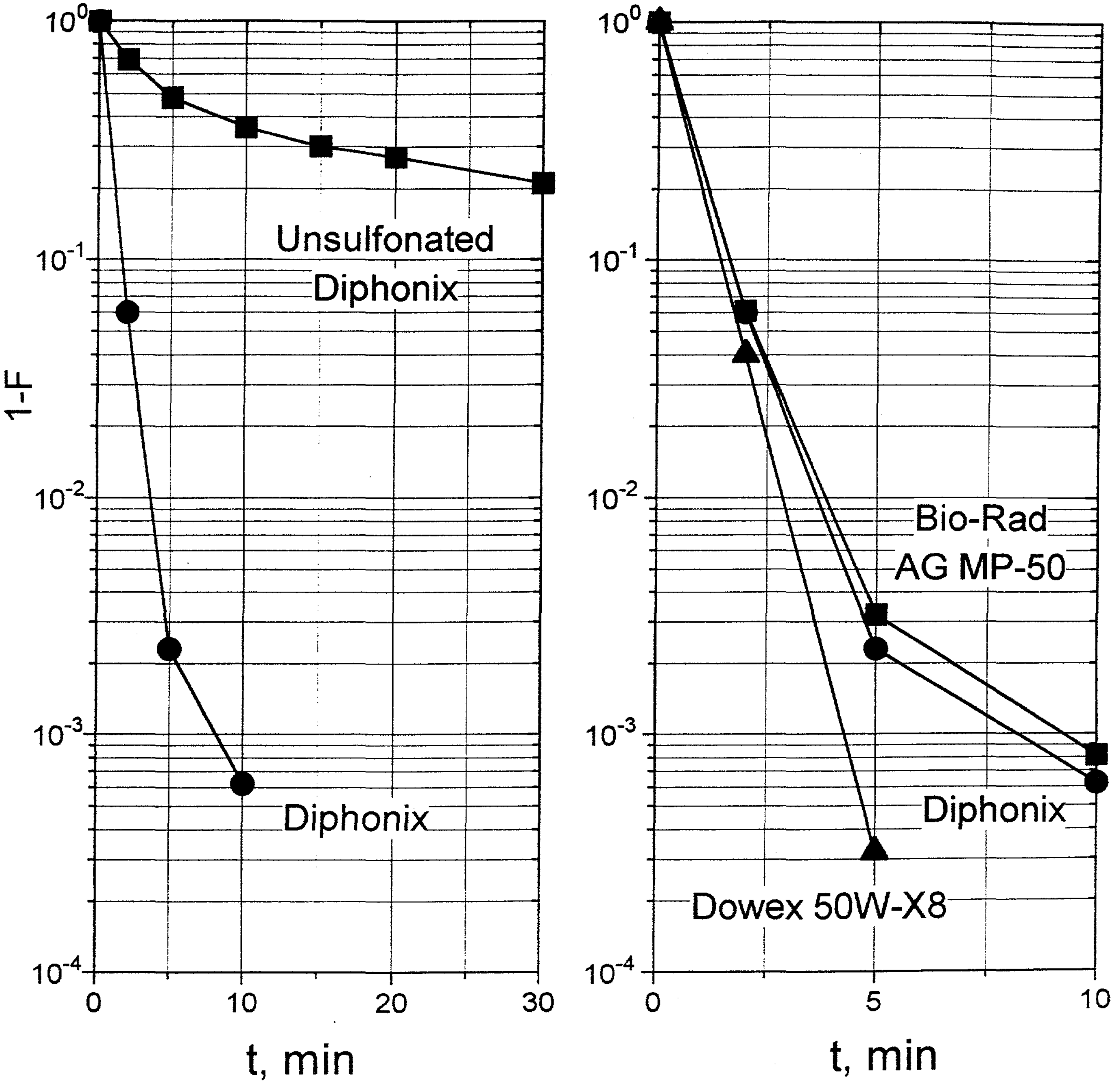

U(VI)
Pu(IV)
Fe(III)
● Diphonix
■ Monophosphonic
▲ Sulfonic
D (mL/g)
10^1
10^2
10^3
10^4
10^5
10^6
10^7
10^{-1}
10^0
10^1
[HNO_3], M

Fig. 7



D (mL/g)
10^6
10^5
10^4
10^3
10^2
10^1
10^0
U(VI)
Fe(III)
Bi(III)
10^-1
10^0
10^1
[HCl], M
10^6
10^5
10^4
10^3
10^2
10^1
10^0
Fe(III)
Mn(II)
Co(II)
Zn(II)
10^-1
10^0
10^1
[H2SO4], M

Fig. 8



1-F
10^0
10^-1
10^-2
10^-3
10^-4
0
10
20
30
t, min
Unsulfonated Diphonix
Diphonix
10^0
10^-1
10^-2
10^-3
10^-4
0
5
10
t, min
Bio-Rad AG MP-50
Diphonix
Dowex 50W-X8

Fig. 9

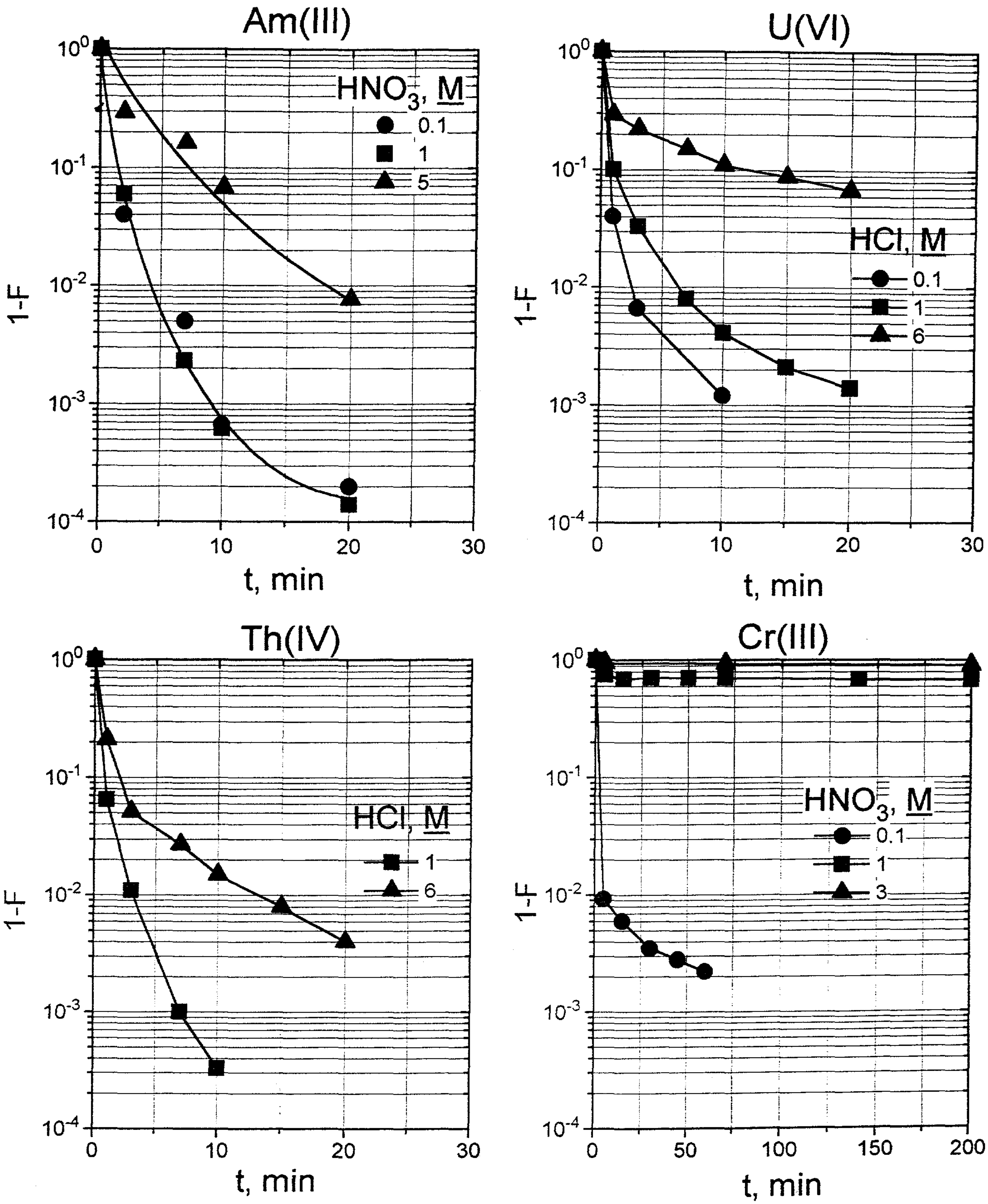

Am(III)
HNO$_3$, M
0.1
1
5
1-F
t, min
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0
10
20
30
U(VI)
HCl, M
0.1
1
6
1-F
t, min
Th(IV)
HCl, M
1
6
1-F
t, min
Cr(III)
HNO$_3$, M
0.1
1
3
1-F
t, min
0
50
100
150
200

Fig. 10

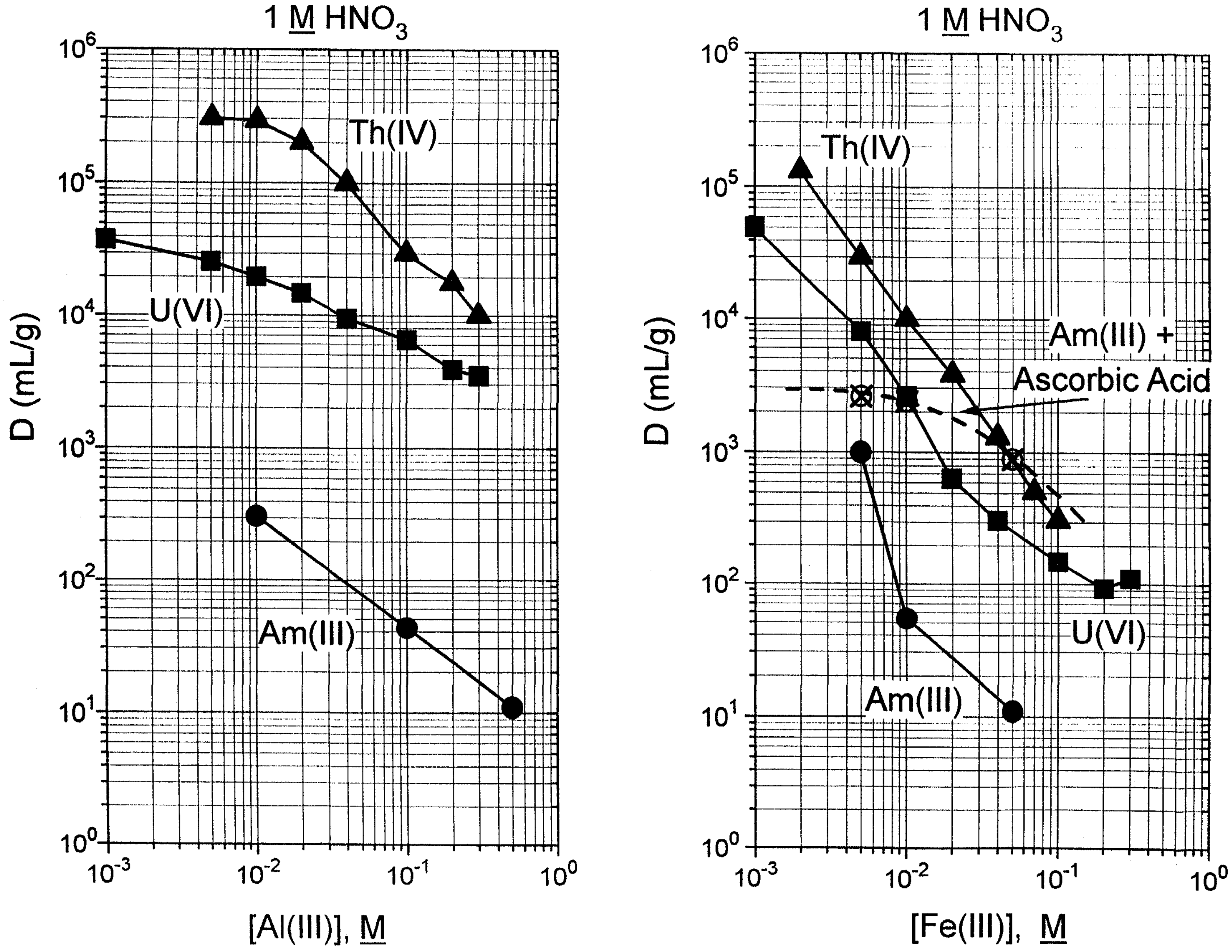

1 M HNO$_3$
D (mL/g)
10^6
10^5
10^4
10^3
10^2
10^1
10^0
Th(IV)
U(VI)
Am(III)
10^{-3}
10^{-2}
10^{-1}
10^0
[Al(III)], M
1 M HNO$_3$
D (mL/g)
10^6
10^5
10^4
10^3
10^2
10^1
10^0
Th(IV)
Am(III) +
Ascorbic Acid
U(VI)
Am(III)
10^{-3}
10^{-2}
10^{-1}
10^0
[Fe(III)], M

Fig. 11

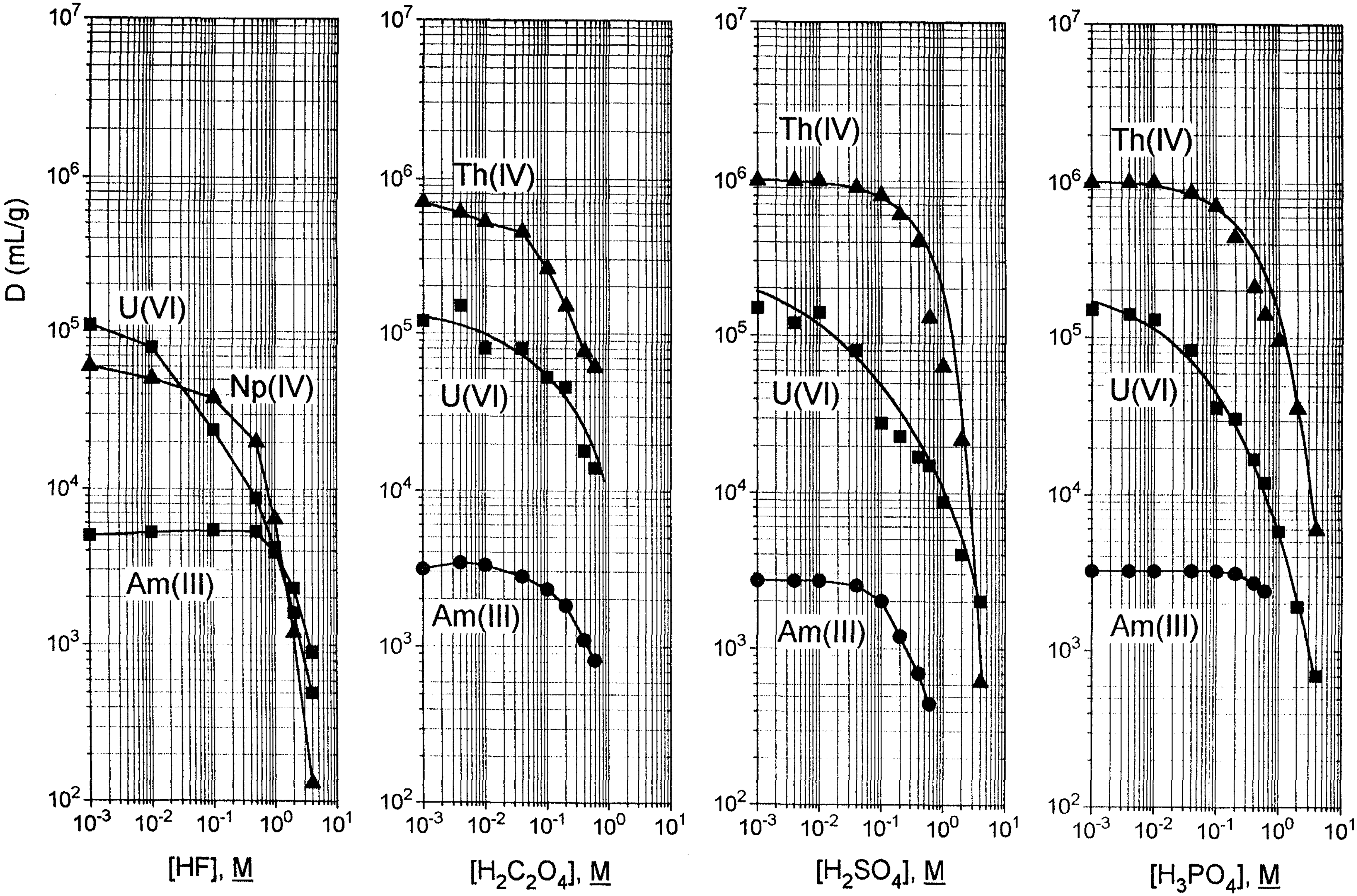

D (mL/g)
10^7
10^6
10^5
10^4
10^3
10^2
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
U(VI)
Np(IV)
Am(III)
[HF], M
Th(IV)
U(VI)
Am(III)
[$H_2C_2O_4$], M
Th(IV)
U(VI)
Am(III)
[H_2SO_4], M
Th(IV)
U(VI)
Am(III)
[H_3PO_4], M

Fig. 12

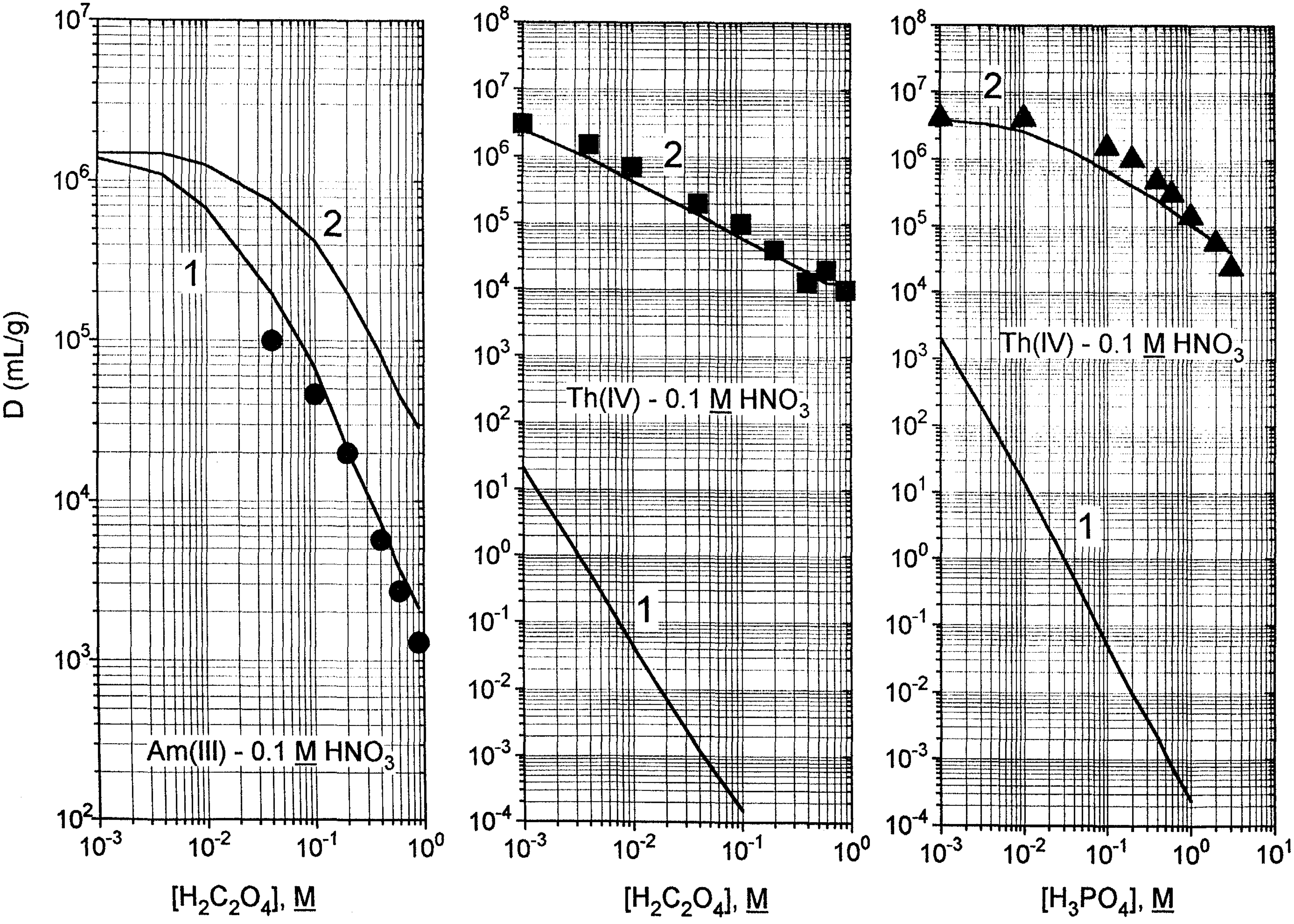

D (mL/g)
10^7
10^6
10^5
10^4
10^3
10^2
1
2
Am(III) - 0.1 M HNO_3
10^{-3}
10^{-2}
10^{-1}
10^0
$[H_2C_2O_4]$, M
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
2
1
Th(IV) - 0.1 M HNO_3
10^{-3}
10^{-2}
10^{-1}
10^0
$[H_2C_2O_4]$, M
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
2
1
Th(IV) - 0.1 M HNO_3
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
$[H_3PO_4]$, M

Fig. 13

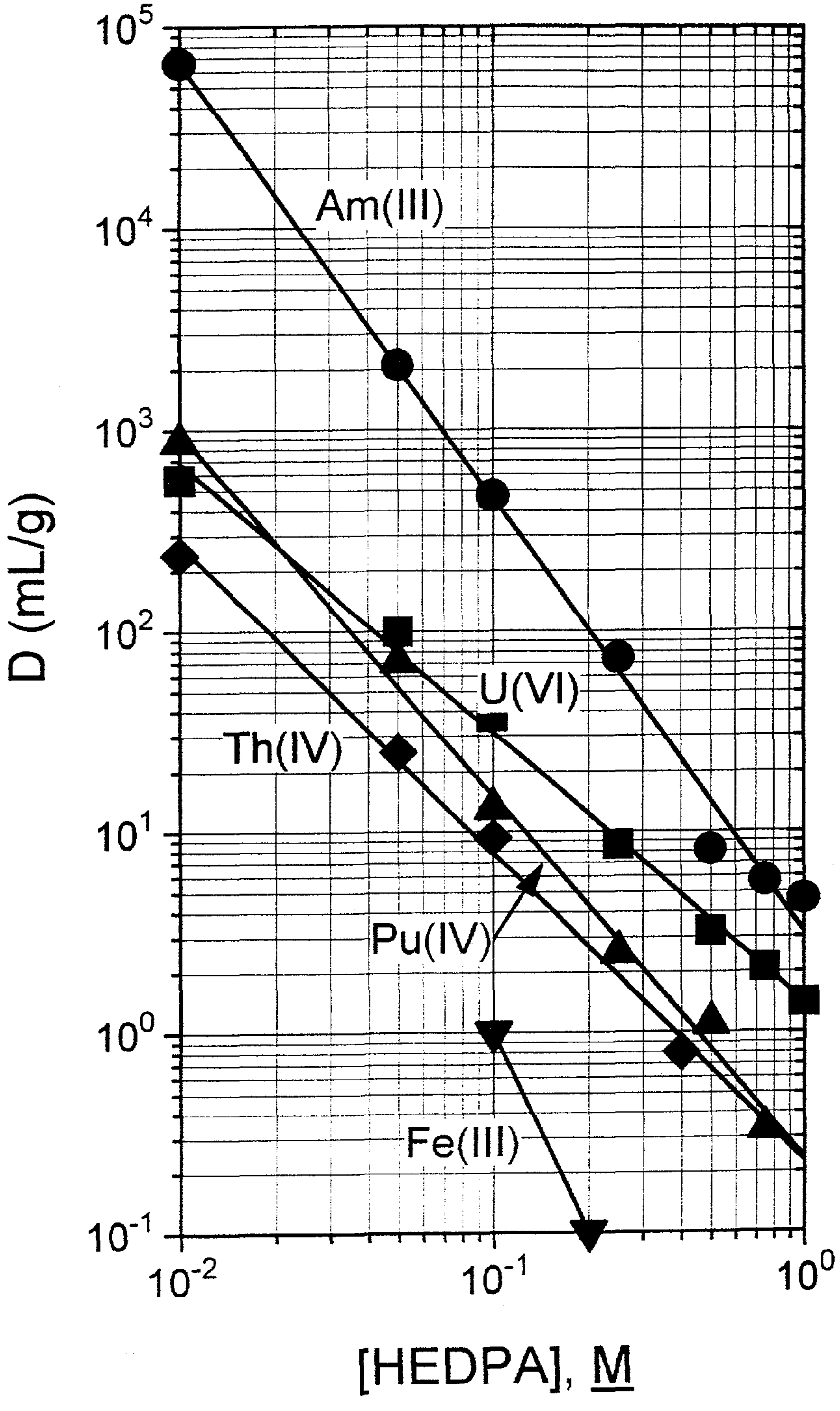
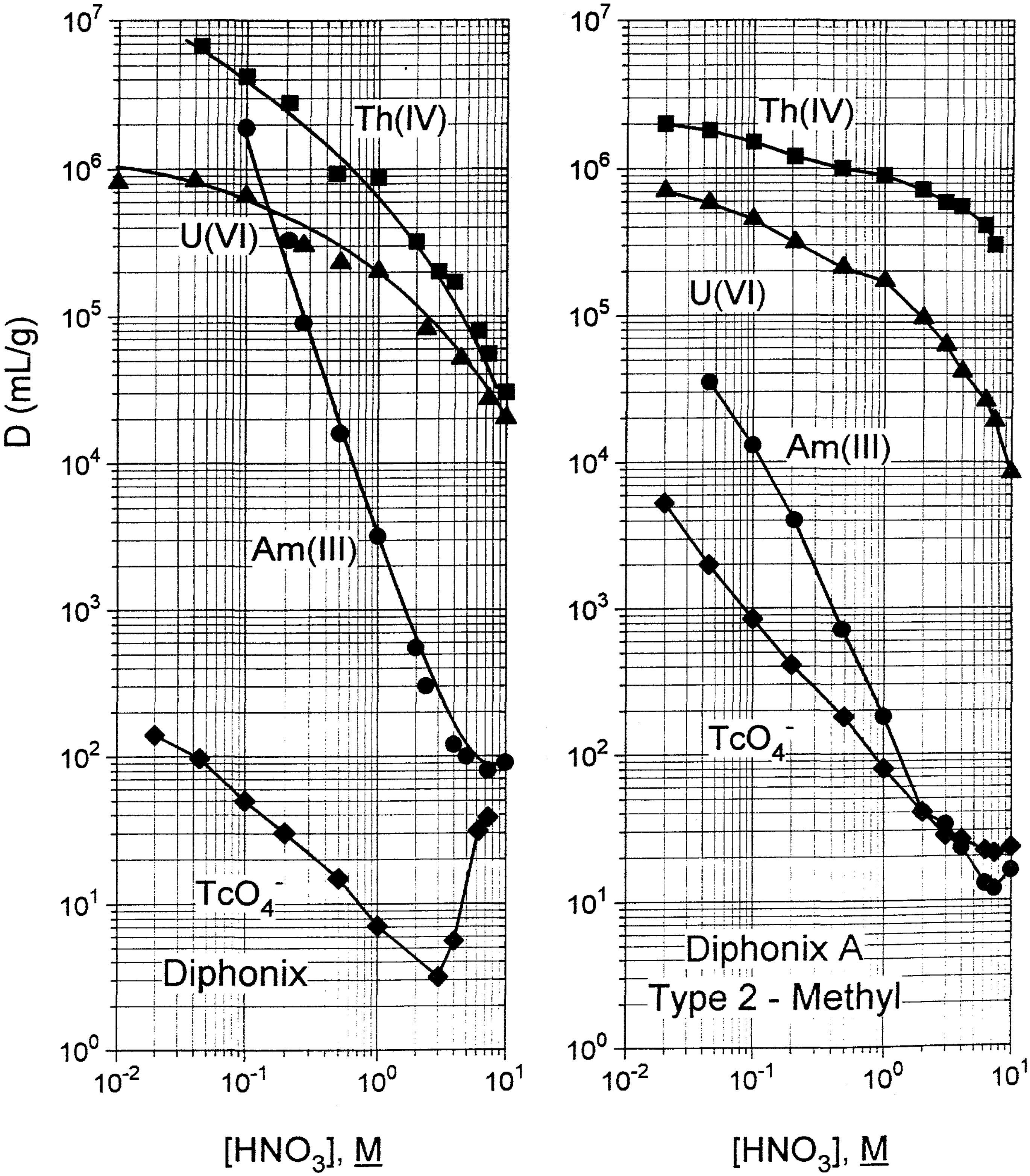

10^5
10^4
10^3
10^2
10^1
10^0
10^-1
D (mL/g)
Am(III)
U(VI)
Th(IV)
Pu(IV)
Fe(III)
10^-2
10^-1
10^0
[HEDPA], M

Fig. 14



D (mL/g)
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
Th(IV)
U(VI)
Am(III)
TcO_4^-
Diphonix
10^{-2}
10^{-1}
10^0
10^1
[HNO_3], M
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
Th(IV)
U(VI)
Am(III)
TcO_4^-
Diphonix A
Type 2 - Methyl
10^{-2}
10^{-1}
10^0
10^1
[HNO_3], M

Fig. 15

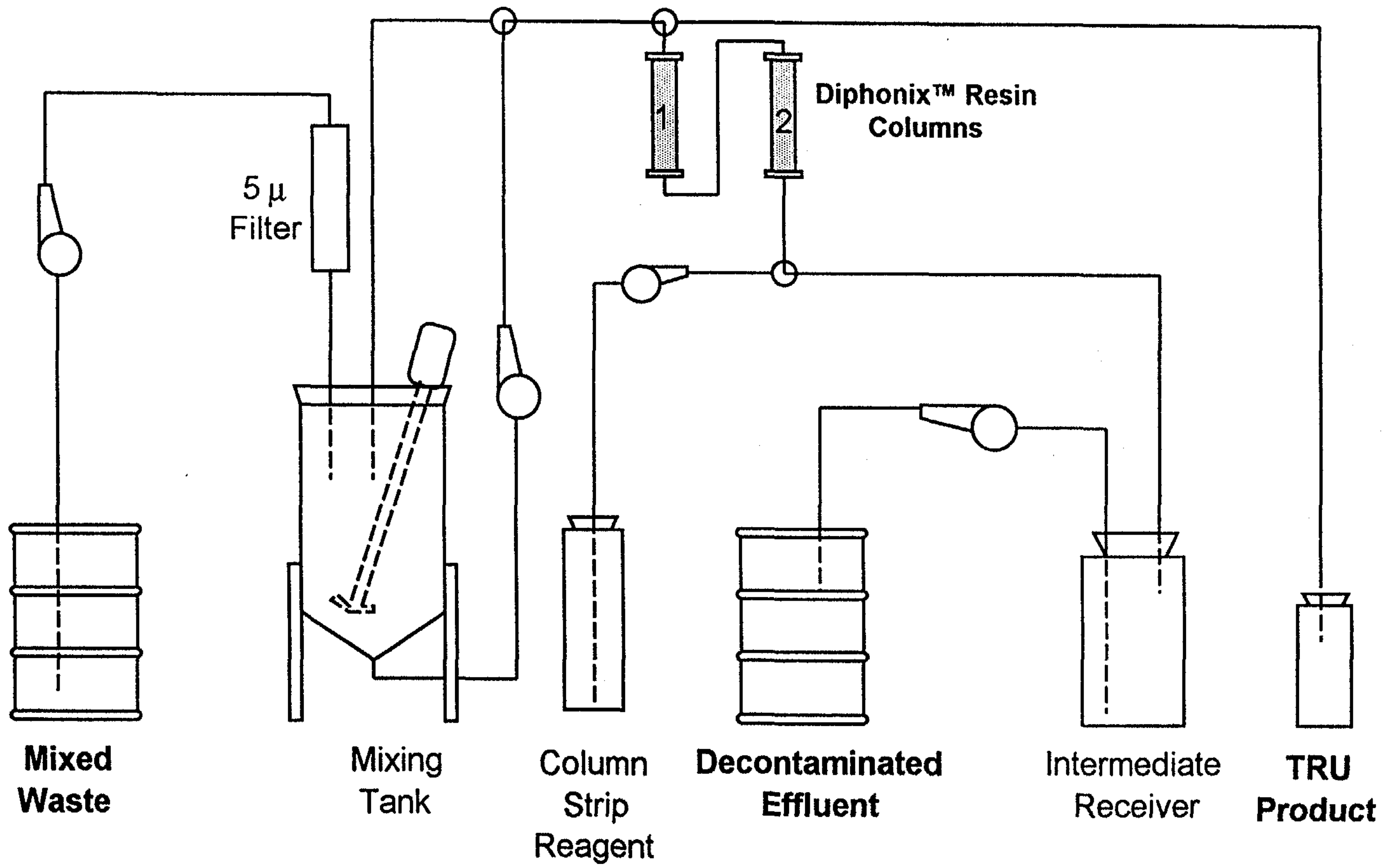

Diphonix™ Resin Columns
1
2
5 µ Filter
Mixed Waste
Mixing Tank
Column Strip Reagent
Decontaminated Effluent
Intermediate Receiver
TRU Product

Fig. 16

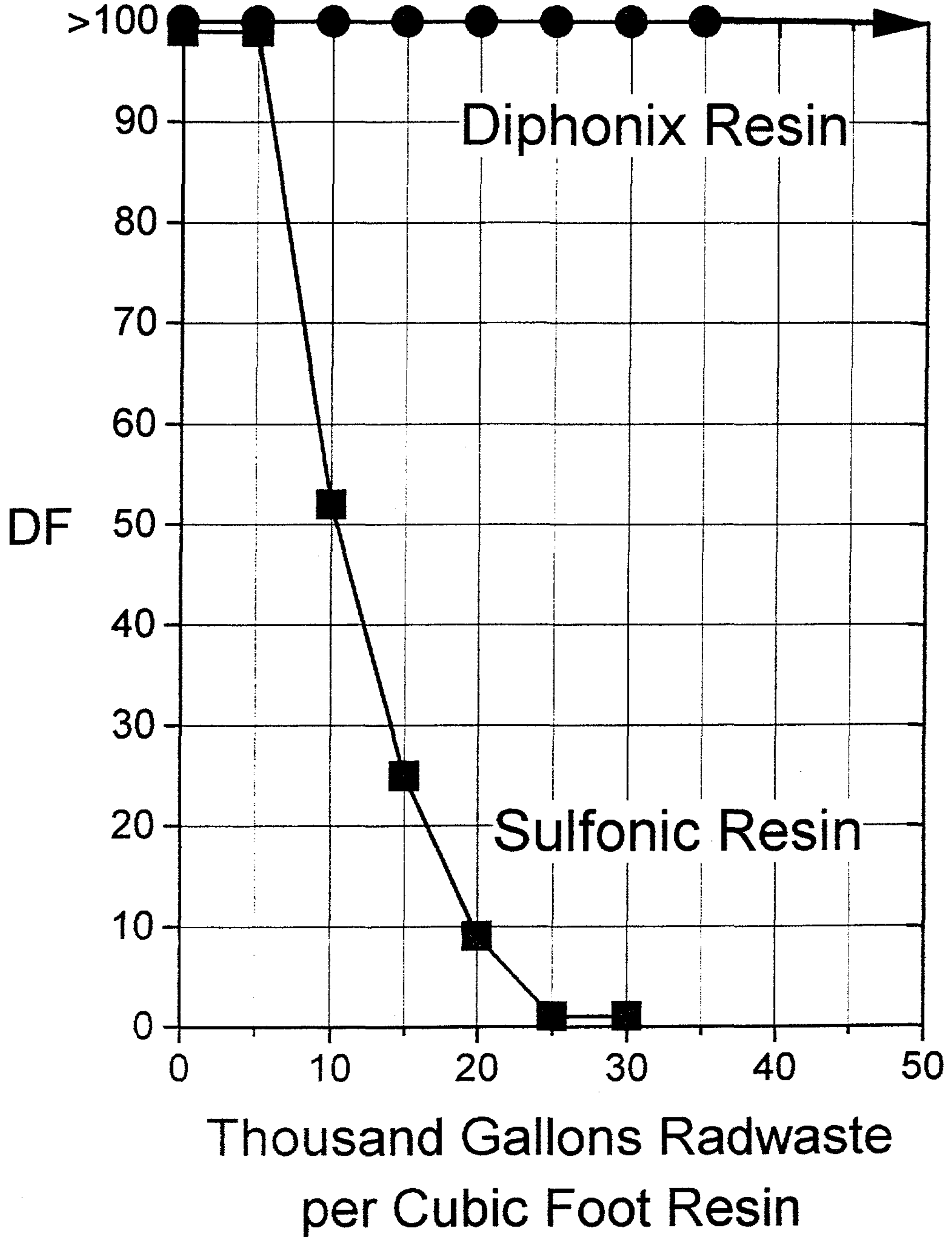

>100
90
80
70
60
50
40
30
20
10
0
DF
Diphonix Resin
Sulfonic Resin
0
10
20
30
40
50
Thousand Gallons Radwaste
per Cubic Foot Resin

Fig. 17

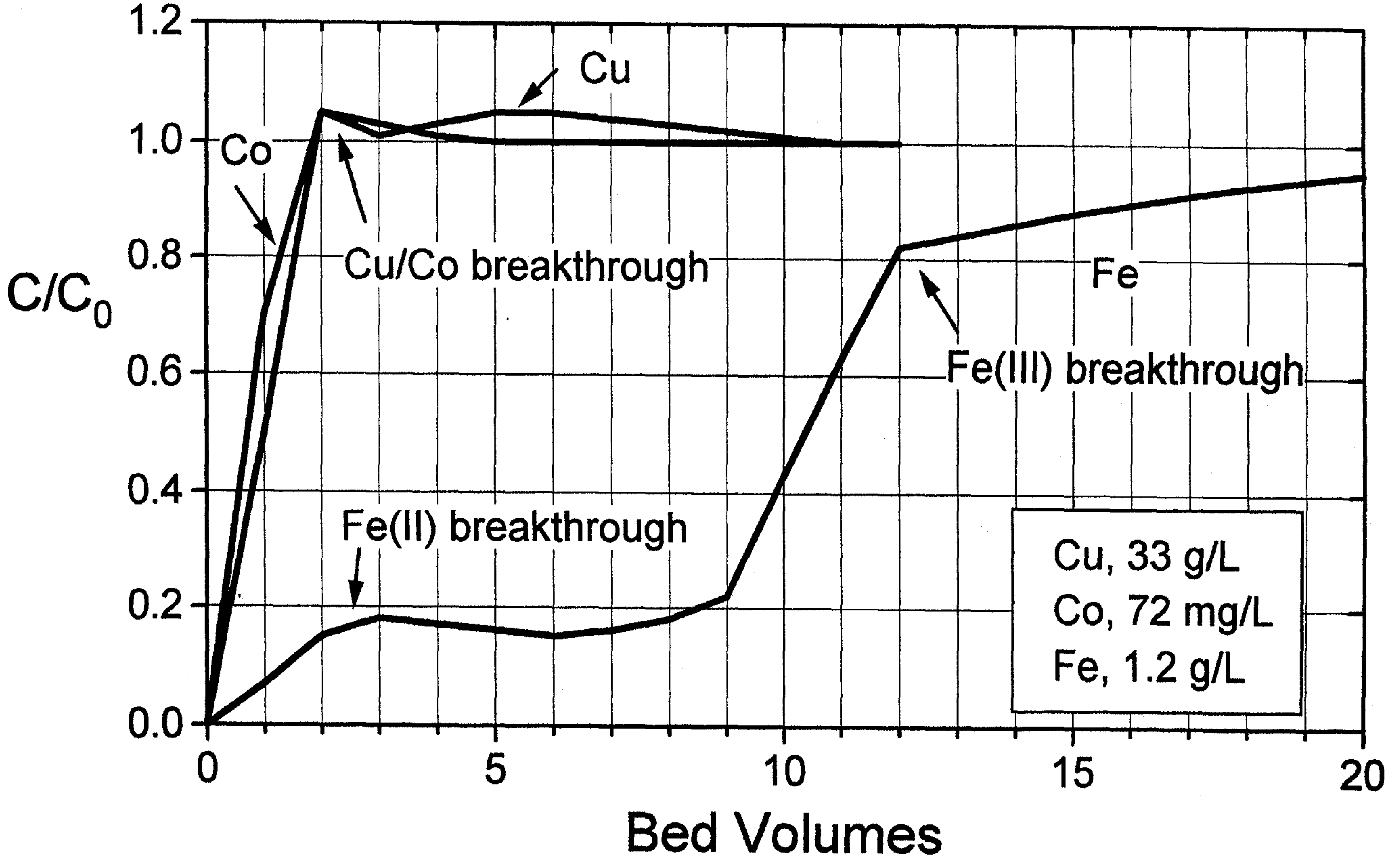

C/C$_0$
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
Bed Volumes
Cu
Co
Cu/Co breakthrough
Fe
Fe(III) breakthrough
Fe(II) breakthrough
Cu, 33 g/L
Co, 72 mg/L
Fe, 1.2 g/L

Fig. 18