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AMBERLITE XAD-2 AND XAD-4 AS CATION-EXCHANGE RESINS OF LOW CAPACITY

AN INVESTIGATION USING AN ATOMIC FLUORESCENCE DETECTOR DIRECTLY COUPLED TO A LIQUID CHROMATOGRAPH

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SUMMARY

A four-channel atomic fluorescence detector, directly coupled to the output of a chromatography column, has been used to monitor the adsorption of magnesium, iron, zinc and copper by Amberlite XAD resins and the subsequent elution of these metals by disodium dihydrogenethylenediamine tetraacetate or ammonia. All the metals can be adsorbed from aqueous solution at pH 2.5 but the adsorption of iron is strongly pH dependent and this influences the adsorption of the other metals since iron forms the strongest complexes in the pH range 1.5–2.5. The adsorption capacity of XAD-4 is approximately halved by washing with methanolic hydrochloric acid and evidence is presented for the existence of a number of different, but unknown, impurity sites on these resins. These results are of special significance to the use of these resins for studying trace metal speciation in natural waters.

INTRODUCTION

The chemical speciation of trace metals in seawater and other natural waters has been the subject of much discussion. It is generally agreed that biologically important metals such as copper, zinc and iron exist mostly in forms other than the simple cations, but the actual chemical species present are unknown. While there is undoubtedly some metal present as inorganic complexes or as inorganic or organic colloidal material, there is increasing evidence that significant amounts of these metals may exist in natural waters as metal–organic complexes. The donor groups of any ligating organic compound are probably hydrophilic moieties such as –COOH, –OH and $-NR_2$ and hence the metal–organic compounds would tend to be more hydrophobic than the parent organic molecules and should be more readily adsorbed on hydrophobic resins. The Amberlite XAD resins have been widely used for extracting organic compounds from nautral waters and in some cases metal organic complexes have been extracted. Thus Mantoura *et al.*[1] used XAD-2 resin to extract humic substances from natural waters and found that the humic compounds contained trace

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metals and Riley and Taylor[2] found that added vitamin B_{12} could be quantitatively removed from seawater by adsorption onto Amberlite XAD-1. These studies are not directly relevant to trace metal speciation in seawater since, in the first case, the seawater was acidified to pH 2.2 to remove the humic compounds and this could change the speciation significantly while, in the second case, the seawater was spiked with vitamin B_{12} at a concentration about three orders of magnitude higher than occurs naturally.

Sugimura *et al.*[3,4] used XAD-2 resin to extract trace metals from seawater and Lyons *et al.*[5] used XAD-2 to extract iron from anoxic nearshore sediment pore fluids. These authors assumed that any metal adsorbed by these resins was in the form of organic complexes since it had been reported[2–7] that simple inorganic cations were not adsorbed. Recent experiments[8] have shown that this is not the case and that Amberlite XAD-1 and XAD-2 adsorb significant amounts of iron, copper and zinc from distilled deionized water spiked with simple cations of these metals. This adsorption of simple cationic species of copper and zinc was presumed to be the reason that these metals could not be reproducibly extracted from seawater by XAD-1[8].

The Amberlite resins (XAD-1, XAD-2 and XAD-4) are all made by the polymerization of styrene–divinylbenzene mixtures and differ primarily in pore size and effective surface area. In principle, they contain no functional groups that can coordinate trace metals, although Puon and Cantwell[10] found that XAD-2 was capable of adsorbing 1 μmole H_3O^+ or 0.2 μmole OH^- per gram of resin depending on pH. The acrylic ester resins (XAD-7 and XAD-8) have been reported as possessing a very low ion-exchange capacity —in the order of 10 μmole g^{-1} in the case of XAD-8[11]— but these authors also reported that the cross-linked polystyrene resins (XAD-1, XAD-2 and XAD-4) possessed no ion-exchange capacity and it is possible that there could be batch to batch variations in these resins. The manufacturer of these resins was unable to provide any information as to the nature or concentration of potential impurity sites.

In a previous paper[9] the adsorption of trace metals from water by XAD-2 was studied by means of a multichannel atomic fluorescence detector (AFD) coupled directly to the output of a chromatographic column packed with the resin. The measurements on XAD-2 are extended in this paper under more rigorously controlled conditions and the results are compared with similar experiments on the chemically identical resin XAD-4.

EXPERIMENTAL

Standard solutions containing 1 g l^{-1} of metal were made by dissolving analytical-reagent grade metal sulphates (ammonium-ferric-alum in the case of iron) in distilled deionized water (DDW) from a Milli-Q system. The stock solution was made by diluting 10 ml each of these solutions to a litre and contained 10 mg l^{-1} of magnesium, iron, zinc and copper. This solution gradually precipitated ferric hydroxide and was acidified drop wise with analytical-reagent grade sulphuric acid until the precipitate disappeared. The final pH was 2.50. A subsample of this stock solution was acidified to pH 1.50 and another subsample was adjusted to the same pH in the presence of $10^{-2}M$ analytical-reagent grade acetic acid. The solutions used for eluting the columns were 10^{-3} M analytical-reagent grade disodium dihydrogenethylenediamine tetraacetate (H_2Y^{2-}) and 5% Aristar-grade ammonia (NH_3). DDW was used in all cases.

The chromatographic equipment was the same as described previously[9] and was of the Cheminert type manufactured by Laboratory Data Control. A CMP-3K pump was used and the chromatography columns were 6 mm I.D. and contained about 4 ml of resin. Two columns, containing XAD-2 and methylated XAD-2 respectively, were the same columns as used previously[9]. The third column was packed with XAD-4 resin that had been soxhlet extracted for 16 h with methanol and 8 h with acetonitrile.

The AFD has been described earlier[9] but the magnesium lamp was operated at 5mA rather than 20 mA. Careful alignment of the optics had resulted in much stronger fluorescence signals for all metals and at higher lamp currents the magnesium fluorescence was so intense that it interfered severely with the iron and copper signals. Under the conditions used in this paper, there was no interference between the separate channels.

The general experimental procedure consisted of injecting 500 μl of stock solution (containing 5 μg each of magnesium, iron, zinc and copper) onto the column with DDW at a flow-rate of 100 ml h^{-1}. The effluent from the column passed directly into the variable nebulizer of the AFD and the nebulizer was adjusted so that the uptake rate was identical to the flow rate through the column. Any adsorption by the column resulted in a reduced signal from the detector. Even allowing for a reduction in the maximum concentration in the effluent due to band broadening and/or adsorption, the peak concentration was generally higher than the linear region of the fluorescence versus concentration calibration curve. This saturation effect is less important for iron than for copper and zinc and previous experiments[9] showed that significant departures from linearity occur at concentrations of 600 μg l^{-1} (Zn), 1000 μg l^{-1} (Cu) and $\geqslant$ 1600 μg l^{-1} (Fe). Thus a small decrease in the copper or zinc fluorescence signal corresponds to considerable adsorption of these ions by the resin. Saturation effects were not apparent for magnesium which is surprising since Larkins[12], using similar equipment, reported non-linear effects at concentrations above 400 μg l^{-1} (Mg), 300 μg l^{-1} (Zn) and 2000 μg l^{-1} (Fe). No attempt was made to quantify the amounts of trace metal in the effluent from the column since this is difficult using the AFD at the concentrations involved and the main interest was in comparing the adsorption properties as a function of resin type, pH, number of loadings etc. The fluorescence signals were compared by measuring the peak heights and half-widths. The "tailing" of the peaks was determined by measuring the width at one tenth of peak height. The fluorescence signals for iron and, particularly, zinc and copper are generally truncated due to saturation effects. Hence the experimentally determined half-width is actually the width at a much lower fraction of the maximum signal intensity. Any reduction in the concentration of copper and zinc (and to a lesser extent iron) initially leaves the peak height almost constant but the line shape changes as the truncation effect is reduced. This leads to an apparent decrease in the experimentally determined half-width. However, any interaction with the column will also cause line broadening and the resultant line width is a compromise between these two opposing tendencies. The concentrations of metal in the H_2Y^{2-} and NH_3 eluates were usually much lower than in the column effluents and the metal concentrations should be roughly proportional to peak height.

After the fluorescence signals in the effluent returned to background levels, the columns were eluted at 100 ml h^{-1} with H_2Y^{2-} or NH_3 and the eluate was monitored by the AFD. All washing and preconditioning of the columns was done at a flow-rate of 500 ml h^{-1}. The columns were also eluted after two, three and five successive injections of stock solution.

The iron, zinc and copper fluorescence signals were recorded on a three-pen recorder and the magnesium fluorescence on a separate recorder. The recorder traces shown in this paper were made by superimposing the signals from both recorders. The traces have been offset slightly for clarity.

RESULTS AND DISCUSSION

XAD-2

Five successive samples of stock solution at pH 2.50 were injected onto a column of XAD-2 and the fluorescence signals in the effluent are shown in Fig. 1a. The recorder traces for the last four injections are identical but the first injection is distinguished by a slightly diminished copper peak while the tailing is a little more pronounced for the iron peak and a little less pronounced for the zinc peak. The differences are small but are reproducible. Figs. 1b–e show the elution peaks when the column was eluted with H_2Y^{2-} after separate experiments where the column was loaded with 5, 3, 2 and 1 injection of stock solution, respectively. The small magnesium fluorescence in all the elutions and the zinc fluorescence after 5 and 3 injections may be due to insufficient time being allowed for all the stock solution to pass through the column before the elution with H_2Y^{2-}.

Inspection of the elution peaks in Figs. 1b–e reveals that the four metals interact quite differently with XAD-2. In the presence of iron, copper and zinc, the adsorption and subsequent elution of magnesium is negligible. The amount of zinc adsorbed by the resin decreases markedly on the second injection and becomes negligible after

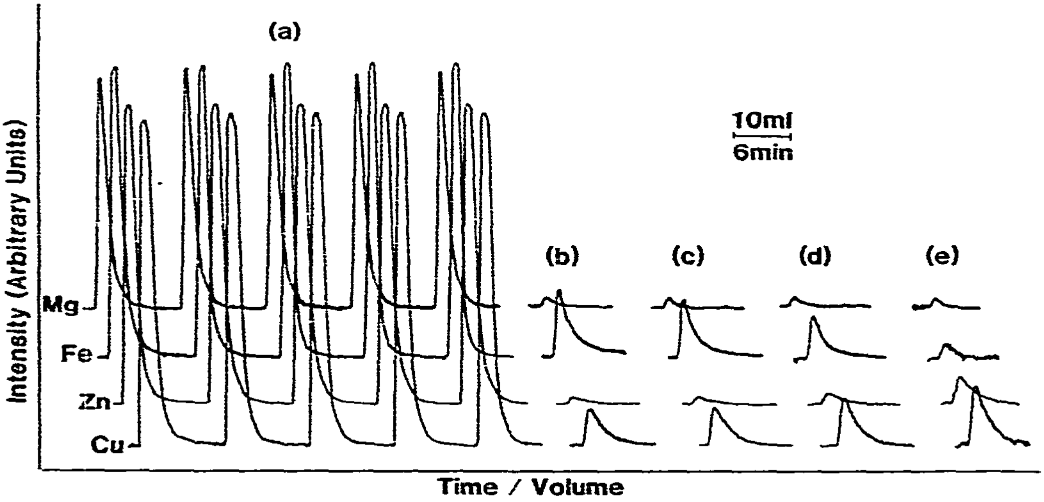

Fig. 1. (a), Atomic fluorescence signals from the effluent from a column of XAD-2 resin after five successive loadings of 500 μl of stock solution at pH 2.50. (b)–(e), Atomic fluorescence signals from the eluent when the column was eluted with H_2Y^{2-} after 5, 3, 2 and 1 loading, respectively.

the third injection. A decrease in the amount of adsorbed copper is also observed but the decrease is much less marked and the amount adsorbed appears to be approaching some equilibrium value. The amount of iron adsorbed by the resin increases on successive injections and it is apparent that iron is able to completely displace adsorbed zinc and partially displace adsorbed copper. The strength of interaction of these four metals decreases in the sequence $Fe^{3+} > Cu^{2+} > Zn^{2+} > Mg^{2+}$.

Although there is significant adsorption of zinc on the first injection, the peak height of the zinc fluorescence in the effluent is indistinguishable from the peak height on the second injection when zinc is actually being added to the effluent due to the displacement of zinc by iron. This is caused by the saturation of the zinc fluorescence signal but it appears that zinc is rapidly adsorbed on the first injection since the effluent band is slightly narrowed. Iron obviously reacts more slowly with the resin since the total amount of adsorbed iron increases steadily with successive additions and this gives rise to a broader signal with more pronounced tailing on the first injection. The rate of adsorption of copper appears to be somewhat between the rates for iron and zinc with the net result that the line shape of the effluent peak remains unaltered although the peak height increases slightly after the first addition.

The adsorption of these metals by methylated XAD-2 resin[9] closely parallels the behaviour of the unmethylated resin. The same small differences exist between the fluorescence signals of the effluent from the first injection relative to all subsequent injections and the fluorescence signals are essentially indistinguishable from those of the unmethylated resin as shown in Fig. 1a. The amount of iron, copper and zinc eluted from the column by H_2Y^{2-} is about 20% less than for the untreated resin and this reduction in adsorption capacity is independent of the number of injections of stock solution. This implies that the functional groups that had been methylated were representative of the donor sites on the resin and did not have a special affinity for any of the metals studied.

When stock solution at pH 1.50 was injected onto the column of XAD-2, the fluorescence signals of the effluent solution were similar to those obtained at pH 2.50. The effluent peaks after a single injection were also different from those of subsequent loadings and in addition to the slight differences observed at pH 2.50, it was found that both the half-width and tailing of the copper signal were slightly larger for the first peak relative to all subsequent peaks. However, the total amount of metal adsorbed onto the resin at pH 1.50 was less than half the amount adsorbed at pH 2.50 although the general pattern was similar with negligible adsorption of magnesium and little adsorption of zinc which was displaced from the resin after the second injection of stock solution. The displacement of copper by iron was much less pronounced at the lower pH and after five loadings, the final iron and copper signals in the H_2Y^{2-} eluate were approximately the same whereas, at pH 2.50, the iron fluorescence was approximately double that of copper (Fig. 1b).

The column of XAD-2 was also loaded by successive injections of a stock solution at pH 1.50 in the presence of 10^{-2} M HOAc and the results are indistinguishable from those obtained in the absence of acetic acid. The stock solution had a total metal concentration of $9 \cdot 10^{-4}$ M and was also 10^{-2} M in undissociated acetic acid and $3 \cdot 10^{-2}$ M in hydrogen ions and one would expect at least some adsorption of undissociated acetic acid onto the resin. If the complexing sites on XAD-2 were similar to isolated carboxyl groups, there should be increased adsorption of trace metals by the resin in the presence of acetic acid. Since this does not occur, either a negligible amount of acetic acid is adsorbed or else the impurity donor sites are different from simple carboxylate groups.

In order to confirm that the results obtained above were not due to adsorbed ethylenediamine tetraacetic acid, the column of XAD-2 was extensively washed with NH_3 solution and DDW and the previous experiment was repeated. The results after this treatment were identical to those obtained prior to washing with ammonia.

XAD-4

The adsorption of trace metals by XAD-4 at pH 1.50 is comparable to that of XAD-2 at the same pH and, as found earlier, the presence of 10^{-2} *M* acetic acid has no effect. The traces for successive loadings and elutions are shown in Fig. 2. The copper fluorescence signal in the first column effluent is much less truncated than is found in subsequent effluents while tailing effects are more pronounced. The copper in the effluent has been spread out over a larger volume with a subsequent decrease in the maximum concentration. This implies a significant interaction between copper and XAD-4. A similar but less pronounced effect is observed for iron after the first addition even though negligible iron is removed from the resin on elution with H_2Y^{2-} (Fig. 2e). However, the resin is capable of adsorbing iron as is apparent from Fig. 2b where iron is found in the H_2Y^{2-} eluate after the column had been loaded five times. As before, this adsorption of iron occurred at the expense of copper and zinc. The desorption peaks from XAD-4 (Figs. 2b–e) are broader than those from XAD-2 (Figs. 1b–e) and it seems that H_2Y^{2-} is a less effective eluent in the former case. In agreement with this, it was found that reproducible behaviour could only be obtained if the column was extensively washed between experiments. The washing time could be reduced by including an ammonia wash between the H_2Y^{2-} and DDW elutions.

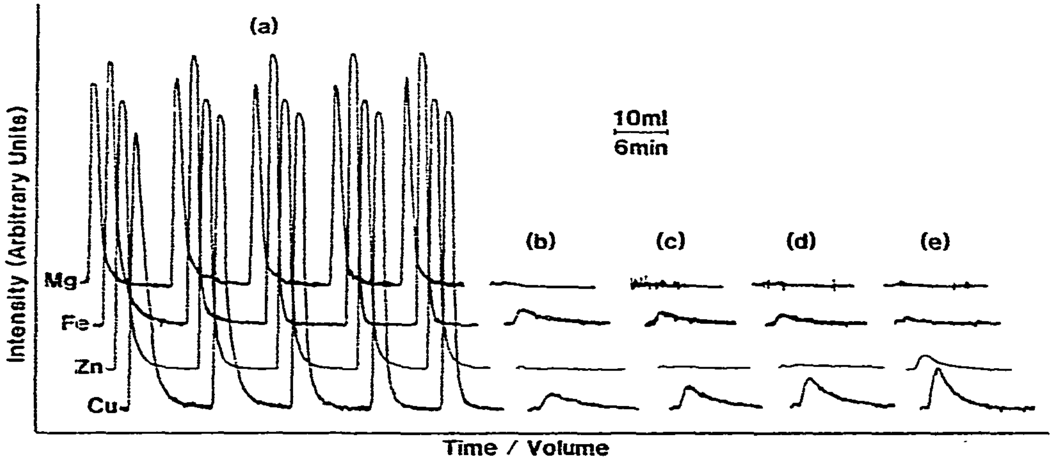

Fig. 2. (a), Atomic fluorescence signals from the effluent from a column of XAD-4 resin after five successive loadings of 500 μl of stock solution at pH 1.50 in the presence of 10^{-2} *M* acetic acid. (b)–(e), Atomic fluorescence signals from the eluent when the column was eluted with H_2Y^{2-} after 5, 3, 2 and 1 loading, respectively.

In the previous experiments, the total amount of metal in each 500 μl injection (450 nmol) exceeded the adsorption capacity of the resin and the competition between the metals for the available coordination sites excluded significant adsorption of zinc and magnesium. The larger surface area of XAD-4 (725 m^2 g^{-1}) compared to XAD-2 (300 m^2 g^{-1}) would be expected to give rise to a greater adsorption capacity by XAD-4 and although this was not observed at pH 1.50, the results at pH 2.50 are very different from those described previously since the adsorption capacity of the resin becomes comparable to the amount of metal in each injection. Under these conditions, the effluent and elution peaks become quite different since on the first injection even magnesium is strongly adsorbed and all the effluent peaks are reduced in height and show no evidence of truncation due to saturation effects (Fig. 3a). The strong interaction between the resin and iron, copper and zinc gives rise to pronounced tailing although this is not apparent for magnesium. The kinetics of adsorption and desorption of magnesium may be more rapid than for the other metals. On elution with H_2Y^{2-}, strong signals are observed for copper, zinc and magnesium with

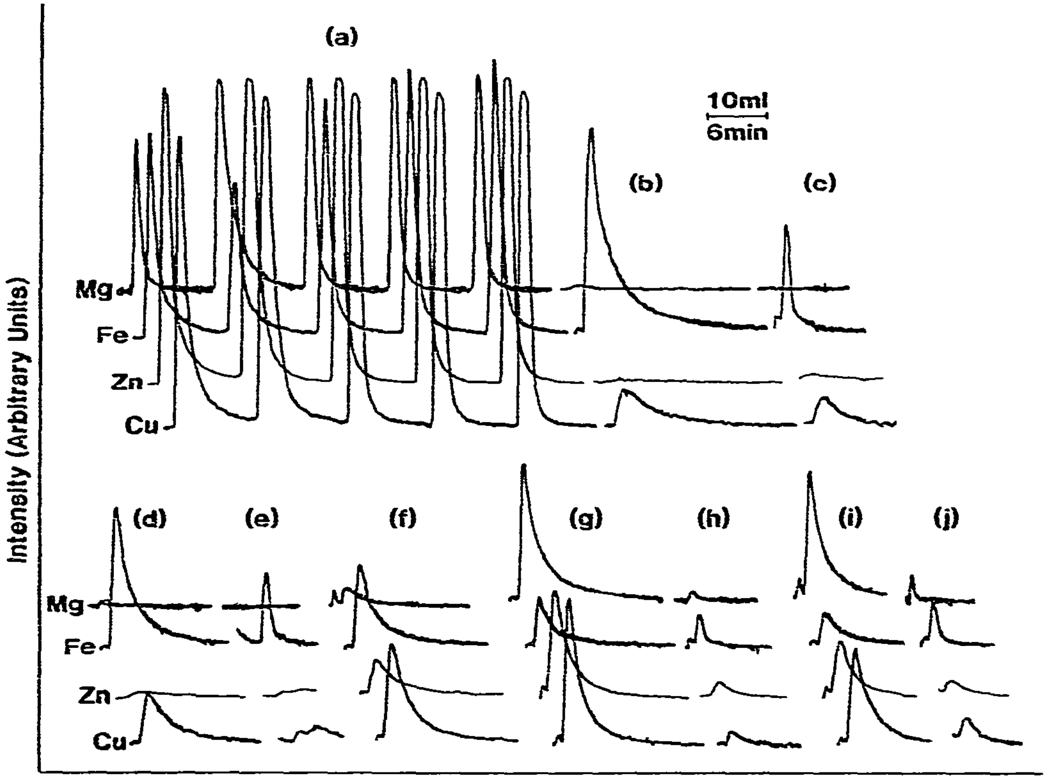

Fig. 3. (a) Atomic fluorescence signals from the effluent from a column of XAD-4 resin after five successive loadings of 500 μl of stock solution at pH 2.50. (b)–(j). Atomic fluorescence signals from the eluents under the following conditions: five loadings and elution with (b) H_2Y^{2-} followed by (c) NH_3; three loadings and elution with (d) H_2Y^{2-} followed by (e) NH_3; two loadings and elution with (f) H_2Y^{2-}; one loading and elution with (g) H_2Y^{2-} followed by (h) NH_3; one loading (at 25 ml h^{-1}) and elution with (i) H_2Y^{2-} followed by (j) NH_3.

a weaker iron signal (Fig. 3g). The elution peaks are broad and asymmetric and subsequent elution with NH_3 gives rise to broad, weak copper and zinc signals, a small, sharp iron signal and a negligible magnesium signal (Fig. 3h).

On further injections of stock solution, the copper and zinc concentrations in the effluent increase until the fluorescence signals in the second effluent are nearly equal to those in the third and subsequent effluents although there is slightly more tailing. The second magnesium effluent peak is much greater than the third and subsequent peaks while the iron peak is even smaller than the first. It is apparent that iron is being strongly adsorbed at the expense of magnesium and from Fig. 3f it is seen that the iron elution peak is much stronger and there is very little magnesium eluted from the column. On the third and subsequent injections, the iron effluent peaks increase but iron is still being strongly adsorbed as is evidenced by the lack of saturation effects and by increasingly strong iron fluorescence in the H_2Y^{2-} elutions (Figs. 3f, d, b). After five injections, only iron and copper remain on the column and the H_2Y^{2-} elution peaks are very broad and asymmetric. Subsequent elutions with NH_3 produced broad copper signals and much sharper iron signals (Figs. 3c, e, h) and the significance of this is discussed later.

The minimum in the iron effluent concentration on the second injections means that iron is more readily adsorbed by the resin on the second injection and hence that the resin was preconditioned by the first loading. There are two ways in which this could occur. Firstly the stock solution had a higher acidity (pH 2.50) than the DDW used to wash the column and the first loading could have protonated impurity groups that existed in their basic form prior to the initial loading. If such protonated groups are still present on the resin when the second loading occurs, and if ferric ions react more readily with such groups, then iron would be more readily adsorbed on the second injection. Alternatively, ferric ions could react more readily with sites coordinated to magnesium and hence the second loading would give rise to an increased adsorption or iron (relative to the first loading) with a concomitant release of magnesium as is observed. It is possible that both processes occur and the chances of observing such an enhancement in adsorption require a serendipitous choice of pH, metal concentrations and resin adsorption capacity.

Iron appears to be absorbed more slowly than magnesium (Fig. 3) and kinetic effects were investigated by loading the column of XAD-4 with one injection of stock solution (pH 2.50) at 25 ml h^{-1}. The column was then eluted with H_2Y^{2-} and NH_3 in the usual way and the results are shown in Figs. 3i and j. The traces are qualitatively the same as obtained when the column was loaded at 100 ml h^{-1} (Figs. 3g and h), although it is difficult to explain why there is less iron, copper and zinc adsorbed at the slower flow rate. However, the important fact is that the relative affinity of XAD-4 for these metals is not affected by changing the loading rate by a factor of four.

In order to get further information on the binding between trace metals and XAD-4, the column was loaded with a single injection of stock solution (pH 2.50) and eluted successively with H_2Y^{2-} and NH_3 (Fig. 4a). The experiment was repeated with the NH_3 elution preceding the H_2Y^{2-} elution and the results are shown in Fig. 4c. As observed earlier (Figs. 3c, e, h and j) iron, copper and zinc can still be eluted by NH_3 even after extensive washing with H_2Y^{2-}. When the elution order is reversed, there is a ready release of copper and zinc, presumably as $M(NH_3)_4^{2+}$. Magnesium and iron do not form ammonia complexes in aqueous solution and any metal liberated from

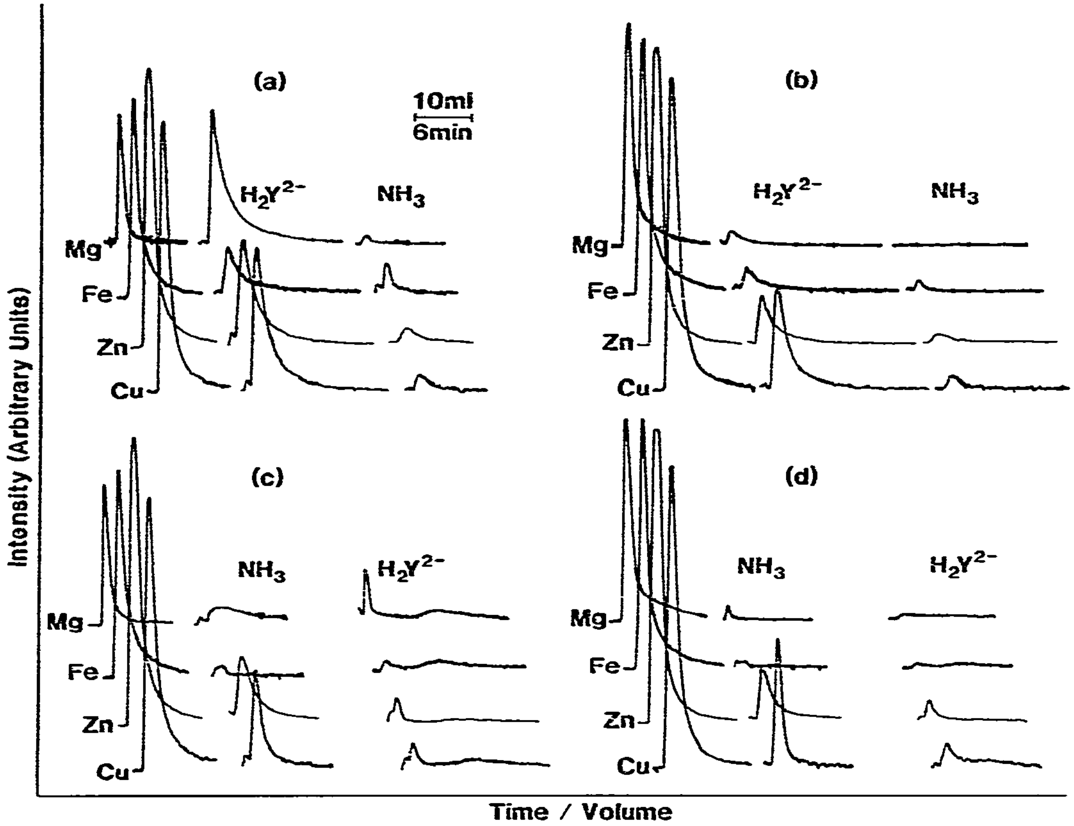

Fig. 4. Atomic fluorescence signals from the effluent from a column of XAD-4 after a single loading of stock solution at pH 2.50 followed by elution with (a) H_2Y^{2-} then NH_3 and (c) NH_3 then H_2Y^{2-}. The resin was then washed with methanolic HCl and the experiments repeated giving the traces shown in (b) and (d).

the resin would be converted into insoluble hydroxides which pass slowly through the column giving rise to rather broad featureless elution bands. On subsequent elution with H_2Y^{2-}, small amounts of copper and zinc are desorbed while magnesium and iron both give rise to two elution bands. The broad weak second bands are probably due to slow dissolution of iron and magnesium hydroxides by H_2Y^{2-}. The origin of the initial sharper peaks is not quite so clear and two possibilities arise: (a) the peaks could be due to the rapid release of iron and magnesium bound to impurity sites on the resin that do not readily release these metals to NH_3, or (b) mixed hydroxy/ethylenediamine tetraacetate complexes may be formed which are more readily eluted due to an increase in the negative charge on the complex. Using tabulated stability constants[13] it can readily be shown that the iron complex $FeY(OH)^{2-}$ is not stable in dilute ammonia (pH $\approx$ 11) but at the interface between ammonia and H_2Y^{2-} (pH 4.5) suitable conditions might exist. Such an explanation could also account for the strong sharp elution peaks of iron when the column was eluted with ammonia in earlier experiments (Figs. 3c and e).

When the column was eluted with NH_3 prior to elution with H_2Y^{2-} the resin required extensive cleaning to remove the precipitated hydroxides of iron and magnesium although the original characteristics of the column could ultimately be reproduced. After all the previous experiments had been completed, the column was washed at 100 ml h^{-1} with 400 ml of 10% methanolic HCl (Merck Suprapure) followed by 125 ml of DDW (500 ml h^{-1}). This procedure had a substantial effect on the adsorption capacity of the resin and comparison of Figs. 4a and b reveals that the column is no longer capable of adsorbing magnesium under the conditions used while the amount of iron, copper and zinc in the eluates is reduced by at least one third. There is also a suggestion that the relative affinity of metals for the resin is altered since the ammonia elution peak for copper (Fig. 4c) is smaller than that observed after the resins had been treated with methanolic HCl (Fig. 4d) contrary to the results for all other elution peaks. It is apparent that some of the functional groups have either been hydrolysed by the methanolic HCl or else have been methylated with a subsequent reduction in Lewis basicity.

In experiments involving only copper and zinc[9] it was found that the adsorption of these metals by XAD-1 and XAD-2 was not strongly dependent on pH. This is not the case where iron is also present since Fe^{3+} forms stronger complexes than zinc or copper and the adsorption of Fe^{3+} is pH dependent. This is of great importance to any investigation of natural waters since iron is generally more abundant than either copper or zinc. Mackey[9] also found evidence for more than one type of impurity donor site on XAD-1 and XAD-2 and the present results on XAD-4 tend to support that idea since some of the adsorbed trace metal is more readily eluted by H_2Y^{2-} than NH_3 while the reverse holds for some adsorbed metal and a significant amount is readily desorbed by either eluant although the desorption is generally slower for XAD-4 than for XAD-2.

The kinetics of adsorption by these resins is interesting and there is no obvious reason for the gradual increase in the amount of iron adsorbed on successive injections nor for the fact that magnesium can be adsorbed from solution even though the column effluent still contains large amounts of iron, copper and zinc (Figs. 3g, 3i and 4a). However, the fact that magnesium can be adsorbed by XAD-4 (and presumably XAD-2), under certain conditions should be borne in mind if these resins are used for speciation studies on seawater where the magnesium concentration may be six orders of magnitude greater than that of the trace metals of interest.

Since iron seems to displace magnesium very readily, this adsorption of magnesium may catalyse the uptake of iron from seawater. In any case, adsorption of trace metals by XAD-2 from natural waters acidified to approximately pH 2.50 cannot be taken as evidence for the existence of organically associated metals in those waters[3-5].

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