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CATION-EXCHANGE BEHAVIOUR OF A RANGE OF ADSORBENTS AND CHROMATOGRAPHIC SUPPORTS WITH REGARD TO THEIR SUITABILITY FOR INVESTIGATING TRACE METAL SPECIATION IN NATURAL WATERS

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SUMMARY

The adsorption of simple cations of iron, copper, zinc and magnesium by a range of adsorbents and chromatographic supports has been investigated using an atomic fluorescence detector directly coupled to a liquid chromatograph. The cross-linked polyaromatic resins (XAD-2, Chromosorb 101 and 102, Porapak P, PS, Q and QS and Benson BN-X4 and BN-X10) all act as cation-exchange resins with capacities of about 0.1–0.5 μequiv. g^{-1}. Octadecyl-bonded silica has a similar capacity provided care is taken to ensure that no alkylgroups are hydrolysed from the surface. Activated charcoal and the polyacrylic ester resins, XAD-7 and XAD-8, have ion-exchange capacities that are higher by one to two orders of magnitude. These cation-exchange capacities, although low, must be taken into account if these resins are used to study trace metal speciation in natural waters.

INTRODUCTION

In recent years there has been increasing evidence that metal–organic complexes play an important role in the biogeochemical cycling of trace metals in natural waters. The low concentration of these elements in unpolluted waters imposes severe restrictions on experiments designed to characterize and identify such species and it would be advantageous to be able to quantitatively isolate metal–organic complexes from natural waters. The hydrophobic cross-linked polystyrene resins XAD-1, XAD-2 and XAD-4 have been used extensively to extract organic compounds from natural waters and it has been assumed that any trace metal adsorbed by these resins[1–3] was associated with organic molecules. However, these resins can also adsorb significant amounts of iron, zinc, copper and magnesium in the absence of organic complexing agents[4,5]. Moreover, these metals can be eluted by disodium dihydrogen ethylenediamminetetraacetate (Na$_2$H$_2$Y) implying that not all metal–organic complexes are adsorbed by these resins[4–6]. Electrically charged molecules are not adsorbed as strongly as neutral species[7] and while this may explain the non-retention of complexes such as CuY^{2-} and FeY^{-}, some positively and negatively charged metal–

organic complexes are quantitatively retained by XAD-2. Thus, Sakai[6] found that the copper(II) chelate of N-(dithiocarboxy)sarcosine is quantitatively adsorbed at pH 7.0 and Willis and Sangster[8] found that the ferrous complex of 1,10-phenanthroline could also be adsorbed by XAD-2. These resins are therefore not suitable for quantitative measurements on trace metal speciation[9] although their low cost, high adsorption capacity and chemical inertness make them suitable for qualitative studies of those trace metal compounds that can be adsorbed from aqueous solution and subsequently eluted by organic solvents. In this paper, I continue my investigations on the adsorption and desorption of Mg^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} by a number of other commercially available adsorbents and chromatographic supports to determine their suitability for extracting and separating metal–organic compounds from natural waters.

EXPERIMENTAL

The adsorbents investigated were Amberlite XAD-2, XAD-7 and XAD-8 (Rohm & Haas), Chromosorb 101 and 102 (Johns-Manville), Porapak P, PS, Q and QS (Waters), BN-X4 and BN-X10 (Benson), activated charcoal Norit A (Nutritional Biochemicals) and octadecyl-bonded silica from Sep-Pak C_{18} cartridges (Waters). Distilled deionized water (DDW) from a Milli-Q system was used in all experiments.

One batch of XAD-2 was ground in a mortar and pestle, sieved and the 50–60 μm fraction collected and compared with a different batch of XAD-2 that had been studied previously[4,5]. The material from six Sep-Pak cartridges was packed into a Cheminert column so that a direct comparison could be made with the other supports. Waters (Aust.) also provided some C_{18}-bonded silica that had been removed from some faulty Sep-Pak cartridges and this material was also investigated.

The experimental procedure has been described in detail[4] and it consists of injecting 500 μl of stock solution (containing 10 mg l^{-1} each of iron, magnesium, copper and zinc at pH 2.50) onto a column and monitoring the effluent for these metals with a four-channel non-dispersive atomic fluorescence detector. After the fluorescence signal in the effluent has returned to background values, the column may either be eluted (10^{-3} M Na_2H_2Y in DDW) or another 500 μl of stock solution injected onto the column. The results from a number of experiments can be combined so that one can measure both the change in composition of the effluent as well as the amounts of trace metal eluted after varying numbers of injections.

The equipment is the same as described previously[4] except that the rhodium plated burner bowl was replaced by a titanium bowl. The voltages applied to the photomultiplier tubes were reduced and the copper fluorescence was detected by a Hamamatsu R106 photomultiplier at 358 V and shielded by a Schott UG11 filter, while iron, zinc and magnesium were detected by a single Hamamatsu R166 photomultiplier at 488 V. The reduction in dynode voltages greatly extended the linear range of the detector without affecting the sensitivity. Interference effects between the channels were also reduced and, with all lamps operating at maximum current, 100 μg l^{-1} of any of the four metals could be detected in the presence of 10,000 μg l^{-1} of any of the other metals without interference. At a flow-rate of 100 ml h^{-1}, detection limits (defined as signal: noise = 2) were 30 μg l^{-1} (Cu and Fe), 5 μg l^{-1} (Zn) and 8 μg l^{-1} (Mg). The detection limit for magnesium was about 1 μg l^{-1} using a Varian IM-1 amplifier. The detection limits were inversely proportional to flow-rate in the range 25–100 ml h^{-1}.

: The 6 mm I.D. Cheminert chromatography columns were slurry packed to a length of 13 ± 2 cm and were generally loaded and eluted at 100 ml h^{-1} using a Cheminert CMP-3K pump. Back pressures were usually less than 20 p.s.i. The activated charcoal column was connected to a CMP-1K pump and the back pressure was 350 p.s.i. at 50 ml h^{-1}. The back pressures were measured on dummy runs and the gauge was isolated from the system during the experiments so as to avoid metal contamination.

No studies were made on the effect of pH nor whether the adsorbed metals were quantitatively eluted by Na_2H_2Y. However, in those cases where the columns were eluted after various loadings, the results were reproducible implying that non-reversible adsorption was negligible. The measurements on the adsorbents were made under identical conditions and were completed within 3 weeks. Day-by-day fluctuations in detector sensitivity are about 20% and this should be borne in mind when comparing the results.

Properties of adsorbents

The properties of the various adsorbents and chromatographic supports (as well as XAD-1 and XAD-4) are listed in Table I. The resins Porapak P and Q and Chromosorb 101 and 102 are normally used as supports for gas–solid chromatography but the resins with larger surface areas (Porapak Q, Chromosorb 102) have been used to extract organic compounds from aqueous solution[20] and from air[21,22]. Although the Porapak resins should contain no functional groups, such groups are

TABLE I

PROPERTIES OF ADSORBENTS

Adsorbent	Structure	Particle size (μm)	Percentage cross-linking	Surface area (m^2 g^{-1})	Average pore diameter (nm)	Ref.
XAD-1	STY–DVB*	250–850	—	100	10	10
XAD-2	STY–DVB	250–850**	—	300	9	10
XAD-4	STY–DVB	250–850	—	725	4	10
Chromosorb 101	STY–DVB	45–75	—	<50	300–400	11
Chromosorb 102	STY–DVB	45–75	—	300–400	8.5	11
BN-X4	STY–DVB	50	4	70	2.8	12,13
BN-X10	STY–DVB	50	10	35	0.9	12,13
Porapak P, PS	STY–DVB–EVB***	180–300	Large	50	—	14
				Approx. zero 100–200	No real pores —	15 16
Porapak Q, QS	STY–DVB–EVB	180–300	Large	400–700	<100	15
				634	7.5	18
XAD-7	Acrylic ester ⁱ	250–850	—	450	9	10
XAD-8	Acrylic ester ⁱ	250–710	—	160	22.5	10
Sep-Pak	C_{18}-bonded silica	50–100	—	250–300 ⁱⁱ	12.5	15

* Copolymer of styrene and divinylbenzene.
** One sample was ground and the 50–60-μm fraction studied.
*** Copolymer of styrene, divinylbenzene and ethylvinylbenzene.
ⁱ See reference 19 for structure.
ⁱⁱ Surface area of silica particles.

known to be present since the manufacturers supply silanized versions under the names Porapak PS and QS. The Porapak resins are chemically different from XAD-1, 2 and 4 and Chromosorb 101 and 102 in that ethylvinylbenzene is included in the monomer mixture with more ethyl groups present in the Q series resins. The presence of ethyl substituted benzene rings should have little effect on the adsorption characteristics of the resins. Thus Sydor and Pietrzyk[22] found that the differences in the adsorption properties of the Porapak and XAD resins were primarily determined by effective surface area and pore size with the adsorption capacity decreasing in the order Porapak Q > XAD-2 > Porapak P. The Benson resins are gel type polymers, are classed as pseudoporous by the manufacturers[12,13] and are chemically identical to Amberlite XAD-1, 2, 4 and the Chromosorb resins. They are made specifically for liquid chromatography and impurities are quoted as being in the ppm range[12,13].

XAD-7 and XAD-8 are polyacrylic esters, are more hydrophilic than the poly-aromatic resins discussed earlier and are more suitable than the latter[23] for extracting polar compounds, such as fulvic acid, from aqueous solution. Since fulvic acid is often assumed to be important in the complexation of trace metals by natural waters, these resins would seem to be suitable for studying naturally occurring metal–organic compounds. The resins exhibit weak acid–base properties[24] and XAD-8 is reported to have a very low ion-exchange capacity of 10^{-2} mequiv. g^{-1} (ref. 23). However, this is about two orders of magnitude greater than the ion-exchange capacity found for XAD-2[4] and it seems highly probable that not all of the carboxyl groups in the resins have been esterified.

Alkyl-bonded silica particles have been extensively studied and although they dominate the field of reverse phase liquid chromatography they have only recently been used to remove organics from seawater[25]. The metal free construction of Sep-Pak cartridges should make them ideally suited to extract metal–organic compounds from natural waters. However, it is extremely difficult to eliminate all of the hydroxy groups from the silica surface even when the silica is treated with less bulky reagents such as trimethylchlorosilane. The residual silanol groups may cause tailing in some chromatographic separations but this should be of little consequence where the materials are used as adsorbents for organic compounds. Unfortunately these groups will have a strong affinity for trace metal cations particularly Class-A cations[26] such as Fe^{3+} and Mg^{2+} and the usefulness of alkyl-bonded silica is limited by the concentration of residual silanols.

RESULTS

Amberlite XAD-2
For the unground resin (Fig. 1) the adsorption of iron increased after the first loading while the other metals were little affected by additional loadings. In contrast, the ground resin initially adsorbed no magnesium, only a trace of zinc and adsorbed iron selectively since this metal was able to displace the copper (and zinc) that was initially adsorbed (Fig. 2). The first loading also predisposed the resin to adsorb iron since the iron signal from the second effluent was less than the first and the behaviour was similar to that observed previously for XAD-4[5]. The smaller particle size of the ground resin resulted in narrower effluent peaks with less tailing, particularly after the first loading had reduced the number of donor sites on the resin. There is no obvious
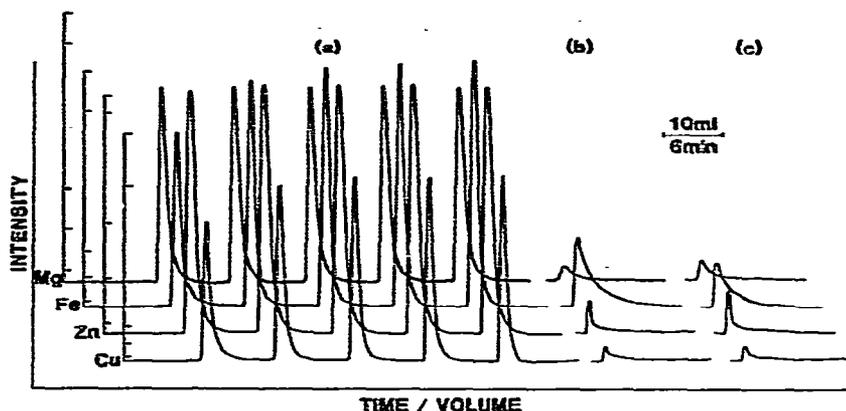
Fig. 1. a, Atomic fluorescence from the effluent from a column of XAD-2 resin after five successive loadings of 500 μl of stock solution. b and c, Atomic fluorescence from the eluent when the column was eluted with Na_2H_2Y after 5 and 1 loading respectively. The scale bars at the left give the approximate signals for 100, 500, 1000, 5000 and 10,000 μg l^{-1}.
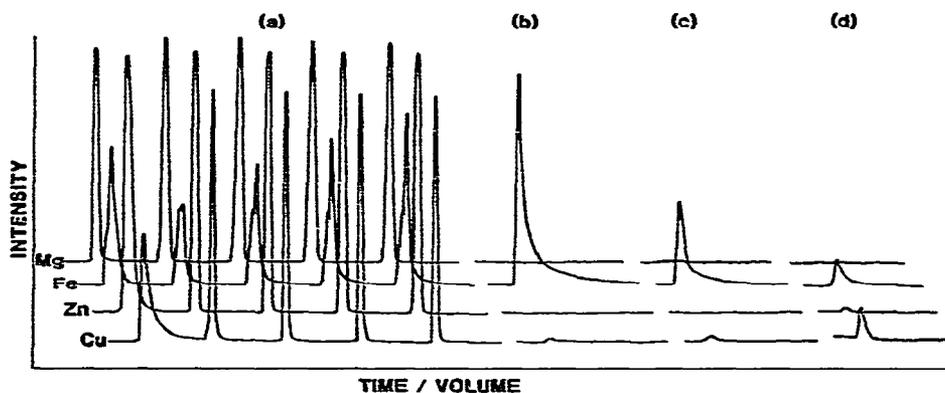

Fig. 2. a, Atomic fluorescence from the effluent from a column of XAD-2 resin (50–60 μm) after five successive loadings of 500 μl of stock solution. b–d, Atomic fluorescence from the eluent when the column was eluted with Na_2H_2Y after 5, 2 and 1 loading respectively. See Fig. 1 for scale.

explanation for the shoulder on the iron effluent peaks (Fig. 2) and no structure was observed in experiments on any of the other resins. The two samples of XAD-2 gave quite different results (Figs. 1 and 2) and it seems that there may be considerable batch to batch variation in these resins. Grinding should have a negligible effect on the surface area of a macroporous resin, such as XAD-2, and the two samples are quantitatively and qualitatively different in their behaviour toward trace metals.

Chromosorb 101 and 102

Chromosorb 101 adsorbed small amounts of all four metals and apart from iron there was no change in the amount of trace metal adsorbed after the first loading (Fig. 3). Both the effluent and eluate peaks were symmetric and the adsorption of the metal ions was non-selective. The behaviour of Chromosorb 102 was quite different (Fig. 4) and the resin had a much greater affinity for iron than for the other metals. Some of the iron was strongly bound since the eluate peaks showed more tailing than
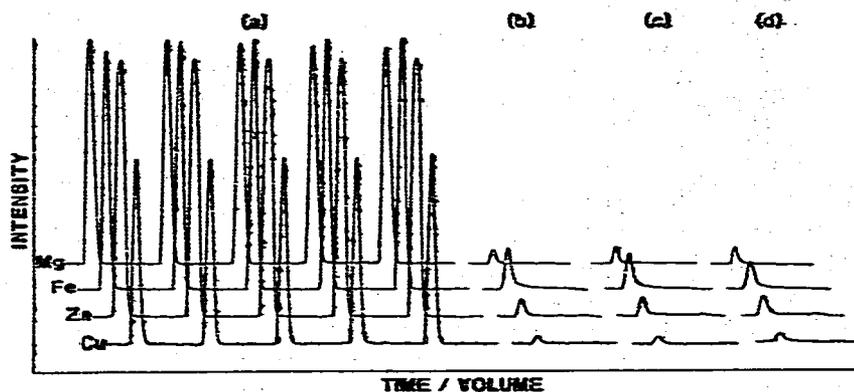
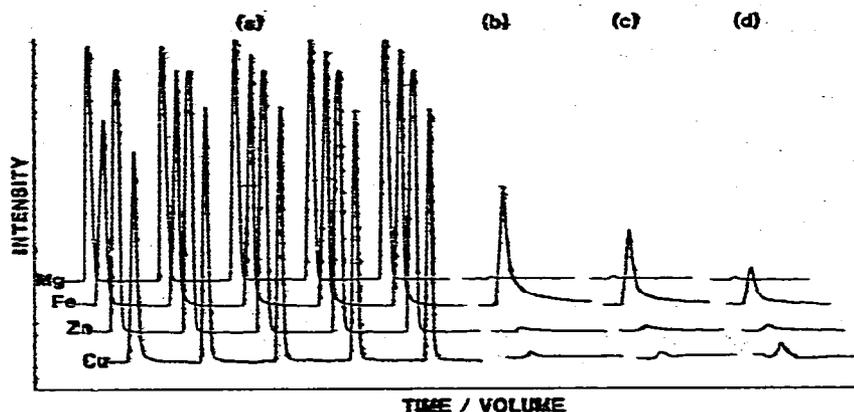Fig. 3. As for Fig. 2 using a column of Chromosorb 101.

Fig. 4. As for Fig. 2 using a column of Chromosorb 102.

was observed for Chromosorb 101 and it is interesting that the manufacturers de-
scribe Chromosorb 101 and 102 as non-polar and slightly polar respectively even
though they are stated to have the same chemical composition[11].

The behaviour of Chromosorb 102 is like that of one of the samples of XAD-2
(Fig. 2) although there was no evidence of structure in the iron effluent peak from the
Chromosorb 102 column nor did the first loading precondition the column so that an
increased amount of iron was adsorbed on the second loading. While this may be
expected in view of the similarity in structure, surface area, pore size and particle size
(Table I) it implies that the two products manufactured for different purposes by
different companies have a similar concentration of impurity sites with similar rela-
tive affinities for iron, copper, zinc and magnesium.

Porapak P, PS, Q and QS

The two resins Porapak P and PS were indistinguishable in their behaviour and
the results for Porapak PS are shown in Fig. 5. The eluate peaks from a column of
Porapak QS were all about 30% smaller than those from a column of Porapak Q and
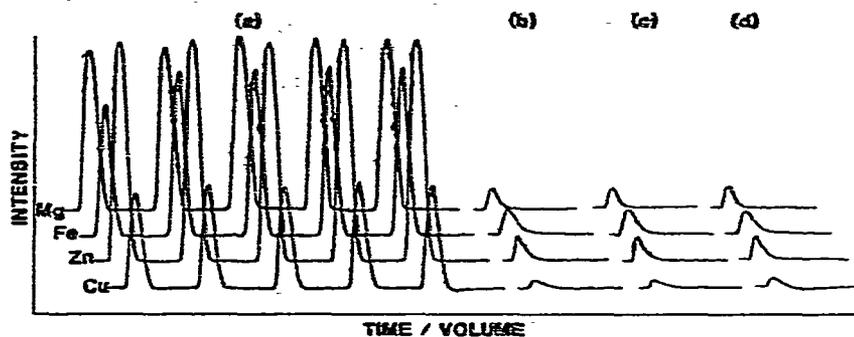
Fig. 5. As for Fig. 2 using a column of Porapak PS.

since both experiments were carried out the same day it is likely that the ion-exchange capacity of the silanized resin was lower than the untreated one although batch variations could also be important. Since all the eluate peaks were reduced, the donor groups that were silanized must have been representative of all the donor groups in the resin. The effluent peaks from columns of Porapak Q and QS were almost identical and the results for the former are shown in Fig. 6.
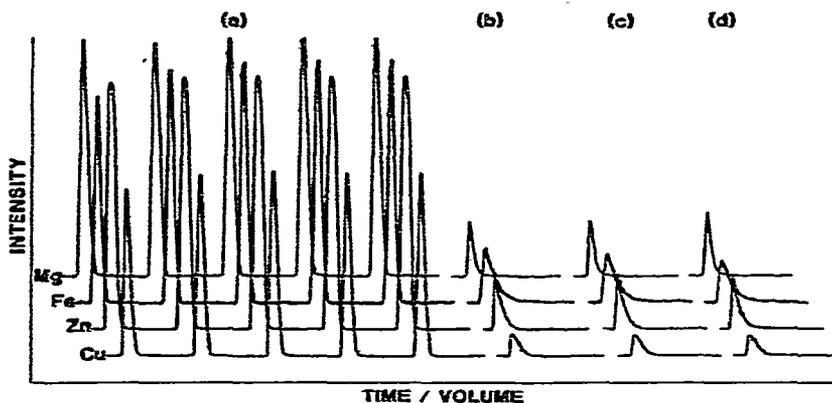

Fig. 6. As for Fig. 2 using a column of Porapak Q.

The behaviour of Porapak P and PS was different from all the other adsorbants in that the effluent peaks were broad and symmetric with half-widths of 2.0–2.5 ml. Most of the trace metals were adsorbed on the first injection and there was little change in the effluent or eluate peaks on subsequent loadings. The resins were non-specific for the four metals and there was no tendency for iron to displace the other metals.

Porapak Q and QS were also non-specific in their affinity for trace metals but the effluent peaks were stronger and narrower than was observed for Porapak P and PS and the eluate peaks were stronger and more asymmetric implying greater interaction between the resin and the adsorbed metals.

BN-X4 and BN-X10

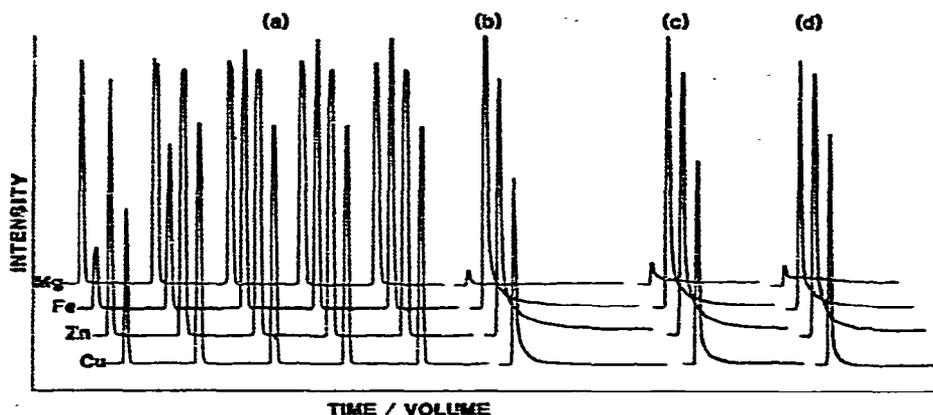Although chemically identical to the Chromosorb and XAD resins discussed

Fig. 7. As for Fig. 2 using a column of BN-X4.

previously, these resins behaved quite differently (Figs. 7 and 8). After the first injection the effluent peaks were strong and the half-widths were comparable to those obtained when the column was isolated from the system. Most of the adsorption occurred on the first loading and iron, zinc and copper were adsorbed more readily than magnesium. The behaviour was therefore intermediate between those resins (*e.g.*, Porapak PS) that have comparable adsorption for all metals (Fig. 5) and those resins (*e.g.*, Chromosorb 102) that have a great selectivity for iron relative to the other metals (Fig. 4). There was a small tendency for iron to displace copper and zinc after the first loading as is apparent both from the change in the eluate peaks after different numbers of loadings as well as from the enlarged copper effluent peak from the second loading due to the desorbed copper. For both resins, the first magnesium elution peaks showed considerable tailing which became less apparent on subsequent loadings and elutions. Copper was desorbed rapidly with little tailing while for zinc and iron there was strong desorption initially with subsequent tailing. The tailing effect for zinc was much more pronounced for BN-X4 (Fig. 7).
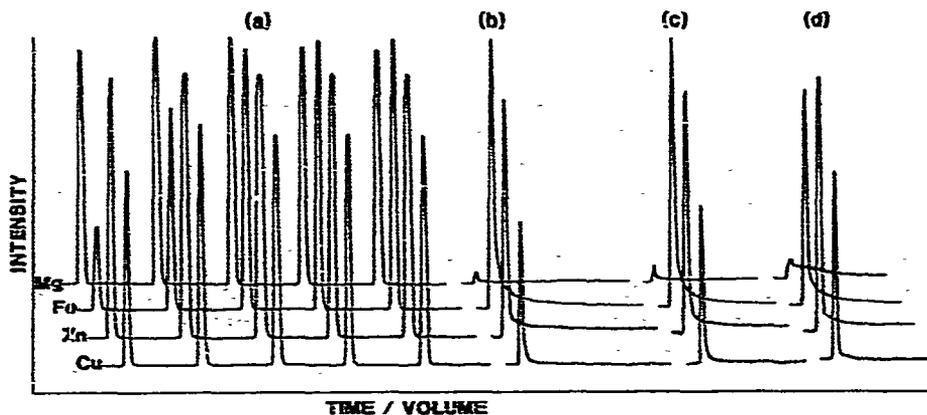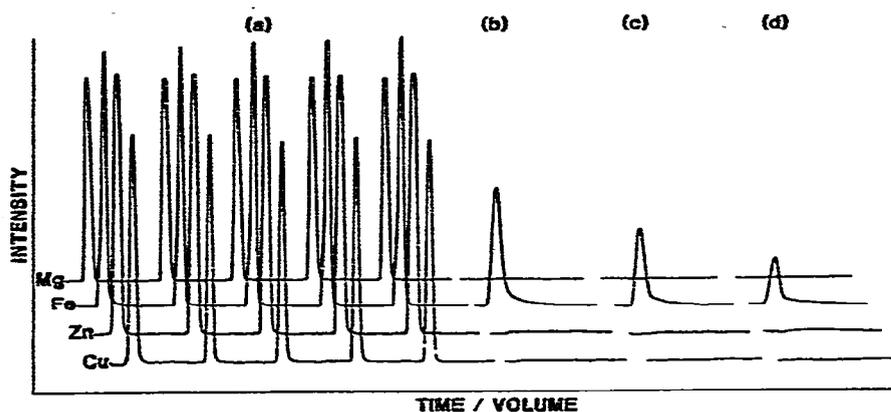
Fig. 8. As for Fig. 2 using a column of BN-X10.

Fig. 9. As for Fig. 2 using a column of C_{18}-bonded silica from Sep-Pak cartridges.

Octadecyl-bonded silica

The results for a Cheminert column packed with C_{18}-bonded silica from six Sep-Pak cartridges are shown in Fig. 9. The effluent peaks were symmetric, showed no evidence of tailing and remained constant in size and shape over five successive loadings. The peaks were narrow but were slightly broader than those of the Benson resins (Figs. 7 and 8). The constancy of the effluent peaks was due to the non-adsorption of copper, zinc and magnesium while the amount of iron adsorbed increased regularly with successive loadings. In contrast to the polymeric resins that adsorb significant amounts of iron (Figs. 2, 4, 7 and 8) the iron elution peaks were almost symmetric with little tendency for an initial rapid release of metal followed by an extended slow release.

The results for the C_{18}-bonded silica supplied by Waters (Aust.) were completely different (Fig. 10) since the column almost totally adsorbed the trace metals in the first three loadings and was still adsorbing iron and copper after five loadings. Magnesium and iron behaved differently from copper and zinc since the latter were readily eluted as sharp symmetric peaks with no evidence of tailing or differential desorption while for the former metals there was initially a rapid release of metal
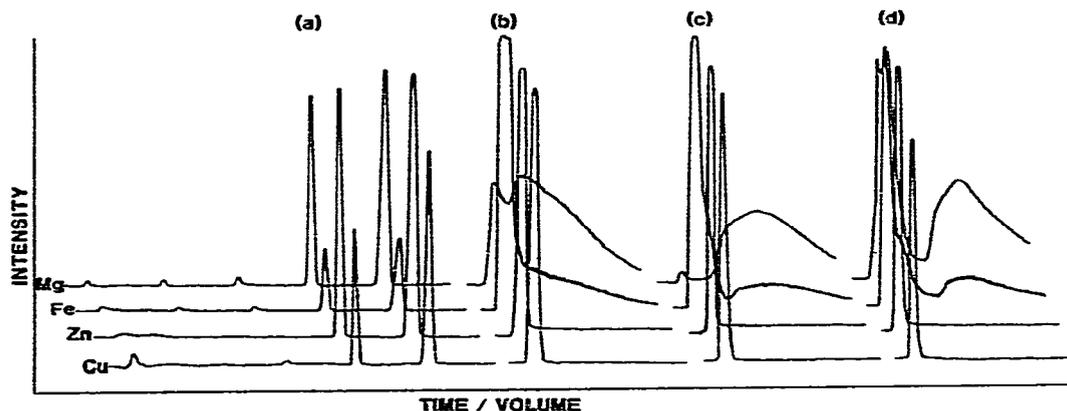

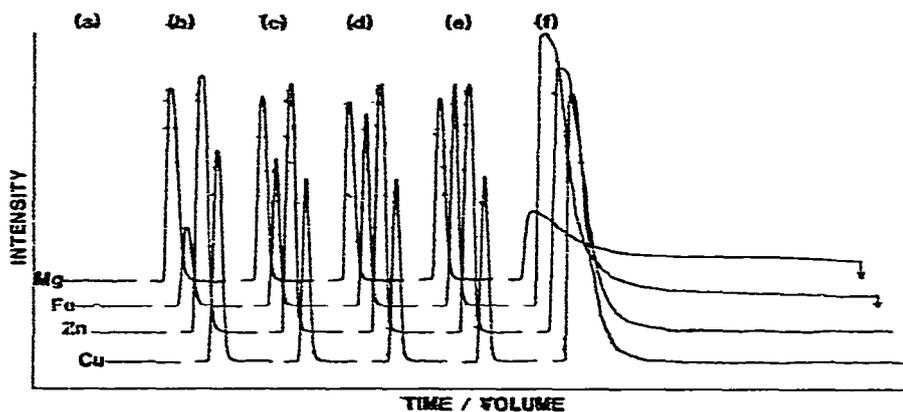Fig. 10. As for Fig. 2 using a column of C_{18}-bonded silica supplied by Waters (Aust.).

Fig. 11. a–e, Atomic fluorescence from the effluent from a column of XAD-8 after 5, 8, 11, 14 and 17 loadings of 500 μl of stock solution. f, Atomic fluorescence from the eluent when the column was eluted with Na_2H_2Y after 17 loadings. The arrows show the baseline levels for magnesium and iron.

followed by slow desorption. Numerous broad elution bands could be identified, tailing was very pronounced and the results were not reproducible. Most of the magnesium and much of the iron was strongly adsorbed.

Amberlite XAD-7 and XAD-8

A column of XAD-8 totally adsorbed the trace metals from the first six loadings and was still slowly adsorbing iron after seventeen loadings (Fig. 11). The magnesium, zinc and copper peaks in the effluent from the eighth loading were greater than succeeding ones due to the displacement of these metals by iron as the concentration of free donor sites decreased. However, large quantities of all four metals were still retained by the resin after seventeen loadings. Iron and magnesium were particularly difficult to remove from the resin and the fluorescence signal from these metals was still significant even after 60 ml of Na_2H_2Y had passed through the column.

The ion-exchange capacity of XAD-7 was even greater than that of XAD-8 and the trace metals from the first 22 loadings were almost totally adsorbed (Fig. 12).
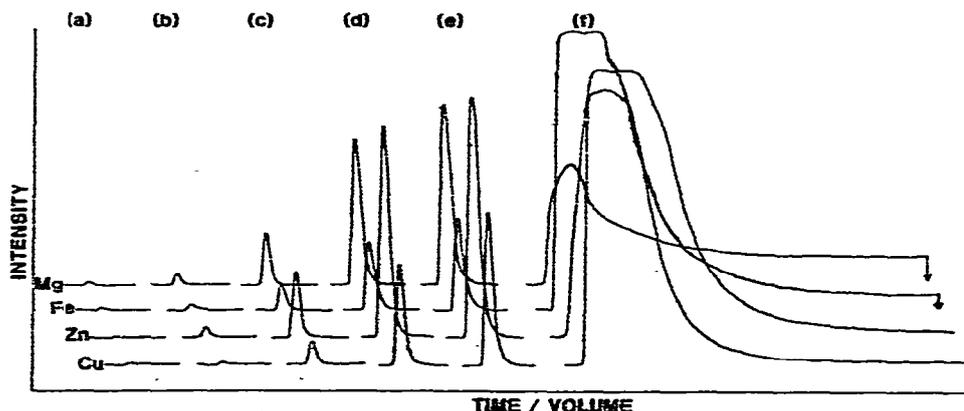

Fig. 12. a–e, Atomic fluorescence from the effluent from a column of XAD-7 after 17, 22, 27, 32 and 37 loadings of 500 μl of stock solution. f, Atomic fluorescence from the eluent when the column was eluted with Na_2H_2Y after 37 loadings. The arrows show the baseline levels for magnesium and iron.

The resin also took much longer to equilibrate with the stock solution and the composition of the effluent was still changing after 37 loadings. Large amounts of all four metals were eluted from the column and, as for XAD-8, the eluate still contained iron and magnesium even after 60 ml of Na_2H_2Y had passed through the column.

Activated charcoal

A column of Norit A totally adsorbed all trace metals from six loadings of the stock solution and the metals were slowly eluted by prolonged washing with Na_2H_2Y.

DISCUSSION

The various cross-linked polyaromatic resins differ appreciably in their behaviour toward competing metals and there also appears to be batch to batch variations as can be seen for the two results for XAD-2 (Figs. 1 and 2). Treatment of these resins to remove trace metals (e.g., washing with methanolic HCl) has been found to alter the adsorption properties of XAD-4[5] and presumably such affects could also occur for other polyaromatic resins. However it does not seem possible to eliminate donor impurity sites either by silanization or by methylation with dimethyl sulphate[4]. Previous studies on XAD-2 (from the same batch as in Fig. 1) gave an ion-exchange capacity of about 0.1 μequiv. g^{-1} and most of the other resins have capacities of about 0.1–0.5 μequiv. g^{-1}. While such low values may be negligible in most applications of these resins they are not so when these resins are used for studies of metal speciation in natural waters. The Sep-Pak cartridges contain about 300 mg of resin and have a capacity in the low milligram range[17]. Assuming a dissolved organic carbon content of about 1 mg l^{-1} and hence a dissolved organic matter content of about 2 mg l^{-1}, a Sep-Pak cartridge should be capable of completely removing all organic matter from about 1 l of seawater. Since only about 10–30 % of organic matter is actually retained by a Sep-Pak cartridge[25] a reasonable protocol would be to pass about 5 l of seawater through each cartridge. If we assume that a typical cartridge has an ion-exchange capacity of 0.3 μequiv. g^{-1} and that the adsorbed cations are divalent then each cartridge could adsorb about 50 nmole of trace metal. In open ocean surface waters 5 l of seawater would contain 2.5–7 nmole Cu, 5–10 nmole Ni, 0.01–0.05 nmole Cd[27] and 1.5–15 nmole Mn[28] and hence the ion-exchange capacities quoted in this paper are sufficient to remove all trace metals from the volume of seawater that can be processed without overloading the adsorption capacity of the resin for organic compounds.

The acrylic ester resins XAD-7 and XAD-8 have much higher cation-exchange capacities than any of the other resins and are quite unsuitable for studies of trace metal speciation in natural waters. Both of these resins contain potential donor groups as an integral part of their structure and the cation-exchange capacities are comparable to other chromatographic supports containing functional groups. For example, it has been found that many supports used in gel filtration chromatography can bind trace metals and capacities for Zn of up to 164 μg ml^{-1} gel have been reported[29]. Activated charcoal would also be of little use to studies of metal speciation. The adsorption of cations by this material has been reported before[30] and the possible adsorption of trace metals should be borne in mind when this material is used to remove organic matter from natural waters in order to make culture media for aquatic organisms.

Most of the polyaromatic resins studied are macroreticular although Porapak P is described as microreticular with no real pores in the dry state[15] and the Benson resins are gels and have a pseudopore[13]. These resins have lower surface areas than the others yet the Benson resins adsorb comparatively large amounts of metal and have totally different ion-exchange properties from Porapak P. The physical structure of these resins does not appear to be an important variable.

Charge transfer complexation can also occur between these resins and solute molecules that can act as π-electron acceptors and this type of interaction has been proposed to explain the difficulty in eluting fulvic acids (and presumably metal fulvates) from polyaromatic resins using only organic solvents[23]. Acidic or basic solvents, such as methanolic HCl or methanolic NH_3, have been found to desorb simple trace metal cations from XAD-2 and XAD-4[4,5] and would lead to an overestimate of the amounts of metal–organic complexes adsorbed by these resins.

Octadecyl-bonded silica may be more suitable for investigating metal–organic compounds in natural waters since the material has little affinity for other trace metals in the presence of ferric ions. The absence of aromatic groups on this support eliminates the possibility of irreversible desorption due to charge-transfer complexation and it is more likely that metal–organic complexes can be completely desorbed using only organic solvents. The range of eluents is necessarily restricted since hydrolysis and dissolution of the material occurs outside the pH range 2–8. Care must be taken to ensure that the silica surface is bonded to as many alkyl groups as possible since free silanol groups will bond strongly to trace metals, particularly Class-A metals such as iron and magnesium (Fig. 10).

It has been suggested[4,5] that there were a number of different types of donor impurity groups on XAD-2 and XAD-4 and that this resulted in some of the adsorbed ions being more readily eluted than others. This seems to be characteristic of many of the polyaromatic resins studied and the different behaviour of C_{18}-bonded silica may be due to the fact that the ferric ions are bonded mainly to isolated silanol groups and that only one type of adsorption site is significant.

ACKNOWLEDGEMENTS

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