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THE ADSORPTION OF SIMPLE TRACE METAL CATIONS ON AMBERLITE XAD-1 AND XAD-2

A STUDY USING A MULTICHANNEL NON-DISPERSIVE ATOMIC FLUORESCENCE DETECTOR WITH QUANTITATION BY BATCH MEASUREMENTS

D. J. MACKEY

Division of Oceanography, CSIRO Marine Laboratories, P.O. Box 21, Cronulla, N.S.W. 2230 (Australia)

SUMMARY

The macroreticular resins Amberlite XAD-1 and XAD-2 are unsuitable for quantitative studies of trace metal speciation in natural waters since significant amounts of the simple cations of copper, iron and zinc are readily adsorbed by the resins. These cations are not desorbed by methanol although they are eluted by methanolic HCl, methanolic NH_3 and sodium dihydrogen ethylenediaminetetraacetate. The interactions have been studied using Cheminert chromatographic equipment directly coupled to a multichannel non-dispersive atomic fluorescence detector, and the results quantitated by batch measurements using graphite furnace atomic absorption spectroscopy. XAD-2 resin adsorbed more trace metals than XAD-1, and the adsorption capacity could be reduced by methylation. The adsorption of copper and zinc was not strongly dependent on pH, and there were differences in the behaviour of XAD-1 and XAD-2 toward competing trace metal ions. Contrary to its usual role in the analysis of natural waters, XAD-2 was capable of removing copper and zinc from acetonitrile, and at least some of this adsorbed metal could be eluted with distilled, deionized water.

INTRODUCTION

The cross-linked polystyrene resins Amberlite XAD-1, XAD-2 and XAD-4 have been widely used to adsorb organic compounds from natural waters at concentrations down to the parts per billion (10^9) level and, in contrast to activated charcoal, this adsorption is often reversible. These resins are therefore suitable both for the quantitative determination of some ecologically important man-made compounds (*e.g.* DDT) as well as for the extraction of naturally occurring organics such as the humic acids. These resins would seem to be ideally suited for separating trace metal organic compounds from seawater and thereby providing a quantitative estimate of the extent of organic complexation of a given metal. However, not all organic com-

plexes are retained by these resins, and some metal–organic compounds may be irreversibly adsorbed. If these affects are important, this would preclude the use of these resins for quantitative measurements of the concentration of naturally occurring metal–organic compounds in seawater, although the adsorption of a trace metal from seawater and its subsequent elution from the resin could provide an estimate of the minimum concentration of such compounds.

Sugimura *et al.*[1,2] passed seawater through a column of XAD-2 resin and found that, for all thirteen metals investigated, between 7% and 100% of the metal was retained by the resin and could be eluted with either methanol or dilute aqueous ammonia. However, their conclusion —that most of the minor elements in seawater are present in organic forms— is valid only if other chemical forms of the elements are not reversibly retained by the XAD-2. In particular, it was assumed that simple inorganic ions were not retained by the resin. Lyons *et al.*[3] made the same assumption in their investigation of iron in nearshore pore fluids. Although there have been numerous reports in the literature that simple cations are not adsorbed[1,2,4–6], the use of these resins to investigate trace metal speciation requires that the resins have a cation exchange capacity of less than 10^{-2} μequiv g^{-1}, and such a low value may well be considered negligible in many applications of these resins.

In an earlier paper[7] it was found that Amberlite XAD-1 was unsuitable for the quantitative determination of the speciation of copper, zinc and iron in seawater. The amount of metals removed from seawater was not reproducible and did not vary linearly with the volume of seawater passed through a column of the resin. The behaviour suggested that the column capacity was being exceeded and it was suggested that the resin adsorbed simple inorganic ions as well as metal–organic species. It was thought that these inorganic ions were adsorbed on to a small number of polar impurity sites, as have been observed in closely related resins used as supports for gas chromatography[8,9]. This paper reports on the adsorption of simple inorganic ions of copper, zinc, iron and magnesium on to XAD-1 and the chemically identical XAD-2.

Although batch techniques are useful in providing quantitative information on the adsorption and desorption of trace metals, the procedure provides low resolution and is very time consuming, particularly if several metals are being investigated. For this reason, a multichannel non-dispersive atomic fluorescence detector (AFD) has been built and its use, in conjunction with batch experiments, provides more detailed information on the interaction between trace metals and the resins XAD-1 and XAD-2.

EXPERIMENTAL

Reagents

Amberlite XAD-1 and XAD-2 resins (20–50 mesh) were Soxhlet extracted with analytical-reagent grade methanol, acetonitrile and diethyl ether and stored under quartz-distilled methanol. Distilled deionized water (DDW) from a Milli-Q system was used in all experiments. XAD-2 resin (25 ml) was washed with DDW, soaked in DDW–tetrahydrofuran (THF) (1:1), vacuum filtered and drained at the pump. It was then resuspended in 80 ml of DDW–THF (1:1) to which were added 3 g of NaOH and 10 ml of dimethyl sulphate. The mixture was then refluxed gently for 5 h. The methylated resin was collected by vacuum filtration, washed and stored under methanol.

The columns were eluted and preconditioned with 10 % Merck Suprapure HCl in double-quartz-distilled methanol (H), 5 % Merck Suprapure NH_3 in the same methanol (N) and a 10^{-3} M solution of disodium dihydrogen ethylenediaminetet-raacetate in DDW (Na_2H_2Y). Metal stock solutions contained 1 g l^{-1} of metal and were BDH standard solutions for atomic absorption spectroscopy or were prepared by dissolving analytical-reagent grade zinc in Merck Suprapure HCl or by dissolving the appropriate analytical-reagent grade metal sulphate in DDW. The pH of the solutions was not controlled, so there was no interference from potential organic complexing agents (except acetate from the BDH standard zinc solution). All glass-ware was acid soaked and, unless otherwise stated, all organic solvents were double quartz distilled.

Chromatographic equipment

A Laboratory Data Control Cheminert CMP-3K pump was used in conjunc-tion with 6 and 9 mm I.D. columns. All fittings were of the Cheminert type, and the only materials in contact with the solutions were borosilicate glass, PTFE and Kel-F. The pressure gauge was stainless steel and was isolated from the rest of the system by a film of PTFE tape inserted between the Cheminert fittings connecting the gauge. The tape tended to leak after a while and the gauge was removed from the system when quantitative measurements were being made. A diagram of the apparatus is shown in Fig. 1. The valve system allowed the two columns to be loaded and eluted separately or jointly depending on the experiment. The eluant could either be col-lected for batch analysis or pass directly to the nebulizer of the AFD.
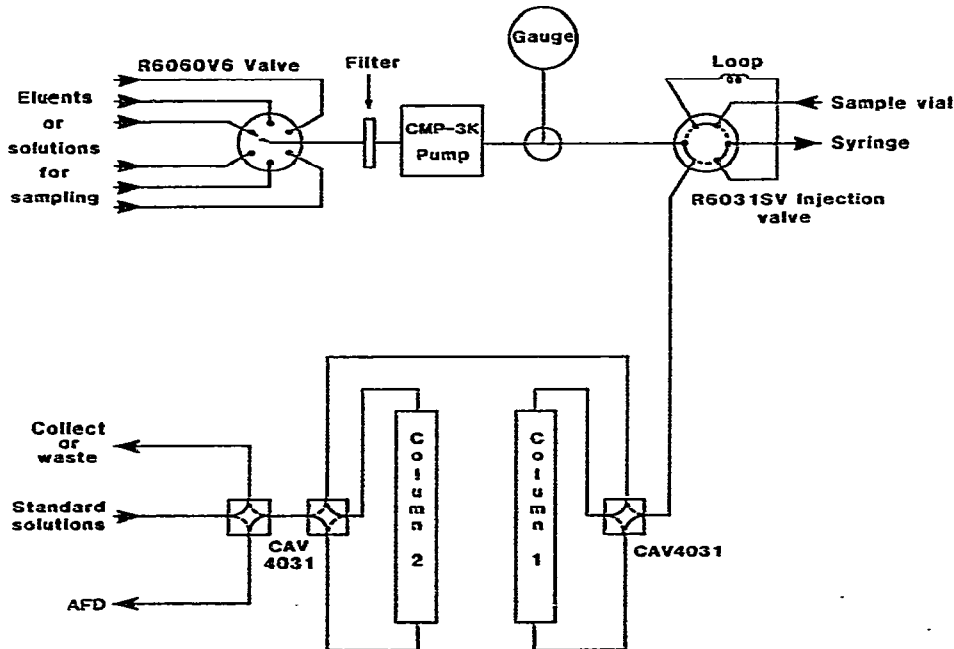

Fig. 1. Schematic diagram of the Cheminert chromatography equipment. The CAV 4031 valves enable the columns to be loaded and eluted separately or jointly while the output can be sampled by batch techniques or directly using the AFD. The detector response can be calibrated via standard solutions.

Metal analyses

For quantitative measurements, aliquots (usually 10 ml) of eluant were collected in acid-soaked polyethylene vials and were analysed by graphite furnace atomic absorption spectroscopy (GFAAS) using a Varian AA6 fitted with a CR-63 furnace. These analyses were performed in a Class-100 clean room.

Atomic fluorescence detector

A four-channel non-dispersive AFD was designed and built along the general lines of those of Larkins[10] and Van Loon et al.[11]. The amplifiers and power supplies were of two different types. For the detection of copper, zinc and iron, separate Varian AA4 indicator modules (IM-1) and lamp power supplies (MLS1-A) were used. The modulation frequencies of two of the indicator modules were altered to 263 Hz (Cu) and 313 Hz (Fe) while the third operated at the standard frequency of 285 Hz (Zn). In addition, a three-channel indicator unit, lamp supply and photomultiplier high-voltage source were specially made by GBC Scientific Equipment Pty. The frequencies could be easily varied from 180 to 330 Hz. For the experiments described here only one channel was used for the detection of magnesium at 217 Hz. No interference was observed between the lock-in amplifiers at the frequencies used. The Varian hollow cathode lamps were operated at their maximum rated currents of 15 mA (Cu and Zn), 20 mA (Mg) and 25 mA (Fe). The copper fluorescence was detected by a Hamamatsu R106 photomultiplier operated at 490 V and shielded by a Schott UG11 filter and a 6-mm iris. The iron, zinc and magnesium fluorescence was detected by a single Hamamatsu R166 solar blind photomultiplier operated at 595 V and shielded by a 9-mm iris. The lenses were made from Suprasil I, were 40 mm in diameter and had a focal length of 50 mm. The light intensity within the flame was approximately doubled by using mirrors to reflect the light back through the flame. These mirrors were 35 mm in diameter, had a 103 mm radius of curvature and were coated with aluminium and a protective layer of either UV-transmitting glass or magnesium fluoride. The lenses, filter, irises, mirrors, radiation shields and photomultiplier housings were mounted on an aluminium disc and all metal parts were painted matt black to reduce stray reflections. The lamps were supported on a second aluminium disc rigidly bolted to the first one. The positions of the lamps, lenses and mirrors were separately adjustable over a limited range. The mirrors could be replaced by lenses and additional lamps mounted on the bottom disc to produce an eight-channel detector. The overall sensitivity of the system would be reduced by a factor of ca. 2 owing to the loss of reflected light and a small loss due to splitting the photomultiplier outputs over more channels.

The nitrogen-sheathed burner assembly was made of titanium and was identical to that of Larkins[10]. The burner bowl was a Varian AA4 model, rhodium-plated to reduce contamination, and the bakelite plug at the bottom of the bowl was replaced by a PTFE plug. An air–acetylene flame was used and the mixture controlled by a Varian GCU-2 unit. The output from the chromatography equipment was connected directly to a Varian adjustable tantalum nebulizer. A constant pressure of air (100 kPa) was applied and the uptake rate of the nebulizer was adjusted to be identical to the flow-rate through the chromatography columns (100 ml h^{-1}).

With inflammable organic solvents in the nebulizer the supply of acetylene had to be reduced otherwise the flame became much too rich. There were difficulties
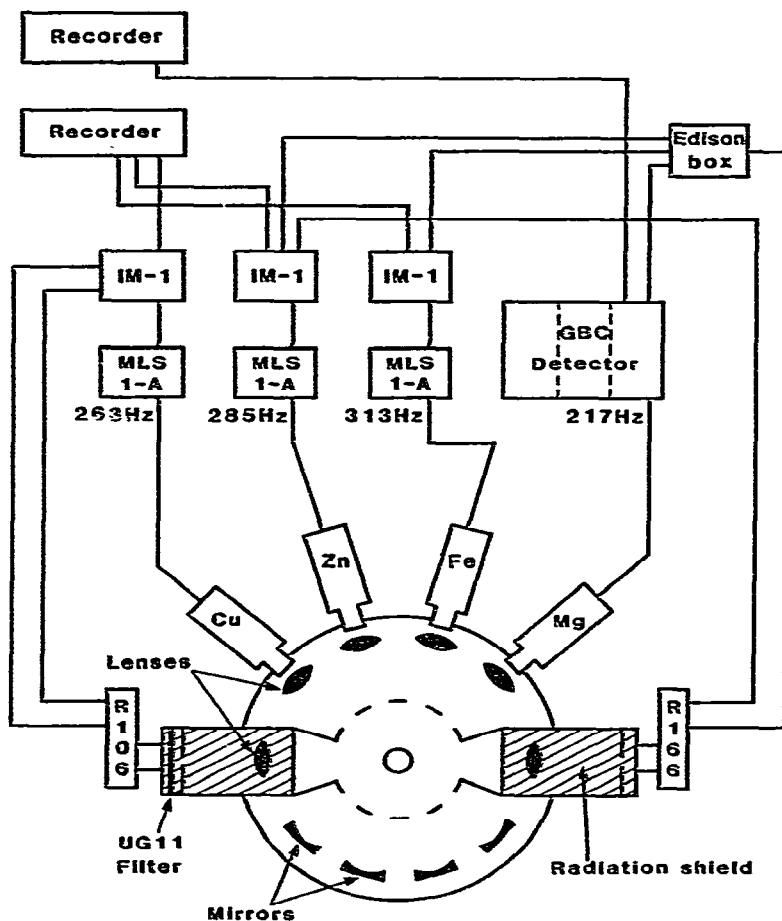
Fig. 2. Schematic diagrams of the non-dispersive multichannel AFD. For copper, zinc and iron, the lamp supplies (MLS1-A) and amplifiers (IM-1) are Varian AA4 units while for magnesium the lamp supply and amplifier are part of a three-channel unit supplied by GBC Scientific P/L. The copper fluorescence is detected by a R-106 photomultiplier and a UG11 filter, while the iron, zinc and magnesium signals come from a R-166 photomultiplier. The signal is split into three by an edison box. The recorders are YEW-3056 models, and Varian hollow cathode lamps are used. The silica lenses have a focal length of 50 mm while the mirrors have a radius of curvature of 103 mm.

involved in changing solvents since the fluorescence signals became very noisy for lean mixtures and the flame tended to go out for rich mixtures. The acetylene flow-rate either had to be changed continuously with the composition of the eluting solvents or maintained at a compromise level with a subsequent increase in noise, particularly when an oxidizing flame was used. The latter approach was adopted here. The iron, copper and zinc fluorescence signals were recorded on a 3-pen recorder while the magnesium signal was recorded on a separate 2-pen recorder. A diagram of the apparatus is shown in Fig. 2.

TABLE I

RECOVERY OF ADSORBED INORGANIC COPPER AND ZINC FROM TWO COLUMNS OF XAD-1 CONNECTED IN SERIES

See text for conditions of elution.

Load (µg)	Sample composition*	Sample volume (ml)	pH (approx.)	DDW wash volume (ml)	Copper		Zinc	
					Col. 1 (µg)	Col. 2 (µg)	Col. 1 (µg)	Col. 2 (µg)
50 / 100	Zn(OAc)₂ / CuCl₂	50	2.7	50	0.97	1.15	0.61	0.66
50 / 50	Zn(OAc)₂ / CuCl₂	10	2.3	75	1.18	1.02	0.94	0.75
50 / 50	Zn(OAc)₂ / CuCl₂	10	2.3	150	0.58	2.35**	1.39	7.62**
5 / 5	Zn(OAc)₂ / CuCl₂	10	3.3	75	0.53	0.40	1.03	0.57
5 / 5	Zn(OAc)₂ / CuCl₂	10	3.3	75	0.58	0.27	2.1	0.87
500	CuCl₂	10	1.3	75	1.20	1.03	—	—
500	ZnCl₂	10	—	75	—	—	0.92	0.94

* HOAc = acetic acid.
** Samples were apparently contaminated.

Batch experiments on XAD-1

DDW was spiked with copper and zinc using BDH standard solutions for atomic absorption spectroscopy. The solutions were cupric chloride in 1 M HCl and zinc acetate in 1 M acetic acid. The pH of the solutions ranged from *ca.* 1.3 to 3.3. In order to eliminate the possibility that acetate complexes may be involved in the adsorption, some experiments were conducted using only metal chlorides. An aliquot of solution, containing zinc or copper or both, was passed through two 9-mm columns connected in series. The first and second columns contained 6.5 ml and 10 ml of XAD-1 resin, respectively, and before each experiment the columns were preconditioned by washing them successively with 200 ml (H), 200 ml methanol, 200 ml (N) and 50 ml of DDW. The columns were loaded and preconditioned at a flow-rate of 250 ml h⁻¹. The columns were eluted with 6 × 10 ml (H), 3 × 10 ml (methanol) and 3 × 10 ml (N) at 50 ml h⁻¹ and the aliquots analysed separately as described earlier. The results are summarized in Table I, and only the total amounts of copper and zinc recovered are listed.

Experiments on XAD-2

Atomic fluorescence detector. Samples of DDW were simultaneously spiked with BDH standard solutions of copper, zinc and iron and were aspirated into the nebulizer at 100 ml h⁻¹. The fluorescence peak heights are plotted as functions of concentration in Fig. 3.

The adsorption of copper, zinc, iron and (sometimes) magnesium on XAD-2 was investigated using the chromatographic arrangement shown in Fig. 1. A stock solution containing these metals (and also nickel and manganese) at a concentration
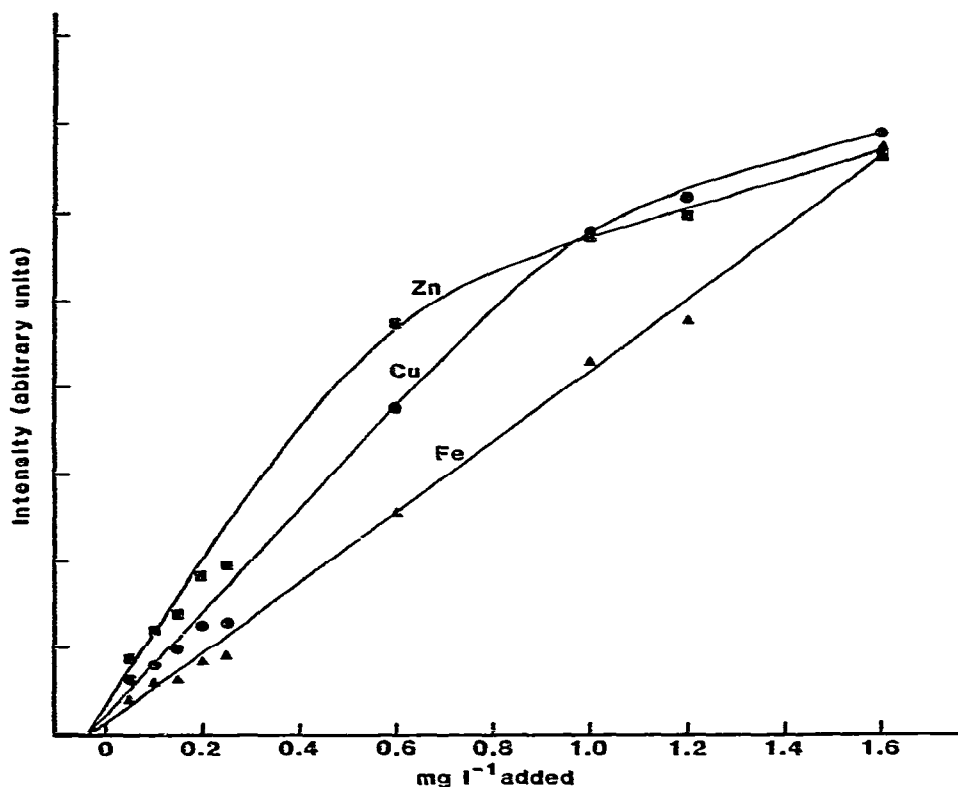
Fig. 3. The AFD response (peak heights) for the simultaneous determination of iron, copper and zinc in aqueous solution.

of 10 mg l^{-1} each was made from BDH standard solutions. The pH of the solution was *ca.* 1.5, although the effective pH on the column may have been significantly higher owing to retention and dilution effects. A 6-mm column, containing 4 ml of XAD-2 resin, was washed with 40 ml of Na$_2$H$_2$Y and DDW. The flow-rate of the DDW was 100 ml h^{-1} and, after 20 ml had passed through the column, 500 μl of stock solution (containing 5 μg of each metal) was injected on to the column while the effluent was monitored for copper, iron and zinc. When the fluorescence signals had returned to background levels, another sample was injected on to the column and the whole procedure was repeated until the column had been loaded five times. The column was then eluted with methanol (analytical-reagent grade), acetonitrile (analytical-reagent grade) and Na$_2$H$_2$Y, and the results are shown in Fig. 4a. The higher noise level during the elutions was due to a compromise fuel–air mixture being used as the solvent system was changed.

The experiment was repeated using the same column but eliminating the methanol and acetonitrile elutions and monitoring the magnesium fluorescence as well (Fig. 4b). Finally the previous experiment was repeated using a column which contained 4 ml of XAD-2 which had been methylated with dimethyl sulphate (Fig. 4c).

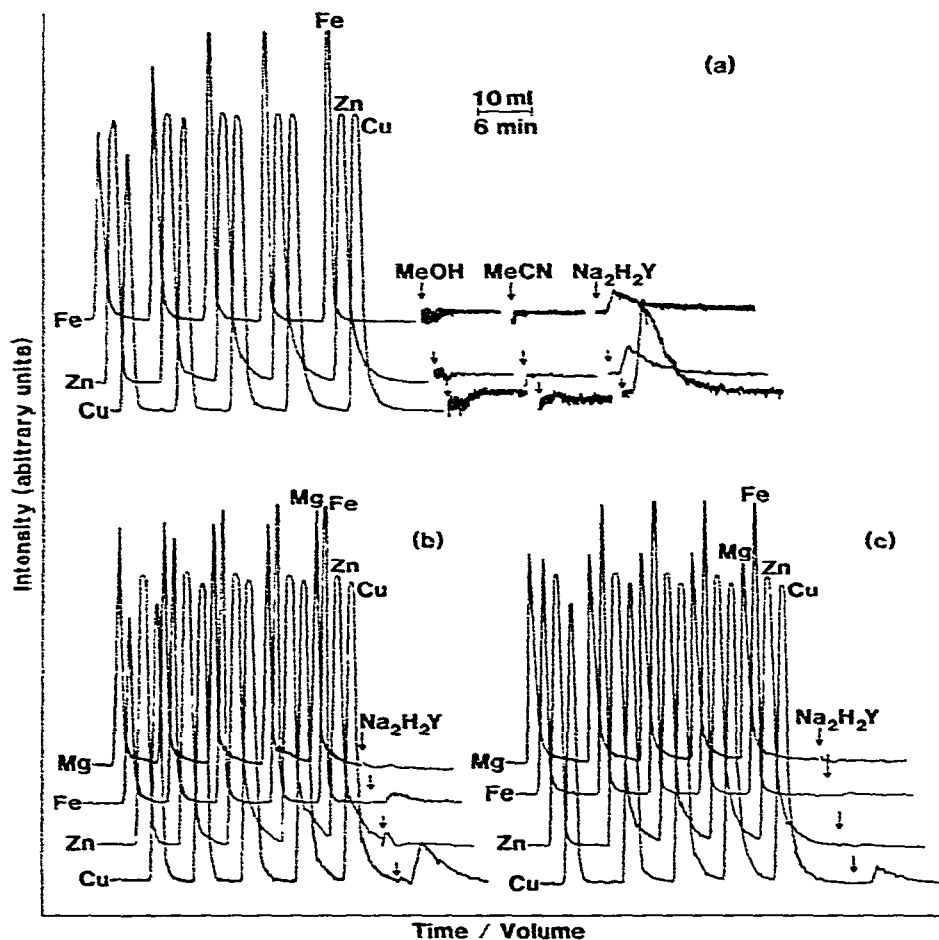*Batch experiments.* The atomic fluorescence experiments described above

Fig. 4. (a) Iron, zinc and copper fluorescence signals from the effluent from a column of XAD-2 after five successive 500-μl injections of stock solution containing 5 μg of iron, copper, zinc, magnesium, manganese and nickel. The column was then eluted successively with methanol (MeOH), acetonitrile (MeCN) and 10^{-3} M disodium dihydrogen ethylenediaminetetraacetate. (b) Same as (a), except that the magnesium fluorescence was also monitored and the MeOH and MeCN elutions were eliminated. (c) Same as (b), except that the resin had been methylated with dimethyl sulphate. The signals were recorded simultaneously but have been offset for clarity.

showed that XAD-2 adsorbs trace metals not only from aqueous solution but also from organic solvents, and this effect was investigated further. The copper and zinc levels of DDW, methanol (analytical-reagent grade) and acetonitrile (analytical-reagent grade) were measured before being pumped through the same 6-mm column of XAD-2 used in the atomic fluorescence experiments. The pump and lines were then flushed out with the appropriate solvent, and 25 ml were passed through the column in the order methanol, acetonitrile and DDW. The copper and zinc levels were measured in the solutions prior to being passed through the column and in successive 5-ml aliquots of the effluent, and the results are given in Table II in terms of absorbance units.

TABLE II

GFAAS MEASUREMENTS (ABSORBANCE UNITS*) ON 5-ml ALIQUOTS OF METHANOL, ACETONITRILE AND DDW AFTER BEING PUMPED THROUGH A COLUMN OF XAD-2 RESIN

	Methanol		*Acetonitrile*		*DDW*	
	Cu	*Zn*	*Cu*	*Zn*	*Cu*	*Zn*
Analytical-reagent grade solvent***	0.003	0.085**	0.017	0.390	0.003	0.060
Analytical-reagent grade solvent ⁵	0.003	0.020	0.020	0.405	0.002	0.065
(Double quartz distilled)	<0.001	0.020	<0.002	0.045	–	–
Aliquot 1	0.004	0.280**	0.009	0.260	0.018	0.210
Aliquot 2	0.003	0.045	0.006	0.045	0.008	0.210
Aliquot 3	0.003	0.025	0.008	0.035	0.009	0.155
Aliquot 4	0.003	0.025	0.009	0.035	0.004	0.080
Aliquot 5	0.003	0.025	0.013	0.055	0.004	0.085

* Approximate conversion factors: 0.100 absorbance units are equal to 120 $\mu g \, l^{-1}$ (Cu) and 2 $\mu g \, l^{-1}$ (Zn).
** These fractions appear to be contaminated.
*** Sampled from solvent container.
⁵ Sampled directly prior to the column.

The adsorption capacity of methylated and unmethylated XAD-2 were compared in batch experiments in which two columns of XAD-2 (6-mm diameter containing 4 ml of resin) were connected in series and loaded with inorganic copper and zinc. The first column contained methylated resin. The columns were loaded with a 500-μl sample loop with metal concentrations of 10, 100 and 500 mg l^{-1} giving metal loadings of 5, 50 and 250 μg, respectively. The columns were loaded with copper and zinc using diluted BDH standard solutions or analytical-reagent grade metal sulphates.

The columns were preconditioned by washing successively with Na_2H_2Y (100 ml), DDW (25 ml), methanol (25 ml), methanolic NH_3 (100 ml) and finally DDW (100 ml). The columns were loaded at 250 ml h^{-1} by passing 10 ml of DDW through the sample loop. The column was eluted at the same flow-rate with 6 × 10 ml fractions of Na_2H_2Y, and the results are given in Table III.

RESULTS AND DISCUSSION

There are two mechanisms whereby simple inorganic ions could be adsorbed on to XAD-1. In the first case, adsorption could occur via polar impurity groups in the resin itself, such as occur on styrene–divinylbenzene copolymers used as supports for gas chromatography[8,9,12]. In the second case, organic ligating agents could be strongly adsorbed on to the resin and these adsorbed molecules could then interact with the inorganic species. The adsorbed molecules would probably contain aromatic rings, since these are known to bind strongly to XAD-1, and polar functional groups such as –OH, –NR₂ or –COOH. It has been reported[7] that methanolic HCl removed virtually all of the copper, zinc and iron from XAD-1. This solution would be expected to remove most neutral polar molecules and particularly molecules that could be protonated to acquire a positive charge, but it may not remove strongly bound

TABLE III

RECOVERY OF ADSORBED COPPER AND ZINC FROM TWO COLUMNS OF XAD-2 CON-NECTED IN SERIES

The columns were eluted separately with 6 × 10 ml aliquots of Na_2H_2Y and only the total amounts recovered are listed. The resin in column 1 had been methylated with dimethyl sulphate. The columns were loaded by injecting 500 μl samples of standard solution (SS).

SS conc. $(mg\ l^{-1})$	Load (μg)	Sample* composition	pH (approx.)	Copper Col. 1 (μg)	Col. 2 (μg)	Zinc Col. 1 (μg)	Col. 2 (μg)
10	5	Zn(OAc)₂ ⎫	2	1.96	3.11	**	**
10***	5	CuCl₂ ⎭					
10	5	Zn(OAc)₂ ⎫	2	2.85	3.61	0.37	0.57
10***	5	CuCl₂ ⎭					
100	50	Zn(OAc)₂ ⎫	1	5.96	7.36	0.60	0.85
100	50	CuCl₂ ⎭					
500	250	Zn(OAc)₂ ⎫	0.3	5.15	6.57	0.68	0.37
500	250	CuCl₂ ⎭					
500	250	ZnSO₄ ⎫	4	3.62	7.35	0.61	0.61
500	250	CuSO₄ ⎭					
500	250	ZnSO₄	5	§	—	§	3.03
500	250	CuSO₄	4	§	6.00	§	—

* HOAc = Acetic acid.
** Samples were contaminated.
*** Total copper recovered exceeds load amount.
§ Column 1 was not used.

organic molecules that remain electrically uncharged in strongly acid solutions (*e.g.* aromatic carboxylic acids). These would probably be removed by methanolic NH_3 and it is unlikely that any organic molecule capable of binding inorganic ions would remain adsorbed on XAD-1 after washing with both methanolic HCl and methanolic NH_3. However, inspection of Table I shows that in all experiments, significant amounts of copper and zinc were recovered from both columns, and it must be concluded that the coordinating sites are on the resin itself and not on adsorbed organic molecules. Virtually all of the copper and zinc recovered from the columns was found in the first two methanolic HCl aliquots, but there was occasionally some tailing observed for zinc as was reported earlier[7]. Although methanolic NH_3 was capable of eluting zinc and copper from XAD-2, no copper or zinc was observed in the methanolic NH_3 fractions, implying that these metals had been removed previously by the methanolic HCl.

Both columns appear to be saturated with copper and zinc at loadings of less than 5 μg because there is no significant increase at loadings of 500 μg. The recovery rate shows no significant correlation with pH. The results for the second column in one run are anomalous. It is thought that these samples were contaminated. When these values are excluded, the average recovery of copper and zinc from the second column (0.77 ± 0.41 μg and 0.76 ± 0.15 μg, respectively) is less than that from the first column (0.84 ± 0.31 μg and 1.17 ± 0.52 μg, respectively). This result is surprising since the second column contained 50 % more XAD-1 resin than the first and may

be due to an inherent variability in the amount of metal retained by the resin since the results have larger standard deviations than expected. Alternatively, it may be due to contamination of the system by metal–organic complexes which are trapped on the first column. The Milli-Q Water system had a mixed cation–anion exchange resin bed in the final position, and it is possible that organic complexing agents could bleed from the resin and complex copper and zinc with the resultant compounds being adsorbed by the resin. However, this is unlikely since there is no correlation between the amount of copper and zinc recovered from the columns and the amount of DDW passed through the columns.

The amount of copper recovered is independent of the amount of zinc in the solution and *vice versa*. This implies that the two metals are competing for different sites. Although copper generally forms stronger complexes than zinc, the two metals tend to form similar complexes with the types of donor groups likely to exist as impurities on XAD-1 resin. It seems improbable that the resin would contain approximately equal numbers of copper- and zinc-specific coordination sites, and a more likely explanation is that similar functional groups are involved but that the specificity is due to the stereochemical requirements of the two metals since copper prefers square planar (or tetragonal) coordination while zinc prefers tetrahedral coordination.

The AFD, although good for qualitative monitoring of the adsorption and desorption of metals from various chromatographic packing materials, is less useful for quantitative measurements since the response is linear with respect to concentration over a limited range. From Fig. 3, the iron fluorescence signal remains linear up to at least 1600 μg l^{-1} while the copper and zinc signals deviate from linearity at *ca.* 1000 and 600 μg l^{-1}, respectively. The departure from linearity occurs at a metal concentration of *ca.* 20 times the detection limit as defined by Larkins[10]. While this restricted linear range is not desirable for quantitative measurements, it is advantageous to its use as a chromatographic detector since the recorder sensitivity does not have to be adjusted as often when samples of unknown concentration are being studied.

In the experiments with XAD-1, it was found that the trace metals could be completely removed with methanolic HCl. However, this solvent is volatile and corrosive and when used with the AFD it causes the magnesium fluoride coatings on the mirrors to become opaque. Batch experiments showed that Na_2H_2Y released copper and zinc as well as methanolic HCl, and hence this solution was used in the atomic fluorescence experiments. The use of Na_2H_2Y, rather than methanolic HCl, also eliminated the possibility of hydrolysis of the methylated XAD-2 resin.

The method of loading the columns of XAD-2 differs from the one used in the batch experiments on XAD-1 in that the local metal concentration is much higher but there is less time for reaction to occur. The hydrogen ion concentration is also higher when the BDH standard solutions are used but, as mentioned earlier, the pH of the solution on the column is probably not well defined.

The low sensitivity of the AFD relative to GFAAS batch methods precludes any measurement of the tailing effects at elution volumes of 20 ml or more, but it is apparent that most of the metals are eluted within a volume of *ca.* 10 ml. Although Larkins[10] reported a short-term variability of *ca.* 20% and a long-term variability of about a factor of two, the traces shown in Fig. 4a and b are virtually

identical for the separate 5-μg loadings of iron, copper and zinc.

Much information about the interaction between trace metals and XAD-2 can be obtained from the size and shape of the peaks in the effluent from successive injections of 500-μl aliquots of trace metal solution on to the XAD-2 column. Since magnesium cannot compete with the other metals for coordination sites, there is no difference between the first and last effluent peaks nor is there any significant difference between the methylated and unmethylated resin. In addition, no magnesium is observed in the Na_2H_2Y elution. The iron effluent peaks become successively larger and reach a constant height at the third injection, and this is interpreted as being due to ferric ions being adsorbed on to the resin up to the third injection. In agreement with this, an iron fluorescence signal is observed when the column is eluted with Na_2H_2Y. The signal is smaller than expected and this could be due to the slow kinetics of the reaction between ferric ions and Na_2H_2Y[13] leading to the gradual release of ferric ions at concentrations too low to be detected by atomic fluorescence. Copper appears to interact much more strongly with the resin since the peaks show a successively greater tailing with subsequent injections of stock solution. The effluent peaks grow in intensity up to the third injection and, as expected, a strong asymmetric copper fluorescence signal is observed on elution with Na_2H_2Y. In contrast to the behaviour of copper, no zinc fluorescence is observed in the Na_2H_2Y eluate and the peak heights in the column effluent remain constant over the five injections. While this suggests that zinc is not adsorbed by the resin there is obviously some interaction since the peaks show even more tailing than is observed for copper. The increased tailing of copper and zinc with successive injections suggests that these metals interact more strongly with the resin as the metal loading increases, but the reason for this is not clear.

Although unreacted vinyl groups have been observed on the chemically similar Chromosorb 100 series resins[8], such groups are unlikely to contribute significantly to the complexation and binding of heavy metals. The donor sites on XAD resins are probably carboxyl groups, phenolic groups or similar entities which are capable of being methylated. The resultant esters and ethers would be weaker Lewis bases and hence should not interact so strongly with heavy metals. In agreement with this, it is found that methylated XAD-2 adsorbs significantly less copper, zinc and iron than the unmethylated resin, as can be seen in the smaller elution peaks in Fig. 4c. However, the methylated resin still adsorbs significant amounts of these ions, and it seems that some coordination sites remain after methylation.

If XAD-2 does contain polar coordinating sites that are capable of removing inorganic ions from aqueous solution at low pH then it is unlikely that the adsorbed ions would be readily removed by organic solvents. This is confirmed in Fig. 4a where no copper, iron or zinc is observed in the methanol or acetonitrile elutions. However, the amount of iron and copper eluted by Na_2H_2Y is much greater in this experiment where the elution was preceded by methanol and acetonitrile elutions. Moreover, zinc is observed in the Na_2H_2Y eluate whereas no zinc fluorescence was observed in the Na_2H_2Y eluate when the column had not been previously eluted with organic solvents (Fig. 4b and c). These organic solvents had not been quartz distilled and it was known that the acetonitrile contained appreciable amounts of heavy metals. The most likely explanation was that the XAD-2 resin was removing heavy metals from the organic solvents and that these were being eluted by Na_2H_2Y.

The adsorption of trace metals from organic solvents was investigated by batch experiments on XAD-2 and the results are shown in Table II. There appears to be no contamination of any of the solvents from the pumping system, and the analytical-reagent grade methanol was essentially free of copper and zinc. Apart from one fraction of methanol eluent which appears to have been contaminated, the concentration of copper and zinc in methanol was uniformly low and was not affected by the XAD-2 column. On the other hand, the analytical-reagent grade acetonitrile was contaminated with copper and zinc but the levels decreased on passing through the XAD-2 column. When DDW was subsequently passed through the column, large amounts of copper and zinc appeared in the first aliquot and then the levels gradually decreased toward background values. Thus XAD-2 can remove copper and zinc from an organic solvent (acetonitrile), and at least some of this adsorbed metal can be subsequently eluted using only DDW. This behaviour is in direct contrast to the use of this resin to remove trace metals from seawater followed by elution with organic solvents (e.g. methanol) to remove the organically complexed trace metals.

Experiments using the AFD suggested that methylation of XAD-2 reduced, but did not eliminate, adsorption of inorganic ions. This effect was investigated by batch experiments and the results are summarized in Table III. It is seen that methylated XAD-2 (column 1) adsorbs significantly less copper than the unmethylated resin, in agreement with the atomic fluorescence results. At pH <2 and at loadings high enough to ensure saturation of the column, methylation decreases the amount of copper adsorbed by XAD-2 resin by ca. 20%. This effect is not nearly so pronounced for zinc, and in one experiment the unmethylated resin adsorbed less zinc than the methylated column. When the unmethylated resin (column 2) was loaded separately with 250 μg of zinc or copper, the amounts of metal eluted (6.0 and 3.0 μg, respectively) should represent the maximum amounts that can be retained by the column. The recovery of up to 7.4 μg of copper from column 2, is probably due to uncertainties in the measurements, and the amount of copper adsorbed by the resin does not appear to be affected by the presence of zinc. The amount of zinc that can be retained by column 2 is approximately-half the amount of copper that can be retained but the amount decreases to one-fifth in the presence of an equivalent amount of copper. This behaviour is different from that observed for XAD-1 (see Table I), but it does offer an explanation for the absence of adsorbed zinc in the atomic fluorescence experiments where zinc had to compete with ferric, nickel, manganese and magnesium ions in addition to copper. The different adsorption capacities of XAD-2 for copper and zinc suggest that there is more than one type of adsorption site on the resin. While this was also postulated for XAD-1 resin, XAD-2 behaves differently in that the adsorption of zinc is strongly dependent on the amount of copper present. An alternative explanation is that there is only one type of site present but that zinc reacts more slowly with the resin than does copper and that the lower capacity of the resin for zinc is an artifact. This could be significant in the present experiment where a concentrated solution is passed rapidly through the column, but it implies that the adsorption capacity for copper is best represented by combining the copper and zinc values from those experiments, using these metals together (neglecting the difference in atomic weights). This would then increase the discrepancy between these experiments and the one where only copper was loaded on to the column. The true situation is probably a combination of these effects.

At loadings of 5 μg each of copper and zinc the reproducibility of the results is not very good, and in one case a total of 6.5 μg of copper was recovered from both columns. Despite the poor reproducibility it is apparent that the adsorption of copper and zinc is not very dependent on pH in agreement with the results on XAD-1.

The surface areas of XAD-1 and XAD-2 are *ca.* 100 and 300 m^2 g^{-1}, respectively, and one would expect that XAD-2 would therefore have about three times the adsorption capacity. If it is assumed that any metal–organic impurities would be trapped on the first column then, from Table I, 10 ml of XAD-1 is capable of adsorbing 1.0 μg of copper and 0.9 μg of zinc. For XAD-2, the same volume of resin could adsorb *ca.* 15.0 μg of copper and 7.5 μg of zinc. The column packings were not weighed but it is clear that XAD-2 adsorbs far more copper and zinc, relative to XAD-1, than would be expected on the basis of surface area alone. The adsorption capacity of XAD-2 for inorganic copper and zinc is appreciable, and it is interesting to compare the figures given above with the results of Puon and Cantwell[14] who found that XAD-2 was capable of adsorbing 1 μmole of H$_3$O$^+$ per gram of resin. The observed copper adsorption could be accounted for if *ca.* 5 % of the hydrogen binding sites were capable of binding copper, and it is surprising that other authors[1,2,4] have reported that XAD-1 and XAD-2 do not adsorb inorganic ions. This could be due to batch variations, so each batch should be tested to determine its adsorption capacity for each ion. The procedure would be further complicated by possible kinetic effects and the fact that different ions would be competing for the limited number of polar donor groups on the resin. It is obvious that this testing cannot be accomplished on a natural water sample of unknown composition. Elution of columns of XAD-1 and XAD-2 resins by organic solvents such as methanol or acetonitrile probably removes only metal–organic complexes from the resin but it is unlikely that adsorbed naturally occurring metal–organic compounds would be quantitatively removed by organic solvents. Any elutions with hydrochloric acid, ammonia or complexing agents would also remove inorganic ions. It is also apparent that some electrically charged metal–organic compounds are not retained by XAD-1 and XAD-2 since iron, copper and zinc can be rapidly and completely removed from these resins by elution with Na$_2$H$_2$Y, presumably as the CuY^{2-}, ZnY^{2-} and FeY$^-$ complexes. This is in agreement with the results of Sakai[5]. Since metal–organic complexes can be neither totally adsorbed nor totally eluted from the resins without contamination from inorganic species, these resins cannot be used to obtain quantitative information on metal speciation in natural waters.

CONCLUSIONS

(1) Contrary to earlier reports in the literature, XAD-1 and XAD-2 resins adsorb appreciable amounts of inorganic iron, copper and zinc. It is logical to assume that many other inorganic ions can also be adsorbed.

(2) Compared with XAD-1, XAD-2 adsorbs larger amounts of copper and zinc than would be expected on the basis of their relative surface areas.

(3) The adsorption of copper and zinc ions is not strongly dependent on pH even down to values as low as 0.3.

(4) For XAD-1, the amount of zinc adsorbed is independent of the amount of copper present and *vice versa*. This is not true for XAD-2 and the results using the

AFD suggest that zinc is not adsorbed in the presence of iron, copper, nickel, manganese and magnesium.

(5) Ethylenediaminetetraacetate complexes are not adsorbed and Na_2H_2Y can rapidly and completely remove iron, copper and zinc from XAD-1 and XAD-2. This is probably true for many other electrically charged metal–organic species.

(6) Methanol and acetonitrile do not remove adsorbed inorganic copper, zinc and iron from these resins.

(7) The adsorption of inorganic ions by XAD-2 can be reduced, but not eliminated, by methylation with dimethyl sulphate.

(8) XAD-2 is capable of removing iron, copper and zinc from acetonitrile. Some of this adsorbed metal can be eluted using only DDW.

(9) The multichannel, non-dispersive AFD provides a rapid and convenient means of investigating the interaction between trace metals and XAD resins or any other chromatographic support.

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