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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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K. S. Subramanian^a; J. C. Méranger^a; C. C. Wan^b; A. Corsini^b

^a Environmental Health Directorate, Health and Welfare Canada, Ottawa, Ontario, Canada ^b

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada

To cite this Article Subramanian, K. S. , Méranger, J. C. , Wan, C. C. and Corsini, A.(1985) 'Preconcentration of Cadmium, Chromium, Copper and Lead in Drinking Water on the Polyacrylic Ester Resin, XAD-7', *International Journal of Environmental Analytical Chemistry*, 19: 4, 261 – 272

To link to this Article: DOI: 10.1080/03067318508077037

URL: <http://dx.doi.org/10.1080/03067318508077037>

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Preconcentration of Cadmium, Chromium, Copper and Lead in Drinking Water on the Polyacrylic Ester Resin, XAD-7

K. S. SUBRAMANIAN and J. C. MÉRANGER

Environmental Health Directorate, Health and Welfare Canada, Tunney's Pasture, Ottawa, Ontario, K1A 0L2, Canada

and

C. C. WAN and A. CORSINI

Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1, Canada

(Received 16 October, 1984)

The conditions (e.g. pH, resin, particle size, foreign ions) affecting the uptake of Cd(II), Cr(III), Cu(II) and Pb(II) from aqueous solution by the SM-7 (also called XAD-7) resin, were studied. Based on these studies, a two-column method was developed to overcome the effect of complexation by humic substances. The method was successfully tested with the NBS multielement water standard, SRM 1643a, and was subsequently applied to enrich Cd(II), Cr(III), Cu(II) and Pb(II) in 15 drinking water samples from Hamilton, Ontario. The metals were determined using graphite furnace atomic absorption spectrometry. The results for the drinking water samples showed that leaching of copper and lead occurred from the distribution system.

KEY WORDS: Preconcentration, XAD-7 resin, trace metals, tap water, determination, graphite furnace atomic absorption spectrophotometry.

INTRODUCTION

Recent studies link the occurrence of certain cancers and cardiovascular diseases with the presence of toxic trace metals such as Cd and Pb in local drinking water supplies^{1,2}. Excessive or deficient

levels of essential micronutrients such as Cr and Cu may also have detrimental effects on health.³ However, the ultratrace levels at which these metals are present in drinking water,⁴ coupled with the possibility of matrix effects from the major ions (Ca^{+2} , Mg^{+2} , Cl^- , humic substances, etc.) necessitate the use of some form of preconcentration prior to analytical measurements. Procedurally, a good preconcentration method should provide a large enrichment factor, provide matrix normalisation (i.e. make the matrix of the sample the same as that of the standard by eliminating matrix effects), concentrate several metals simultaneously and be simple, fast, inexpensive and amenable to automated on-line analysis. The column percolation techniques, based on chelate ion-exchange or adsorption, were found to meet these criteria more satisfactorily than other preconcentration methods such as liquid-liquid extraction and coprecipitation.⁵

Recently, Corsini *et al.*⁶ showed the potential of the macroreticular acrylic ester resin, SM-7, for the direct adsorption of some metal ions including Cd(II), Cr(III), Cu(II) and Pb(II) from aqueous solution. Also, this resin is commercially available, modestly priced, requires no affixation of chelation sites (unlike Chelex-100, for example), and presents minimal contamination problems. In view of these favourable characteristics the feasibility of using this resin for the enrichment of Cd, Cr, Cu and Pb from drinking water samples was explored. The results of this study are reported here.

EXPERIMENTAL SECTION

Apparatus

The concentrations of Cd, Cr, Cu and Pb were determined using a Perkin-Elmer Model 373 atomic adsorption spectrophotometer equipped with a Model HGA-2200 graphite furnace atomizer and a deuterium arc background corrector. Single element hollow cathode lamps were used as the resonance line sources of the elements to be determined. Argon was the purge gas. Its flow was interrupted during the atomization of Cd, Cr and Pb; a flow of 60 ml/min was used during the atomization of Cu.

Reagents and resin

The ammonia and nitric acid were Baker Instra-analyzed grade and all other reagents were reagent-grade. Ammonium acetate and chloride were passed through a 200–400 mesh Chelex 100 column to remove any metal-ion impurities. Appropriate standard solutions of metal ions were prepared daily as required by serial dilution of Fisher Scientific 1000 mg/l stock solutions. All solutions were prepared in distilled-deionized water (DDW). Soil humic material (Aldrich Chemical Co., Milwaukee) was used to simulate marine humic substances. Stock solutions containing about 1 mg/ml were prepared.

The resin was either Bio-Beads SM-7 (Bio-Rad) or Amberlite-XAD-7 (Rohm and Haas), each supplied as 20–50 mesh. The resins were ground and sieved to provide a resin size of 80–100 mesh. Prior to use, the resins were washed under suction with 5% HNO_3 , 2–3% aqueous ammonia, DDW and methanol. The Amberlite resin was first washed with methanol, diethyl-ether and acetone to remove organic impurities. Borosilicate columns⁶ were slurry-packed with resin of appropriate mesh size. For the percent retention/pH study, 20 cm \times 1 cm i.d. columns of 20–50 mesh resin were used. The bed height was 7 cm. For analytical work, 10 cm \times 1 cm i.d. columns of 80–100 mesh were used. The bed height was 3 cm (0.5 g dry resin). Newly packed columns were subjected to a gentle back-flow of DDW to ensure uniform packing and then about 200 ml of 1% HNO_3 was percolated to ensure removal of metal-ion contaminants, followed by dilute ammonia and DDW until the effluent was about pH 8. Used columns were washed with 50–100 ml of 1% HNO_3 . Prior to passage of a sample for preconcentration, the analytical column was conditioned with about 50 ml of $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer (pH 8).

Sample collection

The drinking water samples were taken from taps at 15 sites in the Regional Municipality of Hamilton-Wentworth, Hamilton, Ontario. The samples were collected and stored in 1-l screw-cap polypropylene bottles, and acidified to 1% with nitric acid. Before use the bottles were cleaned as described by Dabeka *et al.*⁷ The samples were refrigerated at 4°C until analyzed.

Procedure

All glass and plastic ware was cleaned as recommended by Dabeka *et al.*⁷ Solutions were prepared and columns loaded and stripped in a horizontal laminar-flow work station (bench-top model, Canadian Cabinets, Ottawa, Ontario).

Optimization of solution conditions The effect of pH on metal ion uptake was studied by passing a 100 ml aliquot of a solution containing 1 ng/ml Cd(II), 5 ng/ml Cr(III), 10 ng/ml Cu(II) and 5 ng/ml Pb(II) through a 1 cm × 7 cm, 20–50 mesh SM-7 resin column at pH values ranging from 1 to 9. A flow rate of 1 ml/min was maintained. The retained metal ions were eluted with 10 ml of 1% HNO₃.

The effect of particle size and of humic substances on metal uptake was studied by determining the distribution ratios at 20–50 and 80–100 mesh at optional pH. A batch-equilibrium procedure was used.⁸ The effect of humics on retention was also shown by column percolation of a solution containing both metal ions and humic materials.

Analysis of NBS water standard (SRM 1643a) and samples Humic materials were removed by acidification of samples to pH 1.6–1.7 and passage through a precolumn (1 × 3 cm bed) of 80–100 mesh XAD-7. The effluent was adjusted to pH 8 with ammonia and passed through a second 3 cm column (analytical column) to preconcentrate the metal ions. This two-column procedure was tested with aliquots of the SRM 1643a standard to which had been added humic material and then allowed to equilibrate for 48 hr. The standard was diluted 10-fold because of the high level of metal ions. A 100 ml aliquot of sample or standard was passed at a flow rate of 1 ml/min. The retained metal-ions were stripped from the analytical column with 5.00 ml of 1% HNO₃ and subsequently determined by GFAAS. Aliquots of 10, 20 or 50 μl were injected into the pyrocoated graphite tube with an Eppendorf pipette. Each metal was atomized under the optimized instrumental conditions shown in Table I. The determinations were done in triplicate. Blanks consisting of solutions of the appropriate reagents in DDW were determined and the results for the water samples were then corrected. In certain samples, the Cu(II) could be determined directly without preconcentration. The standard additions method was used to calculate concentrations.

TABLE I
Graphite furnace atomic absorption spectrometric parameters for
Cd, Cr, Cu and Pb

Spectrometer PE 373	Cd	Cr	Cu	Pb
Wavelength (nm)	228.8	357.9	327.4	283.3
Spectral band width (nm)	0.7	0.2	0.7	0.7
Current (mA) HCL	4.0	15.0	10.0	8.0
Peak height readout time (sec)	5.0	7.0	7.0	5.0
<i>HGA 2200 Furnace</i>				
Drying temp. (°C)	100	100	100	100
Drying time (sec/10 μ l)	20	20	20	20
Ashing temp. (°C)	250	800	800	350
Ashing time (sec)	20	20	20	20
Atomization temp (°C)	2100	2600	2600	2300
Atomization time (sec)	5	7	7	5
Internal argon flow, 60 ml min				
Atomization stage	interrupt	interrupt	flow	interrupt

^aTemperatures (°C) represent the meter settings on the control panel of the HGA-2200 temperature programmer.

RESULTS AND DISCUSSION

The direct retention of metal ions on SM-7 or XAD-7 without prior formation of organometallic complexes or affixation of organic ligands on the resin was reported earlier.⁶ Subsequently, an adsorption mechanism involving charge-dipole interaction (between the metal ion and the resin C=O site) was postulated; the effect of a number of parameters such as pH, resin particle size and ionic strength on adsorption capacity was noted; and application of XAD-7 column to the preconcentration of trace metals in seawater and lakewater were described.^{8,9} As shown below, preconcentration of Cu(II), Cd(II), Pb(II) and Cr(III) in drinking water is readily effected with XAD-7.

Investigation of experimental variables

The effect of pH on the retention of the four ions on a 1 \times 7 cm XAD-7 (20–50 mesh) bed is shown in Figure 1. The behaviour of the

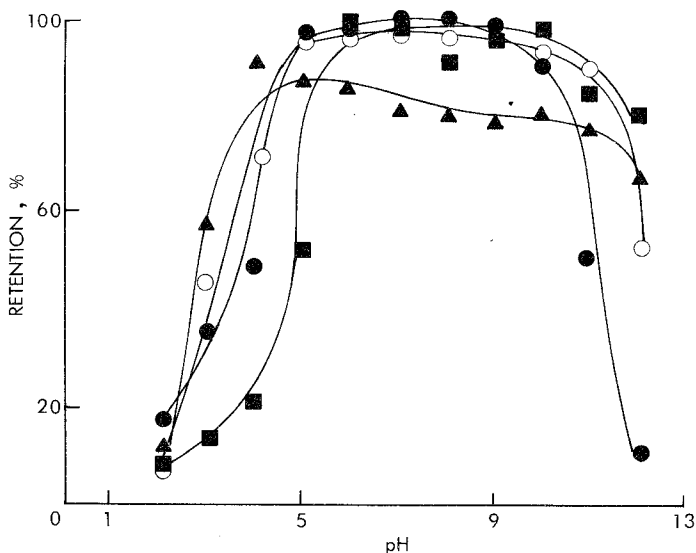


FIGURE 1 Effect of pH on the retention of Cd(II) (■), Cr(III) (▲), Cu(II) (○) and Pb(II) (●) on a 1×7 cm XAD-7 resin bed (20–50 mesh). Flow rate, 1 ml/min.

divalent ions is identical, with maximum uptake (close to 100%) occurring in the range pH 6–9; for Cr(III) maximum retention is >85% between pH 4–6 and ~80% between pH 6–8. Thus, simultaneous retention of the four ions can be brought about in the range pH 6–8. The pH dependency of the adsorption of various ions on XAD results from the fact that protons are also adsorbed and thus compete for active sites; this aspect has been discussed elsewhere.⁸

Table II shows the effect of particle size on the uptake expressed in terms of the distribution ratio. The distribution ratio, D_R , is defined as the moles of metal adsorbed per kg of dry resin to the moles of metal unadsorbed per litre of solution. Use of 80–100 mesh resin relative to the 20–50 mesh increases D_R for Cd(II), Cr(III), Cu(II) and Pb(II) by 68%, 53%, 230% and 124%, respectively. The higher D_R values are consistent with the fact that the column breakthrough volumes are about three times higher for 80–100 mesh than for 20–25 mesh.⁹ Although D_R increases with mesh size, sizes greater than 100 mesh result in flow rates that were too low to be practical (<1 ml/min). For this reason, 80–100 mesh was selected ultimately as the optimum particle size for analytical work.

TABLE II
Effect of SM-7 resin particle size on distribution ratio^a

Ion	pH	D_R , l/kg	
		20-50 mesh	80-100 mesh
Cd(II)	8.0	697	1168
Cr(III)	5.0	209	320
Cu(II)	7.0	329	1086
Pb(II)	8.0	369	827

^aDistribution ratio, $D_R = \frac{\text{moles of metal adsorbed/kg of dry resin}}{\text{moles of metal unadsorbed/l of solution}}$

The effect of some potentially interfering species on metal-ion retention was examined. Up to 200 mg/l of alkali and alkaline-earth metal ions and up to 400 mg/l of Cl^- , 800 mg/l of Br^- and 600 mg/l of NO_3^- had little effect on the retention of Cd(II), Cr(III), Cu(II) and Pb(II) at concentration 10 and 20 times above the detection limit. Since these ions constitute the major inorganic matrix of drinking water samples, no interference can be expected from inorganic species.

Drinking water also contains humic substances which form complexes with a number of trace metal ions including those of this study.¹⁰ The effect of complexation on the adsorption of Cd, Cr, Cu and Pb is illustrated in Figure 2. The D_R values of the four ions (20 $\mu\text{g/l}$ each) in the presence of humic material (10 mg/l) are substantially reduced compared to those in Table II at the corresponding pH. Although 60-100 mesh resin was used to obtain the data of Figure 2 and so cannot be directly compared to the D_R values for 80-100 mesh resin, it is to be noted the values in the presence of humics are substantially lower than even those for 20-50 mesh resin (humics absent). At higher concentrations of humic material, the D_R values decrease further. These results show that for total metal preconcentration, the metal humates must first be dissociated and the humic ligands removed from the sample solution. This could be done at pH 1-2 since the humic substances are retained by the resin at low pH but not the metal ions. Thus, a two-column procedure was used to overcome this interference. The

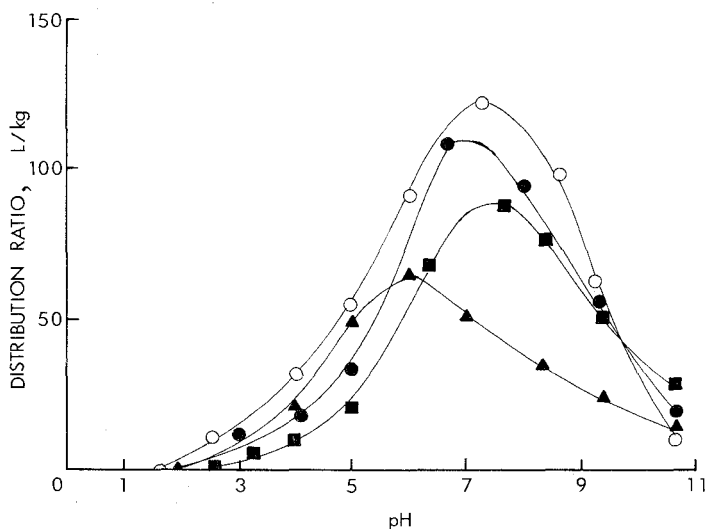


FIGURE 2 Distribution ratio as a function of pH for the adsorption of Cd(II) (■), Cr(III) (▲), Cu(II) (○) and Pb(II) (●), in the presence of humic material on XAD-7 (60–100 mesh). Concentration of each metal ion, 20 ng/ml; humic concentration, 10 mg/l.

acidified sample (pH 1.6–1.7) was passed through the first column (precolumn) operated at about pH 1; the pH of the effluent was then raised to 8 and passed through the second (or analytical) column to preconcentrate the metal ions.⁹ Table III shows the effect of humic material on the recovery of the four ions when a single column is used (i.e. humics not removed). Excellent recovery is obtained when the two-column procedure is used.

The adsorbed metal ions are readily eluted from the XAD-7 column with dilute HNO_3 . Other acids (e.g. HCl , H_2SO_4) give rise to matrix effects in the GFAAS measurement of some elements. Concentrations of up to 10% (v/v) HNO_3 were used but 1% HNO_3 was eventually chosen to reduce the risk of contamination from reagents. A 1% solution is adequate to strip the weakly held metal ions from the column. In contrast, 14% HNO_3 has been used to strip ions from the strongly bonding Chelex-100 column,¹¹ Not only are lower blank values more readily achieved by use of the more dilute HNO_3 solution but also Harnly and Kane¹² have reported that a 5% HNO_3 matrix results in severe irreproducibility if a

TABLE III
Recovery of metal ions from aqueous solutions containing humic substances by single and two-column methods.^a

Ion	Recovery (%) ^b	
	Single-column	Two-column
Cr(III)	37(pH 6)	81(pH 6)
Cu(II)	77	97
Pb(II)	69	94
Cd(II)	73	99

^aFor 100 ml of test solution containing 20 $\mu\text{g/l}$ of each metal ion and 10 mg/l of humic substances. Results represent single determination only. Calibration was by standard curve method. Analytical column was at pH 8 except for Cr(III).

pyrolyzed tube is used in the GFAAS measurement. This effect is not observed when 1% HNO_3 is used.

For a given bed height, the elution profiles of the four ions are essentially the same. The use of a short column allows for larger preconcentration factors. For the analytical work, a 1×3 cm resin bed was used, which permitted the ions to be quantitatively stripped with 5 ml of 1% HNO_3 . For the usual 100 ml sample volume this represents a 20-fold enhancement; higher enrichment factors can be obtained by using larger sample volumes. The capacity of a 1×3 cm bed of 80–100 mesh resin (0.5 g dry weight) exceeds the combined level of Cd(II), Cr(III), Cu(II) and Pb(II) in 100 ml of the NBS SRM 1643a standard (Table IV) by a factor of ~ 175 ; it exceeds the combined level of the ions in 100 mL of the most dilute water sample (no. 15, Table V) by ~ 2700 times and of the most concentrated sampled (no. 14) by ~ 23 times.

No attempt was made to further reduce the size of the resin bed since a reduction in capacity was not desirable; also, volumetric errors would be more significant and channelling problems would arise.

The precision and reliability of the two-column procedure was tested using the NBS "Trace Elements in Water" standard reference material, SRM 1643a, with and without humic material. The results

TABLE IV
Analysis of NBS SRM 1643a, "Trace Elements in Water" standard.

Element	NBS value (ng/ml)	Found (ng/ml) ^a	
		Without HA	With HA ^b
Cu	18.3 ± 2.0	19.5 ± 3.2	17.1 ± 3.8
Pb	27.4 ± 1.0	24.1 ± 0.8	28.9 ± 9.1
Cd	10.2 ± 1.0	10.6 ± 0.2	11.4 ± 2.9
Cr	17.2 ± 2.0	18.1 ± 2.9	16.4 ± 3.1

^aTriplicate determination, by standard additions. The precision measure is the standard deviation.

^bAdded concentration of humic substances (HA) 1000 ng/mL.

TABLE V
Determination of Cd(II), Cr(III), Cu(II) and Pb(II) in some drinking water samples from Hamilton (Ontario) region.

Sample no.	Concentration (ng/ml)			
	Cd(II)	Cr(III)	Cu(II)	Pb(II)
1	0.152 ± 0.010	0.564 ± 0.003	20.7 ± 3.4	1.88 ± 0.48
2	0.138 ± 0.034	0.502 ± 0.079	18.0 ± 2.2	1.32 ± 0.53
3	0.112 ± 0.016	0.629 ± 0.025	74.5 ± 1.3	12.28 ± 0.10
4	0.054 ± 0.009	0.340 ± 0.098	21.2 ± 2.4	1.19 ± 0.02
5	0.080 ± 0.016	0.371 ± 0.047	21.08 ± 0.88	0.938 ± 0.057
6	0.186 ± 0.030	0.510 ± 0.050	23.8 ± 0.9	5.72 ± 0.06
7	0.383 ± 0.032 ^a	0.155 ± 0.068	382.2 ± 7.6	10.9 ± 0.3
8	0.242 ± 0.007 ^b	1.85 ± 0.006	200 ± 9	3.09 ± 0.10
9	0.110 ± 0.005	0.776 ± 0.019	110.9 ± 1.5	1.19 ± 0.07
10	0.123 ± 0.006	0.090 ± 0.032	96.3 ± 1.4	2.12 ± 0.18
11	0.171 ± 0.021	0.198 ± 0.039	103 ± 9	1.33 ± 0.27
12	0.131 ± 0.008	0.189 ± 0.017	27.3 ± 0.9	1.32 ± 0.01
13	0.326 ± 0.003	not detectable	29.5 ± 0.2	2.44 ± 0.04
14	0.282 ± 0.009 ^c	not detectable	405.9 ± 8.1	2.70 ± 0.42
15	0.148 ± 0.006	0.156 ± 0.090	2.67 ± 0.16	1.97 ± 0.16

^aSame sample as no. 6 but left to stand 24 h in Cu pipe before collection.

^bSame location as no. 9 but left to stand 12 hr in Cu pipe.

^cSame location as no. 13 but left to stand 24 hr in Cu pipe.

in Table IV are gratifying, both in terms of precision and recovery, especially in view of the simple preconcentration procedure used.

The detection limit (concentration in pg/ml corresponding to 3 SD of the blank value) for Cd, Cr, Cu and Pb was 0.3, 1, 2 and 5, respectively, taking into account the 20-fold concentration factor and based on a 50 μ l injection volume.

Application to drinking water samples

The two-column procedure was applied to the analysis of 15 drinking water samples in the Hamilton-Wentworth region. The results are presented in Table V. The cadmium values for each sample show good within-run precision, suggesting that the various aliquots taken from a given sample were homogeneous. The grand mean Cd value for the 12 samples (excluding sample nos. 7, 8 and 14, which were left to stand 12 or 24 hr in the pipe prior to collection) was 0.144 ± 0.068 ng/ml. The grand precision indicates a relatively narrow range of cadmium concentration distributed in the area. The good within-run precision for Cr is also indicative of sample homogeneity. The grand average was 0.333 ± 0.249 ng/ml. The broad range shows that Cr is unevenly distributed in the water supplies in West Hamilton and the surrounding region. Since XAD-7 resin retains only Cr(III), the results in Table V give only the Cr(III) value, not total Cr, i.e. Cr(III) + Cr(VI).

The values for copper fall into three groups: (i) about 20 ng/ml for samples from West Hamilton; (ii) about 100 ng/ml for samples collected from Dundas, a region adjacent to West Hamilton; and (iii) > 200 ng/ml for samples collected after a 12- or 24-h standing period in copper pipes (sample nos. 7, 8 and 14). These results suggest that the copper value is considerably dependent on the leaching process within the copper distribution pipes.

For Pb, the concentrations were in general < 3.0 ng/ml. Exceptions are sample nos. 3, 6 and 7. The high lead values in these cases are possibly due to severe leaching of the solder joints.

The Cd, Cr, Cu and Pb levels in all the water samples analyzed were well below the maximum acceptable limit contained in the guidelines for Canadian drinking water quality.¹³

The two-column XAD-7 procedure leads to a simple matrix of essentially 1% HNO₃, relatively free of humic material. It has been

shown⁹ that for such a matrix, the standard calibration curve method rather than the standard additions method can be used to obtain the trace metal concentrations. The former method is preferable (except for Cr(III)) because of savings in time and sample consumed. The standard additions method is superior for Cr(III) because this species is not quantitatively retained by XAD-7 and a low recovery is returned by the calibration curve method. Because Cr(III) was included in the present study and because there was an ample supply of samples, the standard addition method was used.

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