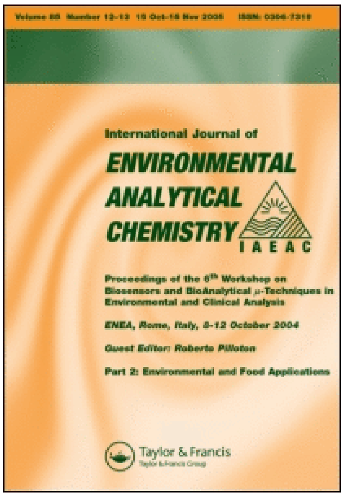

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On-site Sampling with Preconcentration for the Determination of Some Chelex-Labile Trace Metals in Drinking Water

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An on-site pump-integrated water sampler-preconcentration device is described. The preconcentration of trace metals is effected using the Chelex-100 chelating cation exchange resin. Preliminary studies showed this on-site device to be satisfactory for the monitoring of Cd, Cu, Pb and Zn in drinking water samples.

KEY WORDS: On-site sampling-preconcentration, trace metals, potable water, determination.

INTRODUCTION

The determination of metals in drinking water supplies is becoming increasingly popular in recent years because of the public awareness of the toxic effects of several of these metals; also, increasing incidence of water re-use especially in densely populated areas has made the monitoring of potable waters for metal contamination of increasing importance. However, almost all metals in drinking water are present at ng/mL or sub-ng/mL levels requiring the use of highly trained analysts, extremely sensitive analytical instruments and some means of preconcentration. As a result, on-site analysis is rarely practicable. In most cases samples must be transported to a distant laboratory entailing a time delay between sample collection and analysis. Because a natural waterbody is in a state of continuous physical, chemical and biological change, the data obtained in the laboratory may not reflect the actual composition of the sample at the time of collection.[1] Attempts to circumvent this problem through filtration and preservation at the point of sampling invariably contaminates the sample with trace metals introduced from the containers, the filters and the preservation medium.[1] Another problem is the difficulty involved in collecting and transporting large volumes of water samples to a laboratory for analysis.

The above problems of sample integrity can be largely minimized if the sample can be collected *in situ* and the trace metals in the sample can be simultaneously converted to non-labile species through some method of preconcentration. The advantages of such an approach are: (i) preconcentration enables a large, fairly representative sample to be concentrated to a sample of smaller volume; (ii) a concentrated sample in controlled chemical form will be more stable; and (iii) transportation and storage of large volumes of water will no longer be needed. Despite these advantages on-site sampling with preconcentration of metals from drinking waters (and natural waters in general) is not yet well developed.

From a survey of available preconcentration methods, we found the use of the chelating ion-exchange resin known as Chelex-100 the most satisfactory.[2] Thus this short note describes a pump-integrated water sampler coupled with a Chelex-100 preconcentration system designed to sample and concentrate trace metals from drinking water samples *in situ* and thereby minimize some potential sources of sampling contamination and loss of sample integrity. Data are reported for Cd, Cu, Pb and Zn in some drinking water samples, and are compared with those obtained using an on-site batch-integrated sampling-preconcentration (Chelex-100) system.

EXPERIMENTAL METHODS

Figure 1 shows the basic setup of the pump-integrated sampler. The tap from which drinking water is to be sampled is connected through a 0.625 cm inner diameter Tygon tubing† (Cat. No. 6408-45, Cole Palmer) and Teflon adapters to a custom-made 250-mL polyethylene reservoir. The reservoir outflow is connected to a Masterflex peristaltic pump equipped with a 12 rpm pump head (Cat. No. 7543-10 and 7015-20, respectively, Cole Palmer). The reservoir overflow tube is led into the drain. The pump outflow tube is attached to the Bio-Rad filter assembly and resin column. The filtration system is equipped with a 4.7 cm diameter filter holder, a prefilter, a polycarbonate 0.4 μm micropore membrane filter and a disposable polyester drain disc (Cat. No. 342-0008, 334-0648, 331-6648 and 334-0648, respectively, from Bio-Rad Laboratories). The filtrate then percolates through a 10 cm height × 2 cm outer diameter × 1.5 cm inner diameter chromatography column (Canus Plastics) loaded with 2.0 g Chelex-100 resin, 50–100 mesh. The effluent from the column may be received either in a collection vessel or may be led into a drainage basin. The entire set-up is housed in a wooden box. The filter assembly and the column are clipped into position inside the box itself.

The batch-sampler consisted of a 4-L heavy-walled polyethylene percolator (18 cm diameter × 41 cm hieght, Cat. No. F42300, Canus Plastics Ltd., Ottawa) modified to accept a cover and an overflow drain at the 3.5 L level. The drinking water from the tap to be sampled is introduced into the percolator through a 0.625 cm tubing (Cat. No. 6408-45, Cole Palmer) by gravity-controlled downflow. The water in the percolator is then filtered and the filtrate is subsequently passed through the Chelex-100 column as described in the case of the pump-integrated sampler.

Atomic absorption apparatus

The electrothermal atomic absorption measurements of Cd, Cu, Pb and Zn were made using a Perkin–Elmer Model 603 atomic

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†The Tygon tubing was made contamination-free by soaking in 1% nitric acid (Baker Ultrex) overnight followed by several rinses using high-purity water.

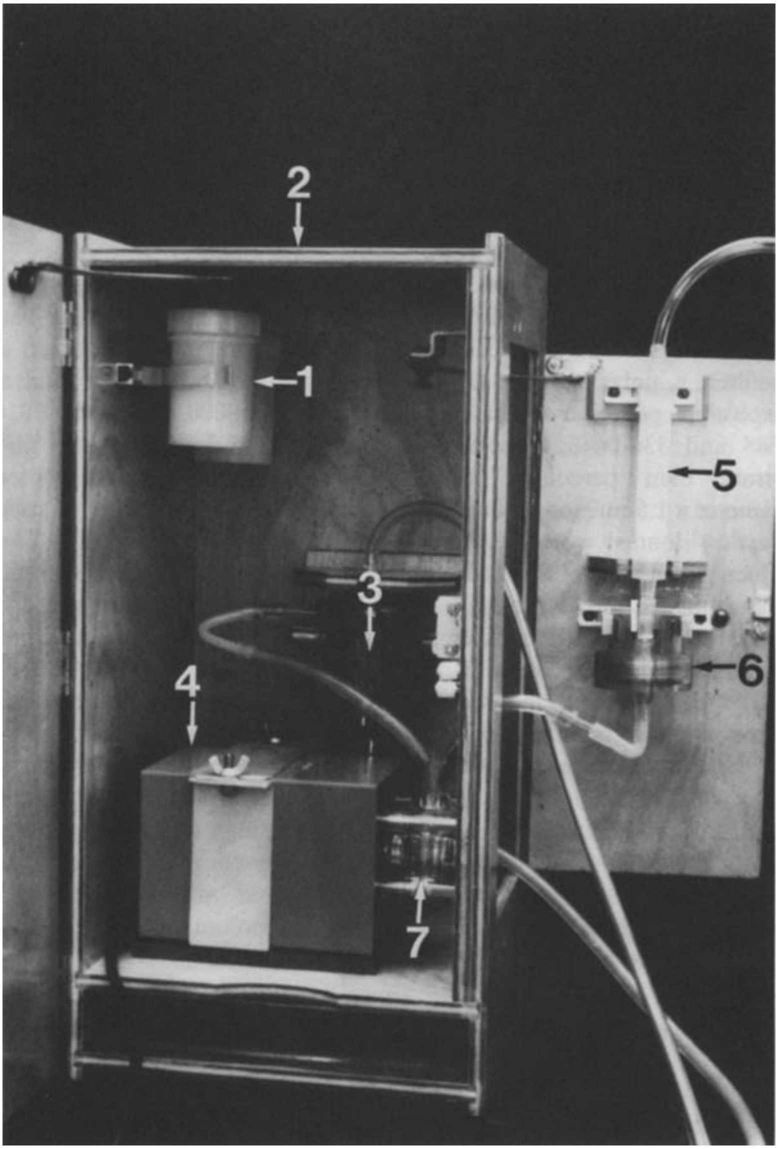

FIGURE 1 Pump-integrated sampler. 1. Extra space for storing resins. 2. Wooden box, 25 cm × 50 cm × 25 cm. 3. 250-mL polyethylene reservoir. 4. Masterflex peristaltic pump. 5. Ion-exchange column. 6. Filtration assembly. 7. 12 rpm pump-head.

absorption spectrophotometer equipped with a Perkin–Elmer Model 500 graphite furnace and a deuterium arc background corrector. Single-element hollow cathode lamps were used as narrow line sources. Nitrogen was used as the purge gas and its flow was interrupted during the atomization of cadmium and lead.

Other equipments used included a Fisher Scientific Model 210 pH meter and 125-mL Pyrex glass separatory funnels fitted with polytetrafluoroethylene stopcocks and polyethylene stoppers.

Reagents

High-purity water was obtained by passing tap water through a cellulose absorbent and two mixed bed ion-exchange columns followed by distillation in a Corning Model AG-11 distillation unit.

A 20% (w/v) solution of ammonium citrate buffer and a 2% (w/v) solution of ammonium pyrrolidinedithiocarbamate used in the solvent extraction study were prepared and purified as described in a previous publication.[3]

The Chelex-100 resin (Cat. No. 142-2832, 50–100 mesh, sodium form, Bio-Rad Laboratories) was purified and converted to the ammonium form as outlined by Sturgeon *et al.*[4]

Appropriate standard solutions of Cd, Cu, Pb and Zn were prepared in 1% HNO_3 (Baker Ultrex) immediately before analysis by serial diluation of the 1000 mg/L stock solution (Fisher Scientific) stored in polyethylene bottles.

All other reagents and solutions used were of the highest purity available.

Sampling procedure

Nine sampling sites were chosen at random in the Ottawa Valley region. The sampling was done at the kitchen or bathroom taps of each of the selected homes. At each site, water from the taps were run to waste at their maximum flow rate for 1 h in order to minimize concentration fluctuations during sampling. For pump sampling-preconcentration, the sampler was connected to the tap. When a steady flow of water was maintained in the 250-mL reservoir, the pump was started and sampling-preconcentration proceeded. The process was continued until approximately 4 L of water had passed through the resin column ($\approx$3.5 h). For batch sampling-preconcentration, the 4-L percolator was filled to the overflow level with drinking water from the tap to be sampled. The stopcock was then opened to let the water pass through the filtration assembly and the Chelex-100 column. The ion-exchange was continued until all the water had passed through the resin bed ($\approx$4.8 h). The sampling-preconcentration was done in duplicate.

Analytical procedure

All the labware used was decontaminated from possible traces of the metals of interest by the cleaning procedure recommended by Laxen and Harrison.[5]

The Chelex-100 column used in conjunction with the pump-integrated and batch-integrated samplers were prepared for ion exchange as follows. A small amount of precleaned glass wool was placed at the bottom of the column. About 2 g of the resin was slurry-loaded into the column allowing the water to drip out of the column as the slurry settled. Two 20 mL portions of 3M HNO_3 were passed through the column followed by two 20 mL portions of high purity water and 10 mL of 2M ammonia. The column was then washed with high purity water until the effluent pH was near neutral. The column was then incorporated into the pump integrated sampler-preconcentration assembly.

On completion of exchange the column was disconnected, rinsed once with 10 mL high-purity water, thrice with 10 mL aliquots of 1M ammonium acetate buffer (pH 5.2), and finally with two 10 mL portions of high-purity water. The resin and glass wool were now transferred from the column into a 10 mL polyethylene conical flask and equilibrated for 1 h with 30 mL of 3M HNO_3. The contents of the flask were then vacuum-filtered through a Pyrex glass frit of medium porosity. The filtrate was collected in a 50-mL Pyrex glass volumetric flask. The glass frit was washed thrice with small jets of water. The flask was brought to the 50-mL mark with high-purity water.

For the determination of a given metal, a 20 μL aliquot was withdrawn from the volumetric flask with an Eppendorf pipette fitted with disposable plastic tips and injected into the pyrocoated graphite tube mounted in the graphite furnace of the atomic absorption spectrometer. Prior to use the tips were decontaminated from traces of the metals by soaking them for 24 h in 1% HNO_3 (Baker Ultrex) followed by four rinses with high-purity water. The sequential dry-char-atomize program of the HGA-500 given in Table I was followed and the peak absorbance noted. The amount of each metal in the drinking water sample was obtained by the method of standard addition.

TABLE I

Optimized GFAA parameters for Cd, Cu, Pb and Zn.[a]

Parameter	Cadmium	Copper	Lead	Zinc
Wavelength, nm	228.8	324.8	383.3	213.9
Slit, nm	0.7	0.7	0.7	0.7
Drying temperature, °C	100	100	100	100
Drying time, ramp-hold, s	20–20	20–20	20–20	20–20
Ashing temperature, °C	250	600	350	400
Ashing time, ramp-hold, s	20–20	10–30	20–20	20–20
Atomization temperature, °C	1900	2400	2100	2000
Atomization time, ramp-hold, s	1–4	1–4	1–4	1–4

[a] Perkin–Elmer Model 603 AA spectrometer equipped with the HGA-500 graphite furnace and dueterium arc background corrector.

RESULTS AND DISCUSSION

Choice of the preconcentration method

The factors that may be considered as contributing to the effectiveness of a field preconcentration method are: (i) quantitative recovery of metals at the ng/mL level; (ii) favourable concentration factors; (iii) stability of the collected sample; (iv) freedom from contamination; and (v) selectivity (i.e. separation of trace metals from the major constituents of drinking water, namely, calcium and magnesium salts). Based on our review of the methods currently available for preconcentrating trace metals from drinking waters and natural waters, the chelating ion-exchange resin known as Chelex-100 was found to meet the above criteria more satisfactorily than any other method of preconcentration.[2] The Chelex resin is almost ideal for the preconcentration of trace metals from natural waters and potable waters because the exchange for metals species is rapid at the pH of natural waters, namely pH 6–8.[6] In addition, the resin in the ammonium form yields low blanks after purification,[3] is simple to use, easy to purify, well characterized, available commercially on a routine basis and is modestly priced. All these factors prompted us to use this chelating cation exchange resin as the preconcentrating agent.

The resin was used in the NH_4^+ form rather than the Na^+ or Ca^{2+} form in order to minimize any matrix problems with the GFAA analysis. For example, salts of sodium, calcium and magnesium are known to suppress the atomic absorption signal of Pb determined by GFAA.[7] A 50–100 mesh resin was used because Pakalns *et al.*[6] found that the exchange, though efficient, was considerably slow with the 100–200 and 200–400 mesh resins.

Note that the Chelex-100 used in the manner described will remove only that fraction of the trace metal level which has become known under the operational definition of "Chelex-labile"; only 44–63% of the Pb and Cu present in some tap waters may be Chelex-labile.[8]

Field testing of the sampler

Table II compares the results for Cu, Pb, and Zn in drinking water samples collected and preconcentrated *in situ* from different sites in the Ottawa area using the pump-integrated sampler with those obtained using the batch-integrated sampler. As can be seen, the agreement between the two methods is satisfactory. Also note that the values (ng/mL) range from 10.0 to 58.8 for Cu; $\leqq 1.0$ to 34.6 for Pb; and $\leqq 3.0$ to 27.4 for Zn. The values for Cd in all the samples analyzed were $\leqq 0.1$ ng/mL.

CONCLUSION

The pump-integrated sampler described in this paper enables the on-site collection-preconcentration of a representative and stable sample. By suitable modification, the sampler can be used for concentrating trace metals from almost any volume of water. This *in*

TABLE II

Levels of Cu, Pb and Zn in some drinking water samples by the pump-integrated and batch-integrated sampling methods.[a]

	Cu, ng/mL		Pb, ng/mL		Zn, ng/mL	
Sample no.	P	B	P	B	P	B
1	<10.0	<10.0	34.6±2.0[b]	38.7±3.1	10.6±0.7	12.5±1.3
2	58.8±3.0	46.9±3.4	20.7±1.2	24.8±2.2	10.9±1.0	11.7±1.2
3	<10.0	<10.0	13.6±1.1	12.7±1.5	9.8±0.9	10.8±1.3
4	14.1±0.5	13.7±0.9	<1.0	<1.0	11.8±0.5	10.7±0.7
5	<10.0	<10.0	<1.0	<1.0	24.0±3.1	28.7±2.6
6	<10.0	<10.0	<1.0	<1.0	10.3±1.1	9.7±1.2
7	<10.0	<10.0	<1.0	<1.0	14.4±0.4	16.6±0.8
8	<10.0	<10.0	<1.0	<1.0	9.1±0.8	9.8±1.0
9	29.3±1.4	23.3±1.7	14.2±0.9	12.7±1.1	27.4±2.2	29.4±2.5

[a] All samples analyzed contained Cd below the detection limit (3SD of blank) of graphite furnace atomic absorption spectrometry, namely 0.1 ng/mL. The GFAA detection limits for Cu, Pb and Zn are (ng/mL): 10.0, 1.0 and 3.0, respectively.

[b] The measure of precision is the average deviation of duplicate determinations.

P = Pump-integrated sampler, B = Batch-integrated sampler.

situ sample-preconcentration device can be applied to the monitoring of Chelex-labile trace metal levels in water samples and can also be adapated for speciation studies by replacing the Chelex-100 column with other chelating resins specific for trace metal species.

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