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Use of an On Site Integrated Pump Sampler for Estimation of Total Daily Intake of Some Metals from Tap Water

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An on-site pump-integrated water sampler-preconcentration device combined with a pressure sensitive switch to allow sampling of water from kitchen taps as a direct function of use is described. The sampler was used in the analysis of 18 tap water samples in the Montreal Metropolitan area for Cd, Cu, Pb and Zn during six days of normal use. The sampler-preconcentration device has the potential for giving a more accurate estimate of the total daily intake of the above metals from drinking water.

KEY WORDS: On-Site sample preconcentration, trace metals, tap water, determination, total daily intake.

INTRODUCTION

The traditional grab sampling techniques used in drinking water surveys for the determination of inorganic contaminants are associated with a number of analytical difficulties such as inadequate sensitivity, poor sample stability during storage and contamination from containers and stabilizing agents. We sought to overcome these problems through the use of an on-site pump-integrated preconcentration sampler based on the Chelex-100 chelating ionexchange resin.² Another drawback of the grab sampling approach is its unsuitability for the estimation of total daily intake of metals from drinking water supplies. This is because taking a water sample for trace metal determinations at the consumer's tap may result in readings that are exceedingly high or misleadingly low depending on whether first flush samples or standing grab samples or running grab samples were taken.3 In other words the grab sample bears no definable relation to patterns of consumption. Furthermore, the total daily intake of metals from drinking water depends on the total volume of water consumed in a day and not on the volume of a grab water sample collected at any instant.⁴ The pump-integrated sampler,² on the contrary, enables us to sample at different time intervals and thus give an overall average for the metal ion concentration as a function of time. Also, the pump-integrated sampler may be attached to a domestic tap and switched when the tap is in use. This means samples are collected during operation of the tap for consumption under the flow conditions used in consumption. Thus the pump-integrated sampler equipped with a switch would allow sampling of water as a direct function of use.

In this paper, we describe such a pump-integrated sampler modified to accept a pressure-sensitive switch device to allow sampling of drinking water in a manner approaching use. Results are reported for Cd, Cu, Pb and Zn from 18 kitchen tap waters from the Montreal metropolitan area.

EXPERIMENTAL METHODS

The pump-integrated sampler has been described earlier.² However, as shown in Figure 1, the sampler has now been equipped with an automatic pressure-sensitive switch made of polysulphone and a right angle piece of plastic pipe with a side arm. Tygon tubing was used for connecting the pressure-sensitive switch to the kitchen faucet, and also for connecting the plastic pipe to the pump. The

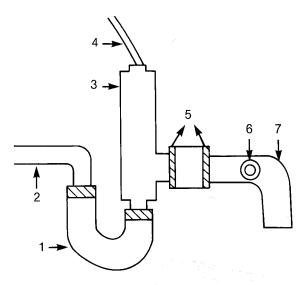


FIGURE 1 Schematic representation of pressure-sensitive switch system attached to faucets. 1. Large diameter Tygon tubing. 2. Faucet. 3. Pressure switch. 4. Leads to 12 V control relay circuit. 5. Tubing clamp. 6. Tygon tubing connection to pump-integrated sampler shown in reference 2. 7. Plastic pipe elbow.

Tygon tubing and the plastic pipe were soaked in 1% HNO₃ (Baker Ultrex) overnight followed by several rinses with high-purity water until the levels of Cd, Cu, Pb and Zn were below the detection limit of graphite furnace atomic absorption spectrometry.

Apparatus

All the work was done using a Perkin–Elmer Model 503 atomic absorption spectrophotometer equipped with hollow cathode lamps of Cd, Cu, Pb and Zn as narrow line sources. Copper and zinc were determined in the flame mode using a 4 inch single shot burner and air-acetylene flame (oxidizing). The burner was set parallel to the beam in the case of copper while it was set at an angle of 30° to the beam in the case of zinc. Lead and cadmium were determined using a Perkin–Elmer Model HGA-2100 graphite furnace with the dry-ashatomize parameters optimized at 110°C (40 s)—250°C (40 s)—2100°C (7 s) for Cd, and 110°C (40 s)—500°C (40 s)—2300°C (7 s) for Pb. The

nitrogen purge gas flow was interrupted during atomization of Cd and Pb. The slit was set at 0.7 nm for all the elements. The resonance lines were set at 228.8, 324.8, 217.0 and 213.9 for Cd, Cu, Pb and Zn, respectively. The deuterium arc background corrector was used for Cd, Pb and Zn.

Reagents

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

Appropriate standard solutions of Cd, Cu, Pb and Zn were prepared in 1% HNO₃ (Baker Ultrex) immediately before analysis by serial dilution of the 1000 mg/L stock solution (Fisher Scientific) stored in polyethylene bottles.

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.*⁵

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

Sampling procedure

The sampling sites were kitchen sinks in 18 locations distributed over the Montreal metropolitan area representing nine apartments, four cottages, three bungalows, one duplex and one single home. The reported plumbing materials included copper (12 locations), steel (3 locations) and PVC (one location). Two locations did not report the type of plumbing materials used. The buildings ranged in age from 10 years to 70 years. The sampling was done for periods of six days at each site. For comparison, the sampling was also done for one day using the previously described pump-integrated sampler but without the switching device.²

The analytical procedure was identical to that described elsewhere.²

RESULTS AND DISCUSSION

The concentration values for Cd, Cu, Pb and Zn in the one-day and

the six-day collection are given in Table I and Table II, respectively. Also included are the results of the repeat studies on site 9 (Table I). Note from Table II that the mean volume of water consumed is 1.850 L with a range of 0.325 to 4.050 L.

It should be pointed out 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 copper and 46–56% of the Pb present in some tap waters may be Chelex-labile.⁶

TABLE I
Levels of Cda, Cu, Pb and Zn in 4-L one-day pumpintegrated samples.

Sample site	Cu, ng/mL	Pb, ng/mL	Zn, ng/mL
1	20	0.38	34
. 2	9	0.70	71
3	12	0.28	68
4	73	0.50	11
5	74	0.42	59
6	18	0.48	171
7	16	0.42	10
8	15	2.78	174
9	231	0.38	10
9ь	175	0.40	14
9°	220	0.33	18
10	6	0.45	87
11	20	1.42	116
12	24	0.95	20
13	12	0.42	30
14	13	0.98	133
15	11	0.40	5
16	44	0.48	6
17	8	0.80	87
18	25	0.52	22
Median	17	0.44	26
Extreme	(6–231)	(0.28-2.78)	(5-174)

The Cd content of water from all the sites was below the detection limit of graphite furnace atomic absorption spectrometry, namely, 0.05 ng/mL.

^bRepeat sampling at the kitchen sink.

^{&#}x27;Sampling from a tap near the entry point of water to the building.

TABLE II
Levels of Cd, Cu, Pb and Zn in six-day pump-integrated samples.

Sample site	Volume collected, mL	Cd, ng/mL	Cu, ng/mL	Pb, ng/mL	Zn, ng/mL
1	4250	0.70	40	0.38	90
2	1750	0.11	130	0.63	76
3	2075	0.19	45	0.34	98
4	2050	0.10	160	0.78	36
5	2275	0.09	68	0.66	94
6	2025	0.10	81	0.64	167
7	4050	0.07	28	0.25	10
8	2125	0.14	18	1.18	48
9	2500	0.24	265	2.76	175
10	1800	0.11	59	0.83	52
11	1500	0.07	38	1.00	191
12	1750	0.06	28	0.57	20
13	2000	0.10	120	0.44	70
14	325	0.46	117	2.06	167
15	1900	0.12	208	0.99	36
16	1250	0.34	42	0.30	51
17	1900	0.09	87	0.89	73
18	750	0.24	21	0.53	95
Median	1850	0.11	64	0.65	75
Extreme	(325–4050)	(0.06-0.46)	(18-265)	(0.25-2.76)	(10–191)

The data given in Table I and Table II are for determinations on a single sample. Based on our previous work,² the precision, expressed as the percent average deviation, was ± 3.5 to 5.1 for Cu; ± 5.8 to 8.1 for Pb; and ± 4.2 to 12.9 for Zn.

The first test which the present system must pass is that of its acceptability in homes. The unit requires space near the sink for its filter, column and pump box. In favourable cases this may be in a floor level cabinet displacing something like a waste can but more commonly it is 25 cm by 25 cm of counter top space. This must be far enough removed from the sink for electrical safety. (The pressure switch is operated with a 12 V circuit to reduce shock hazard). Finally, the mounting of tubing and switch on the faucet itself somewhat reduces the mobility of faucets that swing to different positions over the sink. The response from the participants on the

acceptability of this device in a kitchen for a week was somewhat encouraging. The unit was rated "convenient" by one respondent, "slightly inconvenient" by 11, "moderately inconvenient" by 4, and "very inconvenient" by one; one respondent did not respond. It would appear that recruiting volunteers for future studies using this apparatus will not be very difficult.

As can be seen from Tables I and II, the levels of Cd, Cu, Pb and Zn are higher in the six day samples than in the one day samples for the majority of the sites studied. Variations in trace metals concentrations in drinking water arise from a number of factors such as the time of sampling, "standing time" of water in the distribution system, and the extent to which hot and cold water are used by the consumer. The influence of these factors on the trace element content of the water samples clearly emphasizes the importance of attempting to go beyond grab samples for the purpose of assessing total daily intake of metals from drinking water.

Note the high value of copper in the samples from site 9 (Tables I and II). Such high values can arise by the leaching of copper from the distribution system and plumbing fixtures.⁷⁻¹⁰ We explored the origins of the high copper value at site 9 by repeated one-day measurements at that site. Sample 9^b (Table I) shows that the high value was repeatable 24 days after the first measurement. Sample 9^c (Table I) shows that the high value found from the kitchen sink is repeated at a tap near the entry point of water to the building. This suggests that plumbing within the buildings may not be the dominant factor.

Based on a national survey of trace metals in drinking water supplies, we estimated the total daily intake of Cd, Cu, Pb and Zn by the average Canadian adult to be (μ g/day): Cd \leq 0.03, Cu \leq 13.0, Pb \leq 1.3 and Zn \leq 13.0. Based on the present study, these values for the 1-day sample would be: Cd \leq 0.07, Cu 22.1, Pb 0.59 and Zn 33.8; and for the 6-day collection they are: Cd \leq 0.14, Cu 83.2, Pb 0.85 and Zn 97.5. All these values are based on an average daily consumption of 1.3 L.8 A national survey of drinking water supplies using the pump-integrated sampler is planned to obtain a more accurate estimate of the total daily intake data.

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