APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 11, 551–558 (1997)

Organotin Leachates in Drinking Water from Chlorinated Poly(vinyl chloride) (CPVC) Pipe

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A solid-phase extraction method, using a phenyl-bonded silica sorbent, was developed for the isolation of mono- and di-methyltin, -butyltin and -octyltin from drinking water. Recoveries averaged 92% over two tested sample weights and spiking levels. Ethyl derivatives were made by Grignard reaction for determination by gas chromatography–atomic absorption spectrometry (GC–AAS). Static and repetitive extraction studies were conducted at 24 and 65°C. Butyltins rapidly leached into drinking water kept in chlorinated poly(vinyl chloride) (CVPC) pipe samples. Monobutyltin and dibutyltin levels reached 19.8 (13.4 as Sn) and 197 (100.4 as Sn) ng g^{-1} respectively in water samples collected from CPVC pipe heated to 65°C. Butyltins were still leached from CPVC pipe after 20 repetitive extractions, suggesting that new CPVC water systems would contaminate water with organotins for some time after installation. © 1997 by John Wiley & Sons, Ltd.

Appl. Organometal. Chem. **11**, 551–558, (1997)
No. of Figures: 3 No. of Tables: 5 No. of Refs: 16

Keywords: chlorinated poly(vinyl chloride); organotins; drinking water; gas chromatography; atomic absorption spectrometry; ICP–MS

Received 6 September 1996; accepted 28 August 1996

INTRODUCTION

In 1993, the US used 2.8×10^9 kg of poly(vinyl chloride) (PVC) for building and construction products.[1] About 40% of the PVC was in the form of pipe for use in water mains, sewers and domestic water systems. A variant of PVC, chlorinated poly(vinyl chloride) (CPVC), is widely used for high-temperature water distribution systems.[2]

Dimethyltins, dibutyltins or dioctyltins are added to protect PVC resin from thermal degradation during processing or usage and to protect the final product from light-induced degradation. The corresponding monoalkyltin is added with the dialkyltin stabilizer to produce a synergistic effect. These compounds protect the PVC by (a) inhibiting the dehydrochlorination reaction by exchanging their anionic group, X, with the allylic chlorine atoms in the polymer, (b) reacting with the HCl produced, (c) producing the compound HX which may inhibit other side reactions, and (d) preventing atmospheric oxidation of the polymer by acting as antioxidants.[3]

Organotins exhibit toxicity dependent on the size and number of organic groups attached to the tin atom.[4] Trialkyltins are generally more toxic than the corresponding dialkyl or monoalkyl derivatives. Within the trialkyltin compounds, the lower homologues, triethyltin and trimethyltin, have the greatest acute toxicity (LD_{50} values 4 and 9 mg kg^{-1} respectively in the rat). Various dialkyltin and trialkyltin compounds have an immunotoxic effect. Pennicks[5] established a tolerable daily intake of 0.25 μg kg^{-1} of body wt per day for tribultyltin, based on immune system studies. However, the dibutyltin metabolite probably caused the immunosuppression.

Organotin has been found to leach from PVC pipe,[6–8] but there have been no reports on organotin leachates from CPVC pipe. In a previous study, we found that organotin levels present in CPVC pipe were much higher than those in PVC pipe intended for water delivery systems.[9] The present study examines the levels and species of organotin compounds in water which has been in contact with new and used CPVC pipe.

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CCC 0268–2605/97/070551–08 $17.50

MATERIALS AND METHODS

Reagents and standards

Distilled-in-glass grade solvents (Caledon Laboratories Ltd, Georgetown, and BDH Inc., Toronto, Canada) and ACS reagent chemicals were used. Tropolone and ethylmagnesium chloride were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI, USA). Monooctyltin trichloride ($OcSnCl_3$) was obtained from Gelest, Inc., Bensalem, PA, USA. Dioctyltin dichloride ($OcSnCl_2$) was purchased from MTM Research Chemicals, Windham, NH, USA. Dimethyltin dibromide (Me_2SnBr_2) and monomethyltin trichloride ($MeSnCl_3$) were obtained from Alfa, Johnson Matthey, Ward Hill, MA, USA. Octyltin and methyltin salts were used as received. Monobutyltin trichloride ($BuSnCl_3$), purchased from Research Organic/Inorganic Chemical Corp., Belleville, NJ, USA, was vacuum-distilled prior to use. The source and purity of the dibutyltin dibromide (Bu_2SnBr_2) has been previously reported.[10] Ethyl derivatives of the butyltins, octyltins and dimethyltin dibromide were examined by GC–AAS and found to contain only the expected tin compound. The triethylmethyltin (from $MeSnCl_3$) was 97% pure (Sn basis). The ethylalkyltin standards were synthesized and isolated as previously reported[11] using a 50- rather than a 100-fold excess (molar basis) of Grignard reagent. Ottawa city tap-water was collected and used for all extraction studies.

Statistical method

The SAS™ procedure GLM was used to perform an analysis of variance (ANOVA) to examine the effect of parent pipe source on leachable organotin levels. The ANOVA model used daughter pipes (i.e. adjacent pipe sections) nested within the parent pipe as the source of error for performing the ANOVA *F*-test.

Instrumentation

Details of the gas chromatograph (GS)–atomic absorption spectrometer (AAS) used in this study have been previously described.[12,13] For this study, the GC was fitted with a 1.8 m × 6 mm o.d., 2 mm i.d., glass column packed with 3% OV-101 on Chromosorb 100/120 WHP. Operating conditions were: carrier gas, He, 30 ml min^{-1}; injector temperature, 225 °C; transfer line temperature, 250 °C; column temperature program, 50 °C (30 s hold) ramped to 320 °C (30 s hold) at 25 °C min^{-1}. AAS operating conditions were: wavelength, 224.6 nm; bandpass, 0.5 nm; Hamamatsu tin hollow-cathode lamp current, 10 mA. The quartz furnace was operated at 750 °C with a hydrogen–air flow rate of 26.4 and 22.6 sccm (standard cubic centimeters per minute), respectively, and a 2.0 sccm hydrogen make-up gas flow rate.

A Varian Vista 6000 GC coupled to a VG 7070EQ mass spectrometer was used for mass spectrometric (MS) analysis. The system was operated in the electron impact mode (40 eV) at a mass resolution of 1000. GC operating conditions were: DB-5 capillary column (15 m × 0.25 mm i.d., J&W Scientific, Folsom, CA, USA); carrier gas, He (55.2 kPa); injector temperature programmed from 80 to 250 °C at 40 °C min^{-1}; column temperature program, 70 °C (2 min hold) followed by a 5 °C min^{-1} ramp rate to 90 °C, then a 15 °C min^{-1} ramp rate to 280 °C. Selected monitored ion masses were: *m/z* 233.0502, 235.0509 for $BuEt_3Sn$ and Bu_2Et_2Sn, 289.1129, 291.1135 for $OcEt_3Sn$ and Oc_2Et_2Sn.

Total tin was determined with a VG PlasmaQuad II ICP–MS at the most abundant Sn mass (120 a.m.u.). The system was equipped with a V-groove nebulizer fitted to a VG-supplied Scott-type refrigerated spray chamber. Data were collected using a scanning mode. System operating conditions are given in Table 1.

CPVC tubing

CPVC pipe lengths (3.05 m × 1.27 cm o.d., 1.18 cm i.d.) were purchased at a local hardware outlet and cut into 1 m lengths with a tubing cutter. Interior debris was removed by briefly attaching the pipe sample to a vacuum source. Each 1 m pipe sample was sealed at one end with

Table 1 ICP–MS operating conditions

Forward power	1350 W
Reflected power	0–2 W
Sample uptake flow rate	0.9 ml/min^{-1}
Nebulizer flow rate	0.94 l/min^{-1}
Cooling flow rate	14 l/min^{-1}
Auxiliary flow rate	0.9 l min^{-1}
Spray chamber temperature	5 °C
Mass monitored	120 a.m.u.
Dwell time	0.32 ms

Table 2 Mean recoveries of organotin compounds from tap-water

Analyte	Sample (g)	Spiking level (ng g^{-1})	Mean recovery ± SD[a] (%)
$MeSnCl_3$	10	11.3	92 ± 4
		56.7	91 ± 2
	50	11.3	84 ± 4
		56.7	84 ± 4
Me_2SnBr_2	10	13.8	98 ± 3
		69.2	102 ± 1
	50	13.8	97 ± 2
		69.2	102 ± 2
$BuSnCl_3$	10	10.2	93 ± 5
		51.0	97 ± 2
	50	10.2	97 ± 2
		51.0	92 ± 2
Bu_2SnBr_2	10	14.8	89 ± 2
		74.2	92 ± 2
	50	14.8	86 ± 1
		74.2	90 ± 1
$OcSnCl_3$	10	10.9	91 ± 11
		54.6	94 ± 1
	50	10.9	96 ± 7
		54.6	87 ± 2
Oc_2SnCl_2	10	14.4	84 ± 3
		72.2	94 ± 2
	50	14.4	91 ± 1
		72.2	87 ± 2

[a] $n = 4$.

a CPVC end cap (attached with CPVC solvent cement) and threaded at the other end to accept a Teflon-lined cap. The pipe lateral surface area to volume ratio was 3.4:1.

Experimental studies

Two types of extraction studies were each conducted at 24 and 65 °C.

Single static extraction

Randomly selected CPVC tube samples were filled with tap-water and sampled after extraction times ranging from 1 h to 28 days. Water was analysed from three CPVC tubes for each extraction time interval.

Repetitive extraction

Two adjacent 1 m lengths of CPVC tube were selected from two different 3.05 m parent pipes. Each of these four pipe samples was emptied and filled with tap-water repetitively at 24 h intervals. The water samples were collected and analysed at 1, 2, 5, 10, 15 and 20 extraction cycles.

Analytical methods

Total tin

Samples and tin standards were made up to 10% (v/v) HCl. Rhenium (final concentration 100 ng ml^{-1}) was added as an internal standard.

Organotin

A tap-water sample (30 g) was filtered through 6 mm diameter Whatman 114 paper held in an empty SPE assembly (Fisher Scientific, cat. no. 11–186–47). Tropolone (12 mg dissolved in 2.0 ml 30% $MeOH/H_2O$) and 2.0 ml of 1.0 M sodium citrate buffer were added. The sample pH was adjusted to 6.7 with 0.5 M HNO_3 and the sample allowed to stand for at least 30 min in the dark. C_{PH} (1 ml/100 mg) SPE columns (Bond Elute, Varian Associates) were preconditioned with 2 ml MeOH and then 4 ml deionized water. The samples were passed through at a flow rate of 5 ml min^{-1} and the column then rinsed with 4 ml of deionized water. The organotins were eluted from the column with 2 + 5 ml portions of 0.1% (v/v) HCl/tetrahydrofuran (THF). The pooled eluates were rotary-tumbled (25 rpm) with 100 mg of $NaHCO_3$ for 5 min and then vortexed for 30 s after adding 100 mg anhydrous Na_2SO_4. Each eluate was transferred to a pre-calibrated 10 ml screw-cap centrifuge tube with two THF washes (1 ml each) and, while being heated in a 45 °C water bath, reduced to a volume of 1 ml under a nitrogen stream; this was repeated after the addition of 5 ml THF and then 5 ml hexane. Ph_3SnCl was added as an internal standard. The samples were then derivatized as described below.

Derivatization

THF (1.0 ml) and 0.5 ml of ethylmagnesium chloride (2.0 M in THF) were added to the sample. The tube was capped under nitrogen and then tumbled at 25 rpm for 10 min. While cooling on ice, 0.9 ml iso-octane was added to each sample and then vortexed gently. Prechilled nitric acid (0.5 M) was slowly added up to a total sample of 10 ml. The sample was then tumbled (25 rpm, 5 min). After centrifugation (2500 rpm, 2 min) the aqueous layer was discarded. The sample volume was again made up to 10 ml with deionized water and the wash repeated. After removing the aqueous layer, the sample volume was adjusted to 2.0 ml with iso-octane. Approximately 30 mg each of sodium hydrogen carbonate and anhydrous sodium sulphate were added, the sample vortexed momentarily, centrifuged and then stored in an autosampler vial.

Quantification

Quantification was by comparison with external ethylbutyltin and ethyloctyltin standards by GC–AAS. A 7.5 μl sample volume was injected by autosampler. Sample blanks were run concurrently with each set of leachate samples. Analyte limits of detection (LOD) ranged from 4.4 to 5.3 pg Sn and method detection limits (MDL) varied from 44 to 47 pg Sn g^{-1} (67–129 pg ionic alkyltin g^{-1}). Details regarding the LOD calculations have been reported elsewhere.[13]

Recovery experiments

Tap-water samples (10 or 50 ml volume) were spiked at two levels (10–14.4 and 51–74 ng alkyltin g^{-1}) with a mixture containing $MeSnCl_3$, Me_2SnBr_2, $BuSnCl_3$, Bu_2SnBr_2, $OcSnCl_3$ and Oc_2SnCl_2. Ph_3SnCl was added as an internal standard just prior to derivatization. Recoveries were determined by comparison with ethylated standards prepared from the spiking solution(s).

RESULTS AND DISCUSSION

Method

Organotin recoveries from tap-water averaged 92% (Table 2) with neither sample weight nor analyte level appearing to have any appreciable effect on the recoveries. Preliminary work sug-

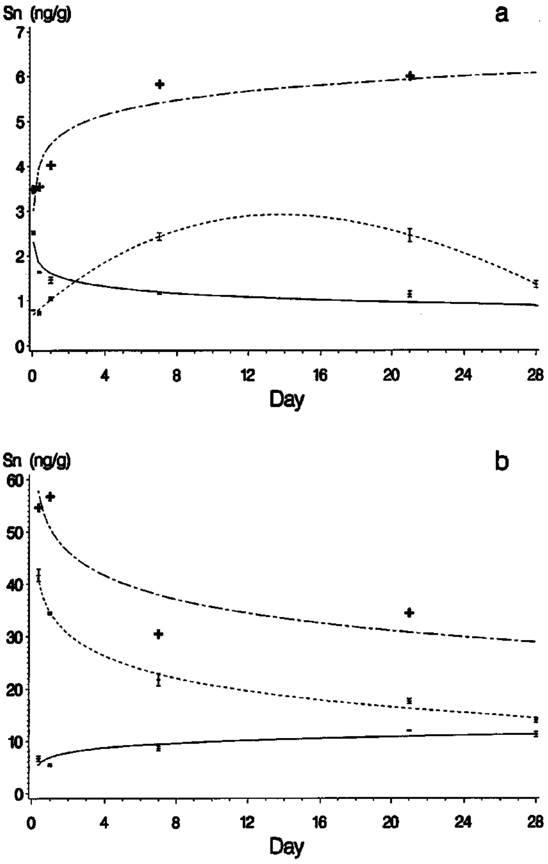

Figure 1 The levels of (——) monobutyltin, (---) dibutyltin, and (–––-) total tin in tap-water after a single static extraction at (a) 24 °C and (b) 65 °C over time. Error bars on monobutyltin and dibutyltin indicate ±SD from triplicate analyses. The trends in (a) for monobutyltin, dibutyltin and total tin are described respectively by the fitted models: $y=1.61–0.219 \ln x$, $y=0.676+0.356x-0.016x^2+0.000156x^3$ and $y=4.49+0.466 \ln x$. The fitted models in (b) for monobutyltin, dibutyltin and total tin levels are respectively: $y=6.85+1.33 \ln x$, $y=34.62-6.04 \ln x$ and $y=50.66-6.55 \ln x$.

Table 3 Monobutyltin (MBT), dibutyltin (DBT) and total tin levels[a] (ng Sn g^{-1}) in tap-water from CPVC pipe leached repetitively at 24 °C

Extraction	Tube A1		Tube A2			Tube B1		Tube B2	
cycle	MBT	DBT	MBT	DBT	Total Sn	MBT	DBT	MBT	DBT
1	2.5	4.5	2.3	5.9	7.9	2.7	3.7	1.2	1.9
2	1.1	2.7	0.9	3.1	5.3	1.0	2.5	0.7	1.8
5	0.5	1.7	0.5	1.7	3.3	0.5	1.2	0.4	1.0
10	0.4	0.8	0.4	1.0	1.0	0.4	0.7	0.3	0.7
15	0.3	0.7	0.3	1.0		0.3	0.7	0.3	0.7
20	0.4	0.7	0.3	0.8	1.5	0.2	0.5	0.2	0.6

[a] Uncorrected for recovery.

gested that the method could be extended to a 100 g sample but sufficient sensitivity had already been achieved with the tested 10–50 g sample weight range. Initial studies with disposable filter units indicated that butyltin and octyltin recoveries were suppressed when the sample was filtered through nylon, hydrophilic polypropylene, Supor™, polytetrafluoroethylene (PTFE) or glass membranes; methyltin recoveries were unaffected. Attempts to extract the retained organotins with aqueous solutions were unsuccessful. Although organic solvents could recover some of the retained organotins, this approach would not have been suitable as organotins would probably be released from any CPVC particulates present on the filter membrane. Whatman 114 paper was selected as none of the analytes was retained.

Tropolone was added to the sample prior to extraction to enhance the retention of monomethyltin, dimethyltin and monobutyltin on the C_{PH} sorbent. The polar, acidic eluant selected (0.1% (v/v) HCl/THF) was necessary to ensure a complete, rapid release of all the organotins from the sorbent.

Single static extraction study

Appreciable levels of monobutyltin and dibutyltin were released into the tap-water from the CPVC (Fig. 1a, b). At 24 °C, both monobutyltin and the total tin levels changed rapidly and then began to plateau towards the end of the exposure period (Fig. 1a). Total tin levels increased to 6 ng g^{-1} while monobutyltin levels dropped from an average of 2.5 ng Sn g^{-1} to 0.9 ng Sn g^{-1} over the extraction time. Initial changes in dibutyltin levels were not as rapid as for monobutyltin or total Sn levels. Dibutyltin levels reached an average of 2.4 ng Sn g^{-1} and decreased towards the end of the study rather than reaching a plateau. The levels of total and organic tin released into the tap-water increased considerably when the CPVC pipe was heated to 65 °C, a temperature typical of hot-water delivery systems (Fig. 1b). In addition, the trends of

Table 4 Monobutyltin (MBT), dibutyltin (DBT) and total tin levels[a] (ng Sn g^{-1}) in tap water from CPVC pipe leached repetitively at 65 °C

Extraction	Tube C1		Tube C2			Tube D1		Tube D2	
cycle	MBT	DBT	MBT	DBT	Total Sn	MBT	DBT	MBT	DBT
1	6.8	35.2	5.5	31.2	49.5	10.0	72.4	13.4	100.4
2	3.8	23.8	3.6	21.0	20.0	4.8	38.8	6.4	53.2
5	1.3	6.4	1.1	5.4	9.4	1.8	12.2	2.0	13.2
10	0.7	2.8	0.6	2.2	3.7	1.2	6.9	1.1	6.3
15	0.7	3.3	0.5	2.2	5.3	1.0	6.1	0.9	5.1
20	0.4	2.2	0.3	1.3	1.6	0.6	3.7	0.4	2.8

[a] Uncorrected for recovery.

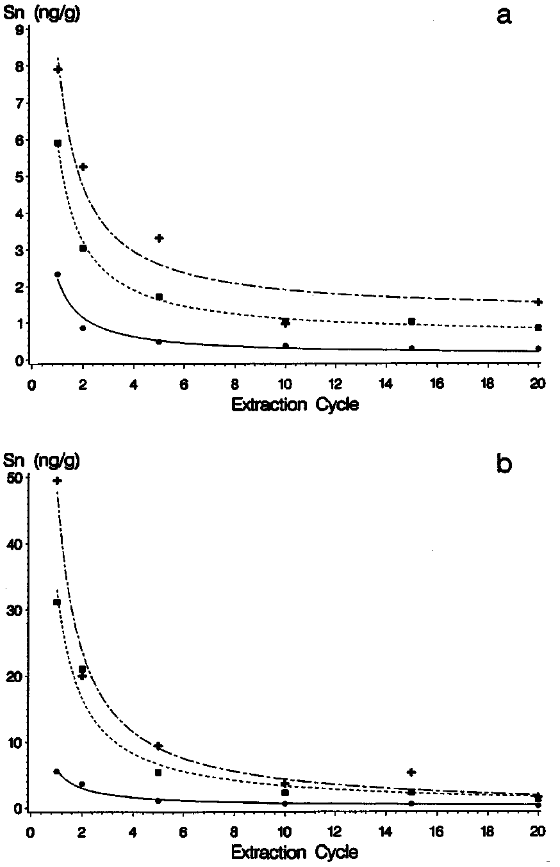

Figure 2 The effect of repetitive extraction on (●) monobutyltin, (■) dibutyltin and (+) total tin levels in tap-water at (a) 24 °C and (b) 65 °C. The trends in (a) for monobutyltin, dibutyltin and total tin levels are described respectively by the fitted models: $y = 0.0946 + 2.11\ x$, $y = 0.575 + 5.27\ x$ and $y = 1.19 + 7.03\ x$. The fitted models in (b) for monobutyltin, dibutyltin and total tin levels are respectively: $y = 0.120 + 5.66/x$, $y = -0.0116 + 33.06/x$ and $y = -0.544 + 48.33/x$.

monobutyltin, dibutyltin and total tin levels changed from those found at 24 °C. Total tin levels dropped (initially rapidly) from 54.7 ng g^{-1} to 34.3 ng g^{-1}. Similarly, dibutyltin levels dropped from 41.7 ng Sn g^{-1} to 14 ng Sn g^{-1} over the exposure period. Monobutyltin levels, however increased from 6.7 ng Sn g^{-1} to 11.3 ng Sn g^{-1} (Fig. 1b).

The observed levels of total tin, monobutyltin and dibutyltin probably result from a combination of several factors: (a) leaching rates of inorganic tin, monobutyltin and dibutyltin from the CPVC material, (b) adsorption processes between the CPVC surface and the analytes, and (c) degradation of dibutyltin to monobutyltin and of monobutyltin to inorganic tin. The decreasing changes to monobutyltin and total tin levels over time suggest that leaching and adsorption processes were approaching an equilibrium. However, the continuous decrease in dibutyltin levels in pipe heated to 65 °C coincided with an increase in monobutyltin levels, suggesting that some of the dibutyltin was degraded to monobutyltin. At 24 °C, monobutyltin levels remained relatively stable while dibutyltin levels dropped during the last seven days of the extraction period, suggesting adsorption to the CPVC substrate. Dibutyltin has been shown to be more adsorptive than monobutyltin or tributyltin in storage experiments.[14] The observed trends are similar to those reported by Quevauviller *et al.*[7] although the butyltin levels are up to 40 times greater; this would be expected as one of our leaching temperatures (65 °C) was higher and more organotin stabilizers are present in CPVC than in PVC pipe.[9]

Repetitive extraction study

Initial levels of monobutyltin, dibutyltin and total tin in tap-water extracts from the repetitive samples were comparable or even higher (Tables 3 and 4) than the static extraction samples. Dibutyltin levels reached 100.4 ng Sn g^{-1} at 65 °C and 5.9 ng Sn g^{-1} at 24 °C. Monobutyltin levels were lower, not exceeding 13.4 ng Sn g^{-1} at 65 °C and 2.7 ng Sn g^{-1} at 24 °C. Organic and total tin levels dropped rapidly during the first five days as the CPVC tubes were extracted repetitively at 24 h intervals (Tables 3, 4) and then continued to decrease at a much slower rate. The trend shown for CPVC pipe lengths A2 and C2 in Fig. 2(a, b) is typical for the other samples. Since measurable levels of monobutyl and dibutyltin continued to leach into tap-water even after 20 extraction cycles (Tables 3, 4) it is likely that new CPVC water distribution systems would contaminate the supplied water with organotins for some time after installation. PVC and CPVC plumbing installations may, therefore, be a significant source of the monobutyltin and dibutyltin found in municipal waste water.[15,16]

GC–MS analysis of tap-water samples from the extraction studies (Fig. 3) confirmed the presence of monobutyltin [$BuEt_3Sn$ (*m/z* 235 [$^{120}M - C_2H_5{}^+$)], dibutyltin [Bu_2Et_2Sn (*m/z* 235 [$^{120}M - C_4H_9]^+$)] and also low levels of mono-octyltin [$OcEt_3Sn$ (*m/z* 291 [$^{120}M - C_2H_5]^+$)] not found by GC–AAS.

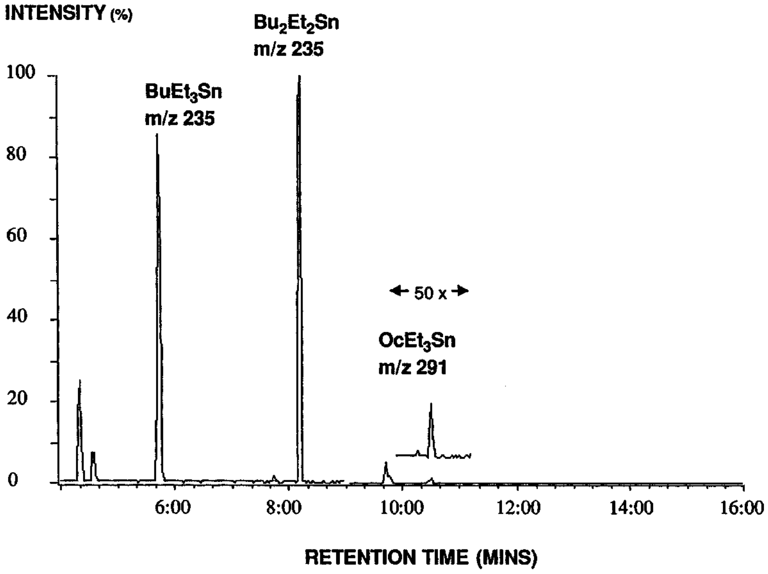

Figure 3 GC–MS confirmation of a tap-water sample containing monobutyltin {as $BuEt_3Sn$ (*m/z* 235 $[^{120}M - C_2H_5]^+$)}, dibutyltin {as Bu_2Et_2Sn [*m/z* 235 {$^{120}M - C_4H_9]^+$)} and monooctyltin {as $OcEt_3Sn$ (*m/z* 291 $[^{120}M - C_2H_5]^+$)}.

An analysis of variance to examine the effect of parent pipe source (Table 5) showed that the four pipe samples (originating from two parent pipes) in the 24 °C repetitive study released similar amounts of monobutyltin and dibutyltin (excluding day 5). On day 5, dibutyltin levels were significantly greater ($P = 0.02$) from tubes A1 and A2 than from tubes B1 and B2. However, one of the parent pipes (sampled as tubes D1 and D2) selected for the 65 °C repetitive study consistently released significantly ($0.01 \leqslant P \leqslant 0.07$) higher levels of monobutyltin and dibutyltin than the other parent pipe (sampled as tubes C1 and C2). The extractable levels of organotin present in the CPVC pipe can, therefore, vary considerably from one parent pipe to the next when compared to within parent pipe variability.

Table 5 Analysis of variance for effect of parent pipe on leachable butyltin levels

Temperature (°C)	Extraction cycle	Effect of parent pipe, P[a]	
		Monobutyltin	Dibutyltin
24	1	>0.1	>0.1
24	2	>0.1	>0.1
24	5	>0.1	0.02
24	10	>0.1	>0.1
24	15	>0.1	>0.1
24	20	>0.1	0.09
65	1	0.07	0.03
65	2	>0.1	0.05
65	5	0.06	0.02
65	10	0.03	0.01
65	15	0.07	0.07
65	20	>0.1	>0.1

[a] Probability.

CONCLUSIONS

Monobutyltin and dibutyltin were quickly leached by tap-water from CPVC pipe designed for potable water delivery. Levels of extracted organotins were increased by heating (65 °C) the tap-water. Repetitive extraction experiments show that organotin levels initially decrease rapidly and then much more slowly, suggesting that long-term leaching of organotins from new CPVC water delivery systems is probable. Leachable organotin levels probably vary considerably among manufactured CPVC pipes. Long-term studies, of new CPVC plumbing in residential housing, are desirable to further examine the leaching of organotins as the CPVC ages.

Acknowledgements The authors thank R. Dabeka and A. MacKenzie for determination of total tin, D. Weber for GC–MS analyses and S. Hayward for help with the statistical analysis.

REFERENCES

1. M. S. Reisch, *Chem. Eng. News* 30 (22 May 1995).
2. M. S. Reisch, *Chem. Eng. News* 20 (20 May 1994).
3. R. J. Maguire, Water Pollut. Res. J. Canada **26**, 243 (1991).
4. N. J. Snoeij, A. H. Pennicks and W. Seinen, *Environ. Res.* **44** (1987).
5. A. H. Pennicks, *Food Addit. Contam.* **10**, 335 (1993).
6. W. Wu, R. S. Roberts, Y.-C. Chung, W. R. Ernst and S. C. Havlicek, *Arch. Environ. Contam. Toxicol.* **18**, 839 (1989).
7. Ph. Quevauviller, A. Bruchet and O. F. X. Donard, *Appl. Organomet. Chem.* **5**, 125 (1991).
8. J. C. Meranger, *J. Assoc. Off. Anal. Chem.* **58**, 1143 (1975).
9. D. S. Forsyth, R. Dabeka, W. F. Sun and K. Dalglish, *Food Addit. Contam.* **10**, 531 (1993).
10. D. S. Forsyth and C. Cleroux, *Talanta* 38, 951 (1991).
11. D. S. Forsyth, D. Weber and C. Cleroux, *Food Addit. Contam.* **9**, 161 (1992).
12. D. S. Forsyth, *Sci. Total Environ.* **89**, 299 (1989).
13. D. S. Forsyth and S. Hayward, *Fresenius J. Anal. Chem.* **351**, 403 (1995).
14. Ph. Quevauviller and O. F. X. Donard, *Fresenius J. Anal. Chem.* **339**, 6 (1991).
15. K. Fent, M. D. Muller, *Environ. Sci. Technol.* **25**, 489 (1991).
16. Y. K. Chau, S. Zhang and R. J. Maguire *Sci. Total Environ.* **121**, 271 (1992).