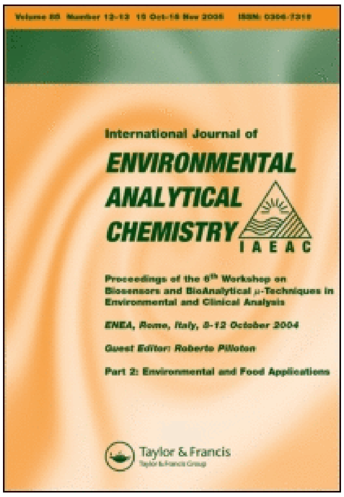

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ANALYSIS OF POLYCHLORODIBENZO-P-DIOXINS IN RAW AND TREATED WATERS. PART 2: OPTIMIZATION OF AN XAD-2 RESIN COLUMN METHODOLOGY

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Several operating parameters were evaluated to assess the efficiency of an XAD-2 resin column for use in an automated sampling unit to be developed for the analysis of polychlorodibenzo-p-dioxins (PCDDs) in water. Direct standard addition of mass labelled congeners onto the column were used to evaluate the capacity of the resin for PCDDs. Ratios of resin volume and bed volume flow rates were systematically varied. Flow rates of 3 to 24 bed volumes per minute were used without observable breakthrough. Column behaviour was evaluated using the continuous standard addition technique to determine the optimum flow rate for minimal breakthrough, which was found to be 3 bed volume/min. PCDD recoveries were quantitative (>75%) except for octachlorodibenzodioxin where lower recoveries (approximately 40%) were due to losses in the cleanup procedure and not to the sampling. Recoveries of the five congeners used in this study confirm that XAD-2 resin exhibits an extracting capability of organic contaminants from water equal to that of liquid-liquid extraction and allows both a much larger sample size and easier sampling.

KEY WORDS: PCDD, dioxin, XAD-2 resin, water analysis.

INTRODUCTION

In the previous paper,[1] optimization of a liquid-liquid extraction procedure was described for the analysis of polychlorodibenzo-p-dioxin (PCDD) contaminants in large volume grab samples of water. However, for ultra-trace (pg/L) analysis the essential difficulty of transporting large volumes of water from collection sites to the analytical laboratory remains. As well, liquid-liquid extraction of such samples is time consuming and labour intensive. One way of avoiding these problems is by performing the liquid-liquid extraction at the sampling location. A large volume

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aqueous-phase liquid extractor (APLE)[2] was designed for this purpose and recently tested for the on-site extraction of 200 L samples for determining PCDDs. While this instrument provides an improvement over grab sampling, it is cumbersome and difficult to transport. Other attempts have been made to avoid grab sampling such as the development of the continuous liquid-liquid extractors (CLLE).[3,4] The drawback of liquid-liquid extraction devices is that solvent losses can occur when extracting large sample volumes since many solvents such as DCM are significantly soluble in water. The discharge of extracted water can therefore contaminate the environment.

An alternative approach for an on-site preconcentration method is based on removal of organics from water by contact with hydrophobic solid sorbents such as macroreticular resin, packed in a column through which the water sample is passed. One such system has been developed by Seakem Oceanography[5] using XAD-2 resin. A similar type of sampler utilizing XAD-7 and Sephadex QAE[3] has been developed by Water Quality Branch, Pacific and Yukon Region. Adsorbent methodology has been used successfully for the isolation of PCDD congeners down to the 1 pg/L level[6,7] and for many other organochlorine,[8–10] organophosphate[11] and polyaromatic hydrocarbon compounds.[12,13] The advantages of this technique are the elimination of potential contamination problems posed by on-site liquid-liquid extraction and the adaptation to a compact and convenient instrumentation for the preconcentration of treated or raw water samples. Based on this approach, a project was undertaken to establish suitable parameters for the use of an XAD-2 resin column, in an automated sampling unit, for the preconcentration and measurement of PCDD contaminants in Ontario waters.

EXPERIMENTAL

Materials

Materials and solvents were obtained and glassware cleaned as previously described.[1] The evaluation study was carried out using tetra to octa labelled ^{13}C-dioxins as representative congeners. Standard solutions consisting of ^{13}C-PCDD were prepared as previously described.[1]

The Amberlite XAD-2 resin (Rohm and Haas Company) required cleaning prior to use in ultratrace organic analysis. The resin (454 g) was covered with tap water in a 1.5 L beaker and stirred gently. After allowing the resin to settle for approximately 5 minutes, the supernatant water was decanted to remove fines. This process was repeated until the supernatant was clear. The resin was transferred to a large scintered glass filter funnel and the water was removed by aspiration. It was then transferred to a large beaker, covered with acetone and sonicated for 5 minutes. The filtering and sonication cycle was repeated once more with acetone and twice each with hexane, methylene chloride and acetone in this sequence. Each time the solvent was added, the resin was stirred to dislodge trapped air and allowed to soak for 10 minutes. The solvent was removed by aspiration and the resin was stored under acetone in a clean brown bottle with a Teflon-lined cap.

Columns were built as described by LeBel *et al.*[11] with tube lengths of approximately 18 cm and 9 cm respectively. The dimensions permitted resin bed-volumes of approximately 22 mL and 11 mL, representing one half and one quarter the size of column bed-volumes evaluated previously.[6] The pump used was a liquid chromatograph pump, Eldex Model B-100-S. Columns were packed with a measured amount of clean XAD resin and prepared for sampling as described by LeBel *et al.*[11] The resin was washed by passing 250 mL of acetone and 1 L of purified water through the column.

Methods

All runs were performed in triplicate together with 1 blank column. Each set of experiments was carried out with two columns in series to detect potential breakthrough of the analyte.

Standard Addition on Column

An aliquot containing 2.5 ng ^{13}C-1,2,3,4-TCDD and 5.0 ng each of ^{13}C-1,2,3,7,8-PnCDD, ^{13}C-1,2,3,6,7,8-HxCDD, ^{13}C-1,2,3,4,6,7,8-HpCDD and ^{13}C-OCDD was added to the top of the resin in the column. The columns were flushed with 500 mL of purified water and were then inverted and connected to the tap water line.[6,14] Flow rates were set using the fine-metering valves. For each run, 200 L Ottawa tap water was passed through each column to give an equivalent standard addition level of 12.5 pg TCDD/L or 25 pg/L of the other congeners.

Standard Addition to Sample Stream

Apparatus

The columns were assembled as previously described.[6,14] A high pressure LC pump was connected by a tee junction between the blank column and those to be spiked. In the initial assembly a 1 m length of 6 mm copper tubing ran between the LC pump and the columns to provide mixing of the standard addition solution with the tap water. A 0.75 m length of Teflon tubing was used to siphon the standard addition solution from the reservoir into the LC pump. In subsequent runs, the mixing line was replaced by a set of tee and elbow joints to provide a more tortuous mixing path. Also, the portion of Teflon line immersed in the standard addition solution was replaced by a 25 cm piece of 3.2 mm stainless steel tubing to minimize adsorption of standard additives on these lines.

A column bed volume of 22 ml was used for all experiments while other parameters such as flow rates and standard addition ratios were varied.

Standard Addition Solutions

The standard addition solutions were prepared to provide a total load of 5 ng of each congener over the sampling period. The sampling time, depending on flow rate used, was varied to provide a sample size of 200 L, giving a concentration of 25 pg/L of each congener. The solvent used for the standard addition solutions varied from 25% methanol in purified water to 100% methanol. The standard addition solution was contained in a clear glass Winchester (or amber 4 L solvent) bottle reservoir with a Teflon-lined cap previously rinsed well with toluene, acetone, methylene chloride and methanol.

Extraction and Elution Procedures

As previously described.[11,14]

Isolation of Extracted PCDDs

The isolation method has been previously described.[1,6] To keep errors at a minimum the internal standards were added just prior to analysis of isolated samples to correct for possible variation of detector response as well as for variations in extract and injection volumes.

Instrumental Analysis

Gas chromatography

The isolated samples were analyzed by capillary GC/ECD on a Varian GC as described previously.[1]

RESULTS

Standard Addition to Column

The results are presented in Table 1. Samples were run in quadruplicate for the 140 mL/min experiments and in triplicate for the 280 mL/min experiments. No breakthrough was observed in the backup column. The standard deviation represents mostly procedure errors since reading errors were small in comparison to the observed deviation.

Optimization of Standard Addition to Sample Stream

The conditions for the optimization experiments are reported in Table 2. Seven

Table 1 % recovery of ^{13}C-PCDD standard addition on column from 200 L treated water using XAD-2 column at 140 and 280 mL/min flow rates

PCDD Congener	*11 mL^{a} XAD-2 resin*		*22 mL^{a} XAD-2 resin*	
	140 mL/min	*280 mL/min*	*140 mL/min*	*280 mL/min*
n	4	3	4	3
TCDD	52(3)^{b}	126(44)	86(17)	79(17)
PnCDD	102(11)	131(4)	97(19)	103(5)
HxCDD	98(10)	122(4)	92(14)	88(8)
HpCDD	92(10)	114(3)	90(15)	96(3)
OCDD	53(7)	61(3)	51(8)	44(5)

n = number of replicates

[a] Resin was measured in acetone.

[b] Mean % recovery, values in brackets are standard deviations.

Each column was directly loaded with 2.5 ng of TCDD and 5.0 ng of PnCDD, HxCDD, HpCDD and OCDD.

Table 2 Parameters for standard addition to sample stream experiments

Expt (no.)	*Flow Rate (mL/min)*	*Samp Time (hr)*	*Pump Rate (mL/min)*	*Std addition Mix (% MeOH/H$_2$O)*	*% MeOH in Effluent*
1	140	24	2.0	25	0.12
2	280	12	4.0	25	0.12
3	140	24	1.0	50	0.12
4	140	24	2.0	100	0.48
5	70	48	0.5	100	0.24
6	140	24	0.5	100	0.12
7	280	12	1.0	100	0.12

Amount of analyte loaded onto the column was 5 ng or 25 pg/L of each analyte.

The volume of water passed through the columns (22 mL resin) in each experiment was 200 L.

experiments were performed to maximize recovery of standards from the sample stream and prevent breakthrough out of the adsorption column.

In the continuous standard addition technique, the delivery to the resin of a uniformly mixed standard addition solution of known concentration presented some difficulties. An earlier evaluation[6] indicated incomplete delivery of PCDD to the resin from a 100% aqueous standard addition solution. It was suspected that PCDDs could be adsorbing on the glass bottle or the Teflon line since they are highly hydrophobic and the slow pump flow rate of 1.0 mL/min provides a lengthy contact time. Therefore, in the first experiment the standard addition solution in the reservoir was prepared in 25% methanol to increase the solubility of the PCDD in the standard addition solution while keeping the concentration of methanol in the final water stream at a minimum. In spite of this change, the results in Table 3 show low recoveries for all congeners.

The second experiment was carried out in an attempt to improve on the low recoveries from the first experiment by modifying the standard addition delivery apparatus. The flow rate and pump rate were doubled to allow a shorter sampling

Table 3 Percent recovery of ^{13}C-PCDD standard addition to sample stream in 25% methanol from 200 L tap water using XAD-2 column[a]

PCDD Congener	*Test column*[b]	*Backup column*[c]
TCDD	16(9)[d]	ND[e]
PnCDD	34(18)	ND
HxCDD	5(1)	ND
HpCDD	7(2)	0.9
OCDD	5(1)	0.7

[a] For flow conditions see Table 2, Experiment 1.

[b] Test column = primary column for adsorption of analyte.

[c] Backup column = secondary column for adsorption of analyte.

[d] Mean % recovery, values in brackets are standard deviations.

[e] Not detected; limited of detection = 0.6%.

Table 4 % recovery of ^{13}C-PCDD standard addition to sample stream from 200 L tap water using XAD-2 column at various flow rates

PCDD Congener	*70 mL/min*		*140 mL/min*		*280 mL/min*	
	Test[a]	*Backup*[b]	*Test*	*Backup*	*Test*	*Backup*
n	*3*	*3*	*3*	*3*	*3*	*3*
TCDD	104(3)[c]	2(1)	87(14)	3(1)	76(5)	14(1)
PnCDD	50(18)[d]	2	53(4)[d]	5(1)	98(6)	14(4)
HxCDD	97(3)	2	89(1)	5(1)	78(1)	10(1)
HpCDD	78(2)	2	83(2)	4(1)	72(2)	8(1)
OCDD	36	1	39(4)	3(1)	37(6)	4(1)

Standard addition 25 pg/L, XAD column 22 mL bed volume

[a] Primary column for adsorption of analyte.

[b] Secondary column for adsorption of carryover analyte.

[c] Mean % recovery, values in brackets are standard deviations.

[d] ECD background interference just prior to congener, resulting in quantitative uncertainty.

period. The portion of teflon siphon line submerged in the standard addition solution was replaced by stainless steel tubing. Also, the mixing line between the entry of standard addition solution entry and the column was replaced by a series of tees to provide thorough mixing. The changes were adopted for all further evaluation runs, but the congener recoveries did not improve, indicating still incomplete delivery of the PCDDs to the columns.

The concentration of methanol in the standard addition solution was increased in the third experiment to 50% and no problems in the delivery of congeners were encountered. To ensure this behaviour, all other runs were made using 100% methanol standard addition solution. This gave a methanol concentration of 0.12 to 0.48% in the final water stream.

The fourth experiment was performed to observe whether increasing the methanol standard addition rate would cause increased breakthrough of dioxin standard to the back-up column. No difference was noted.

Three more experiments were undertaken to optimize flow rate for minimal PCDD breakthrough. These results are presented in Table 4. Reading errors were small and the observed variation is again attributed to procedure errors. A background interference was present, using ECD, just prior to the penta congener, resulting in quantitative uncertainty.

DISCUSSION

The applicability of XAD resin for the analysis of PCDD in water has been previously studied.[6] However, additional data on column size, sampling rate and standard addition procedures for field use were required to optimize the use of XAD resin columns in any potential automated sampling unit. A reduced column size was desirable in order to minimize the volume of the sampler for easier field use. Sampling rate and standard addition procedures had to be established in order to set parameters for minimal breakthrough.

Standard Addition on Column

To evaluate the adsorbent capacity of the columns, a series of runs were made using the technique of standard addition onto the column and employing various flow rates and column sizes. The results, given in Table 1, show comparable recoveries at the two flow rates (140 and 280 mL/min) used for the two column sizes. The flow rates correspond to 6 to 24 bed volumes per minute which are well above the rate of 3 bed volumes per minute used for PCDDs previously.[6] No PCDDs were found in any of the back-up columns which suggests that once PCDDs are adsorbed to the nonpolar resin surface they are not eluted by water.

Standard Addition to Sample Stream

The technique of standard addition continuously into the sample stream before the resin is more representative of sample collection in which dilute aqueous solutions of contaminants continually flow through the resin bed. Therefore, this standard addition technique was used for all further evaluation. The results from the optimization experiments, Table 4, show the effects of flow rate on the recovery of the PCDD congeners. The data show essentially quantitative recoveries (>75) for the PCDD except for OCDD where lower recoveries (approximately 40%) were expected due to losses in cleanup procedures.[1] The results indicate that significant breakthrough of congeners into the backup columns increases when using higher flow rates. Even though the standard deviation increases with the higher flow, a student's "t" test showed that there is a significant difference (95% confidence level) in breakthrough recovery values between the different flow rates for all congeners, except TCDD which shows minimal breakthrough from 70 through to 140 mL/min. This suggests that the optimum water flow through the column is

70 mL/min (3 bed-volume/min). Higher flow rates may be acceptable when using on-site standard addition onto the sample stream to correct recoveries.

CONCLUSION

An XAD-2 resin column can be used effectively to replace liquid-liquid extraction for PCDD analysis in water. Evaluation of parameters for its use in the design of an automated sampling unit indicates that the sampling rate is important for efficient adsorption. For the 22 mL resin bed-volume column, a flow rate of 3 bed volumes/minute is the most efficient rate with the least amount of breakthrough. However, the flow rate can be increased whenever some breakthrough, such as 10%, is deemed acceptable. The breakthrough can be corrected by an on-site standard addition to the stream by using appropriate internal standards. The detection limit can be improved by using longer sampling times and hence larger total collection volumes. A 100 L sample size can be obtained at 3 bed volumes/min for 24 hours or sampled for 48 hrs to obtain 200 L. Methanol is the preferred solvent if continuous standard addition to the stream is required in the field. The methanol does not affect analyte breakthrough for up to 0.5% methanol in the standardized water stream.

The addition of standards directly on the column prior to use does not entirely simulate actual continuous sampling. However, it may be used if it is undesirable to have standard addition in the field or if internal standards are required for quality assurance or quality control purposes.

Since the XAD-2 resin technique provides the assurance of acceptable accuracy and precision in preconcentration of PCDDs under continuous standard addition to the water stream, it becomes possible to exploit the much greater convenience and safety of liquid-solid extraction in the design of a field sampling unit. In comparison to field samplers using liquid-liquid extraction, a liquid-solid unit can be many times smaller and lighter, provide for valid duplicate samples in easily removed, self sealing columns and achieve preconcentration of 100 L samples in a few hours. Based on the recovery values for the experiments in this paper, there is no difference in either accuracy or precision between the liquid-liquid extraction described in an earlier paper[1] and the XAD-2 resin extraction method. This observation was achieved through the use of a student "t" test which compared the 20–25 pg/L PCDD standard recovery levels in the continuous standard addition XAD-2 resin experiment against those obtained from the liquid-liquid extraction experiments.

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