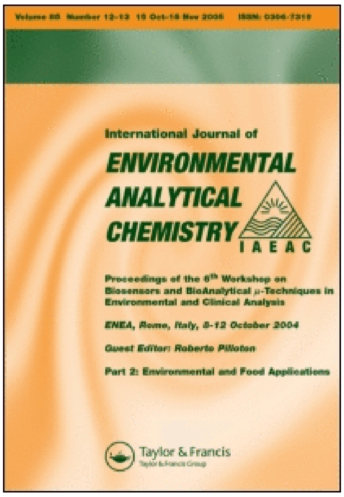

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Solid Phase Extraction of Polychlorodibenzodioxins and Polychlorodibenzofurans Dissolved in Particle-Free Water Containing Humic Substances

P. Bonifazi[a]; A. R. Mastrogiacomo[a]; E. Pierini[a]; F. Bruner[a]
[a] Istituto di Scienze Chimiche e Centro di Studio per la Chimica dell'Ambiente e le Tecnologie Strumentali Avanzate, Università degli Studi-Piazza Rinascimento, Urbino, Italy

To cite this Article Bonifazi, P. , Mastrogiacomo, A. R. , Pierini, E. and Bruner, F.(1994) 'Solid Phase Extraction of Polychlorodibenzodioxins and Polychlorodibenzofurans Dissolved in Particle-Free Water Containing Humic Substances', International Journal of Environmental Analytical Chemistry, 57: 1, 21 — 31

To link to this Article: DOI: 10.1080/03067319408033099

URL: http://dx.doi.org/10.1080/03067319408033099

Intern. J. Environ. Anal. Chem., Vol. 57, pp. 21-31
Reprints available directly from the publisher
Photocopying permitted by license only

SOLID PHASE EXTRACTION OF POLYCHLORODIBENZODIOXINS AND POLYCHLORODIBENZOFURANS DISSOLVED IN PARTICLE-FREE WATER CONTAINING HUMIC SUBSTANCES

P. BONIFAZI, A. R. MASTROGIACOMO, E. PIERINI
and F. BRUNER*

*Istituto di Scienze Chimiche e Centro di Studio per la Chimica dell'Ambiente e le Tecnologie Strumentali Avanzate, Università degli Studi—Piazza Rinascimento, 6
61029 Urbino, Italy*

(Received, 23 August 1993; in final form, 23 December 1993)

The effect of dissolved organic materials, such as humic acids, on the recovery of PCDDs and PCDFs from particle-free water is demonstrated. Experiments are carried out in a range of concentrations and using materials for water container that allow a correct evaluation of the binding properties of humic acids toward the compounds of interest. A method to destroy the humic acids prior to the preconcentration procedure is described, which allows to obtain good recovery of PCDDs and PCDFs from particle-free water. Examples of application to river water spiked with 1 ng/L of PCDDs and PCDFs are reported to show the applicability of the method described to real samples in the case of severe water pollution.

KEY WORDS: Humic substances, SPE, PCDDs, PCDFs.

INTRODUCTION

In the recent years, a growing interest has been shown by environmental researchers and analytical chemists about the capability of humic and fulvic acids to form various complexes with metal ions[1]. A noticeable difference in the solubility of several classes of organic compounds, such as polynuclear aromatic hydrocarbons[2], herbicides and pesticides[3-6] has been observed and this fact is usually attributed to binding effects that humic and fulvic acids show toward organic compounds, although well defined complexes have not been identified yet. An analogous behaviour has been observed by Servos *et al.* [7] for a particular PCDD, 1,3,6,8-TCDD, and this leads to the idea that also other compounds of the same class and of the analogous class of PCDFs will suffer the same effect.

The major consequence of binding occurring between organic compounds and humic and fulvic acids is in a strong enhancement of their water solubility in the presence of these substances. This fact should be seriously considered in the analytical procedure followed in the extraction and enrichment of these compounds from water. Also it should be remembered that the distribution coefficient between sediments (solid phase) and water is altered in favour of the latter when humic acids are dissolved in the liquid phase[7]. Among the various techniques used for enriching PCDDs and PCDFs from water, solid phase extraction has been successfully used for drinking and river water by Rappe *et al.*[8]. Due to the extremely low concentration of these compounds in these media (20–25 ng/L), samples of water as large as 100–200 L must be used in order to obtain the necessary amount of sample (0.2 pg) in the final injection for GC-MS determination.

At our best knowledge, a systematic approach to the analytical procedure using SPE for the determination of PCDDs and PCDFs in particle-free water in the presence of humic acids has not yet been performed. It should be noted that by "free" water we mean a sample of water which has been previously filtered to eliminate any suspended sediment or solid material being well aware of the fact that the major part, up to 90%[9–10] of the compounds of interest are adsorbed on the solid phase.

In this paper we report an analytical procedure that allows the SPE extraction of PCDDs and PCDFs from particle-free water in the presence of humic acids. Due to the limited sensitivity and resolution of our GC-MS system and to the necessity of spiking water with PCDDs and PCDFs, these experiments are limited to rather high values of concentration (1 ng/L).

We realise that for these reasons the present method has at the moment an applicability only to that range of concentrations, excluding in most cases drinking and river water. However, in a recent report Miller[11] states that in some rivers, higher concentrations of PCDDs such as 6.5 ng/L can be observed downstream some chemical plants.

Also, in the unlucky circumstance of an industrial accident, when the concentration range is higher, the method described can be applied. Also, an original method to destroy the humic acids is described which allows the use of SPE for the extraction procedure.

Preliminary experiments have been carried out to validate the analytical procedure and to eliminate possible adsorption of the compounds of interest on the container's walls when spiking with rather high concentrations of PCDDs and PCDFs.

EXPERIMENTAL

Materials and instrumentation

Six PCDDs and six PCDFs have been chosen for the experiments according to the fact that the most toxic compounds of this classes are those where chlorine atoms are present in the 2,3,7,8 positions[12]. These compounds have been obtained from Lab. Service Analytica, (Bologna, Italy). ^{13}C marked TCDD, used as an internal standard was obtained by CIL, Cambridge Isotope Laboratories, (Woburn, MA, USA). Solvents such as acetone, toluene, methanol, n-hexane and methylene chloride, of the pesticide grade have been obtained from

Janssen Chemicals, (Geel, Belgium). Potassium permanganate 0.2 M of the RPE grade, sulphuric acid 96% and hydrogen peroxide 30% were obtained from Farmitalia Carlo Erba (Milan, Italy).

LC_{18} silica, 30–70 μm, stock 211502 was obtained from Alltech Ass. (Deerfield, ILL, USA). This material has been pretreated with 10 mL methanol containing 10% concentrated HCl, then with 10 mL methanol, 10 mL toluene, 1 mL acetone and 1 mL H_2O according to a procedure previously described[13].

The empty polypropylene tubes (0.9 cm i.d., 6 cm 1.) with the PTFE frits (20 μm), stock 211104, were from Alltech.

Humic acids, as sodium salts, technical grade, stock 12.086.58, were obtained from Janssen. Alumina (basic), stock 417214, obtained from Carlo Erba (Milan, Italy) is activated at 300 °C for 2 hours immediately prior to use.

PTFE containers, 1 L, were made according our drawing by Sirtres s.r.l. (Muggiò, Milano). Connections to the SPE cartridges were also made of PTFE tubing. Mineral water from a mountain spring, used for the experiments, had the following characteristics:

- pH, at the spring: 7.8; total unvolatile mineral content: 72.5 mg/L.
- COD (Kubel method): 0.3 mg/L.

The river Metauro water, used after filtration with 0.22 μm polyvinylidene difluoride filters, GUMP 04700, (Millipore, Bedford, MA, USA), had a pH of 6.6 and a COD of 1.8 mg/L.

A HP 5890 gas chromatograph coupled with a HP 5970 quadrupole mass spectrometer is used. The GC, equipped with a split-splitless injector was used only in the splitless mode. A capillary column 60 m, 0.25 mm i.d. coated with SP-2331, 0.20 μm film thickness, was used. Temperature programme and other GC conditions were:

Carrier gas pressure: $2 kg/cm^2$. Initial gas velocity:24 cm/sec. Temp. programme: 2 min isoth. 200 °C then programmed 10°C/min to 270°C.

MS analysis was made in SIM according to the programme shown in Table 1.

Preliminary "blank experiments" with mineral water additioned of humic acids and river water could not show any interferences at the elution time and m/z of PCDDs and PCDFs. The same waters artificially polluted with PCDDs and PCDFs, (water concentration was 1 ppt), were analyzed after the proposed treatment with $KMnO_4$ and H_2O_2 monitoring two ions of the isotope cluster per compound to verify the correct isotope ratio.

After that, we decided to use one ion per compound in order to achieve a better sensitivity in the following experiments. The dwell times were chosen considering the peak widths (about 11 sec) to get a satisfactory number of points (15–20) per peak, according to the well accepted procedure for analytical mass spectrometry (see for example)[14].

Solutions and cartridges

From the original vials, where PCDDs and PCDFs are contained at a concentration of 10–50 μg/mL in *n*-nonane, a mother solution in acetone was prepared at a concentration 0.5 μg/mL

Table 1 SIM programme for the analysis of PCDDs and PCDFs.

Retention time (min.)	*m/z*	*Dwell time (msec.)*	*Compounds*
13	322	300	1) TCDD=2,3,7,8-tetrachlorodibenzo-p-dioxin
	334	"	i.s. $^{13}C_{12}$ TCDD=2,3,7,8-tetrachlorodibenzo-p-dioxin
15	306	300	2) TCDF=2,3,7,8-tetrachlorodibenzofuran
	340	"	3) PCDF=1,2,3,7,8-pentachlorodibenzofuran
17.44	354	600	4)PCDD=1,2,3,7,8-pentachlorodibenzo-p-dioxin
19	374	600	5) H_6CDF=1,2,3,6,7,8-hexachlorodibenzofuran
21.5	390	300	6)H_6CDD=1,2,3,6,7,8-hexachlorodibenzo-p-dioxin
		"	7) H_6CDD=1,2,3,7,8,9-hexachlorodibenzo-p-dioxin
24.5	410	600	8)H_7CDF=1,2,3,4,6,7,8-heptachlorodibenzofuran
	374		9) H_6CDF=1,2,3,7,8,9-hexachlorodibenzofuran
28	424	600	10)H_7CDD=1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin
35	444	300	11)OCDF=octachlorodibenzofuran
	460	"	12) OCDD=octachlorodibenzo-p-dioxin

of each compound. This solution was used to prepare the final spiking solutions with different concentrations, namely 10, 2 and 1 ng/mL. Spiking was made by adding to 1 L water 1 mL of the spiking solution chosen under stirring and subsequent sonication at 50 watts for 30′. Thus, the final solutions spiked had concentrations of 10, 2 and 1 ng/L, respectively. The humic acids (sodium salt) were dissolved in water in a concentration of 1 mg/mL. The solution was then centrifuged at 3000 rpm to separate the insoluble part of the technical grade product. Water was spiked with this solution to obtain a 10 mg/L concentration. The resulting COD value (Kubel) was 2.7 mg/L.

The C_{18} cartridge, 6 cm × 1.0 cm i.d. is packed with 600 mg of the adsorbent in the absence of humic acids and with 900 mg in the presence of these compounds. The material was treated before use as stated above.

For the adsorption procedure the water flow rate was about 20 mL/min. The desorption flow rate was 1 mL/min.

Recovery experiments without humic acids

A preanalytical procedure in the absence of humic acids has been followed. 1 L water was placed in a glass container and spiked with different concentrations of PCDDs and PCDFs. This was passed through the C_{18} cartridge, which was then extracted with 2 mL toluene. The solution obtained was evaporated to dryness and 50 μL of toluene containing ^{13}C TCDD at a concentration similar to the final concentration of the compounds of interest were added. This compound was used as an internal standard.

This solution was directly analyzed by GC-MS. The recoveries obtained with the various concentrations are reported in the left columns of Table 2.

Table 2 PCDDs and PCDFs recoveries from mineral water with different spiking concentrations using a glass container.

	10 ng/L				*2 ng/L*				*1 ng/L*			
	Cart.	*Glass cont.*	*Tot.*	*RSD*	*Cart.*	*Glass cont.*	*Tot.*	*RSD*	*Cart.*	*Glass cont*	*Tot.*	*RSD*
2,3,7,8-TCDD	69	27	96	17	108	10	116	10	104	nd	104	19
2,3,7,8-TCDF	51	25	76	15	111	0	111	12	87	nd	87	18
1,2,3,7,8-PCDF	51	37	88	21	71	12	83	12	82	nd	82	21
1,2,3,7,8-PCDD	48	41	89	20	68	14	82	15	95	nd	95	14
1,2,3,6,7,8-H_6CDF1	38	49	87	22	60	29	89	16	77	nd	77	16
1,2,3,6,7,8-H_6CDD1	34	61	95	17	64	31	95	9	81	nd	81	18
1,2,3,7,8,9-H_6CDD2	36	55	91	20	57	30	87	10	87	nd	87	20
1,2,3,4,6,7,8-H_7CDF	31	57	88	21	51	38	89	11	67	nd	67	24
1,2,3,7,8,9-H_6CDF2	36	51	87	23	72	31	103	14	79	nd	79	18
1,2,3,4,6,7,8-H_7CDD	28	64	92	17	54	44	98	14	66	nd	66	26
OCDD	27	70	97	15	54	56	110	16	64	nd	64	18

Then, the PTFE container was tested. The better results obtained are reported in Table 3. Therefore, PTFE was always used in the following experiments.

Before use, the PTFE container was cleaned with 10 mL acetone, 10 mL toluene and 10 mL acetone. These last ones were concentrated to about 0.1 mL under a slight N_2 flow and injected in the mass spectrometer to test the container blank, wich resulted free of impurities. The container was then rinsed with some mineral water.

ANALYTICAL PROCEDURE WITH HUMIC ACID

Sample preparation

1 L of spring water is placed in the PTFE container and added with 10 mL water solution

Table 3 PCDDs and PCDFs recoveries from mineral water with different spiking concentrations using a PTFE container.

	10 ng/L				*2 ng/L*				*1 ng/L*			
	Cart.	*PTFE cont.*	*Tot.*	*RSD*	*Cart.*	*PTFE cont.*	*Tot.*	*RSD*	*Cart.*	*PTFE cont.*	*Tot.*	*RSD*
2,3,7,8-TCDD	63	22	85	7	95	nd	95	18	101	nd	101	8
2,3,7,8-TCDF	66	22	88	8	93	nd	93	18	99	nd	99	9
1,2,3,7,8-PCDF	55	28	84	8	82	15	97	9	100	nd	100	8
1,2,3,7,8-PCDD	58	29	87	8	80	14	94	8	96	nd	96	5
1,2,3,6,7,8-H_6CDF1	43	46	90	11	76	18	95	11	98	nd	98	8
1,2,3,6,7,8-H_6CDD1	42	50	92	16	76	19	95	14	96	nd	96	10
1,2,3,7,8,9-H_6CDD2	41	43	84	13	78	18	96	9	100	nd	100	5
1,2,3,4,6,7,8-H_7CDF	30	52	82	14	75	19	95	6	88	nd	88	6
1,2,3,7,8,9-H_6CDF2	42	46	86	13	80	18	99	19	99	nd	99	6
1,2,3,4,6,7,8-H_7CDD	30	57	87	20	73	23	96	9	90	nd	90	6
OCDF	29	66	96	21	74	29	103	11	97	nd	97	6
OCDD	30	67	97	20	70	23	92	12	95	nd	95	6

containing 10 mg of humic acids. It should be considered that the actual concentration is lower because of the centrifugation procedure described above.

After 5 min. stirring, the solution becomes clear and pale brown in color. 1 mL of the acetone solution containing PCDDs and PCDFs at the desired concentration is added to the water solution, stirring and sonicating for half an hour. The resulting solution is acidified with conc. H_2SO_4 until pH 1 is reached. After this, a solution of $KMnO_4$ 0.2 M is added drop by drop, until a persistent violet color is observed. The solution is stirred for 15 min. and H_2O_2 (30%) is added until the solution becomes colourless and clear. The solution is neutralized by adding a few drops of sodium hydroxide 6 N.

If $KMnO_4$ is added in lower amounts than requested for full oxidation, the solution containing humic acids yields a brilliant yellow color, probably due to the formation of strongly colored intermediate compounds.

The 1L water solution is now passed through the cartridge containing 900 mg of C_{18} silica. Then, the cartridge is dried under a flow of about 100 mL/min of nitrogen for 1 hour and extracted with 2 mL toluene using a PTFE test tube for collecting the extract. The toluene extract is then dried under a flow of nitrogen at room temperature.

The PTFE tube is now added with 50 μL toluene containing the ^{13}C labelled TCDD. The resulting solution is added with 1 mL of *n*-hexane and passed on the freshly activated alumina column (0.5 cm i.d., 10 cm 1.). Another mL of *n*-hexane is added to the empty PTFE test tube and also this is passed through the alumina column. Now 10 mL are passed through the alumina column to eliminate all organics except PCDDs and PCDFs. According to the well accepted EPA procedure 10 mL of a solution of *n*-hexane and methylene chloride 1:1 are now added to the alumina column in order to elute the PCDDs and PCDFs. The solution from the alumina column is dried and added with 50μL toluene. The effect of gravity was sufficient to obtain the necessary flow out of the alumina column.

This solution is ready for GC-MS analysis.

RESULTS AND DISCUSSION

Recovery experiments without humic acids

The extraction and preconcentration procedure has been tested to establish weather it would yield reliable results for what recovery of the compounds of interest is concerned. A glass container has been used first and the results obtained are reported in Table 2. These results were compared with those from a PTFE container shown in Table 3.

The left column of Tables 2 and 3 reports the recoveries from the C_{18} cartridge. The center column shows the recoveries obtained by washing three times with 10 ml methylene-chloride the glass container. The right column is the sum of the two recoveries yielding the overall recovery.

Three typical concentrations have been adopted to confirm the so called "container effect", i.e. the fact that a competition between water solution and adsorption on the glass container walls takes place especially for those compounds that show a very low solubility in water[15]. This effect increases with the decrease of the water solubility, that is from 2,3,7,8-TCDD whose water solubility is about 200 ng/L, to OCDD (0.4 ng/L)[16]. The results exposed in Table 2 confirm this hypothesis as was found for pesticides in previous works[17]. This effect decreases when the water concentration decreases. This is shown by the figures reported in the center column of Table 2. When the concentration of PCDDs and PCDFs is 1 ng/L, the recovery improves noticeably, but still the higher MW compounds are partially adsorbed on the glass container walls. The recoveries at the same 1 ng/L concentration with the PTFE container, shown in Table 3, are almost complete. The columns showing the recoveries from the container walls are void in this case, because the MS peaks are close to the detection limit of our GC-MS instrumentation (S/N = 2 was about 4 pg).

Also at the 2 ng/L concentration, PTFE gives better results even though oversaturation contribute to causing incomplete recoveries. These results show that PTFE should be preferred to glass.

The right column of Tables 2 and 3 indicates that the C_{18} cartridge works nicely, the overall recovery being acceptable.

These experiments then demonstrate that in the absence of humic acids a complete recovery of PCDDs and PCDFs is obtained using SPE with C_{18} in the cartridges, provided that a PTFE container is used and the concentration range is kept around 1 ng/L at the maximum.

Preliminary experiments with river water

River water, containing naturally dissolved organic material as described in the experimental part, after filtration has been spiked with the PCDDs and PCDFs in a concentration of 1 ng/L of each compound, and the procedure described above has been followed for the extraction and preconcentration of these compounds.

The recovery obtained ranged around 20–25% for all compounds. These findings are in full agreement with the results already obtained[7] who found that the solubility of 1,3,6,8-TCDD is strongly enhanced by the presence of humic acids. Thus, destruction of these materials is necessary in order to analyse PCDDs and PCDFs when dissolved organic material is present in water.

We attributed the scarce recovery to the fact that at least a part of the organic material present in the river water should be humic substances, as stated by Thurman and Malcolm[18] who examined several river waters with this aim.

Destruction of humic acids prior to preconcentration

The same water used for the blank experiments has been spiked with humic acids in a total concentration of these compounds of about 8 mg/L, which yielded a COD of 2.7 mg/L after centrifugation. This water, spiked with 1 ng/L of PCDDs and PCDFs according to the procedure previously described, was treated for extraction and preconcentration, but the recovery was again around 20% for all compounds.

Thus, the need for eliminating humic substances prior to extraction and preconcentration treatments became evident, and the procedure described has been followed. $KMnO_4$ oxidises the humic substances and the excess of it is reduced with H_2O_2.

Table 4 Percent recovery from mineral water spiked with 8 mg of humic acids and 1 ng/L of PCDDs and PCDFs. The procedure for humic acids destruction is followed. Ten different experiments are reported. Last column contains the average recovery with the overall standard deviation.

Experiment N°	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*X ± RSD*
TCDD	114	97	92	84	87	104	95	101	102	89	96 ± 9
TCDF	87	80	108	97	94	93	87	89	80	91	91 ± 9
PCDF	97	103	98	87	84	91	87	110	86	99	94 ± 9
PCDD	91	101	97	82	103	100	100	87	92	91	94 ± 7
H_6CDF1	77	88	102	86	97	92	110	88	85	87	91 ± 10
H_6CDD1	97	101	100	88	101	109	108	118	103	105	103 ± 7
H_6CDD2	81	98	96	82	104	99	104	100	101	88	95 ± 9
H_7CDF	97	103	100	85	109	116	107	115	103	89	102 ± 9
H_6CDF2	88	96	100	86	117	99	108	97	93	86	97 ± 10
H_7CDD	111	112	97	86	112	112	107	117	84	93	103 ± 11
OCDF	81	79	98	105	111	115	118	112	96	86	100 ± 13
OCDD	96	100	99	105	108	118	135	108	105	90	106 ± 11

The pH value of water is then adjusted to about 6 since acid solutions may hydrolyse the C_{18} of the cartridge.

The water sample, treated in this way is passed through the C_{18} cartridge and then purified through the alumina column.

The results obtained in the analysis of the final solution reported in Table 4 show recoveries for all the compounds considered that are quite similar to those found for the water free of humic substances. In this table the results reported refer to ten complete water treatments, each time using 1 L water. The overall average standard deviation on all measurements of the single PCDDs and PCDFs is 9.5%.

On a single water sample, the overall average standard deviation becomes lower, as it could be expected, namely 5.8%.

The significantly high standard deviation found is probably to be imputed to the analytical system. Much better results could be obtained using a high resolution mass spectrometer, which is presently unavailable in our laboratory.

Experiments with river water

In Table 5 the results obtained on a real sample of a lowland river water are reported. The sample, similar to the one examined before, showed a COD (Kubel) of 1.8 and has been treated for the elimination of humic substances. Also for this sample recoveries are now satisfactory. The procedure has been applied to the same water sample, five times using each time 1 L of the sample.

In Figure 1a a typical mass chromatogram obtained on a sample of lowland river water spiked with 1 ppt of each compound is shown according to the SIM program of Table 1.

In Figure 1b the mass chromatogram expanded at the retention time of OCDD and OCDF obtained with the sum of the intensities of m/z 444 and 460 is reported.

In Figure 1c the mass chromatograms related to the single m/z values cited are shown. In the same way the peaks corresponding to TCDD and TCDF have been analyzed.

Table 5 Percent recovery from a sample of lowland river water spiked with 1 ng/L of PCDDs and PCDFs. The procedure for humic acids destruction is followed. Five different experiments, from a sample of 5 liters of river water are reported. The last column contains the average recovery with the relative standard deviation for all the experiments.

Compounds	*Exp. 1*	*Exp. 2*	*Exp. 3*	*Exp. 4*	*Exp. 5*	*X*	*RSD*
2,3,7,8-TCDD	100	92	84	79	105	92	10
2,3,7,8-TCDF	86	75	81	75	106	85	13
1,2,3,7,8-PCDF	88	85	93	80	104	90	8
1,2,3,7,8-PCDD	78	85	74	80	98	82	9
1,2,3,6,7,8-H_6CDF1	105	87	110	87	95	97	10
1,2,3,6,7,8-H_6CDD1	104	88	94	85	92	93	7
1,2,3,7,8,9-H_6CDD2	93	81	104	88	90	91	8
1,2,3,4,6,7,8-H_7CDF	113	108	92	95	99	100	9
1,2,3,7,8,9-H_6CDF2	109	83	106	89	95	96	10
1,2,3,4,6,7,8-H_7CDD	109	114	95	90	101	102	9
OCDF	101	110	90	85	100	97	9
OCDD	100	115	84	82	100	96	13

CONCLUSIONS

The results of the experiments here reported show the following facts:

Good recoveries for PCDDs and PCDFs can be obtained from particle-free water spiked with these compounds using SPE with C_{18} silica and purification on alumina.

A careful procedure using proper materials for the containers is advisable for reliable results. The concentration of the compounds of interest should be kept, whenever possible below the solubility limit of each compound.

Humic substances, when present, are probably responsible for the low recoveries obtained even though the entire preanalytical procedure is correct, so that they should be removed prior to the extraction procedures.

It has been shown that dissolved organic material may be eliminated by using $KMnO_4$ and H_2O_2, obtaining in this way very good recoveries.

The method presented here is valid for rather high concentrations as it has been stated in the introduction, and should be tested for lower concentrations. In fact, unless the procedure for the destruction of humic substances is followed prior to preconcentration, it is impossible to state weather PCDDs and PCDFs are present and in which concentration in the sample.

In order to analyze properly PCDDs and PCDFs at lower concentration ranges, the use of a high resolution mass spectrometer, operating at a resolving power of at least 10000 is imperative. We hope that the method presented in this paper will be tested in laboratories where such instrumentation is available. The inconvenience due to the scarce overall sensitivity using a quadrupole MS could be overcame for lower concentration by using a much larger water volume, but this could yield an increase of the impurities, so that the only solution can be found in HRMS.

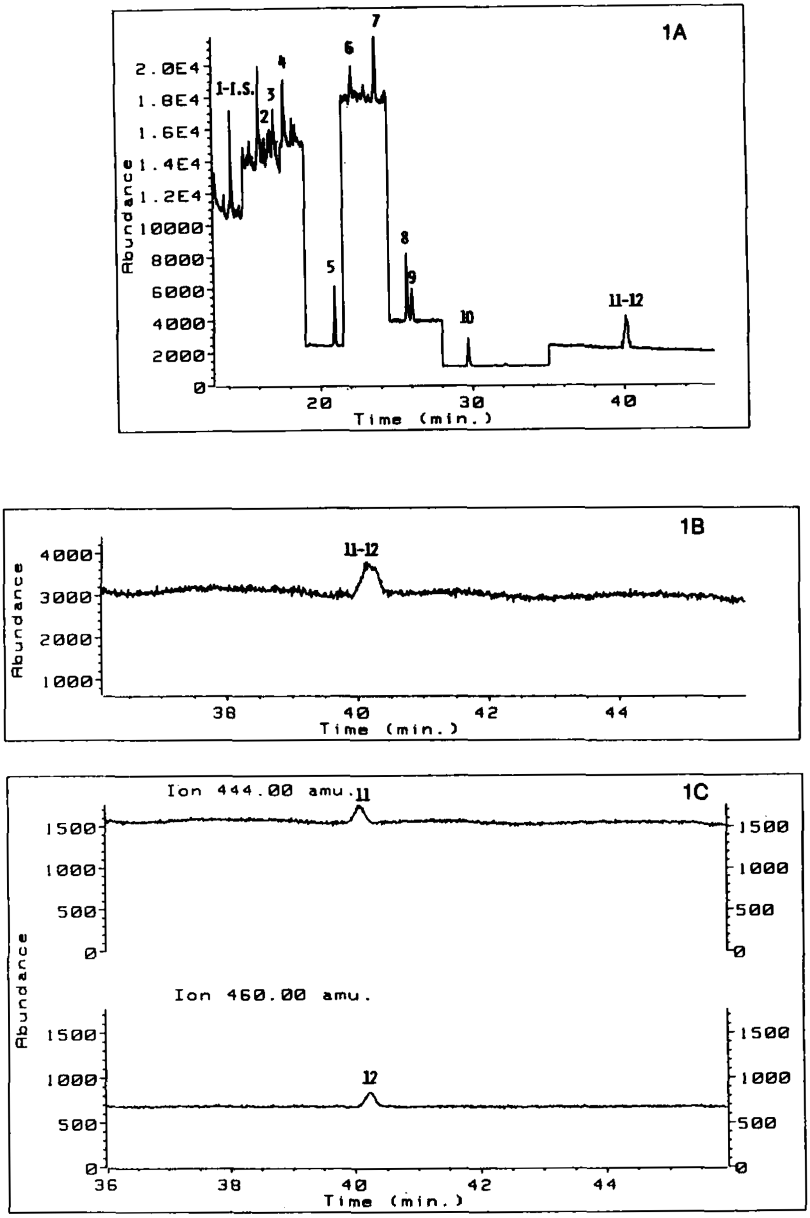

Figure 1 Typical mass chromatogram of the extract of a lowland river water spiked with 1 ng/L of each compound and treated for the elimination of humic substances.
SIM programme and peaks identification: according to Table 1:
Column: 60 m × 0.25 mm i.d. × 0.2 μm d.f. SP2331.
Carrier gas pressure: 2 Kg/cm^2. Initial linear gas velocity: 24 cm/sec.
Temp. programme: 2 min isoth. 200°C then programmed 10°C/min to 270°C.

References

1. B. A. Brown and C. T. Driscoll, *Environ. Sci. Technol.*, **27,** 915–922 (1993).
2. M. A. Shlautman and J. J. Morgan, *Environ. Sci. Technol.*, **27,** 961–969 (1993).
3. T. C. Chiou, R. L. Malcolm, T. I. Brinton and D. E. Kile, *Environ. Sci. Technol.*, **20,** 502–508 (1986).
4. W. E. Johnson, N. J. Fendinger and J. R. Plimmer, *Anal. Chem.*, **63,** 1510–1513 (1991).
5. M. Senesi and C. Testini, *Chemosphere*, **13,** 461–468 (1984).
6. M. Senesi, E. Loffredo and G. Padovano, *Plant and Soil*, **127,** 41–47 (1990).
7. M. R. Servos and D. C. G. Muir, *Environ. Sci. Technol.*, **23,** 1302–1308 (1989).
8. C. Rappe, L. O. Kjeller and R. Anderson, *Chemosphere*, **19,** 13–20 (1989).
9. L. L. Lamparski, T. J. Nestrick, M. N. Frawley, R. A. Hummel, L. W. Cocher, M. H. Mahle, J. W. McCoy, D. L. Miller and T. L. Peters, *Chemosphere*, **15,** 1445–1452 (1986).
10. M. Oehme, S. Manol and B. Bjerke, *Chemosphere*, **18,** 1379–1389 (1989).
11. A. Miller, *Environ. Sci. Technol.*, **27,** 1014–1015 (1993).
12. J. J. Ryan, A. Schecter, W. F. Sun and R. Lizottein, in: *Chlorinated dioxins and dibenzofurans in perspective* (C. Rappe, G. Choudhary, L. H. Keith, eds. Lewis Publ., inc., Chelsea, Mich., USA, 1986) pp. 6.
13. R. J. Ozretich and W. P. Schroeder, *Anal. Chem.*, **58,** 2041–2048 (1986).
14. D. E. Matthews and J. M. Hayes, *Anal. Chem.*, **48,** 1375–1382 (1976).
15. A. Cappiello, F. Mangani, P. Palma, E. Sisti and F. Bruner, *Chromatographia*, **30,** 357–360 (1990).
16. W. S. Shlu, W. Doucette, F. A. P. C. Gobas and A. Andren, *Environ. Sci. Technol.*, **22,** 651–658 (1988).
17. F. Bruner, G. Crescentini, F. Mangani and R. L. Petty, *Anal. Chem.*, **55,** 793–795 (1983).
18. E. M. Thurman and R. L. Malcolm, *Environ. Sci. Technol.*, **15,** 463–466 (1981).