

Determination of Dioxins and Furans in water sample by HRGC/HRMS and Pretreatment using Solid-Phase Microextraction

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Introduction

For trace analysis of polychlorinated dibenzo-*p*-dioxins(PCDDs) and polychlorinated dibenzofurans(PCDFs) in aqueous sample such as effluent and leachate, conventional pretreatment methods which consist of several steps such as extraction, purification, and concentration require large volume of sample and high-purity solvents, causing reduced sensitivity due to contamination from solvents, need for a lot of time throughout the experiment, and harmful influence on the health of the experimentalists.

In order to minimize the disadvantages of aforementioned pretreatment techniques for analyzing PCDDs and PCDFs in water sample, this report makes an attempt to investigate analysis by solid phase microextraction(SPME) coupled with high resolution gas chromatography and high resolution mass spectrometry.

Materials and Experimental

Materials

Seventeen kinds of 2,3,7,8-substituted isomers of PCDD/Fs (EDF-7999; Cambridge Isotope Lab.) were used as standards, and 15 kinds of 2,3,7,8-substituted isomers in which ¹²C₁₂ substituted with ¹³C₁₂ (EDF-8999; Cambridge Isotope Lab.) were used as internal standards except 1,2,3,7,8,9-HxCDD and OCDF. ¹³C₁₂-1,2,3,4,-TCDD and ¹³C₁₂-1,2,3,7,8,9-HxCDD(EDF-5999; Cambridge Isotope Lab.) were used as recovery standards, and calibration standard (EDF-9999; Cambridge Isotope Lab.) was also used. Perfluorokerosene (PFK, Aldrich Chem. Co.) was used as mass standard.

The glassware was rinsed in 5%-dimethyldichlorosilane (Supelco Park. Bellefonte, PA) for 15 seconds, and washed twice with toluene(Wako. Pesticide grade) and three times with methanol(Wako. Pesticide grade), and dried before use.

SPME system consisted of 4mL vial with PTFE/Silicone Septum (Supelco. Bellefonte, PA, USA), 10x4mm magnetic stir bar (Supelco. Bellefonte, PA, USA), and heat/stir plate (Corning, USA) with temperature range 40~550°C and stirring speed 60~1200rpm. Commercially-available 7 μM -and 100 μM -polydimethyl-siloxane(PDMS) fibre and 85 μM- polyacrylate fibre were used as extraction materials .

Sample solutions were prepared as follows; 25 μl of precision and recovery standard solution (EDF-7999, 40~400ng/ml, CIL) and 25 μl of labeled compound stock solution (EDF-8999, 100~200ng/ml, CIL) were placed in a 100ml-volumetric flask, and water (HPLC-grade) was added to make up to 100ml, giving the concentration of tetrachlorinated isomers 10pg/ml, penta- through

heptachlorinated isomers 50pg/ml, octachlorinated isomers 100pg/ml, tetra- through heptachlorinated isomers of labeled compound 25pg/ml, and octachlorinated isomer 50pg/ml.

Experimental

Three milliliter of sample and magnetic bar were placed in 4ml vial and fitted with PTFE/Silicone septum. The coated fibre was withdrawn into the syringe needle, which was used to penetrate the septum of the sample vial. The fibre was plunged into the sample and it adsorbed analytes for a specified time with magnetic stirring. When adsorption was completed, the fibre was again withdrawn into the needle and the syringe was removed from the septum of the vial. The coated fibre which adsorbed the analytes was directly inserted into the injector of a gas chromatograph. The thermal desorption of the analytes was taken place in the injection port of the GC at high temperature.

Calculation of recovery by double injection technique

Just before injecting of the SPME fibre into the GC injector, 50pg of $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD were injected as recovery standards using a digital syringe(Hamilton, 7001KH) to determine the recoveries of internal standards.

Results and discussion

Determination of extraction modes

In order to determine extraction modes for dioxins and furans, direct SPME was compared with headspace SPME using 7 μM -PDMS fibre. Fig.1 shows that responses of 10pg/ml of 2,3,7,8-TCDF are $1.7\text{E}+05$ with direct SPME and $2.4\text{E}+05$ with headspace SPME. And for 2,3,7,8-TCDD, the responses are $1.9\text{E}+05$ and $9.5\text{E}+04$ with direct SPME and headspace SPME, respectively. Direct SPME was found to give better extraction efficiency than does headspace SPME for all of 17 kinds of isomers of dioxins and furans.

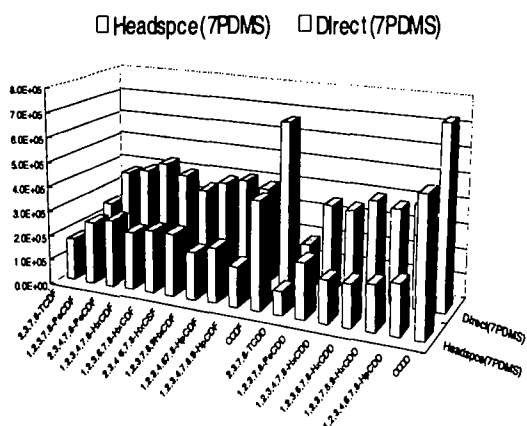


Figure 1. Relative extraction efficiencies according to extraction modes

Selecting the coating materials

To determine the coating materials, the adsorption efficiencies of dioxins and furans were investigated, using 7 μM PDMS, 100 μM PDMS, 85 μM polyacrylate and 75 μM CAR/PDMS fibres. The efficiencies were in order 7 μM PDMS > 100 μM PDMS > 85 μM polyacrylate > 75 μM CAR/PDMS. The extraction efficiencies for 2,3,7,8-TCDF and 2,3,7,8-TCDD at a concentration level of 10pg/ml, using the 7 μM PDMS fibre were $8.1\text{E}+05$ and $6.5\text{E}+05$, respectively. The 100 μM PDMS fibre was also proved to have ability to extract dioxins, the 85 μM polyacrylate and 75 μM

CAR/PDMS fibres, however, were not suitable. Santos¹⁾ had reported that a 100 μM -PDMS fibre was adequate for volatile organic compounds, while a 85 μM polyacrylate fibre was preferred for phenols, which had higher polarity, and Grote²⁾ had reported a 85 μM polyacrylate fibre gave better efficiencies for ethanol, acetone and isopropanol than did a 100 μM PDMS fibre. Llompart³⁾ and Yang⁴⁾ had used a 100 μM PDMS fibre for extraction of nonpolar and high molecular weight PCBs. The result that the 7 μM PDMS fibre gave the highest extraction efficiency for dioxins was in good agreement with these previous reports. Therefore, the PDMS fibre seemed to be fit for extraction of dioxins whose physicochemical properties were similar to PCBs.

Linearity and detection limit on SPME

Calibration was obtained by adding 3 μl of calibration standard solution in the EPA 1613 Method⁵⁾ to 3ml of water, extracting with the 7 μM PDMS fibre for 60 minutes, and analyzing by HRGC/HRMS. The correlation coefficients for all the isomers of dioxins and furans were more than 0.99, with the highest (0.9992) for 2,3,7,8-TCDD, and the lowest(0.9922) for OCDF. The linear ranges of tetrachlorinated isomers, penta- through heptachlorinated isomers, octachlorinated isomers were 0.5~200pg/ml, 2.5~1000pg/ml, and 5~2000pg/ml, respectively. In this study, the calibration curves showed good linearity in a wide range of concentration.

The detection limits of internal standards obtained by OPUSquan quantitative program (Micromass Co.) were between 0.12ng/L and 0.17ng/L; 2,3,7,8-TCDF and OCDF showed the lowest and highest value, respectively.

Recoveries and precision

Recoveries obtained by relative calibration in which the isotope dilution method was used ranged from 81.6% for 1,2,3,4,6,7,8-HpCDD to 119% for 2,3,7,8-TCDD. Relative standard deviations for repeatability were shown in Table 1, illustrating that the highest and lowest values were 22.9% for 2,3,7,8-TCDD and 5.4% for 1,2,3,7,8-PeCDF, respectively.

Conclusion

More efficient extraction of dioxins was achieved on direct SPME than on headspace SPME at room temperature. The adsorption efficiencies according to materials decreased in the order Polydimethylsiloxane, Polyacrylate, Carbowax. The lowest method detection limit(MDL) was 0.15ng/L for 2,3,7,8-TCDF. The precision, as determined by the relative standard deviation, was fairly good, ranging from 7.1 to 22.9% for dioxins, and from 5.4 to 17.5% for furans. It is concluded that SPME can be used as the effective pretreatment method for PCDD/Fs in water sample, allowing extraction, concentration, and injection to be performed in a single step.

Table 1. Spiking levels, estimated concentrations, relative standard deviations and recoveries of water samples analyzed using a 7 μ M-PDMS fiber.

Compounds	Spiking levels (ng/L)	Estimated Mean ^a (ng/L)	MDL	Repeatability	
				Recovery (%)	%RSD
2,3,7,8-TCDF	10	11.599	0.15	115.9	17.5
1,2,3,7,8-PeCDF	50	48.219	0.35	96.4	5.4
2,3,4,7,8-PeCDF	50	49.854	0.45	99.7	8.7
1,2,3,4,7,8-HxCDF	50	47.121	1.18	94.2	7.2
1,2,3,6,7,8-HxCDF	50	48.832	1.21	97.7	9.5
2,3,4,6,7,8-HxCDF	50	46.815	2.54	93.6	8.9
1,2,3,7,8,9-HxCDF	50	48.510	1.69	97.0	6.0
1,2,3,4,6,7,8-HpCDF	50	56.362	2.74	112.7	10.2
1,2,3,4,7,8,9-HpCDF	50	52.684	4.81	105.4	10.2
OCDF	100	114.862	59.26	114.9	14.5
2,3,7,8-TCDD	10	11.911	0.21	119.1	22.9
1,2,3,7,8-PeCDD	50	52.555	0.42	105.1	7.1
1,2,3,4,7,8-HxCDD	50	45.211	1.47	90.4	7.7
1,2,3,6,7,8-HxCDD	50	46.974	1.75	93.9	9.5
1,2,3,7,8,9-HxCDD	50	43.106	1.48	86.2	14.0
1,2,3,4,6,7,8-HpCDD	50	40.788	1.17	81.6	14.9
OCDD	100	100.190	8.43	100.2	8.7

^a: average of sixteen determinations

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