서울特別市 保健環境硏究論文集 第36號 (2000)
Report of S.I.H.E., 36:385~389 (2000)

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

Micropollutant Analysis Team

Seok-won Eom, Yong-suk Choi, Min-young Kim and Jae-young Shin

固狀微細纖維에 依한 前處理와 HRGC/HRMS에 依한 물에서 dioxins의 分析

미량물질분석팀

엄석원 · 최용석 · 김민영 · 신재영

초 록

유기화합물의 분석을 위한 전처리과정으로써 널리 사용되고 있는 액 · 액추출이나 고상추출(solid phase extraction; SPE)는 추출, 정제 및 농축과정의 여러 단계를 거치게되며, 이 과정에서 분석성분이 손실되거나, 사용된 유기용매로부터 방해성분이 유입되어 문제가 되고 있다. 이러한 기존의 전처리 방법에 있는 단점을 보완할 수 있으면서 시료채취와 농축이 한 단계로 이루어지고, 분리컬럼에 직접 분석성분을 주입할 수 있는 방법인 새로운 SPME방법을 이용하여 2,3,7,8 위치에 염소가 치환된 17종의 이성체에 대하여 ppt 수준의 농도가 되도록 제조하여 추출mode에 따른 추출효율, 흡착물질의 종류에 따른 추출효율, 흡착하는 시간에 따라 추출효율의 변화를 관찰하여 최적 추출모드와 흡착물질 및 흡착시간을 찾아 MDL및 재현성을 조사하여 다음과 같은 결론을 얻었다.

수용액 시료로부터 다이옥신류를 추출하여 HRGC/HRMS에 의하여 분석한 결과 SPME추출 mode는 직접 SPME가 헤드스페이스 SPME 보다 더 높은 추출효율을 나타냈다. 흡착물질에 따른 다이옥신류의 흡착효율은 polydimethylsiloxane 〉polyacrylate〉Carboxen™/polydimethylsiloxane순으로 나타났다. 7㎛-PDMS으로 60분간 추출할 때 MDL은 퓨란류는 2,3,7,8-TCDF는 0.15ng/L로 가장 낮고, OCDF는 59.26ng/L로 가장 높았으며, 다이옥신류는 2,3,7,8-TCDD는 0.21ng/L로 가장 낮고, OCDD는 8.43ng/L으로 가장 높게 나타났다. 상대표준편차(%RSD)는 퓨란류는 5.4~17.5이였으며, 다이옥신류는 7.1~22.9로 나타났다. 상관계수는 17종 모두 0.99 이상으로 나타났다. 정량용내부표준물질의 회수율은 회수율표준물질과 SPME섬유의 연속 주입방법을 통하여 계산할 수 있었으며, 정성분석에서 방해성분으로부터의 간섭은 모니터 이온을 증가시킴으로써 보완할 수 있었다. SPME에 의한 전처리와 HRGC/HRMS에 의한 다이옥신류의 분석방법은 전처리에 수 주가 소요되는 표준전처리방법의 실시 전에 예비 분석방법으로 실시하여 신속하게 결과를 획득함으로써 본 실험의 세부계획의 수립에 기초자료를 제공하고, 분석비용의 절감 효과와 다이옥신류의 오염사건에 대한 신속한 대책 마련에 기여할 수 있는 가능성을 보여 주었다.

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

1. 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 $^{12}C_{12}$ substituted with $^{13}C_{12}$ (EDF-8999; Cambridge Isotope Lab.) were used as internal standards except 1,2,3,7,8,9-HxCDD and OCDF. $^{13}C_{12}$-1,2,3,4,-TCDD and $^{13}C_{12}$-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), 10×4mm magnetic stir bar (Supelco. Bellefonte, PA, USA), and heat/stir plate (Corning, USA) with temperature range 40~550℃ and stirring speed 60~1200rpm. Commercially-available 7-㎛ and 100㎛-polydimethyl-siloxane(PDMS) fibre and 85㎛- polyacrylate fibre were used as extraction materials .

Sample solutions were prepared as follows; 25㎕ of precision and recovery standard solution (EDF-7999, 40~400ng/ml, CIL) and 25㎕ 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 octachlorinatd isomer 50pg/ml.

2. 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.

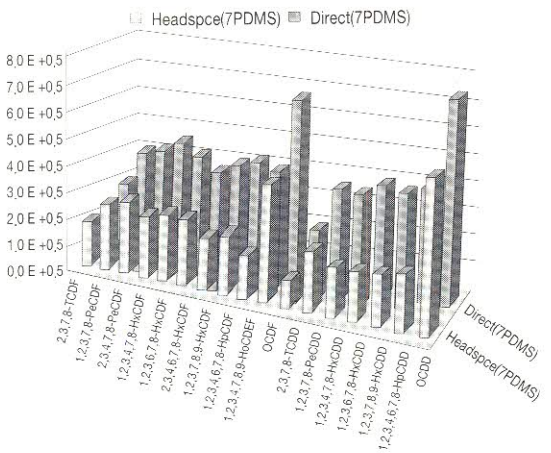

Fig. 1. Relative extraction efficiencies according to extraction modes

3. Calculation of recovery by double injection technique

Just before injecting of the SPME fibre into the GC injector, 50pg of $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-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

1. Determination of extraction modes

In order to determine extraction modes for dioxins and furans, direct SPME was compared with headspace SPME using 7㎛-PDMS fibre. Fig.1 shows that responses of 10pg/ml of 2,3,7,8-TCDF are 1.7E+05 with direct SPME and 2.4E+05 with headspace SPME. And for 2,3,7,8-TCDD, the responses are 1.9E+05 and 9.5E+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.

2. Selecting the coating materials

To determine the coating materials, the adsorption efficiencies of dioxins and furans were investigated, using 7㎛-PDMS, 100㎛-PDMS, 85㎛-polyacrylate and 75㎛-CAR/PDMS fibres. The efficiencies were in order 7㎛-PDMS 〉 100㎛-PDMS 〉 85㎛-polyacrylate 〉75㎛-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㎛-PDMS fibre were 8.1E+05 and 6.5E+05, respectively. The 100㎛-PDMS fibre was also proved to have ability to extract dioxins, the 85㎛-polyacrylate and 75㎛-CAR/PDMS fibres, however, were not suitable. Santos[1] had reported that a 100㎛-PDMS fibre was adequate for volatile organic compounds, while a 85㎛-polyacrylate fibre was preferred for phenols, which had higher polarity, and Grote[2] had reported a 85㎛-polyacrylate fibre gave better efficiencies for ethanol, acetone and isopropanol than did a 100㎛-PDMS fibre. Llompart[3] and Yang[4] had used a 100㎛-PDMS fibre for extraction of nonpolar and high molecular weight PCBs. The result that the 7㎛-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.

3. Linearity and detection limit on SPME

Calibration was obtained by adding 3㎕ of calibration standard solution in the EPA 1613 Method[5] to 3ml of water, extracting with the 7㎛-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 cali-

bration 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.

4. 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-㎛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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