

# SIMPLIFIED DETERMINATION FOR PCDDs/PCDFs WHICH SUBSTITUTED SOLID PHASE MICRO EXTRACTION FOR LARGE VOLUME INJECTION

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## Introduction

Although the large volume injection method (LVI) is widely used for the purpose of improvement in sensitivity in analysis of PCDDs/PCDFs, in order to also inject large amount of interferences simultaneously, it is difficult to continue maintaining equipment in the good state. Therefore application of the solid phase micro extraction (SPME) which is the simple and high sensitivity injection methods can be considered, but it was already reported in water sample that the detection limit of SPME is ng level and it can be used as the effective pretreatment<sup>1</sup>, and Suzuki et al. had presented evidence that PCDDs/PCDFs are easy to volatilize under a nitrogen flow<sup>2</sup>.

Then, the aim of this study is the improvement of not the direct extraction from an environmental sample but the injection ratio to GC/MS which is usually 1-10 $\mu$ l among 100 $\mu$ l, and is the improvement in the ratio of extraction by applying SPME to the sample which was carried out the nitrogen flow just before dryness, and it was investigated that coexistence of maintenance of appropriate analysis apparatus conditions and simplified determination of PCDDs/PCDFs could be possible.

## Method and Materials

### *Materials*

17 kinds of 2, 3, 7, 8- substituted isomers of PCDDs/PCDFs(Wellington Lab.) were used as standards, and 17 kinds of 2, 3, 7, 8- substituted isomers in which <sup>12</sup>C<sub>12</sub> substituted with <sup>13</sup>C<sub>12</sub> were used as internal standards, and <sup>13</sup>C<sub>12</sub>-1,2,3,4-TeCDD, <sup>13</sup>C<sub>12</sub>-1,2,3,4-TeCDF, and <sup>13</sup>C<sub>12</sub>-1,2,3,4,6,9-HxCDF was used as recovery standards. These were diluted into 2 $\mu$ g/ml acetone solution. All solvents used were of dioxin-analysis grades (Wako Pure chemicals).

SPME system consisted of 2ml vial with PTFE/Silicone septum. Commercially-available Polydimethylsiloxane (PDMS) (100 and 7 $\mu$ m) fiber, PDMS / Divinylbenzene (PDMS/DVB) fiber, Carbowax / DVB (CW/DVB) fiber, Polyacrylate (PA) fiber, and DVB / Carboxen (CX) / PDMS fiber were used as extraction materials.

### *Experimental*

Although extraction mode of SPME was usually direct SPME or headspace SPME where liquid phase and air phase were both existed, extraction of this study was performed headspace in the state where there is no liquid phase. Standards were prepared by spiking 2 $\mu$ l of 2ng/ml acetone solution which diluted with acetone the 100 ng/ml mixed standard solution into amber vials of 2ml which specifically were silanized prior to use. The vials put in completely underwater, and were heated by water bath, if needed.

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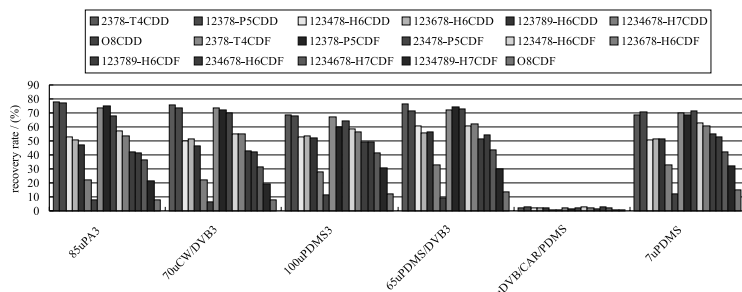


Figure 1 Recovery rate of SPME fiber

## GC/MS analysis

All PCDDs/PCDFs analysis is performed by HRGC/HRMS operating at a resolution of 10,000 in the SIM mode, using a HP6890plus gas chromatograph connected to a JMS-700 mass spectrometer (JEOL Ltd. Japan). The column used was a SP-2331 column (60 m x 0.32 mm x 0.1  $\mu$ m). The column temperature was maintained at 100 °C for 5 min, heated to 200 °C at a rate of 20 °C/min, heated to 260 °C at a rate of 2 °C/min, and maintained at 260 °C for 22 min. The injection temperature was 260 °C, ion source temperature was maintained at 280 °C, carrier gas (helium) rate was 1.5ml/min. The ionization energy was 38eV and ionization current was 500  $\mu$ A, and the other details of instrumental conditions were based on JIS-K0312<sup>3</sup>.

## Calculation of recovery by double injection technique<sup>1</sup>

To determine the recoveries of internal standards, just before injecting of the SPME fiber into the GC injector, 2pg of <sup>13</sup>C<sub>12</sub>-1,2,3,4-TeCDD, <sup>13</sup>C<sub>12</sub>-1,2,3,4-TeCDF, and <sup>13</sup>C<sub>12</sub>-1,2,3,4,6,9-HxCDF were injected as recovery standards using a auto injector (combi-pal ; CTC analysis).

## Results and Discussion

### Determination of extraction fiber

In order to determine extraction fiber, the recovery rates were investigated, using commercially-available 6 kinds of fibers, Polydimethylsiloxane (PDMS) ( film thickness 100 and 7  $\mu$ m), PDMS/Divinylbenzene (PDMS/DVB), Carbowax/DVB (CW/DVB), Polyacrylate (PA), DVB / Carboxen (CAR)/PDMS). The extraction time investigated was 10 minutes, and extraction temperature investigated was maintained at 80 °C. The results are shown in Fig. 1. There was no fiber which extracted all PCDDs/PCDFs well. HxCDDs/HxCDFs also had the recovery rate of TeCDDs/TeCDFs and PeCDDs/PeCDFs as good as 50 %-70 % except the fiber containing Carboxen. However, all of fibers extracted OCDD and OCDF only about 10%. Moreover, the difference of a recovery rate was not seen among fibers other than the fiber containing Carboxen. It has guessed that extraction temperature and extraction time had influenced the recovery rate rather than the coating film of fiber. Previous paper<sup>1</sup> reported that 7  $\mu$ m PDMS was adequate. But 7  $\mu$ m PDMS gave good recovery for interferences as well as PCDDs/PCDFs. Therefore the Polyacrylate fiber that was widely use to extract somewhat alternatively for polar substances such as PCDDs/PCDFs, and was comparatively more stable in high temperature, seemed to be appropriate for extraction of PCDDs/PCDFs.

### Determination of extraction condition

Extraction time and extraction temperature were examined that extraction time was changed from 10 minutes to 50 minutes, extraction temperature was changed to 60-90 °C. Consequently, it turned out

that the recovery rate is better with the increase in extraction time and extraction temperature. However, the measurement time of GC/MS was 62 minutes, the desorption time of PCDDs/PCDFs from a fiber required for 10 minutes, and in order to be efficient analysis, it is necessary to already go into extraction during measurement of a previous sample, the steep increase in the rate of extraction was not expected after 40 minutes or more, as a result extraction time was decided 50 minutes and extraction temperature was decided at 90 °C which all PCDDs/PCDFs were most extracted.

#### *Detection limit on SPME*

To calculate the detection limits of internal standards, a recovery test was performed at a low concentration level (spiked with 0.2 pg). The extraction time was 40 minutes, the extraction temperature was maintained at 90 °C. The results were shown in table 1, the detection limits that have been calculated for 3 times of standard deviation (n=5) were between 0.02 pg and 0.05 pg. As a result, it has checked that there was no demerit by having used SPME.

#### *Influence of solvents*

Since use of pre-concentration (liquid/liquid extraction, solid phase extraction, Soxhlet, or ASE) is indispensable, SPME will be used in the state where it dissolve into certain solvents. But existence of a solvent had very bad influence on recovery rate. The relation between the amount of solvents and the recovery rates was investigated about the acetone supposing the present use. It was investigated that the volume of acetone spiked into 2ml vial was changed from 2 to 200 µl. The result of investigation was that the recovery rate became extremely bad in existence of the acetone more than 50 µl. Under the nitrogen flow, PCDDs/PCDFs was easy to dryness acetone from toluene etc., and considering vial capacity and pressure, it decided to leave 20-30 µl.

#### *Application of environmental samples*

As comparison with the LVI methods, a total of four samples of river sediment 2 samples and industrial waste 2 samples containing incineration ashes were investigated. These samples were extracted over 16 hours by Soxhlet extractor using toluene, respectively. Detailed procedure of sample preparation was described elsewhere<sup>4</sup>. The concentrates just before dryness under nitrogen stream, were dissolved into 200 µl acetone solution of 0.1 pg/µl of <sup>13</sup>C<sub>12</sub>-1,2,3,4,6,9-H6CDF as a spike for a SPME recovery rate check. It divided into two vials and moved to 2 ml vial. It dried by the nitrogen flow until removing acetone to 30 µl, and it was extracted and was injected to GC/MS by SPME. The result of comparison was that the measured value of SPME was about 70 % of measured value of LVI.

#### **Conclusion**

It is concluded that SPME substituted for LVI can be used as injection method which is coexistence of maintenance of appropriate analysis conditions and simplified determination of PCDDs/PCDFs.

#### **References**

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