

Quick and effective analytical methods for PCDDs and PCDFs using ultrasonic Soxhlet extraction and high performance liquid chromatography (HPLC)

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Introduction

During recent years quick and effective analytical methods for PCDDs and PCDFs have been developed^{1,2,3,4,5}. Analytical procedures for these compounds in complex samples are in most cases time consuming and associated with problems concerning recoveries of these compounds. These problems are in many cases due to the many steps involved in the analytical procedures, especially the procedures of extraction and clean-up. HPLC methods have been used to resolve these problems^{2,4}. In this abstract we present the results of an improved analytical method of PCDDs and PCDFs, where ultrasonic Soxhlet extraction and HPLC are used.

Experimental

Sample preparation and Soxhlet extraction: The sample matrix to be subjected to the analytical method was fly ash from a municipal waste combustion incinerator. Fly ash was chosen since it is known to contain all relevant congeners of PCDD/Fs. The fly ash was extracted with toluene in a Soxhlet apparatus for 24 hrs. and our original ultrasonic Soxhlet apparatus for 8hrs. to 24hrs. after HCl treatment.

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Before the extracts can be injected on the HPLC system a cleaning step is necessary in order to remove unwanted substances. In this study the cleaning step consisted of elution through an open multilayer silica-gel column with n-hexane as solvent.

HPLC system: The HPLC system is composed of a waters 600E "multi-solvent-system" equipped with a gradient unit and a Waters 481 UV detector. The injector is a U6K with a 2ml loop. The columns used are GL-Science 150mm x 4.6mm NITRO-column and Nakarai-Tesque 150mm x 4.6mm PYE-column.

GC/MS analysis.: Evaluation of our clean-up method was performed on GC/MS. For polyaromatic hydrocarbons (PAC) this was done on a Hewlett-Packard (HP) 5890 A GC coupled to a HP 5971A mass selective detector. For the PCDD/Fs the analyses were performed on a KRATOS Concept 1S mass spectrometer and Shimadzu 14A GC with a 60m DB-5, DB-17 and SP-2331 capillary column.

Results and Discussion.

Ultrasonic Soxhlet extraction.: Normally Soxhlet extraction of fly ash was performed for 24hrs. Attempts were made to reduce this extraction time by means of ultrasonic Soxhlet extraction. Comparison of the results for extractions performed by normal 24hrs. Soxhlet and ultrasonic Soxhlet extractions, are shown in Table 1.

Table 1. The analytical results of extract using our method

Time(hr.)	Soxhlet	24	4	8	8	8
	ultrasonic	0	4	4	8	4
	Solvent*	T	T	T	T	T+M
PCDD/Fs recovery (%)		100	65	75	98	98

* T: Toluene, T+M: Toluene/Methanol=98/2

As shown in Table 1, recoveries by using the ultrasonic Soxhlet method are the same as those obtained by using the normal extraction method. The time of extraction with the ultrasonic Soxhlet method can be reduced to 8hrs.

HPLC analysis.

We tried to separate the PCDD/Fs from the extracts of the fly ash using HPLC with a NO₂-column and a PYE-column with n-hexane as mobile phase. The NO₂-column when used in a straight phase mode, separates the components according to the number of aromatic rings (dipole-dipole interaction of components with the surface of stationary phase).

The evaluation was made by analyzing standard mixtures run through the HPLC system. The standard mixtures were:

- one mixture of three polycyclic aromatic compounds (anthracene, pyrene, fluoranthene),
- one mixture of native tetra, penta, hexa, hepta and octa-PCDD/Fs,
- one mixture of three co-planar PCBs (3,3',4,4'-tetra, 3,3',4,4',5-penta, 3,3',4,4',5,5'-hexa-PCB).

On HPLC separation using NO₂-column, after the each fraction of HPLC were collected and PCDD/Fs contained in these fractions were analyzed by GC/MS. The results of GC/MS analysis were showed in table 2. The distribution of PCDD/Fs are shown in each fraction; PCDD/Fs mainly elute in the third to fifth fractions and are not detected in the first, seventh and eighth fractions.

Table 2. The distribution of PCDD/Fs in each HPLC fractions.(%)

Fraction	1st	2nd	3rd	4th	5th	6th	7th	8th
T4CDF	-	3	3	85	7	1	1	-
T4CDD	-	67	19	8	6	-	-	-
P5CDF	-	10	24	25	30	11	-	-
P5CDD	-	4	60	28	8	-	-	-
H6CDF	-	3	46	25	23	3	-	-
H6CDD	-	-	17	30	53	-	-	-
H7CDF	-	-	33	57	10	-	-	-
H7CDD	-	1	70	29	-	-	-	-
O8CDF	-	6	72	16	6	-	-	-
O8CDD	-	1	25	74	-	-	-	-

If the third, fourth and fifth fractions were collected on HPLC using a NO₂-column we could obtain the fractions that contain all PCDD/Fs. Since polycyclic aromatic compounds were eluted later, PCDD/Fs were

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separated completely from polycyclic aromatic compounds.

The retention-time of co-planar PCBs (co-PCB) were different from that of PCDD/Fs in the HPLC of a PYE-column, and co-PCBs could be separated from PCDD/Fs. We are going to continue the study to investigate the separation of other PCBs.

Conclusion.

1. The ultrasonic Soxhlet extraction is a very useful method that results in more rapid extractions.
2. PCDD/Fs can be separated from polycyclic aromatic compounds by means of HPLC.

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