

COMPARISON OF ASE AND SOXHLET-APPARATUS EXTRACTION INDETERMINATION OF POLYCHLORINATED DIBENZODIOXINS AND BENZOFURANS

Adam Grochowalski¹, Anna Maślanka²

1 Chemistry Department of Technical University of Cracow, Poland, agrochow@chemia.pk.edu.pl

2 EMIPRO Ltd. Kraków, Poland, Cystersów 15

Introduction

Analysing trace compounds, such as dioxins, in various samples requires the latter to be specially pre-treated, as the concentration level of these compounds is very low – usually ng/kg TEQ. Preparation of samples to determine their contents of these compounds is cost- and labour-consuming and the demand for PCDDs/Fs contents determination in various samples, e.g. in soil, keeps growing, hence it is striven to make the methods of sample pre-treatment more efficient.

This study covers determination of dioxin contents in soil samples taken in the area of deep-water intake for Tarnów, which is adjacent to the power plant of Zakłady Azotowe w Tarnowie. The intent was to compare the contents of dioxins in samples prepared by various methods using accelerated solvent extraction (ASE) with those prepared by extraction in Soxhlet apparatus and efficiency of extract purification by dialysis with the use of semipermeable membranes (SPM) of polyethylene with purification on active carbon.

Methods and Materials

The test material was soil samples taken nearby the power plant of Zakłady Azotowe w Tarnowie in the area of the urban water works – the deep-water intake for Tarnów.

Initial tests showed contents of dioxins in those samples of ~ 2 ng/kg TEQ, which evidences certain, inconsiderable soil contamination with these compounds and provides a good model material.

The first, most important step of sample preparation is extraction of dioxins out of the matrix. In the experiment, the accelerated solvent extraction (ASE) was applied. It is a technique involving use of liquid solvents for extraction under increased pressure and temperature conditions – which makes it possible to obtain extracts very rich in miscellaneous chemical compounds in much shorter time and consuming much less solvents than using other methods.

One of ASE system applications is obtaining extracts intended for determination of PCDDs/Fs contents (Application Note 323, Dionex) [1]. This application was the standard one basing on which the extraction methods of the investigated samples were developed.

The ASE was applied in three methods differing in temperature and solvent dwelling time in the extraction cell.

Method 1st - temperature 200°C, extraction time 15 minutes,

Method 2nd – 150 °C and 5 minutes of extraction,

Method 3rd – 120 °C and 5 minutes of extraction.

In all methods, toluene was applied as the solvent, and the pressure of the system was maintained at 13.8 MPa.

In order to compare efficiency of ASE, the soil samples were also purified in Soxhlet apparatus, by extraction with toluene under a reflux condenser for 16 hours.

Prior to extraction, 1 ml of the recovery standard was added to each sample, both to be extracted in Soxhlet apparatus and using ASE. The recovery standard was a mixture of 15 congeners ^{13}C – 2, 3, 7, 8 – PCDD/F at the concentration of 1.2 ng/ml.

Following the extraction process, the solutions obtained were subjected to further purification steps with the use of semipermeable membranes (SPM) or active-carbon columns.

The SPM purification process is based on the laws of analytes diffusion out of the extract placed in a membrane bag to the solvent outside of the membrane. The membranes applied in the test were made of semipermeable polyethylene film, in form of bags sealed on one side. Through the pores with the diameter ca. 1 nm, the smaller-size analyte molecules pass from the matrix to the accepting solvent, while fats and other high-molecular pollutants remain inside the membrane. It is a non-destructive method, easy to carry out, which also enables one to determine contents of other substances in the samples being tested.

In the experiment, the extracts had been dissolved in n-hexane and were transferred to the membrane bag placed in a 100 ml glass cylinder. N-hexane was used as the accepting solvent [2,3].

In order to assess the purification efficiency using the SPM method, the extracts were also purified in active-carbon columns. The previously purified active carbon had been put into the glass columns and the sample dissolved in n-hexane was laid on. Following the initial purification, the carbon-adsorbed dioxins were eluted by counter-current extraction with condensing toluene (after having reversed the column) in Soxhlet apparatus for 10 hours.

Afterwards, all samples were purified by shaking with concentrated sulphuric acid, then they underwent further purification in a silica-gel column and an alumina column.

Dioxins in extracts were determined by gas chromatography coupled with mass spectrometry detection, with multistep fragmentation of molecules – GC-MS/MS accordingly to the procedure described Grochowalski et al [4]. Two columns, DB-5 MS and DB-17, were used for chromatographic separation of the PCDDs/Fs congeners.

Results and discussion

For determination of dioxins, the experiment showed that the recovery values of individual congeners were very high (70 –100%) for all samples, and the extraction methods applied allow one to achieve high level of analyte recovery out of the matrix (Tab. 1A and 1B, Fig. 1).

Table. 1A. Conditions of Sample Preparation for PCDDs/Fs Analysis

Extraction using Soxhlet apparatus.

Extraction conditions	Sample A	Sample B
Solvent	Toluene	Toluene
Temperature	ca. 110°C	ca. 110°C
Extraction time	16 h	16 h
Extract purification	SPM	carbon column

Table. 1B. Conditions of Sample Preparation for PCDDs/Fs Analysis

Extraction using ASE technique						
Extraction parameters	Sample C	Sample D	Sample E	Sample F	Sample G	Sample H
Solvent	Toluene	Toluene	Toluene	Toluene	Toluene	Toluene
Temperature	200°C	200°C	150°C	150°C	120°C	120°C
Pressure	13.8 Mpa (2000 psi)	13.8 Mpa (2000 psi)	13.8 Mpa (2000 psi)	13.8 Mpa (2000 psi)	13.8 Mpa (2000 psi)	13.8 Mpa (2000 psi)
Static time	15 min	15 min	5 min	5 min	5 min	5 min
Flowing solvent volume	60 % of cell volume	60 % of cell volume	60 % of cell volume	60 % of cell volume	60 % of cell volume	60 % of cell volume
Purging time	100 s	100 s	100 s	100 s	100 s	100 s
No. of cycles	2	2	2	2	2	2
Extract purification	SPM	carbon column	SPM	carbon column	SPM	carbon column

The recovery values for the samples analysed using the ASE technique (under the most extreme conditions) and, for comparison, using the Soxhlet apparatus are very close to each other. At lower ASE temperature, the recovery value of dioxins becomes reduced.

Purification of samples by dialysis using semipermeable membranes (SPM) and carbon columns results in very similar recovery values.

Extracts obtained by means of the ASE technique under the most severe conditions, allow one to get the highest PCDD/Fs recovery values, of 95-85%, but they are loaded with a considerable amount of contaminants which impede further steps of samples treatment prior to chromatography. For the extracts obtained by means of the ASE technique under milder conditions, a little lower recovery values have been ascertained, of 80-85%, but the amount of contaminants extracted from the soil samples is much less, and does not raise any difficulties in sample treatment prior to chromatography.

One can notice that the profiles of PCDD/Fs recovery for the samples purified using Soxhlet-apparatus extraction approximate those of the samples purified by means of the ASE technique, which is also an indicative of accelerated solvent extraction appropriateness to prepare samples for determination of dioxin and furan contents (Fig. 2).

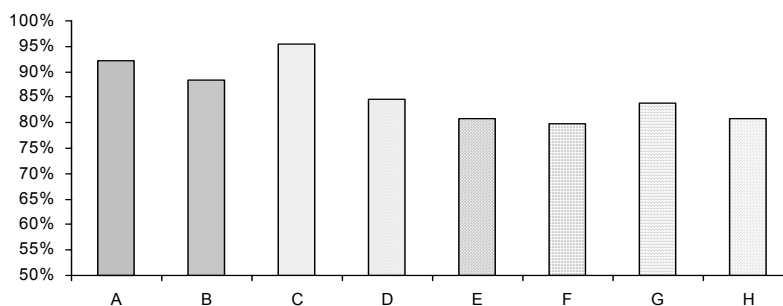


Fig. 1. Average PCDDs/Fs recovery values for individual samples

- A** – sample extracted in Soxhlet apparatus and purified in the active-carbon column,
- B** – sample extracted in Soxhlet apparatus and purified by means of SPM,
- C** – sample extracted by ASE technique (method 1 – temp. 200 °C, extraction time 15 minutes) and purified in the active-carbon column,
- D** - sample extracted by ASE technique (method 1 – temp. 200°C, extraction time 15 minutes) and purified by means of SPM,
- E** - sample extracted by ASE technique (method 2 – temp. 150°C, extraction time 5 minutes) and purified in the active-carbon column,
- F** - sample extracted by ASE technique (method 2 – temp. 150°C, extraction time 5 minutes) and purified by means of SPM,
- G** - sample extracted by ASE technique (method 3 – temp. 120°C, extraction time 5 minutes) and purified in the active-carbon column,
- H** - sample extracted by ASE technique (method 3 – temp. 120°C, extraction time 5 minutes) and purified by means of SPM,

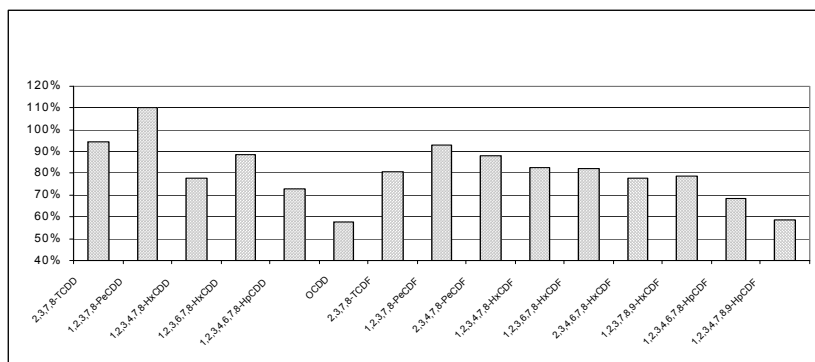


Fig. 2. PCDDs/Fs recovery values for individual congeners, for sample **E** and **F**.
E - sample extracted by ASE technique (method 2 – temp. 150°C, extraction time 5 minutes) and purified in the active-carbon column,

References

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