

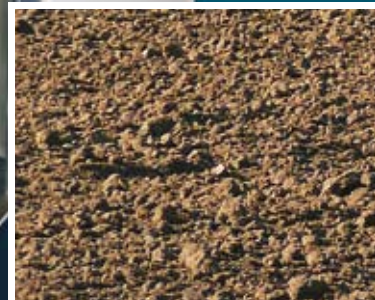
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Extraction System B-811
Extracting PCDD/F from Soil and Grass Samples

Environmental Analysis – Extracting PCDD/F from Soil and Grass Samples

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Abstract

We are presenting the use of Büchi's Extraction Unit B-811 for isolating polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) from solid environmental samples (soil, grass) under standard conditions and by means of hot extraction. The extracts received will be further processed by means of an internationally recognized method [1] and analyzed with high-resolution GC/MS in the single-ion monitoring (SIM) mode.

Introduction

One of the most important steps in processing solid samples for PCDD/F is extraction. Here, it is essential that the analytes are dissolved during extraction with the greatest amount of yield from the sample matrix. EPA 8290 describes the sample preparation and quantification of PCDD/F. The samples are extracted according to matrix-specific extraction procedure. Soxhlet extraction with toluene is approved for soil.

The extraction times are between 16 and 48 hours according to EPA 8290, EN and VDI guidelines, the Sewage Sludge Ordinance, [1 to 5]. This results in long investigation times and additional safety problems since the extraction is not monitored outside of working hours. Strict safety regulations can only be met if very costly automatic carbon dioxide extinguishing systems are installed.

For exactly these two reasons, dioxin analysts are always on the lookout for efficient extraction methods that are less time consuming. The Büchi B-811 Extraction System focuses on these aspects and is of particular interest because it is possible to use hot extraction for processing dioxide-contaminated sample materials with this system.

The Instruments

The Extraction Unit B-811 has four similar extraction units, consisting of a solvent beaker, an extractor with a sample thimble and a cooler. Of the four potential extraction techniques, we tested the hot extraction and the Soxhlet standard technique. The hot extraction was developed to speed up the classic Soxhlet extraction. In hot extraction the sample thimble is heated by a second heating unit.

Depending upon the technique, the extraction time and the number of cycles can be programmed, as well as a rinsing and drying step. The rinsing step was used in order to remove residues from the sample.

Extraction Experiments

The sample matrices of soil and grass available for the experiments were analyzed using the Soxhlet standard technique and the hot extraction technique. Each of the techniques was divided up into several steps, whose extracts were processed separately and analyzed by means of HRGC/HRMS.

A purification step was performed after

Condition	Soxhlet-Standard-Extraction
weighted portion	13.38 g grass 101.53 g soil
solvent	toluene r. a.
lower heating	stage 13
partial steps	
first extraction	4 hours
second extraction	4 hours
third extraction	16 hours
rinsing	0.5 hours
condition	hot extraction
weighted portion	9.81 g grass 89.94 g soil
solvent	toluene r. a.
lower heating	stage 13
upper heating	stage 6
partial steps	
first extraction	4 hours
second extraction	16 hours
rinsing	0.5 hours

the rinsing step, and a blank reading control was carried out to ensure that the extraction apparatus did not contain any contaminants.



Figure 1: Extraction Unit B-811

Processing the Extracts

The extracts were processed as follows:

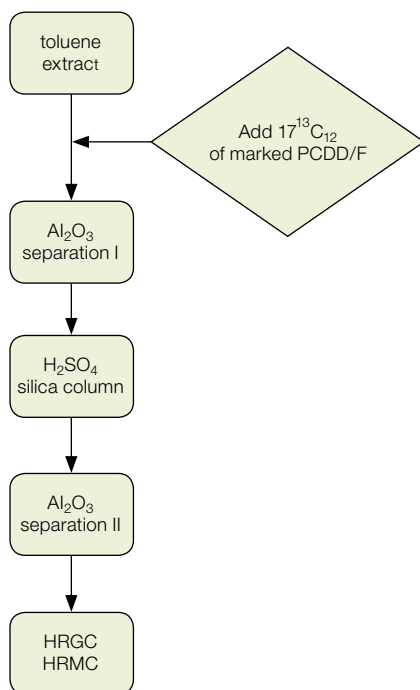


Figure 2: Processing steps

HRGC/HRMS Analysis

The purified extract was transferred into a 100 µl vial and analyzed in the SIM mode by means of HRGC/HRMS. It was qualified with the internal standard added before processing the extracts (refer Figure 2).

Results

An evaluation of the analyzed samples produced the following results:

1. Soil sample analyses
2. Grass sample analyses (refer to 1 and 2 table on the following page).

Discussion

The results of Table 1 show that more than 90% of the PCDD/F is extracted after four hours using hot extraction. In addition, it becomes very obvious that the apparatus can be used again after rinsing without being cleaned any further. This was confirmed by means of a supplementary purification step and a blank reading control [6]. Therefore, it is

only necessary to change the sample thimble. This saves cleaning time and also minimizes solvent use. Since a range of fluctuation of 25% is permissible pursuant to the Sewage Sludge Ordinance [5], extraction can be interrupted without any problems after four hours.

We were able to achieve an even better result with hot extraction of the grass samples (refer to Table 2). With the exception of the OCDD, all of the other PCDD/F was completely extracted after four hours. We were not able to detect any PCDD/F in the rinsing sample or after purification using a similar method as was used for the soil sample. If we compare our results to the Soxhlet standard technique, Table 1 shows that up to 28% of the PCDD/F is still contained in the sample after four hours. Furthermore, we can see that up to 15.79% PCDD/F is in the third extract – i.e., after more than 8 hours. This means that 24 hours are necessary for extraction with the Soxhlet technique. However, it is also nice to see here that no further PCDD/F could be detected in the rinsing extract and that the apparatus could also be reused immediately in this case. All other PCDD/F have been completely dissolved from the grass sample (refer to Table 2) with the exception of the sum of TCDF and the sum of PCDF after four hours of Soxhlet extraction. With the sum of TCDF and the sum of PCDF, it is very noticeable that it was not possible to detect the rest of the TCDF and PCDF in the second extraction, but only in the third extraction. Apparently, there is strong adsorption with the grass sample that can only be destroyed after a longer period of extraction.

Conclusions

The results received during this series of experiments prove unambiguously that a four-hour extraction period is sufficient when using hot extraction. Consequently, eight extractions can be carried out with an extraction system per working day. This ensures that the extraction process is monitored (working hours), which makes it possible to forego the automatic carbon dioxide extinguishing system.

The compact sealing system and the fact that it is possible to forego further purification steps make it possible to save 70% of the solvent. The electronically controlled heating system allows for a reproducible extraction process with a subsequent rinsing process, whose parameters can be recalled as needed.

Literature

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1. Soil Sample Analyses

Components distribution of concentration in %	Soxhlet Standard Technique				Hot Extraction		
	First extraction	Second extraction	Third extraction	Rinsing	First extraction	Second extraction	Rinsing
total TCDD	100	0	0	0	100	0	0
total PCDD	100	0	0	0	100	0	0
total H6CDD	82.81	8	9.19	0	100	0	0
total H7CDD	85.51	4.92	9.57	0	94.04	5.96	0
total TCDF	92.14	2.54	5.32	0	92.98	7.02	0
total PCDF	95.40	1.73	2.82	0	100	0	0
total H6CDF	93.50	3.13	3.37	0	100	0	0
total H7CDF	92.72	1.9	5.38	0	100	0	0
Congenere PCDD/F							
2,3,7,8 - TCDD	100	0	0	0	100	0	0
1,2,3,7,8 - PCDD	100	0	0	0	90.22	9.78	0
1,2,3,4,7,8 - HCDD	72.30	11.96	10.92	0	93.06	6.94	0
1,2,3,6,7,8 - HCDD	84.06	6.52	9.42	0	96.92	4.08	0
1,2,3,7,8,9 - HCDD	84.77	50.80	10.15	0	90.75	9.25	0
1,2,3,4,6,7,8 - HCDD	85.34	6.33	8.32	0	93.85	6.15	0
1,2,3,4,6,7,8,9 - OCDD	97.44	5.64	14.92	0	93.25	5.87	0.37
2,3,7,8 - TCDF	77.37	6.84	15.79	0	92.47	7.53	0
1,2,3,7,8 - PCDF	92.37	2.82	4.80	0	95.73	4.27	0
2,3,4,7,8 - PCDF	89.49	4.28	6.23	0	92.26	7.74	0
1,2,3,4,7,8 - HCDF	95.24	1.72	3.04	0	96.39	3.61	0
1,2,3,7,8,9 - HCDF	94.44	3.33	2.22	0	88.31	11.69	0
1,2,3,6,7,8 - HCDF	91.91	3.88	4.21	0	94.34	5.66	0
2,3,4,6,7,8 - HCDF	89.23	4.62	6.15	0	94.16	5.84	0
1,2,3,4,6,7,8 - HCDF	95.08	2.40	2.51	0	96.86	4.14	0
1,2,3,7,8,9 - HCDF	96.15	1.92	1.92	0	100	0	0
1,2,3,4,6,7,8,9 - OCDF	93.80	2.81	3.39	0	97.07	2.93	0

Table 1: Distribution of PCDD/F Concentration in % with Soxhlet and Hot Extraction of the Soil Sample

2. Grass Sample Analyses

Components distribution of concentration in %	Soxhlet Standard Technique				Hot Extraction		
	First extraction	Second extraction	Third extraction	Rinsing	First extraction	Second extraction	Rinsing
total TCDD	100	0	0	0	100	0	0
total PCDD	100	0	0	0	100	0	0
total H6CDD	100	0	0	0	100	0	0
total H7CDD	100	0	0	0	100	0	0
total TCDF	84.68	0	15.32	0	100	0	0
total PCDF	95.43	0	14.57	0	100	0	0
total H6CDF	100	0	0	0	100	0	0
total H7CDF	100	0	0	0	100	0	0
Congenere PCDD/F							
2,3,7,8 - TCDD	100	0	0	0	100	0	0
1,2,3,7,8 - PCDD	100	0	0	0	100	0	0
1,2,3,4,7,8 - HCDD	100	0	0	0	100	0	0
1,2,3,6,7,8 - HCDD	100	0	0	0	100	0	0
1,2,3,7,8,9 - HCDD	100	0	0	0	100	0	0
1,2,3,4,6,7,8 - HCDD	100	0	0	0	100	0	0
1,2,3,4,6,7,8,9 - OCDD	97.20	2.80	0	0	81.67	18.33	0
2,3,7,8 - TCDF	57.88	0	0	0	100	0	0
1,2,3,7,8 - PCDF	58.33	0	0	0	100	0	0
2,3,4,7,8 - PCDF	42.18	0	0	0	100	0	0
1,2,3,4,7,8 - HCDF	100	0	0	0	100	0	0
1,2,3,7,8,9 - HCDF	100	0	0	0	100	0	0
1,2,3,6,7,8 - HCDF	100	0	0	0	100	0	0
2,3,4,6,7,8 - HCDF	100	0	0	0	100	0	0
1,2,3,4,6,7,8 - HCDF	100	0	0	0	100	0	0
1,2,3,7,8,9 - HCDF	100	0	0	0	100	0	0
1,2,3,4,6,7,8,9 - OCDF	100	0	0	0	100	0	0

Table 2: Distribution of PCDD/F Concentration in % with Soxhlet and Hot Extraction of the Grass Sample

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