EVALUATION OF ACCELERATED SOLVENT EXTRACTION OF PCDDs AND PCDFs FROM NATIVE CONTAMINATED SAMPLES.

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INTRODUCTION
Soxhlet extraction using toluene for isolation of PCDDs and PCDFs from solid matrices is widely accepted as a robust liquid/solid (L/S) extraction technique. However, the interest for supercritical fluid extraction with carbon dioxide (SFE) as alternative has increased mainly because of the need to reduce the organic solvent wastes, better selectivity and ease of automation. The major disadvantage of SFE is that extraction efficiencies are not as robust as Soxhlet extraction. The efficiencies strongly depend on the type of matrix. It is especially difficult to yield good efficiencies for samples where the extraction is limited by strong matrix-analyte interactions (1).This is often the case for low levels (ppt - ppb) analyses of PCDDs and PCDFs in solid matrices. Due to these interactions, it is necessary to optimize the SFE conditions for each type of matrix. Recently, Dionex has developed Accelerated Solvent Extraction (ASE), a new technique for extraction of organic micro pollutants from solids(2), with the robustness of conventional Soxhlet extraction's. ASE uses organic solvents under high temperature and elevated pressure what results in rapid and safe extraction's. ASE reduces both extraction time and solvent consumption and is easy to automate. Typical volume and time for a 10 g sample are about 15 ml and 15 min, respectively. Furthermore, the time for method development is short, because direct conversion of a Soxhlet method into an ASE method is possible. These promising advantages were the reason to test the ASE[tm] 200 from Dionex for:
1. the extraction efficiencies of ASE relative to Soxhlet extraction,
2. carry over,
3. thermal degradation of OCDF. We studied degradation of OCDF, because this congener is less chemical stable than the other PCDDs and PCDFs congeners[3,4].

EXTRACTION AND CLEAN UP
We have used the following samples:
1. A soil sample contaminated with native PCDDs and PCDFs. We dried about 200g of this soil sample for 5 days at 40° C. After drying we homogenized the sample.
2. An alumina matrix impregnated with copper (alumina/ Cu) and highly contaminated with native OCDF. We mixed an amount of nominal 0.5g of this sample with 12g anhydrous sodium sulfate and homogenized it. This matrix was chosen to study possible degradation of OCDF in the presence of a catalytic material.

Extractions
We extracted six sub samples of nominal 5g soil according to Soxhlet using 350 ml toluene for 24 hours in the dark and six sub samples of nominal 5g soil using ASE[tm] 200 extractor, DIONEX. The soil samples were transferred into 11 ml extraction cells. We filled the remaining dead volume with

glass beads. The ASE extraction was performed using toluene as solvent under the following conditions: T= 175°C, P=1500 Psi. The extraction cell was filled with solvent, heated up and pressurized and followed by a static extraction of 5 min. Then the cell was flushed using 2 ml solvent. This cycle was done twice. After the second cycle, the sample was purged with Nitrogen during 99 s. Total volume of toluene that we used was less than 20 ml!

To determine possible degradation of OCDF as function of temperature during ASE, we extracted nominal 1.5 g of the mixture alumina/Cu with sodium sulfate at different temperatures: 80, 100, 150 and 175°C. Each temperature was performed in duplicate. The applied pressure was still 1500 Psi. The samples were transferred into 11 ml extraction cells. The remaining dead volume was filled with glass beads. The extraction cell was filled with solvent, heated up and pressurized and followed by a static extraction of 5 min. Then the cell was flushed using 2 ml solvent. This cycle was done three times. We flushed with nitrogen during 99s, after the last static extraction. Nominal 0.5 g Alumina/Cu sample (without sodium sulfate) was Soxhlet extracted using 350 ml toluene for 24 hours in the dark out to check for differences in degradation of OCDF between ASE and Soxhlet

We determined 'carry over' of PCDDs and/or PCDFs by extracting a blank (glass beads) after each of the above mentioned sample.

Clean up
We added 1 ml n-tetradecane as keeper and seventeen tetra- to octachlorinated $^{13}C_{12}$-labeled 2378-congeners as internal standards to the toluene extracts. These spiked extracts were concentrated to 1 ml n-tetradecane and then cleaned up using multiple column chromatography: silica gel, acid and base modified silica gel, basic alumina and carbon-on-celite.

4.   INSTRUMENTAL ANALYSIS
We analyzed the final extracts using HRGC/MS - an HP5890 series II on line with a HP5971 MSD - equipped with a 60m DB5 XLB column.
Native 2,3,7,8 congeners were quantified using ISTD with the internal standards that were added before the clean up.

RESULTS AND DISCUSSION

In table 1 we present the mean and relative standard deviation (RSD) for the 2,3,7,8-congeners found for ASE and Soxhlet.

The results in Table 1 show there is no statistical difference for concentrations of 2,3,7,8-congeners between ASE and Soxhlet extraction. We did not determine the contents of the homologue group totals, but we visually inspected the isomer patterns for the homologue groups and these showed also no difference between ASE and Soxhlet.

Table 2 shows the LOQs found for the carry over. All blanks showed no presence of PCDD and PCDFs above the LOQs. For the soil samples, we determined the carry over of the most abundant TeCDF- and PnCDF isomer. We used the alumina/Cu sample to determine the carry over of OCDF. The carry over was calculated using the equation:

$$\frac{LOQ_{blank}}{conc_{sample}} \times 100\%$$

Where LOQ_{blank} was the LOQ found for the blank that was directly extracted after the sample and $conc_{sample}$: was the concentration of the isomer in the proceeding sample. The absolute contents of the most abundant isomer of TeCDF, PnCDF and OCDF that were brought into the ASE^{tm} 200 were about 1200 ng, 1200 ng and 3300 ng, respectively.

During Soxhlet extraction using toluene in daylight OCDF can degrade with formation of lower chlorinated furans. 1234678-HpCDF was found to be the main conversion product (2). Therefore, we determined the mass ratio 1234678-HpCDF/OCDF for the ASE extraction's of the alumina/Cu sodium sulfate samples at different temperatures. The same ratio was determined for a Soxhlet extraction of the alumina/Cu using toluene in the dark for 24 hours to compare ASE with Soxhlet. These are shown in table 3.

The alumina/Cu sample that was extracted according to Soxhlet was not diluted with sodium sulfate as the ASE samples and contained about 10 times more OCDF. The table shows that ASE at higher temperatures do not cause more degradation of OCDF. ASE showed also no increase of OCDF degradation compared to Soxhlet, see table 3 and also table 1.

CONCLUSIONS
ASE of native PCDDs and PCDFs from soil using less than 20 ml toluene at a temperature of 175°C and a pressure of 1500 Psi yielded similar extraction efficiencies as Soxhlet extraction. The ASE extraction was done within 20 min.

The carry over calculated for the most abundant congeners was less than 0.01%.

Although we used a matrix with catalytic properties (alumina/Cu) degradation of OCDF was not found, not even at a temperature of 175 °C.

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Table 1: Comparison of extraction effieciencies of
2,3,7,8-congeners between Soxhlet and ASE.

12C12-congeners	Soxhlet		ASE	
	mean (µg/kg)	RSD. (%)	mean (µg/kg)	RSD. (%)
2,3,7,8-TeCDD	0.04	11	0.06	5.7
1,2,3,7,8-PnCDD	0.4	2.9	0.5	16
1,2,3,4,7,8-HxCDD	2.2	2.6	2.2	3.6
1,2,3,6,7,8-HxCDD	0.2	3.5	0.3	7.1
1,2,3,7,8,9-HxCDD	0.1	11	0.1	7.1
1,2,3,4,6,7,8-HpCDD	4.2	4.5	4.1	2.0
OCDD	0.4	9.6	0.4	7.9
2,3,7,8-TeCDF	46	6.7	41	16
1,2,3,7,8-PnCDF	1.9	13.6	1.7	24
2,3,4,7,8-PnCDF	7.0	2.47	7.2	4.5
1,2,3,4,7,8-HxCDF	2.8	3.41	2.9	4.5
1,2,3,6,7,8-HxCDF	0.04	5.09	0.05	5.0
2,3,4,6,7,8-HxCDF	0.02	26.94	< 0.03-	-
1,2,3,7,8,9-HxCDF	0.04	27.62	0.05	24
1,2,3,4,6,7,8-HpCDF	0.2	10.88	0.2	21
1,2,3,4,7,8,9-HpCDF	0.1	13.36	0.1	18
OCDF	13.6	4.81	13.1	3.1
TE(NATO/CCMS)	9.0	3.5	9.0	4.6

1 For ASE, we used the results of 4 samples to calculate the mean and relative standard deviation for 2,3,7,8-TeCDD and to calculate the total toxic equivalent concentration (TE(NATO/CCMS)). Because for two ASE extracted samples the concentration of 2,3,7,8 TeCDD was lower than the limit of quantification (<0.07)

2 Mean and relative standard deviation of 2,3,7,8 TeCDF found for ASE was calculated for 5 samples, because the content in one sample was an outlier.

Table 2: carry-over of most abundant congeners

Most abundant congener of	Carry over %
TeCDF	<0.01
PnCDF	<0.01
OCDF	<0.01

Table 3 Mass ratio of 1234678-HpCDF/OCDF found for the alumina/Cu sample using ASE at different temperatures and using Soxhlet extraction..

Temperature °C	ASE								Soxhlet
	80		100		150		175		111
Ratio	0.06	0.06	0.06	0.06	0.06	0.08	0.06	0.06	0.07