Fast Extraction and Clean-Up Efficiency of Polychlorinated-p-Dioxins and Furans from soil samples

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Introduction

The aim of this study was to maintain good quality, high efficiency and good recoveries when speeding up the analysis and clean-up. This was needed to increase the turnover and reduce the costs. The laboratory was able to increase the amount of samples analysed weekly to 20 samples. The problem occurring in samples from some sites was poor recovery of the labelled internal standards. The extraction used was ASE-extraction followed by only basic alumina (ICN, Super grade I) column clean up. The levels of PCDD&PCDF are normally below 20 ng I-TEQ/ kg dry soil. At Saw Mill sites where the pentachlorophenol containing KY-5 to protect the wood from blue staining fungi have been used[1], the contamination levels are ranging at the low contaminated spots between 50-500 ng I-TEQ/ kg dry soil and in the heavy contaminated spots it can raise > 3000 -9000 ng I-TEQ/ kg dry soil. Due to this fact the samples are normally pre analysed screening the chlorophenol content to be able to avoid cross contamination. This knowledge is also needed to be able to choose right amounts of sample taken to the extraction vessel to avoid overflow in the mass detector.

Methods and Materials

Sample preparation included air drying of the samples over night and sieving through a 2 mm stainless steel sieve[2]. The dry content was measured and 1-5 g was mixed with Dionex^R Prep DE (Diatomaceous Earth) and loaded on 34 ml extraction cells. The internal standard solution EPA-LCS obtained from CIL was added to the top of the extraction cells (40 µl ^{13}C-labelled PCDD/PCDF standard solution (16 out of 17 possible congeners). The ASE-300 was operated at 100 ºC using methylene chloride:acetone 50:50. The initial heating time was 5 minutes followed by two static cycles where the static time was 5 minutes, flush volume 60%, and purge time 90 seconds[3]. The extracts were dried with dry pre-washed sodium sulphate and after addition of 40 µl tetradecane evaporated to dryness. The transfer to the top of the clean-up column was done using a small amount of n-hexane.

The clean up consisted of only basic aluminium oxide (ICN, Super grade I). The column was pre-washed with 25 ml of n-hexane. After the sample has been transferred on-to the column it was first eluted with 20 ml n-hexane which was discarded and then with 10 ml of n-hexane :met-hylene chloride (HEX:DCM) 98:3 V/V (fraction 1 containing PCBs). The PCDD and PCDF where eluted with 30 ml of hexane:methylene chloride 80:20 V/V (fraction 2 containing PCDD and PCDF). This was not always sufficient so additional step of 80 ml of hexane:methylene chloride 50:50 V/V was added to ensure the recovery of the higher chlorinated congeners, especially hexa-CDD/CDF. This is shown in the Tables 1 and 2.

Gas chromatographic-high resolution mass spectrometry-selected ion monitoring (GC-HRMS-SIM) analyses were performed on a JEOL SX-102 double focusing mass spectrometer equipped with a HP-5890 GC Series II. The ionization current was 600 µA, ionization voltage 40 eV. The resolution used was 9000-10000. The certified standards (CRM-614) solutions S 0 - S 5 were used for calculation of response factors and testing the mass spectrometer linearity.

Results and Discussion

In the Table 1 it is presented the dioxin and furan content in the soil sample with different elution sequences, amounts and solvent compositions used to improve the recoveries of the internal standards. The PCDD and PCDF congeners were eluted from sample 201a with 30 ml 98:20 (HEX:DCM) + 30 ml 50:50 (HEX:DCM)) according to the aluminium clean up part in the in-hose method KET1200195, version 7 (This method is the full clean-up method using silica, acid silica, basic silica, basic aluminum oxide and Carbopack C on Celite)[4]. The recoveries of most internal standards were poor so the simplified clean up needs improvement. When adding an additional step using 50 ml of hexane: methylene chloride 50:50 V/V, the recoveries achieved fulfilled the requirements mentioned in EPA-1613 standard method (Table 2). When additionally eluting the same aluminium oxide column with 40 ml hexane:methylene chloride 50:50 V/V, only about 0.6-4.5 percent of the internal standards where additionally recovered. We can draw the conclusion from these experiments that the method using only basic aluminum clean up an additional elution of at least 80 ml hexane:methylene chloride 50:50 V/V is needed to get a sufficient recovery for the 17 2,3,7,8-substituted PCDD and PCDF congeners. Further more the mass spectrometric responses and linearity have to be checked daily. The CRM 614 S-3 was used for this to test the accuracy of the response factors used.

As can bee seen from the Table 1 the results are comparable even at low recoveries of the internal standards added. Only the LOD of the method can contribute to poor results.

The reason for the need of stronger elution power may be caused by pitch in the extract from the woodchips present in the samples.

Table 1. The content of PCDD&PCDF in a Saw Mill soil sample, that gave recovery problems. Sample 201a was ASE extracted eluted with 30 ml of each hexane:methylene chloride 80:20 + hexane:methylene chloride 50:50 V/V. The sample 201b was ASE extracted as sample 201a but the aluminum column was eluted with 30 ml of each hexane:methylene chloride 80:20 V/V and additionally eluted with 80 ml of hexane:methylene chloride 50:50 V/V and all the eluates where combined. The sample 201c is just an additional 40 ml of hexane:methylene chloride 50:50 V/V eluation of the aluminum oxide column and the eluate is threated as a separate sample.

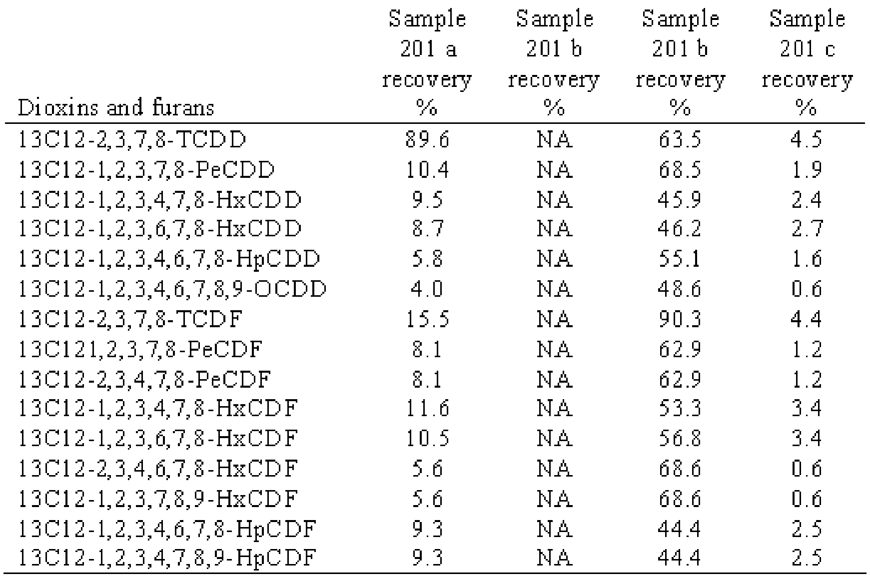
Dioxins and furans	Method Blank pg/g dw	Sample 201a Bl. Sub. pg/g dw	Sample 201b, run 1 Bl. Sub. pg/g dw	Sample 201b, run 2 Bl. Sub. pg/g dw	Sample 201c Bl. Sub. pg/g dw
2,3,7,8-TCDD	< 2	< 2	< 2	< 2	< 2
1,2,3,7,8-PeCDD	< 2	< 2	< 2	< 2	< 2
1,2,3,4,7,8-HxCDD	< 2	< 2	< 2	< 2	< 2
1,2,3,6,7,8-HxCDD	< 2	< 2	11	10	17
1,2,3,7,8,9-HxCDD	< 2	< 2	3.5	4.5	< 2
1,2,3,4,6,7,8-HpCDD	< 2	< 2	69	60	67
1,2,3,4,6,7,8,9-OCDD	< 2	< 2	39	36	36
2,3,7,8-TCDF	< 2	< 2	< 2	< 2	< 2
1,2,3,7,8-PeCDF	< 2	< 2	< 2	< 2	< 2
2,3,4,7,8-PeCDF	< 2	< 2	< 2	< 2	< 2
1,2,3,4,7,8-HxCDF	< 2	< 2	4.2	3.4	< 2
1,2,3,6,7,8-HxCDF	< 2	< 2	2.0	1.4	< 2
2,3,4,6,7,8-HxCDF	< 2	< 2	1.9	2.4	< 2
1,2,3,7,8,9-HxCDF	< 2	< 2	< 2	1.1	< 2
1,2,3,4,6,7,8-HpCDF	21	360	700	730	670
1,2,3,4,7,8,9-HpCDF	< 2	< 2	3.1	3.3	< 2
1,2,3,4,6,7,8,9-OCDF	24	770	420	420	1100
Sum of PCDD and PCDF	45	1100	1300	1300	1900
Dry weight when extracting, %		99.9	99.9	99.9	99.9
Limit of detection (LOD) is 2 pg/g dw					
Sum of I-TEQ as upper limit values		10	15	15	16

bl. sub. = blank reduction

dw = dry weight

Run 1 and 2 of sample 201b is just a duplicate mass spectrometric SIM analysis of the same sample vial.

Table 2. The recovery of the internal labeled standards added to the sample prior to extraction.



Dioxins and furans	Sample 201 a recovery %	Sample 201 b recovery %	Sample 201 b recovery %	Sample 201 c recovery %
13C12-2,3,7,8-TCDD	89.6	NA	63.5	4.5
13C12-1,2,3,7,8-PeCDD	10.4	NA	68.5	1.9
13C12-1,2,3,4,7,8-HxCDD	9.5	NA	45.9	2.4
13C12-1,2,3,6,7,8-HxCDD	8.7	NA	46.2	2.7
13C12-1,2,3,4,6,7,8-HpCDD	5.8	NA	55.1	1.6
13C12-1,2,3,4,6,7,8,9-OCDD	4.0	NA	48.6	0.6
13C12-2,3,7,8-TCDF	15.5	NA	90.3	4.4
13C121,2,3,7,8-PeCDF	8.1	NA	62.9	1.2
13C12-2,3,4,7,8-PeCDF	8.1	NA	62.9	1.2
13C12-1,2,3,4,7,8-HxCDF	11.6	NA	53.3	3.4
13C12-1,2,3,6,7,8-HxCDF	10.5	NA	56.8	3.4
13C12-2,3,4,6,7,8-HxCDF	5.6	NA	68.6	0.6
13C12-1,2,3,7,8,9-HxCDF	5.6	NA	68.6	0.6
13C12-1,2,3,4,6,7,8-HpCDF	9.3	NA	44.4	2.5
13C12-1,2,3,4,7,8,9-HpCDF	9.3	NA	44.4	2.5

NA= not analysed

Acknowledgements

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References

1. Veikko H. Kitunen, (1990) The use and formation of CPs, PCPPs and PCDDs/PCDFs in mechanical and chemical wood processing industries (Thesis), University of Helsinki, ISBN 952-90-2452-5

2. In house method KET4500398 version 6, for dioxin measurements from soil samples using activated carbon clean-up. Last accredited 31.12.2004. Laboratory code FINAS T050

3. DIONEX, Application Note 313

4. In house method KET1200195 version 6, for dioxin measurements from soil, sediment, water, fly-ash, wipe and emission samples (silica, acid silica, basic silica, basic aluminum oxide and activated carbon on Celite). Last accredited 31.12.2004, Laboratory code FINAS T050