Determination of PCDDs/PCDFs in soil using an activated carbon column as a rapid clean-up method

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Introduction

Soils from old sawmill and industrial or waste combustion sites contain polychlorinated dibenzo-p-dioxins and furans (1). These sites often are to be cleaned for living areas, thus they have to be cleaned from contaminants. A sensitive, rapid and accurate method had to be developed for the analysis of these contaminants. A lot of samples had to be analysed in a tigth time schedule and at low cost. The developed method uses a one-step activated carbon column cleanup and sensitive high resolution gaschromatography mass spectrometry in selected ion mode (HRGCMS/SIM). The earlier accreditated method contained complex cleanup-steps which were very labourous and time consuming.

The concentration given in Nordic Toxic equivalent is of great economical importance when the decision is made where to dispose the contaminated soils.

Samples containing more than 500 ng/kg dry weight (dw) dioxins and furans calculated as Nordic-toxic equivalents, have to be transported to a hazard waste incinerator plant (Ekokem in Riihimäki, Finland). Lower contaminated soils can be put into the waste soil dumps. Certified materials are needed for testing of the methods. Intercomparison studies are also needed to be able to keep the method accredited.

Material and Methods

The soil and sediment samples (0.05-5g) are Soxhlet extracted with 200 mL of acetone:dichloromethane (1:1 V/V) for 12 h (2). The internal standards (C^{13}-labelled) are added directly after sample weighing. The extracts are dried with Na_2SO_4 and then 50 µL of tetradecane is added and the extract volume is reduced in a rotavapor and by nitrogen stream at room temperature to dryness. The extract is redissolved in 1 mL of n-hexane.

Method A:

The extract is transferred into a test tube containing active copper chips (removal of sulphur from the samples). If there is very dark colour in the extract, 1 ml of dioxin pure concentrated H_2SO_4 is added. The extract is shaken for some minutes and allowed to settle. The dioxins and furans were extracted with 5-10 ml of n-hexane twice. The volume was reduced to ~ 1 ml by nitrogen stream. The n-hexane extract (1 ml) was transferred to the top of an activated carbon

column. The solvent is changed to dodecane and syringe standard is added (5 μL in nonane). The final volume is 40-60 μl in HP-autosampler vials equipped with 100 μl inserts.

The column used was a DB-dioxin (60 m, 0.32 mm id and 0.25 μm).

Method B:

The extract is transferred to the top of the precolumn. The conventional clean up method used as quality control consists of four columns; a silica/KOH-silica precolumn, an acidic silica column containing copper chips for removal of sulphur (used only for soil and sewage sludge samples), a basic alumina column and an active carbon column. The solvent is changed to dodecane and syringe standard is added (5 μL in nonane). The final volume is 40-60 μL in HP-autosampler vials equipped with 100 μL inserts.

The columns used to separate all 2,3,7,8-congeners were, DB-dioxin, DB-5MS and SP-2330.

The mass spectrometer used was a JEOL SX-102 operated at 10 000 resolution. EPA CS1-CS5 quantitation standards were used for linearity check of the response factors. EPA LCS labelled internal standard solution containing 16 C^{13}-labelled 2,3,7,8-PCDD and PCDF congeners, and EPA ISS syringe spike solution containing C^{13}-labelled 1,2,3,4-TCDD and C^{13}-labelled 2,3,7,8-HxCDD, were used for quantitation and recovery calculations.

Results and Discussion

An already analysed soil sample was analysed to evaluate the performance of the new method accreditated by FINAS (KET4500398, spring -98). The results of the analyses of the soil sample are compared to those obtained with the accreditated reference method (KET1200195, spring -95). The results are presented in Table 1.

The results presented in Table 2, are those we reported in the interlaboratory exercise organised by Dr. Richard Lawn from LGC, UK. The exercise was a part of UK's Valid Analytical Measurement (VAM) program. The procedure required three columns were used (DB-DIOXIN, DB-5MS and SP-2330). The results are presented in Tables 2.

The developed method has shown good reproducibility for this matrix. It has clearly been shown, that a cleanup step, using only an activated carbon column, gives accurate results. Standard deviation of the sum of I-TEQ is less than 5 %. The recovery of labelled standards have been according to EPA-1613 guidelines (3). Extraction efficiencies are over 98 %. This was tested both by re-extraction tests and by standard addition at three different levels.

Participation in Intercalibration Exercises annually is of great importance for the accreditation authorities.

Literature

1. Veikko H. Kitunen, (*Thesis*), *The use and formation of CPs, PCPPs AND PCDDs/ PCDFs in mechanical and chemical wood processing industries*, Helsinki **1990**
2. Lars-Owe Kjeller, *Upparbetning och analys av polyklorerade dibenso-p-dioxiner (PCDD) och polyklorerade dibensofuraner (PCDF) i sediment och jordprover*, Enheten för Miljökemi, Umeå **89-01-23**
3. EPA Method 1613: *Tetra- through Octa Chlorinated Dioxins and furans by Isotope Dilution HRGC/HRMS*, Revision A, October **1990**

Table 1. The content of dioxins and furans in a soil material analysed spring -97 with the reference method (B) and reanalysed with the new method (A) spring -98. All results presented in this table were obtained using only one column (DB-DIOXIN).

Sample	Soil (5g)	st dev ±	Soil (5g)	st dev ±	Soil	st dev ±
	A. mean	(n=4)	B. mean	(n=3)	mean of both methods	both methods
congener	ng/kg dw	ng/kg dw	ng/kg dw	ng/kg dw	ng/kg dw	ng/kg dw
2,3,7,8-TCDD	0.98	0.2	1.1	0,1	1.1	0.1
1,2,3,7,8-PeCDD	5.1*	0.7	6.3*	0,7	5.7	0.9
1,2,3,4,7,8-HxCDD	8.4	1.0	6.2	0,3	7.3	1.6
1,2,3,6,7,8-HxCDD	12	0.7	12	0.2	11.9	0.05
1,2,3,7,8,9-HxCDD	7.2	0.7	7.8	0.4	7.5	0.4
1,2,3,4,6,7,8-HpCDD	96	4.4	78	1.1	87	12
OCDD	279	8.2	219	2.3	249	42
2,3,7,8-TCDF	5.8	0.6	4.2	0.1	5.0	1.1
1,2,3,7,8-PeCDF	11*	2.4	5.9*	0.5	8.3	3.4
2,3,4,7,8-PeCDF	10*	0.9	10*	0.4	10.5	0.4
1,2,3,4,7,8-HxCDF	13*	0.4	20*	1.2	16.2	4.8
1,2,3,6,7,8-HxCDF	11	0.4	12	0.5	11	0.8
1,2,3,7,8,9-HxCDF	0,7	0.5	1.2	0.2	1.0	0.3
2,3,4,6,7,8-HxCDF	12	0.7	11	0.4	12	0.7
1,2,3,4,6,7,8-HpCDF	77	6.9	78	2.5	77	1.1
1,2,3,4,7,8,9-HpCDF	4.8	0.2	4.3	0.2	4.6	0.4
OCDF	62	15	46	0.5	54	11
Sum of I-TEQ	18.3	0.7	19.2	0.5	18.7	0.7

* not pure congeners on DB-DIOXIN
n = number of independent analyses

Table 2. The reported results of dioxin and furans in a soil sample in an interlaboratory exercise, using all procedure required columns to ensure full separation of all 2,3,7,8-PCDD/PCDF congeners. The analyses were done spring -97.

Sample congener	Soil (5g) mean ng/kg dw	st dev ± (n=3) ng/kg dw
2,3,7,8-TCDD	1.1	0.1
1,2,3,7,8-PeCDD	6.3	0.6
1,2,3,4,7,8-HxCDD	6.2	0.3
1,2,3,6,7,8-HxCDD	12	0.2
1,2,3,7,8,9-HxCDD	7.8	0.4
1,2,3,4,6,7,8-HpCDD	84	0.8
OCDD	235	10
2,3,7,8-TCDF	4.2	0.1
1,2,3,7,8-PeCDF	5.9	0.5
2,3,4,7,8-PeCDF*	8.3	0.3
1,2,3,4,7,8-HxCDF	15	1.8
1,2,3,6,7,8-HxCDF	12	0.4
1,2,3,7,8,9-HxCDF	1.2	0.2
2,3,4,6,7,8-HxCDF	11	0.4
1,2,3,4,6,7,8-HpCDF	80	1.8
1,2,3,4,7,8,9-HpCDF	4.3	0.2
OCDF	46	0.5

* = not completely resolved on these three columns
n = number of independent analyses