EVALUATION OF A NEW AUTOMATED CLEANUP SYSTEM FOR THE ANALYSIS OF PCDD/PCDF IN ENVIRONMENTAL SAMPLES

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Introduction

At present, there is ample evidence that chlorinated aromatic compounds with a dioxin-like activity have an adverse effect on exposed metabolisms. In 1997, the International Agency for Research on Cancer (IARC) declared the 2,3,7,8 - tetrachlorodibenzo - p -dioxin (TCDD) to be carcinogenic to humans (Group 1) [1]. Previously, in 1990 the World Health Organization (WHO) established a tolerable daily intake (TDI) of 10 pg I-TEQ/kg body weight (b.w.) for polychlorinated dibenzo- p -dioxins and dibenzofurans (PCDD/PCDF) based on the data available at the moment (toxicity, kinetic in humans and experimental animals, etc.) [2,3]. Since then, new toxicological studies have been carried out and important knowledges mainly related to endocrinological effects have been provided [4]. In 1998, the WHO reevaluated the health risk from PCDD/PCDF and established a new TDI between 1 and 4 pg I-TEQ/kg b.w. [5]. In parallel, stringent regulations governing public health reflect the widespread interest in these compounds. As an example, in 1996, the European Union (EU) member countries set limits for PCDD/PCDF from hazardous waste incineration stack gas emissions of 0.1 ng I-TEQ/Nm^3 [6].

In this connection, monitoring plays an important role in public and sanitary decisions. The growing demand for fast laboratory determinations implies a need to substantially reduce analysis time, without lowering the quality of the results. It is well known that appropiate methods and techniques as well as the application of quality control (QC) measures are required in order to guarantee good quality data. In case of PCDD/PCDF determinations, high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS) operating in a selected ion monitoring (SIM) mode and using isotopic dilution as a quantification method provides accurate sensitivity and selectivity for the analysis. However, an efficient cleanup is unavoidable prior to HRGC-HRMS analysis. Conventional cleanup procedures are usually based on liquid-solid adsorption chromatography at atmospheric pressure. Official organizations internationally recognized suggest sequential steps which include the use of several types of adsorbents such as silica, Florisil, alumina and activated carbon [6-8]. These methods are time-consuming and they require manual sample manipulation, that may give rise to a decrease of precision and accuracy, besides the risks of human exposure. Recently, a new commercial apparatus (Power Prep™ from Fluid Management Systems Inc., Watertown, MA, USA) based on the use of pressured column chromatographic procedures has been presented as an alternative that overcomes most of the disadvantges of the conventional cleanup methods aforementioned owing to its capability to process automatically unattented samples simultaneosly in approx one hour [9-12]. To the best of our knowledge, an exhaustive study evaluating the capability of this new Power Prep system for PCDD/PCDF analysis in abiotic samples has not been reported.

In the present work, an assessment of this new automated cleanup system was performed. The study was firstly carried out against standard mixtures containing labeled and unlabeled PCDD/PCDF. Next, evaluation of the system and quality information were obtained from the analysis of a certified reference material CRM 490 [13,14] and from the participation in an interlaboratory study [15,16]. Finally, in order to evaluate the suitability of the method for real sample analysis a comparison between a well established manual cleanup procedure and the new automated system was also made in different environmental matrices, such as stack gas emissions, fly ashes, sludges, ambient air and soil [6-8].

Materials and methods

Chemicals and materials.

EPA 1613 standard solutions in nonane (CS-1 to CS-5, PAR, LCS, ISS and CSS, Wellington Labs., Guelph, Ontario, Canada) were used for instrument calibration, quantification, recovery and quality control [7]. Solvents (acetone, dichloromethane, toluene, ethyl acetate, n-hexane and cyclohexane) for organic trace analysis were purchased from Merck (Darmstadt, Germany). For the manual cleanup process silica (70-210 mesh) and Florisil (60-100 mesh) both from Merck, alumina (50-200 mesh, ICN, Germany) and activated carbon (Carbopack C 80/100 mixed with celite, both from Supelco, Bellefonte, PA, USA) were employed as adsorbents in glass columns at atmospheric pressure [17-21]. Amberlite XAD-2 was purchased from Supelco (Bellefonte, PA, USA).

Sample collection.

Representative sample collection episodes were carried out depending on the type of matrices. Incineration samples were collected from a municipal waste incinerator (MWI). Flue gas emissions were collected with a stack gas sampler on the filter/condenser method using XAD-2 as an adsorbent. Ambient air samples were collected with a high volume sampler using a polyurethane foam (PUF) as an adsorbent. The sampling process in stack gas emissions and ambient air samples was controlled with CSS standard spiked in the filter or the adsorbents. More details about sample collection are given in previous works [17-21]. Sludge samples were obtained from a waste water treatment plant .

Extraction processes.

Appropiate extraction techniques as well as additional steps were also applied depending on the sample nature. All samples were spiked with a LCS standard solution prior to the extraction process. PCDD/PCDF were removed from the solid matrices (XAD-2, PUF, filters, soils, sludges and fly ashes) by soxhlet extraction using 300 mL toluene for 48 h [20]. Fly ash was treated with 25 mL HCl 3% for 2 h prior to soxhlet extraction. Liquid-liquid extraction with dichloromethane was performed to remove the compounds from condensed water from the flue gas emission samples.

Surfaces of tubes, vessels and other parts of the sampling device in contact with the sample were rinsed first with acetone followed by toluene [17-20].The final extracts were concentrated prior to the cleanup process, except for the sludge samples which were treated with sulphuric acid before the cleanup [21].

Cleanup.

Manual cleanup: The manual cleanup process was based on the sequential use of open chromatographic multilayer silica, Florisil and basic alumina columns. The multilayer silica column was composed of sequential layers of (3g) Na_2SO_4 /(12g) SiO_2-H_2SO_4 /(1g) SiO_2 / (6g) SiO_2-NaOH /(1g) SiO_2 /(2g) SiO_2-$AgNO_3$. 5 g Florisil and 6 g basic alumina adsorbents required to be conditioned at 600ºC and 300 ºC overnight respectively [6-8].

The extract applied to the top of the silica column was eluted with 150 mL of n-hexane and then concentrated until 5 mL prior to Florisil column. Next, interferences were eluted from that column with 250 mL of n-hexane and PCDD/PCDF were then recovered with 150 mL toluene:eter (1:1) solvent mixture. The extract was newly concentrated and transferred to 5 mL of n-hexane prior to alumina column. Interferences were eluted from this column in two separate runs, with 25 mL n-hexane and 20 mL n-hexane:dichloromethane (98:2) solvent mixture. The PCDD/PCDF were recovered with 150 mL n-hexane:dichloromethane (1:1) solvent mixture. Finally, an additional carbon column had to be included for those cases in which some interfering compounds were not removed in the previous columns. The carbon was activated at 130ºC overnight and prerinsed with different solvents in separate runs: 2.5 mL toluene, 1 mL toluene:dichloromethane:MeOH (15:4:1) and 0.5 mL cyclohexane:dichloromethane (1:1). Then, the column was kept at 130ºC overnight. Next, the column was prerinsed with 2.5 mL of n-hexane and the sample extract was applied to the top of the column. The interferences were eluted with 1.5 mL n-hexane and 2 mL dichloromethane:cyclohexane (1:1). PCDD/PCDF were recovered by inverting the column with 30 mL toluene [17-20]. The whole process was accomplished in three or four days.

Automated cleanup: The automated cleanup system Power Prep is based on the sequential use of multilayer silica, basic alumina and PX-21 carbon adsorbents respectively, prepacked in Teflon columns and sealed (Fluid Management Systems Inc., MA, USA). The Power Prep system configuration consists of a valve module, a valve drive module and a pump. All the tubes and connections in contact both with the sample or solvents are made of Teflon. The whole system is computer controlled and can be programmed as required (i.e. volume, flow rates, direction of solvent flow, etc.). The flow rates range from 5 to 15 mL/min without restrictions on solvent volume. The pressure is controlled by a pressure sensor on each pump module that automatically shuts the system off when the pressure exceeds 25 psi.

Prior to the automated cleanup process, the n-hexane extracts had to filtered (particulate size should not exceed 1 µm). Afterwards, they were loaded and pumped through individual sets of multilayer silica followed by a basic alumina columns with 90 mL of n-hexane at 15 mL/min. Interferences were eliminated with 60 mL n-hexane:dichloromethane (98:2) at 12 mL/min. Next, PCDD/PCDF were eluted from the alumina column and transferred to the PX-21 carbon column with 120 mL of n-hexane:dichloromethane (1:1) at 7 mL/min. The interferences were eluted with 12 mL of ethyl acetate:toluene (1:1) in the forward direction at 15 mL/min, and PCDD/PCDF were collected from the carbon column in the reverse direction with 65 mL of toluene at 5 mL/min. The whole process was accomplished in approx one hour.

HRGC-HRMS analysis.

Purified extracts were analyzed by HRGC-HRMS on a GC 8000 series gas chromatograph (Carlo Erba Instruments, Milan, Italy) equipped with a CTC A 200S autosampler and coupled to an Autospec Ultima mass spectrometer (Micromass, Manchester, UK), using a positive electron ionization (EI+) source and operating in the SIM mode at 10000 resolving power (10% valley definition). Verification of the resolution in the working mass range was obtained by measuring perfluorokerosene (PFK) reference peaks. The current trap was 500 µA, the ionization energy was 37 eV and the acceleration voltage was 8000 V. Ion source temperature was 250 ºC. The two most abundant ions in the [M-Cl]+ cluster were monitored at a 50 ms dwell time and a delay time of 20 ms. Chromatographic separation was achieved with a DB-5 (J&W Scientific, CA, USA) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 µm film thickness) with helium as carrier gas at a linear velocity of 35 cm/s (T: 100ºC) in the splitless injection mode (1-2 µL). As a confirmation, a DB-DIOXIN (J&W Scientific, CA, USA) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 µm film thickness) was employed when required. Chromatographic windows for each group of PCDD/PCDF homologues, from tetra- to octachlorinated, were defined on the DB-5 capillary column. Injector temperature was 280 ºC for the DB-5 column and 260 ºC for the DB-DIOXIN column. The interface temperatures for the DB-5 and DB-DIOXIN columns were 280 ºC and 260 ºC, respectively. The temperature program was: 140 ºC (1min) to 200 ºC (1min) at 20 ºC/min, then at 3ºC/min to 300 ºC and held isothermally for 20 min at 300 ºC for the DB-5 column and 140 ºC (1min) to 200 ºC (1min) at 20 ºC/min, then at 2ºC/min to 280 ºC and maintained isothermally for 85 min at 280 ºC for the DB-DIOXIN column [17].

Quantification.

Quantification was carried out by the isotopic dilution method [6-8]. Relative response factors (RRF) for the individual isomers were obtained by analyzing CS-1 to CS-5 standard solution mixtures. The recoveries of labeled standards were calculated using a mixture of two labeled PCDD (ISS) added before the HRGC-HRMS analysis.

Limit of detection.

The limit of detection (LOD) for PCDD/PCDF was defined as the minimum concentration of analyte that produces a clear peak with an acceptable chlorine isotope ratio and with a signal-to-noise ratio equal to 3. In our study, the chlorine isotope ratio for the molecular cluster ions was within ±15% of the theoretical ratio and the peak responses for each of the two selected molecular cluster ions were at least three times the background noise level [6-8].

Results and discussion

Analysis of standard mixtures.

The first step in the evaluation of the system was based on the analysis of a working standard mixture solution in nonane formed by 17 unlabeled

2,3,7,8-substituted PCDD/PCDF in concentrations ranging from 20 to 200 pg/µL and 15 labeled 2,3,7,8-substituted PCDD/PCDF in concentrations of 50 pg/L. Five different aliquots of 10 µL from the working standard solution were transferred through individual sets of 10 mL n-hexane and analyzed using the automated cleanup system. The average recoveries and relative standard deviations (RSD %) of the native PCDD/PCDF congeners are shown in Table 1. The recoveries were consistently high, between 96 and 105 %. In case of the labeled compounds, the values were slightly lower, between 74 and 92% Figure 1, but they still were in good agreement with the minimum requirements of well accepted methods [6-8].

Analysis of Certified Reference Materials.

Accuracy and precision of the automated system were evaluated against a fly ash certified reference material (CRM 490) [13-14] which has matrix and target analytes similar to those found in real environmental samples. The obtained data (mean: 3.24 ng I-TEQ/g (n=3) and RSD<1 %) were comparable to the values reported by BCR for this material (mean: 3.71 ng I-TEQ/g, RSD=7%).

The reproducibility of the method was also verified by analyzing in triplicate the extracts obtained from different matrices such as flue gas emissions, fly ashes and a soil sample Table 2, Table 4. The RSD values were consistent among all the samples (0.29-5.73%) and they were in good agreement with that found in the analysis of the certified reference material [21].

Comparison between manual and automated cleanup procedures.

The suitability of the new automated system in the analysis of real abiotic samples was evaluated against a well established manual cleanup procedure [6-8]. Some different environmental matrices such as flue gas emissions, fly ashes, ambient air, sludges and soils were considered for this study. Figure 2 gives comparison data of PCDD/PCDF, expressed in I-TEQ values, obtained from the analysis of the aforementioned samples. Even though there were remarkable differences among matrices in terms of organic matter content, specific interferences (i.e. coplanar PCB, PAH or PCN) and PCDD/PCDF pattern and profile, the results show a good correlation between the total I-TEQ values using both, manual and automated, cleanup procedures.

The pattern of TCDF chromatograms (m/z:303.9016) of a flue gas emission extract cleaned up by the automated and the manual methods respectively is shown. Significant differences between the two chromatograms were not found, which indicates the capability of the new automated procedure. Furthermore, the congener-specific 2,3,7,8-chlorinated PCDD/PCDF analysis of this flue gas emission sample corroborated the similar performance of the two methods. The values were comparable in both cases, with acceptable recovery rates [6-8] and besides, it has to be pointed out that LOD were slightly better when the automated system was used Table 3.

Intercalibration Exercises.

Additional evaluation of the Power Prep system and quality information were obtained from the participation in a interlaboratory study (the Fourth International Intercalibration Study on incineration and soil/sediment/sludge samples) recently organized by the Institute of Environmental Chemistry of the University of Umea (Sweden). The final report of this intercalibration study has been already published [15,16]. The data about levels of PCDD/PCDF of a fly ash extract, expressed in ng I-TEQ/ampoule, corresponding to the 49 laboratories participating on the incineration exercise. The average is given by the straight line and the standard deviation (SD) by the dotted line. The value reported by our laboratory corresponds to the participant number 70. It has to be remarked that this value was found acceptable on statistical grounds. Therefore, these results confirmed the suitability of the system for the cleanup process in the analysis of PCDD/PCDF in real samples.

Quality assurance.

The criteria for ensuring the quality dioxin analysis include the application of some quality control (QC) measures, such as a continous monitoring of laboratory contamination based on the determination of a blank sample covering the whole analytical procedure, including extraction, cleanup and quantification. Other performance checks considered in this work were: (i) isomer specific GC separation, (ii) sensitivity check of mass spectrometer (MS), (iii) check of MS resolution at 10000, (iv) sufficient recovery (v) parallel analysis of quality control sample and (vi) participation in interlaboratory studies.

In addition, the cleanliness of the automated system was exhaustively evaluated. After analyzing each sample the system was throughly washed with a solvent mixture, afterwards these solvents were analyzed prior to the analysis of the following samples. A classification between low level samples (ambient air or soils) and high level samples (stack gas emissions, fly ashes or sludges) was made and they were always analyzed separately in two different lines in order to avoid eventual contamination episodes. Next, a number of extracts from solvent washes were analyzed to check the cleanliness of the automated system. After the analysis of low level samples no remarkable signals were detected from solvent washes and acceptable blanks were obtained. Special attention was focused on the cleanliness system after the analysis of high level samples. The analysis of 4 g fly ash containing approx 3.5 ng I-TEQ/g was followed by the analysis of four 45 mL n-hexane:dichloromethane (1:1) solvent washes in separate runs. The first wash showed concentrations of less than 1% of the sample value. In the second wash the levels did not exceed 0.1 %, whereas the third wash yielded traces of hepta- and octachlorodibenzo-p-dioxin as well as hepta- and octahlorodibenzofurans at concentrations close to the detection limit. No peaks were found in the fourth solvent analysis. From these findings it was concluded that a 135 mL n-hexane:dichloromethane (1:1) solvent wash allowed to obtain an acceptable blank procedure. However, as a quality assurance measure, an evaluation of the cleanliness of the automated system prior to the analysis of the next sample is always recommended, especially when the expected levels between two samples might present large differences.

Another interesting question related to quality assurance measures concerns the lock-mass, which constitutes an important assessment tool for the quality of the cleanup. From our experience, the lock-mass for each m/z group did not vary by more than ±20% throughout its respective retention time window in the samples analyzed by the automated system . This fact indicated no presence of interferences which might reduce the sensitivity and tuning of the MS. The absence of coeluting sustances did not only improve the HRMS analysis, either in our study an increase in the lifetime of the GC columns and in the quality of the GC separation was observed overall.

Conclusions.

The automated cleanup system Power Prep™ has demonstrated to be successful for PCDD/PCDF determinations in environmental samples (flue gas emissions, fly ashes, soils, ambient air and sludges). In addition, the system offers some advantages over conventional cleanup methods. It allows to process multiple unattended samples, is less time-consuming, reduces sample manipulation and consequently diminishs the risks of human exposure and increases the accuracy of the procedure. Therefore, the new Power Prep apparatus constitutes a considerable improvement on the cleanup process for PCDD/PCDF determinations.

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Table 1. Recovery of a standard mixture analysis

Compounds	**Concentration** (pg/µL)	**Recoveries (%) Mean ± SD** (n=5)
2,3,7,8-TCDF	20	101 ± 1.21
1,2,3,7,8-PeCDF	100	101 ± 1.30
2,3,4,7,8-PeCDF	100	101 ± 0.74
1,2,3,4,7,8-HxCDF	100	99 ± 1.86
1,2,3,6,7,8-HxCDF	100	103 ± 1.38
2,3,4,6,7,8-HxCDF	100	100 ± 1.67
1,2,3,7,8,9-HxCDF	100	101 ± 1.58
1,2,3,4,6,7,8-HpCDF	100	105 ± 1.69
1,2,3,4,7,8,9-HpCDF	100	99 ± 1.81
OCDF	200	97 ± 3.98
2,3,7,8-TCDD	20	100 ± 0.53
1,2,3,7,8-PeCDD	100	101 ± 0.73
1,2,3,4,7,8-HxCDD	100	96 ± 5.07
1,2,3,6,7,8-HxCDD	100	99 ± 1.60
1,2,3,7,8,9-HxCDD	100	100 ± 6.54
1,2,3,4,6,7,8-HpCDD	100	99 ± 0.39
OCDD	200	99 ± 0.35

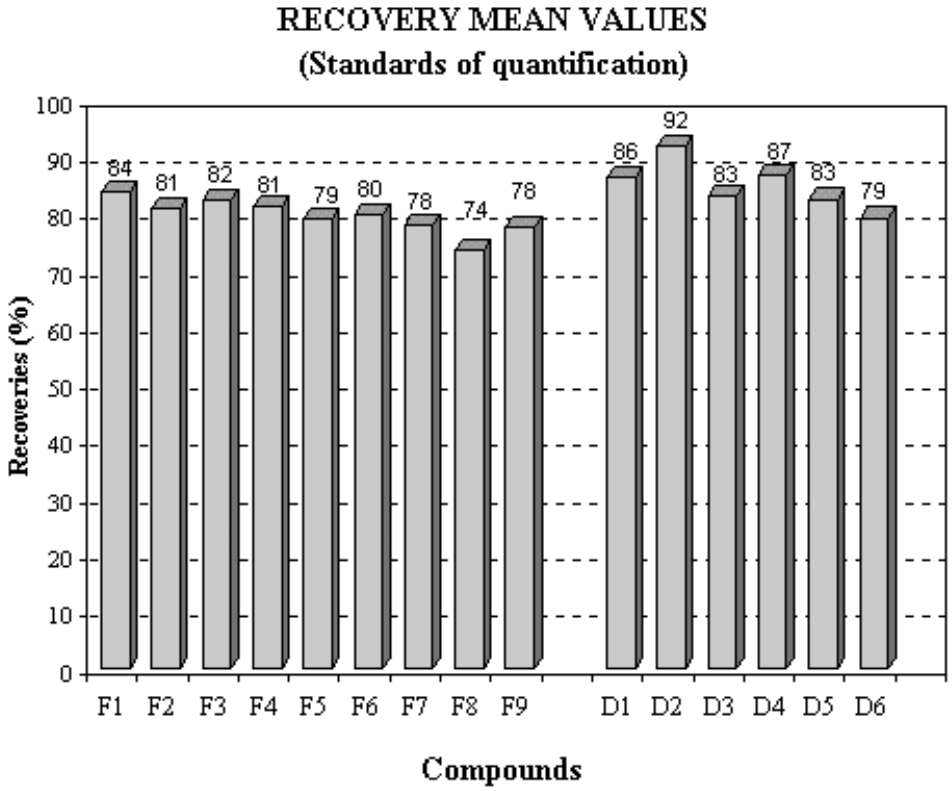
Table 2. Replicate analysis of real samples using the automated system cleanup

Matrices	**Mean** (n=3)	**SD**	**RSD** (%)
Flue gas emissions (pg/Nm3)			
Sample 1	86.19	1.41	1.63
Sample 2	52.13	0.76	1.46
Fly ashes (ng/g)			
Sample 1	1.02	0.06	5.73
Sample 2	3.24	0.01	0.36
Sample 3	0.02	<0.001	3.14
Soils (pg/g)			
Sample 1	7.29	0.02	0.29

Data expressed in I-TEQ

Table 3. Isomer-specific comparison of 2,3,7,8-substituted congeners in a flue gas emission sample

CLEANUP PROCEDURE	Automated			Manual		
COMPOUND	**Conc.** (pg/Nm^3)	**DL** (pg/Nm^3)	$^{13}C_{12}$ **Recovery** (%)	**Conc.** (pg/Nm^3)	**DL** (pg/Nm^3)	$^{13}C_{12}$ **Recovery** (%)
2,3,7,8-TCDF	57.45	0.034	72	58.28	0.157	73
1,2,3,7,8-PeCDF	3.76	0.389	73	8.64	0.638	74
2,3,4,7,8-PeCDF	34.00	0.472	66	36.40	0.866	70
1,2,3,4,7,8-HxCDF	124.72	1.330	75	129.21	1.150	75
1,2,3,6,7,8-HxCDF	71.81	1.310	70	72.22	1.110	73
2,3,4,6,7,8-HxCDF	206.61	1.470	72	198.96	1.320	72
1,2,3,7,8,9-HxCDF	16.22	1.960	67	15.74	1.760	64
1,2,3,4,6,7,8-HpCDF	588.57	0.164	61	600.93	0.280	67
1,2,3,4,7,8,9-HpCDF	252.08	0.247	56	258.31	0.448	57
OCDF	1143.44	0.373		1162.02	0.412	
2,3,7,8-TCDD	0.66	0.045	75	0.25	0.188	73
1,2,3,7,8-PeCDD	2.53	0.055	73	1.95	0.226	75
1,2,3,4,7,8-HxCDD	9.21	0.169	70	9.51	0.304	65
1,2,3,6,7,8-HxCDD	24.64	0.149	70	24.86	0.268	66
1,2,3,7,8,9-HxCDD	16.06	0.160		16.96	0.287	
1,2,3,4,6,7,8-HpCDD	253.97	0.148	65	256.04	0.375	69
OCDD	769.53	0.326	55	771.73	0.455	58
I-TEQ Total (pg/Nm^3)	84.64			85.51		



F1: 13C12-2,3,7,8-TCDF
F2: 13C12-1,2,3,7,8-PeCDF
F3: 13C12-2,3,4,7,8-PeCDF
F4: 13C12-1,2,3,4,7,8-HxCDF
F5: 13C12-1,2,3,6,7,8-HxCDF
F6: 13C12-2,3,4,6,7,8-HxCDF
F7: 13C12-1,2,3,7,8,9-HxCDF
F8: 13C12-1,2,3,4,6,7,8-HpCDF
F9: 13C12-1,2,3,4,7,8,9-HpCDF

D1: 13C12-2,3,7,8-TCDD
D2: 13C12-1,2,3,7,8-PCDD
D3: 13C12-1,2,3,4,7,8-HxCDD
D4: 13C12-1,2,3,6,7,8-HxCDD
D5: 13C12-HpCDD
D6: 13C12-OCDD

Figure 1. Internal standard recovery rates obtained by the analysis of a standard mixture

Table 4. Parallel analysis of quality control samples

Matrix	Aliquote 1	Aliquote 2	Aliquote 3
Flue gas emissions			
Sample 1 *(pg /Nm3)*	87.18	85.19	-
Sample 2 *(pg /Nm3)*	52.67	51.59	-
Fly ash			
Sample 1 *(ng /g)*	0.98	1.00	1.09
Sample 2 *(ng /g)*	3.23	3.25	3.25
Sample 3 *(pg /g)*	0.022	0.023	-
Soil			
Sample 1 *(pg /g)*	7.27	7.30	-

Data expressed in I-TEQ

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