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Automated clean up method for the determination of PCDD/Fs in long term MSWI emissions

Andrea Colombo^{1,4}, Marco Lodi¹, Simone Caimmi², Gianluca Rossetti³ and Andrea Manni³

¹ Istituto di Ricerche Farmacologiche Mario Negri IRCCS, Department of Environmental Health Science, Via La Masa 19, 20156 Milan, Italy;

² Environ-Lab, via don Bosco 3, Genzone (PV), Italy;

³ Chemical Research 2000 Srl, Via Santa Margherita di Belice 16, Rome, Italy.

⁴ Email: andrea.colombo@marionegri.it

Abstract. The aim of the present work is to assess a simplified and automated clean up procedure for the determination of PCDD/Fs from MSWI emission samples obtained from long term monitoring system. Results showed that extraction recoveries satisfactorily fulfill the criteria required by the official methods for the determination and quantification of PCDD/Fs from MSWI emissions.

1. Introduction

In the last decades several studies have been performed in order to investigate levels of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) emitted from Municipal Solid Waste Incinerators (MSWI). PCDD/Fs are well known as unintentionally generated Persistent Organic Pollutants (POPs), which pose serious health and environmental risks on a global scale [1] [2]. These studies however are based on PCDD/Fs analysis from short-term manual sampling measurements. It has been demonstrated that PCDD/Fs emissions might vary significantly over time, showing considerably higher values under unstable conditions such as plant startup or shut-down [3] [4] [5].

The officially Reference European Standard method with respect to the determination and verification of compliance with the legal limits of PCDD/Fs in industrial atmospheric emissions is UNI EN 1948 entitled: Emissions from a fixed source - Determination of the mass concentration of PCDD / PCDF and dioxin PCBs similar - Parts 1 - 2 and 3 respectively related to sampling, extraction and purification and finally the identification and quantification of PCDD/Fs [6].

The recent introduction of EN 1948-5 [7] addressed the principles and minimum requirements for long-term sampling of PCDD/Fs. It offers the advantage to cover all operation periods of the investigated plant, such as start-up and shut-down when levels of PCDD/Fs might be considerably higher. This allows for consequently more representative sampling and lower limit of detections (LODs). The clean-up procedure of EN 1948-2 [6] is suitable for flue gas samples of 10 m³ at 0.1 ng I-TEQ/Nm³, while a Long Term sampling will typically collect a volume from 50 m³ to 400 m³ [7]. These larger volumes, necessary to achieve the enrichment of PCDD/Fs in the extracts, increase the difficulty in removal of many potentially interfering chemicals. The solution provided by the EN1948-5 is to divide the extracts in appropriate fractions (5% to 50%) [7], with a corresponding increase of the uncertainty of the results and LODs.



Reference methods for the quantitative analysis of PCDD/Fs involve successive clean-up steps on various chromatographic adsorbents (multi-layer silica, Florisil, alumina, activated carbon) which considerably increases the time needed for analysis. These methods are generally expensive and slow.

The objectives of this study were to provide a simplified clean-up procedure, capable of working on the long-term sample extract, through the assessment of an automated clean-up system based on gel permeation chromatography combined with an in-line concentration system and solid phase modules able to manage the acid silica/neutral silica and basic alumina purification. The system processes the samples in series.

2. Details experimental

The MSWI investigated has a capacity of 150 tons of wastes per day and is composed of two incinerating units.

The automatic long-term sampling device is a Dioxin Ames System® (Environnement SA, France) and works according to cooled probe method described in EN-1948:1 (CEN, 2006) [6], with adsorption on XAD-2.

The study consisted of a total 28 samples (12 and 16 samples for the first and second incinerating units, respectively) which were spiked with a mixture of ¹³C-labelled PCDD/Fs standards (Wellington Laboratories, Canada). Extraction was performed with an ASE 300 from Dionex (Sunnyvale, CA, USA) and carried out with dichloromethane, using the following instrumental parameters:

- System Pressure: 1500 psi
- Oven Temperature: 80 °C
- Oven Heatup Time: 5 min
- Static Time: 15 min
- Solvent: Dichloromethane
- Flush Volume: 60% of extraction cell volume
- Nitrogen Purge: 1 MPa (150 psi) for 60 s

The extract was concentrated to 5 ml and injected into a 5ml loop of an automated GPC system (AccuPrep MPS™, J2 Scientific). The GPC column was 2.5cm x 43 cm filled with 40 g of BioBeads SX-3 resin working at a flow rate of 5 ml/min using dichloromethane. The eluate was collected between 17:30 and 25 min (37.5 ml) and concentrated through an inline evaporation system (AccuVap™, J2 Scientific) to a final volume of 5 ml. The eluate was concentrated under nitrogen flow to dryness and then diluted with n-hexane to 1ml and was submitted to an automated clean up system (Dioxin/SPE module) using acid silica/neutral silica (Si/5G-44%H₂SO₄/Si, Supelco, USA) and basic alumina cartridges (manually packed with 7g of active Aluminium oxide 90 basic, Supelco USA).

The sample was loaded on acid silica/neutral silica cartridge connected to a basic alumina cartridge and eluted with 75ml of n-hexane. This fraction was discarded. The basic alumina cartridge was eluted with 60 ml of n-hexane/dichloromethane (98:2) and this fraction, containing PCBs was discarded. Then the basic alumina was eluted with 120ml of a mixture of n-hexane/dichloromethane (1:1) and this fraction containing PCDD/Fs was concentrated to 50 µl and spiked with a ¹³C-labelled standard and submitted to instrumental analysis (Wellington Laboratories, Canada).

The flow rate used for all columns was 6ml/min.

The GPC and SPE clean up procedure is shown in Figure 1.

The pollutants were detected by a GC coupled with a high-resolution mass spectrometer, operating in the electron impact ionization (EI+) mode, at 10,000 resolution power. A capillary column (60 m x 0.20 mm x 0.25µm) with splitless injection was used. The PCDD/Fs temperature program for analysis was 160°C for 1 min, 2.5°C/min increase until 300°C, 300°C maintained for 6 minutes.

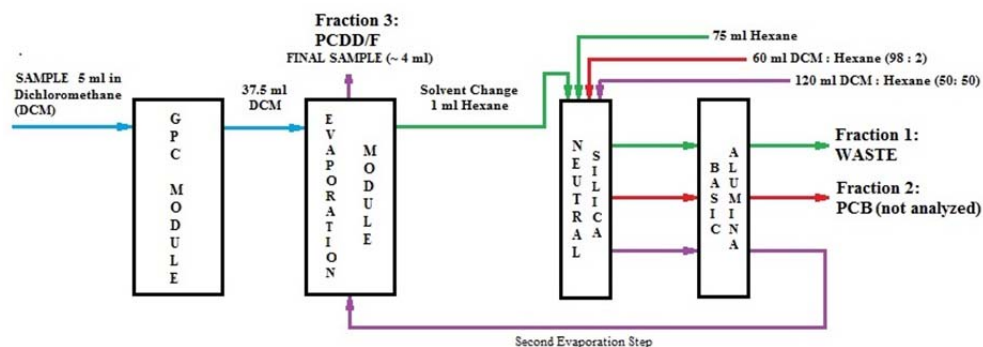


Figure 1. Automated clean up design.

The ions were scanned in the selected ion-monitoring (SIM) mode. The ions monitored were tetra-chlorinated congeners and M+2 and M+4 for penta-, hexa-, hepta- and octa-chlorinated congeners. Peaks were accepted if the isotopic ratio was within 15% of the corresponding ratio in the internal standard (IS). Limits of detection (LOD) were calculated individually for each sample on the basis of a signal-to-noise ratio of 3:1. Field and analytical blanks were run covering the whole sampling and analytical procedure. Blank PCDD/F samples showed no peak.

3. Results and discussion

Table 1 presents the PCDD/Fs concentrations at the MSWI chimney. These values ranged from 0.001 to 0.006 ng I-TEQ/Nm³ in samples collected from the first incinerating unit, and from 0.001 to 0.004 ng I-TEQ/Nm³ in samples collected from the second incinerating unit. The normal state (N) refers to 1 bar, 273.15 K and 11% oxygen content. In general, higher values were found in the first incinerating unit, in spite of a large variability (78% and 67% respectively), the emission values from the chimney were always lower than the emission limit (0.1 ng TEQ/Nm³) adopted from the Italian MSWI regulations.

Table 1. PCDD/F concentrations at the MSWI chimney referred to the volume of stack gas (ng/Nm³).

Congener	First Incinerating Unit n=12		Second Incinerating Unit n=16		
2,3,7,8-TCDF	0.006	0.005	0.0007	±	0.0005
2,3,7,8-TCDD	0.002	0.002	0.0002	±	0.0001
1,2,3,7,8-PnCDF	0.005	0.006	0.0004	±	0.0003
2,3,4,7,8-PnCDF	0.015	0.012	0.0014	±	0.0009
1,2,3,7,8-PnCDD	0.006	0.006	0.0004	±	0.0003
1,2,3,4,7,8-HxCDF	0.013	0.011	0.0008	±	0.0005
1,2,3,6,7,8-HxCDF	0.017	0.014	0.0012	±	0.0008
2,3,4,6,7,8-HxCDF	0.040	0.032	0.0024	±	0.0015
1,2,3,7,8,9-HxCDF	0.002	0.001	0.0002	±	0.0001
1,2,3,4,7,8-HxCDD	0.010	0.008	0.0005	±	0.0003
1,2,3,6,7,8-HxCDD	0.021	0.017	0.0014	±	0.0009
1,2,3,7,8,9-HxCDD	0.016	0.014	0.0007	±	0.0004
1,2,3,4,6,7,8-HpCDF	0.064	0.053	0.0033	±	0.0022
1,2,3,4,7,8,9-HpCDF	0.004	0.003	0.0003	±	0.0002
1,2,3,4,6,7,8-HpCDD	0.129	0.106	0.0070	±	0.0047
OCDD	0.159	0.125	0.0066	±	0.0046
OCDF	0.014	0.010	0.0008	±	0.0005
I-TCDD Eq.	0.027	0.021	0.0019	±	0.0012

In order to evaluate the quantitative performance of the automated system the mean recoveries and their standard deviations of labelled PCDD/Fs were calculated and showed in Table 2.

In all the samples analyzed recoveries are in good agreement with the quality standards requirements of reference method, ranging from 65% to 119% [6].

It has been reported that each source type favors the formation and environmental release of certain mixtures of PCDDs and PCDFs. These mixtures are called congener profiles, pattern or fingerprint, which represents the distribution of total PCDDs and PCDFs present in the mixture. A congener profile may serve as a signature of the types of PCDD/Fs associated with particular environmental sources of these compounds [8] [9]. Consequently, quality data obtained from several MSWI should result in similar 2,3,7,8 chlorine-substituted [10] congeners.

PCDD/Fs congener profiles, obtained dividing the congener specific stack gas concentration by the average total PCDD/F stack gas concentration, are shown in Figure 2 and Figure 3 respectively.

As shown OCDD or HpCDD were the highest in the pattern of PCDDs, while 1,2,3,4,6,7,8-HpCDF was the highest in the pattern of PCDF for all samples, similarly to those reported in other studies [10].

Table 2. PCDD/F recovery and standard deviation.

Congener	Recoveries (Mean±SD) n=28		
2,3,7,8-TCDF	91%	±	10%
2,3,7,8-TCDD	87%	±	11%
2,3,4,7,8-PnCDF	82%	±	16%
1,2,3,7,8-PnCDD	82%	±	12%
1,2,3,4,7,8-HxCDF	91%	±	10%
1,2,3,6,7,8-HxCDF	89%	±	11%
2,3,4,6,7,8-HxCDF	88%	±	9%
1,2,3,4,7,8-HxCDD	91%	±	10%
1,2,3,6,7,8-HxCDD	83%	±	11%
1,2,3,4,6,7,8-HpCDF	91%	±	10%
1,2,3,4,6,7,8-HpCDD	91%	±	12%
OCDD	90%	±	12%
OCDF	93%	±	12%

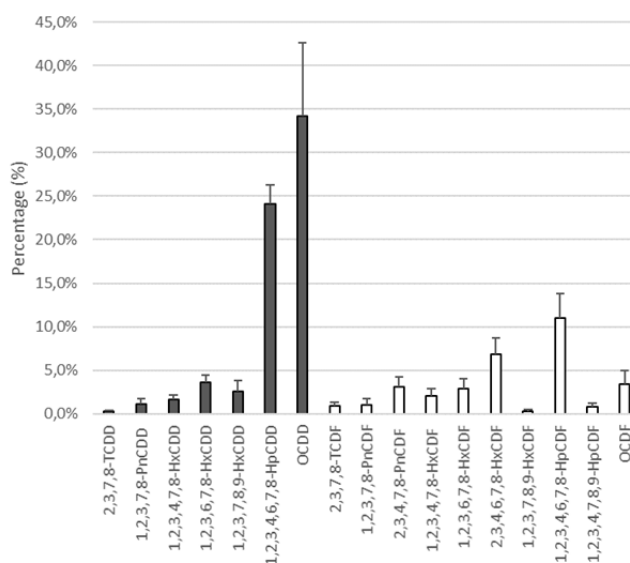


Figure 2: Average PCDD/Fs congener pattern of MSWI first incinerating unit. The percentage indicates the contribution of the different congeners to the total of the 2,3,7,8-PCDD/Fs.

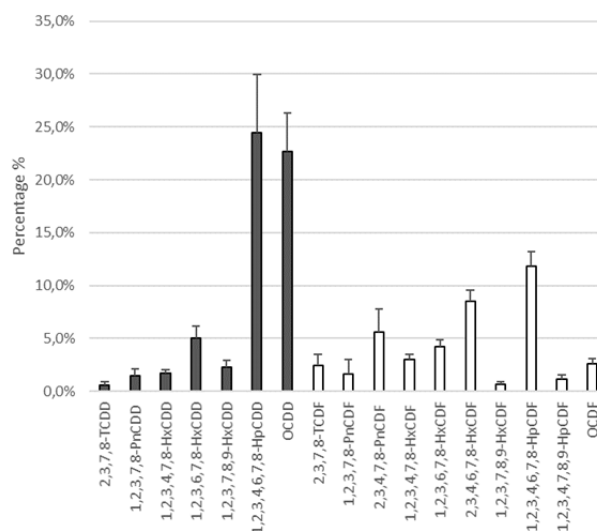


Figure 3 Average PCDD/Fs congener pattern of MSWI second incinerating unit. The percentage indicates the contribution of the different congeners to the total of the 2,3,7,8-PCDD/Fs.

4. Conclusions

This study demonstrated that the automated GPC/SPE purification system is able to satisfy the official EN-1948-2 method specifications and performances. It fits the purposes of the determination and quantification of PCDD/Fs in long term samples obtained from MSWI.

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