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SIMPLIFIED CLEAN-UP METHOD FOR dl-PCBs AND PCDD/Fs IN FLUE GAS EMISSIONS

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Abstract
A method for the analysis of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/Fs) and dioxin-like polychlorinated biphenyls (dl-PCB) in flue gas emissions was developed. Reference methods for the quantitative analysis of PCDD/Fs and dl-PCBs involve successive clean-up steps on various chromatographic adsorbents which considerably increase the time needed for analysis. In order to simplify the clean-up step we used an automated clean-up system based on gel permeation chromatography to perform the purification of co-extractable and potentially interfering compounds combined with an in-line concentration system, followed by a SPE alumina column to separate PCDD/Fs from and dl-PCBs. It was possible to couple the two columns thanks to the in-line concentration system. Different elution conditions were tested starting from the most common procedure applied to separate PCDD/Fs from dl-PCBs: in the final experiment we obtained a complete separation of all dl-PCBs from PCDD/Fs.

Introduction
Fast and not expensive methods for analyses of dioxins and dioxin-like PCB have to be developed allowing to analyze in routinely manner a great number of samples and to provide quick, cheap, and reliable results on the presence of those compounds in the environment, feed and food, as stated in the Community Strategy for dioxins, furans and polychlorinated biphenyls[1].
The analysis of dioxins and dl-PCBs can be carried out on different kind of samples. Sample preparation of dioxin and dl-PCBs extracts is one of the most challenging in analytical chemistry. Many co-extractable and potentially interfering compounds present in the raw extract must be removed in order to achieve the enrichment of PCDD/Fs and dl-PCBs in the extracts, considering the small amount of analytes to be determined. Reference methods[2,3] for the quantitative analysis of PCDD/Fs and dl-PCBs involve successive clean-up steps on various chromatographic adsorbents (multi-layer silica, Florisil, alumina, activated carbon) which considerably increase the time needed for analysis. The cleanup step can be modified to overcome interferences or lower the cost of measurements, provided that all method equivalency and performance criteria are met.
In a previous paper[4] we evaluated a new semi-automated clean-up system based on gel permeation chromatography (AccuPrep MPS™, J2 Scientific)[5] combined with an in-line concentration system (AccuVap™, J2 Scientific)[5], followed by a manual alumina column to separate PCDD/Fs from and dl-PCBs. In this work, an assessment of the suitability of the completely automated system in the PCDD/Fs and PCBs (*ortho*-PCBs and *coplanar* non-*ortho*-PCBs) analysis was performed.

Materials and methods
Samples
In order to evaluate the suitability of the completely automatic system in the PCDD/Fs, *ortho*-PCBs and *coplanar* non-*ortho*-PCBs analysis, many MWI emission samples spiked with labeled PCDD/PCDFs and dl-PCBs congeners (EN-1948 ES and WP-LCS, Wellington Laboratories) were analyzed.
Clean-up
The automated clean-up system configuration consists of a 2.5 cm x 45 cm glass column packed with BioBeads SX-3 resin (J2 Scientific) in 100% methylene chloride, a pump, an auto sampler and the evaporating chamber. The whole system is computer controlled and can be programmed as required (i.e. volume, flow-rates, direction of solvent flow, etc.). The system used a 5-mL sample loop and a flow rate of 5 mL/min with methylene chloride as the mobile phase. The GPC column was calibrated using the method outlined in USEPA Method 3640A[6]. The

autosampler loads the 5 ml sample on the GPC column. The eluate is collected between 18.5 and 27 minutes, concentrated by AccuVap and taken through 2 consecutive washes with methylene chloride and a final wash with hexane 2% dichloromethane up to a final volume of 1.5 ml. The extract is directly sent to the SPE alumina column and eluted as the different experimental conditions.

Analysis

Purified extracts were analysed by HRGC-HRMS on a GC 8000 series gas chromatograph (Fisons Instruments) coupled to an Autospec mass spectrometer (Micromass, Manchester, UK), using a positive electron ionization (EI) source and operating in the SIM mode at 10 000 resolving power (10% valley definition).

Chromatographic separation was achieved with a VF-Xms (Varian) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 mm film thickness) with helium as carrier gas in the splitless injection mode.

Results and Discussion

The non-*ortho* but lateral chlorine substituted coplanar PCBs 3,4,4',5-TetraCB (IUPAC-No. 81), PCBs 3,3',4,4'-TetraCB (IUPAC-No. 77), 3,3',4,4',5-PentaCB (No. 126) and and 3,3',4,4',5,5'-HexaCB (No. 169) are the most toxic PCB-congeners. They are isostereomers to the 2,3,7,8-substituted PCDD/PCDFs. These toxic non-ortho-PCBs are usually present in lower concentrations than other abundant PCB-congeners, but their environmental concentrations are generally higher than those of the PCDD/PCDFs. So these congeners have a significant contribution to the 2,3,7,8-TCDD toxic equivalents (TEQs).

Due to the extremely low concentrations of the non-*ortho*-PCBs and PCDD/Fs and the presence of many other organic compounds at higher concentration levels interfering in their instrumental determination, the analysis of dl-PCBs and PCDD/PCDFs always involves extensive clean-up procedures. Though with activated Florisil and alumina a successful separation between non-planar *ortho*-PCBs, coplanar non-*ortho*-PCBs and planar PCDD/PCDFs is possible, because of the higher affinity of the active centers of the activated sorbents to the planar molecules, non-*ortho*-PCBs and PCDD/PCDFs are more strongly bound to these activated sorbents and thus need a more polar solvent for their desorption[7,8,9]. Changing the solvent polarity in few steps[10] we achieved different congener distributions, obtaining at least a complete separation between PCDD/Fs and dl-PCBs.

In order to evaluate the quantitative performance of the automated system, the mean recoveries and standard deviations (%) of three replicates of labeled PCDD/PCDF and dl-PCB congeners were calculated .

We started from the most common procedure applied to separate PCDD/Fs from PCBs (G1) and, changing solvent amount and polarity (G4) we arrived to the final separation (G8). The elution conditions are reported in Table 1.

	% Hex:DCM (Volume ml)		
Fraction	G1	G4	G8
F1a	98:2 (10)	98:2 (10)	94:6 (20)
F1b		98:2 (5)	
F1c		98:2 (5)	
F2	50:50 (10)	50:50 (10)	40:60 (10)

Table 1. Elution conditions

After sample loading, 10 ml of hexane are discarded.

The F1 fraction involves the PCBs elution, the F2 fraction involves the complete PCDD/Fs elution, with the presence of PCBs congeners depending on elution conditions.

In Figure 1, 2 and 3, respectively, the recovery percentages of dl-PCB congeners are reported, as obtained in experiment G1, G4 and G8. All the experiments were performed in three replicates with standard deviations < 10% .

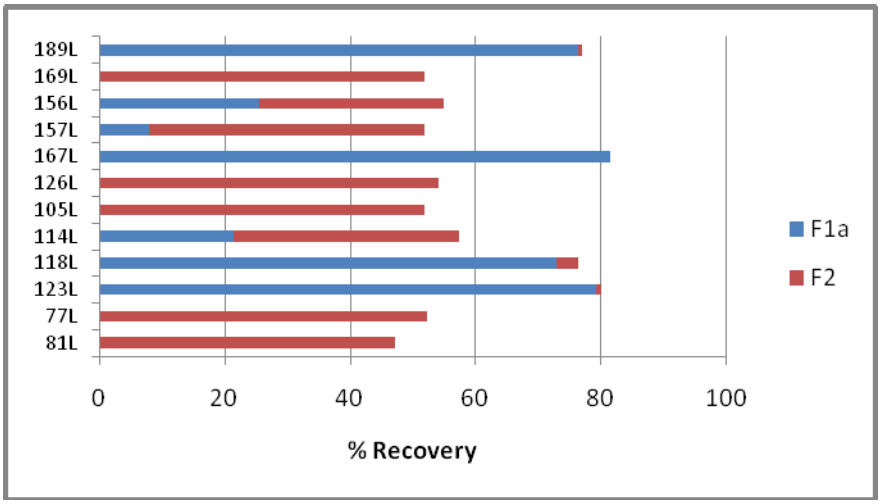

Figure 1: G1 dl-PCBs fractionating

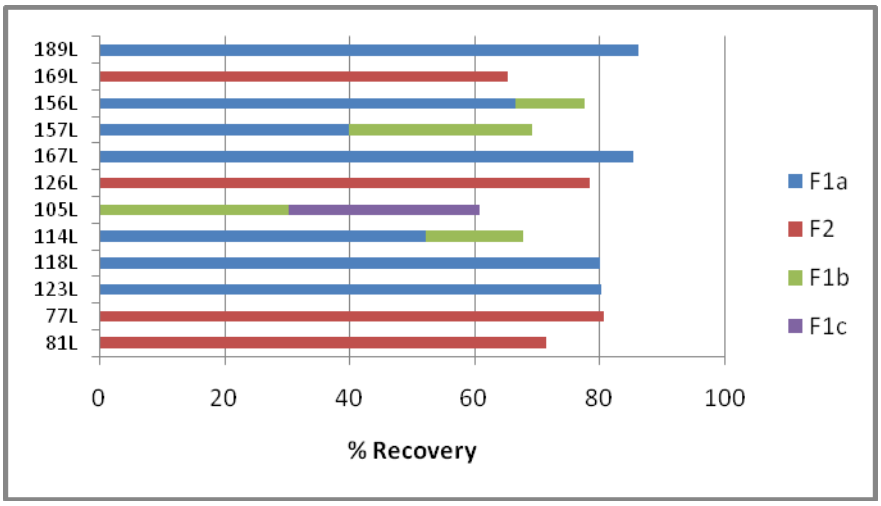

Figure 2: G4 dl-PCBs fractionating