SIMULTANEOUS DETERMINATION OF CHLORINATED ORGANIC COMPOUNDS – DIOXINS, FURANS, DIOXIN-LIKE PCBs AND HEXACHLOROBENZENE IN ATMOSFERIC AIR AND STATIONARY SOURCE EMISSIONS

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Introduction

Human exposure to organohalogen compounds in environment is a major source of concern in our days. Various accidents involving these substances have increased the concern of people and forced governments to adopt specific legislation to prevent new situations. Therefore in response to this repercussion the EU created some Directives such has Directive 82/501/CEE – "*Seveso Directive*",[1] Directive 96/82/EC and Directive 96/59/EC. These Directives were one of the first steps taken, but there is a general opinion that additional measures are needed to prevent human health and the environment. Some of the progresses achieved reports to the "Best Available Techniques – BAT". This action intends to minimize production of these substances in their source without significant affects to the economic sustainable grow.[2,3] In respect to food consumption by humans the EU has adopted other approach. They intend to reduce the presence of these compounds in food chain by adopting several steps. The EU strategy called "Environment and Health" adopted in 2003,[4] issues as main goal to obtain information and knowledge about the relation between human health and the environment focused in one early phase on some priority effects such as the neurological development. Dioxins/Furans and Polychlorinated biphenyls were considered an integrant part of this strategy that began in 2004. So, in order to respond to this need of information and knowledge, analytical tools have been developed to determine concentration and profiles of organohalogen compounds in gas samples (atmospheric air and stationary source emissions).

Material and Methods

This study reports two kinds of samples: samples from atmospheric air and samples from stationary source emissions. Both samples are treated in the same way, except in the sampling procedure. The analytical methodology is based on EN 1948 (NP), parts I, II, III[5,6,7] and on the USEPA Method 1688.[8] The samples were collected with a specific device mentioned in the EN 1948 (filter/cooler method). In a simplest way, the collected gas is forced to pass firstly through one glass fibre filter (to collect the molecules in the solid phase) and secondly through a resin or foam (XAD-2 or PUF – to collect the molecules in the gaseous phase) for a period of time between 6 to 8 hours. The volume of sampling gas was standardized and all the parts of sampling device which contact with the air or gas were washed with toluene/acetone to obtain full recovery of analytes. The filter, the resin (or foam), the condensed water and the wash solvents were submitted to several techniques of sample preparation to determine the organohalogen compounds. Firstly the filter and the resin (or foam) were extracted by soxhlet with toluene for 48 hours. The condensed water was extracted by liquid-liquid extraction with toluene and finally, these extracts were combined with the washing toluene/acetone. Internal standards were added before sampling (EN1948 SS from Wellington Laboratories) and extraction (EN1948ES and WP-LCS from Wellington Laboratories) procedures. The volume of the combined extracts was reduced by controlled pressure evaporation and submitted to a multi-column clean up with silica, alumina and activated carbon columns (Power Prep - Fluid Management System). From this clean up process tree extracts were obtained. The first contained the hexachlorobenzene (HCB), the second contained the dioxin-like polychlorinated biphenyls (PCBs) and the third contained the polychlorinated dibenzo-*p*-dioxins (PCDD) and the polychlorinated dibenzofurans (PCDFs). Internal standards were added to the extracts prior to injection in the GC systems (PCB IUPAC 198, EN1948IS

and WP-ISS from Wellington Laboratories). The HCB determination was evaluated by gas chromatography with electron capture detector (GC/ECD - from Agilent Technologies 6890 series) and for the dioxin-like PCBs and PCDD/Fs it was used a high-resolution gas chromatograph coupled with high-resolution mass spectrometer (HRGC/HRMS – Agilent Technologies 6890 series coupled with a Micromass spectrometer AutoSpec ultima).

Results and Discussion

Figure 1 shows the validation results for this methodology. The graphics show the recovery of internal standards (marked with ^{13}C) added before sampling and extraction stages.

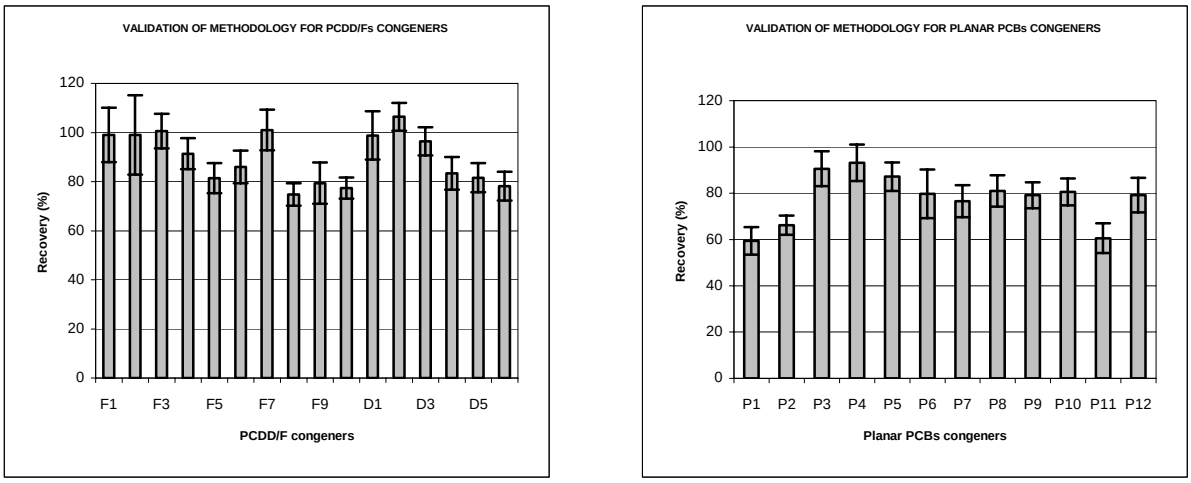

Figure 1. Recovery of internal standards added before sampling and extraction procedures for PCDD/Fs and dioxin-like PCBs.

The mean recovery obtained for HCB with fortified samples was 74% in the tree tests, with a standard deviation of 9 %. Figure 2 represents the obtained data for real samples.

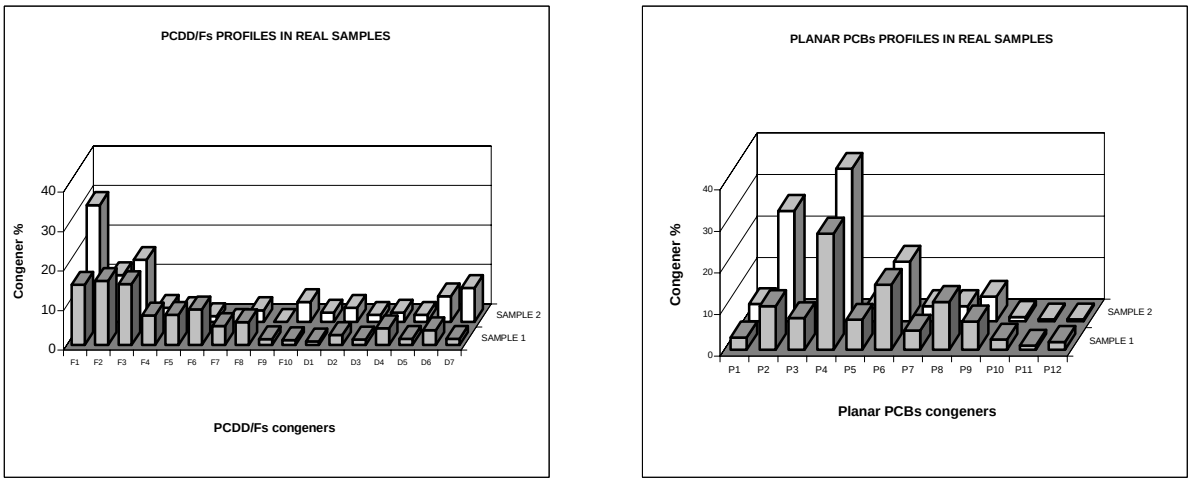

Figure 2. Results obtained for real samples of stationary stable sources; profiles of PCDD/Fs and dioxin-like PCBs.

From the data ilustrated in Figure 2, it was possible to predict the sources for the compounds found in the collected real samples.

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