THE SUPELCO DIOXIN PREP SYSTEM – FLORISIL VERSION : A NEW SAMPLE PREPARATION METHOD FOR FAST ANALYSES OF PCDD/Fs AND WHO-12 PCBs IN ENVIRONMENTAL SAMPLES

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INTRODUCTION

In 1995, the Environment Department of Corus R, D and T set up a Trace Organic Analysis Laboratory (TOAL) to assess the potential release of persistent organic pollutants from its operating plants. Preliminary work focused on the development and validation of sampling and analysis methods for the determination of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs)[1], using analytical procedures derived from US EPA methods 23 and 1613B. TOAL became UKAS accredited (ISO 17025 standard) in 1996 for both the sampling and the analysis of PCDD/Fs. In 1998, the World Health Organisation identified a set of 12 polychlorinated biphenyls (PCBs) exhibiting dioxin-like activities. These so-called WHO-12 PCBs are now included as part of the overall dioxin concentration and should be systematically investigated in industrial emissions. TOAL has subsequently modified its PCDD/F analytical procedure to allow quantitative determination of WHO-12 PCBs using a procedure derived from method US EPA 1668A[2]. Standard US EPA procedures for the determination of PCDD/Fs and PCBs involve successive clean-up steps on various chromatographic adsorbents (multi-layer silica, Florisil, alumina, activated carbon). In order to shorten sample preparation time, Supelco launched in 2003 in Japan the so-called "Dioxin Prep System", a kit for rapid clean-up of PCDD/F samples that was composed of a multi-layer silica gel column connected in series to a dual-layer carbon cartridge. Before it became commercially available in the UK, Corus UK and Hall Analytical (Manchester, UK) were invited to evaluate the "Dioxin Prep System" alongside their existing dioxin analytical procedure. Results showed that it could significantly reduce the sample preparation time while maintaining high accuracy for performing the analysis of PCDD/Fs[3]. However, the "Dioxin Prep System" was not suitable for PCB analyses. In 2005, Corus, Hall Analytical and Supelco agreed to collaborate on the development of an enhanced version of the “Dioxin Prep System” that would allow both the analysis of PCDD/Fs and PCBs. Work was carried out by both accredited laboratories to develop and validate an analytical procedure using the new version of the kit. The so-called "Supelco Dioxin Prep System - Florisil Version", is based on the previous Dioxin Prep System, but the dual-layer carbon reversible column has been replaced by a new micro-column containing activated Florisil connected in series to a multi-layer silica tube. This paper present details of the new Florisil version of the Supelco kit and validation data on a range of environmental matrices.

THE SUPELCO DIOXIN PREP SYSTEM – FLORISIL VERSION

Description

The Supelco "Dioxin Prep System - Florisil Version" is composed of a multi-layer silica gel column connected in series to a micro-column packed with activated Florisil, as depicted in Figure 1. A vacuum manifold and a vacuum adapter provide the option of running a single sample or multiple samples at one time (3 samples per vacuum unit). Up to three units can be handled by a fully trained technician, allowing the clean-up of a batch of nine samples in one day.

Fig.1: The 'Supelco Dioxin Prep System -Florisil Version'

The Supelco multi-layer silica gel column is designed to meet the requirements of Japanese Industrial Standard Methods K-0311 and K-0312. The column has a 15 mm internal diameter and is 35 cm in length. It contains 7 layers of treated silica gels, that oxidize, reduce, and separate polar interferents (Figure 2). The design of the column allows for easy connection to various components including stopcock valves and separatory flasks. Activated Florisil (1g) is provided in flame-sealed ampoules, and packed prior the sample clean up into specifically designed micro-columns that are easily connected to the multi-layer silica gel column using commercially available connectors.

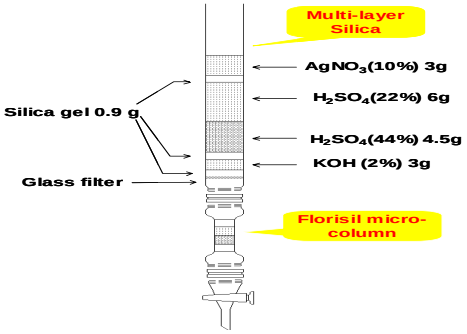

Fig.2: The Supelco "Dioxin Prep System - Florisil Version" : Packing of the multi-layer silica gel column

Experimental

All solvents were pesticide residue grade and were purchased from LGC Promochem (Hadfield, UK). Quantitation of 2,3,7,8 substituted PCDD/F and WHO-12 PCB congeners was by isotope dilution using USEPA methods 23 and method 1668A, respectively. Supelco supplied all materials needed for the "Dioxin Prep System - Florisil Version". Figure 3 describes the analytical procedure used by Corus and Hall Analytical for the validation of the "Dioxin Prep System - Florisil Version". All sample types were extracted with an Accelerated Solvent Extraction system using toluene (150°C for 12 min, 2000 psi). Prior to clean-up, the Dioxin Prep System was set up without the Florisil micro-column to activate separately the multi-layer silica tubes using 150 ml of *n*-hexane and vacuum elution. Afterwards, the entire Dioxin Prep System was set up as depicted in Figure 1, by connecting the activated multi-layer silica tubes in series with micro-columns packed with 1 g of activated Florisil. The sample extracts were loaded onto the silica gel tubes and eluted with 175 ml of *n*-hexane under a light vacuum. The silica gel column was removed and replaced by an empty silica tube, and 25 mL of *n*-hexane/DCM (98:2, v/v) were added to complete the elution of the waste fraction containing PCBs. The Florisil micro-columns were then eluted with 50 mL of DCM under gravity to collect the PCDD/F fractions. Waste fractions containing PCBs were concentrated to 0.5 mL and subjected to an additional clean-up step using basic alumina chromatography. This step removes large amounts of saturated hydrocarbons typically present in the PCB fractions from stationary source emission samples[2]. Analysis of extracts for PCDD/Fs and PCBs was conducted by high resolution gas chromatography - high resolution mass spectrometry using a Hewlett-Packard 6890 gas chromatograph coupled to a Micromass Autospec Ultima high resolution mass spectrometer (Waters, Manchester, UK).

VALIDATION OF THE SUPELCO DIOXIN PREP SYSTEM – FLORISIL VERSION

Corus and Hall Analytical carried out a set of validation experiments using different environmental matrices including a certified reference sediment (DX-3), a certified reference soil (BCR-529), a certified reference sewage sludge (BCR-677), and a certified reference fish tissue (WMF-01). The data are summarised in the next paragraphs.

DX-3 certified reference sediment: PCDD/F and PCB data

DX-3 sediment (National Water Research Institute, Canada) is a "naturally" contaminated lake sediment for which consensus values have been established for the seventeen toxic 2,3,7,8-PCDD/Fs, the total PCDD/F homologue groups, and the WHO-12 PCBs. Corus carried out four replicate analyses using the Supelco "Dioxin Prep System - Florisil Version". As may be seen from Figure 3, the Supelco kit allowed an accurate determination of PCDD/Fs and WHO-12 PCBs in the certified sediment. Concentrations of toxic congeners and total PCDD/F homologue groups were

in good agreement with the certified values. Recoveries of $^{13}C_{12}$ PCDD/F and PCB internal standards were typically within the range 60% to 100% for PCDD/Fs and PCBs, well within the acceptance criteria of US EPA methods 23 and 1668A.

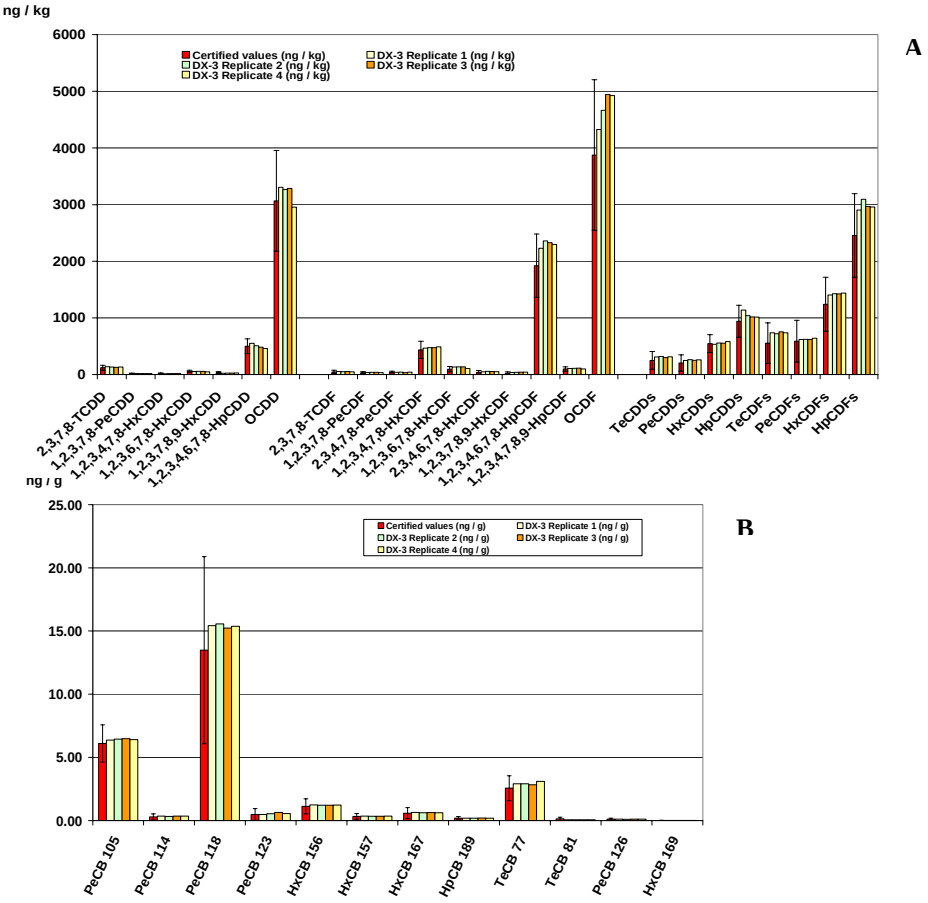

Fig. 3 : PCDD/F and WHO-12 PCB concentrations in DX-3 certified reference sediment determined using the Supelco "Dioxin Prep System - Florisil Version"

For DX-3 sediment, information values are also provided for a series of additional PCB congeners (PCBs 28, 52, 101, 138, 149, 153, 180, 194, 202, 205, 206, 208, 209). Figure 4 shows the data relative to these PCBs using the Supelco kit. Most of the additional PCB congeners that were determined in DX-3 sediment compared favourably with the information values provided with this material. Only PCBs 52, 101, 138 and 149 exhibited concentrations significantly lower than the information values. For these compounds, several co-elutions have been reported in the literature depending on the GC capillary columns that are used for analysis[4]. It is therefore possible that the indicative values reported for these congeners are over estimated depending on the type of GC capillary columns that were used by the participating laboratories at the time this sediment was certified. For these additional congeners, the Supelco "Dioxin Prep System - Florisil Version" brings a significant improvement compared to the previous dual-carbon column that did not allow the determination of non ‘dioxin-like’ PCB congeners.

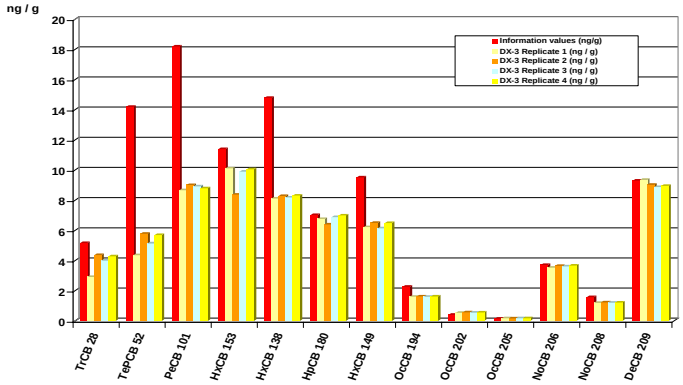

Fig. 4 : Concentrations of selected PCB congeners in DX-3 certified reference sediment determined using the Supelco "Dioxin Prep System - Florisil Version". For these PCBs, Concentrations are information values only.

Certified reference sandy soil (BCR-529) and sewage sludge (BCR-677) : PCDD/F data

BCR-529 and BCR-677 are two reference materials certified by the Institute for Reference Materials and Measurements (IRMM) of the European Commission's Directorate General Joint Research Centre (Belgium). These materials are certified for PCDD/Fs only. Figure 5 illustrates the PCDD/F content of BCR-529 and BCR-677, as determined using the Supelco kit. For BCR-529, analyses showed that all replicates were within an acceptable range of the certified value, apart from 1,2,3,7,8,9-HxCDF (Fig. 5A). For this particular congener, a certified value of 22 ng/kg was provided, but the four replicate analyses that were carried out consistently led to determine a concentration situated around 500 ng / kg (Fig. 5A). No obvious explanation was found to explain these differences. This might be attributed to an interference caused by the co-elution of another HxCDF congener on the DB5-MS GC capillary column. For all analyses, recoveries of $^{13}C_{12}$ PCDD/F internal standards were typically within the range 73% to 108%, well within the acceptance criteria of US EPA method 23. With regard to BCR-677, mean concentrations of 2,3,7,8-PCDD/Fs were all in good agreement with the certified values, as depicted in Figure 5B.

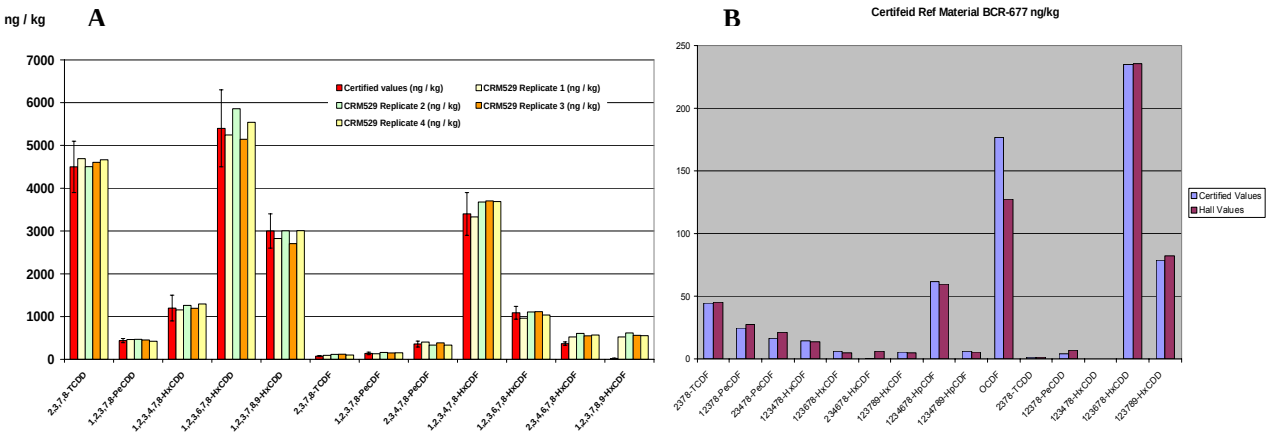

Fig. 5 : Concentrations of PCDD/Fs in BCR-529 (certified reference sandy soil) and BCR-677 (certified reference sewage sludge) determined using the Supelco "Dioxin Prep System - Florisil Version" by Corus and Hall Analytical.

Certified reference Fish tissue (WMF-01) : PCDD/F and PCB data

WMF-01 is a reference 'freeze-dried' fish tissue for organic contaminant analysis. It contains low levels of dioxins and comparatively high levels of WHO-12 PCBs. This material exhibits certified values for the WHO-12 PCBs

and four toxic PCDD/F congeners. These are 2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD and 2,3,7,8-PeCDF. Figure 6 summarises the validation data obtained for WMF-01 certified fish tissue. With regard to the four certified PCDD/F congeners and the WHO-12 PCBs, analytical data obtained using the "Dioxin Prep System - Florisil Version" compared favourably with the certified values. Recoveries of $^{13}C_{12}$ PCDD/F and PCB internal standards were typically within the range 70% to 105% for both PCDD/Fs and PCBs.

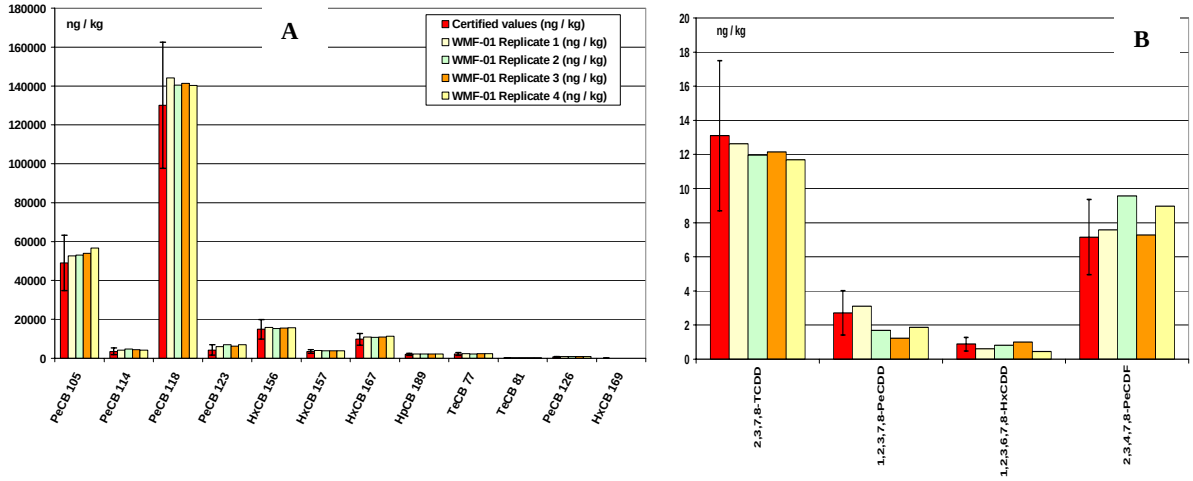

Fig. 6 : Concentrations of WHO-12 PCBs and selected 2,3,7,8-PCDD/Fs in WMF-01, a certified reference fish tissue, determined using the Supelco "Dioxin Prep System - Florisil Version".

CONCLUSIONS

Experiments have been carried out by Corus and Hall Analytical to validate an analytical procedure allowing the analysis of PCDD/Fs and WHO-12 PCBs using the Supelco "Dioxin Prep System - Florisil Version". Results showed that for all sample types (sediment, soil, sewage sludge and fish tissue), the Dioxin Prep System allowed an accurate determination of both PCDD/Fs and WHO-12 PCBs with recoveries of $^{13}C_{12}$ labelled internal standards well within the acceptance criteria of standard US EPA methods. In addition, the "Dioxin Prep System - Florisil Version" allows the determination of 'non-dioxin' like PCBs, which constitute a significant improvement in comparison with the previous dual-carbon column version of the kit. Corus gained UKAS ISO 17025 accreditation for the use of this method in January 2006 and is currently applying it on a regular basis to environmental samples from the steel industry (stationary source emission samples, waste dusts from iron-making). When commercially available, the Supelco "Dioxin Prep System - Florisil Version" could constitute one of the fastest solution for quantitative determinations of PCDD/Fs and WHO-12 PCBs in environmental samples.

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