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RAPID CLEAN-UP FOR DETERMINATION OF PCDD/Fs USING A MULTI-LAYER SILICA GEL COLUMN CONNECTED TO A DUAL-LAYER REVERSIBLE CARBON COLUMN

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Introduction

Reference methods (Methods US EPA 23 or 1613 B ; European method EN-1948) for the quantitative analysis of the seventeen toxic 2,3,7,8-PCDD/Fs involve successive clean-up steps on various chromatographic adsorbents (multi-layer silica, Florisil, alumina, activated carbon) which considerably increase the time needed for analysis. Corus UK and Hall Analytical Laboratories are using for the determination of the 17 targeted 2,3,7,8 PCDD/Fs an analytical procedure, derived from method US EPA 1613B, which consists of a two stage clean-up procedure after extraction of environmental samples[1]. Briefly, the first stage employs a multi-layered silica chromatography column (activated silica, sulphuric acid on activated silica, sodium hydroxide on activated silica). After concentration, cleaned-up extracts are loaded on to micro-columns packed with activated Florisil in order to separate PCBs from PCDD/Fs. As a result, three days of sample preparation are required prior to HRGC / HRMS analysis of PCDD/F fractions. Since 1996, this UKAS accredited methodology has been applied by Corus UK to characterise the emissions and impacts of PCDD/Fs from its integrated steelworks[2,3].

Recently in Japan, Supelco launched a new preparation kit for rapid clean-up of dioxin samples, called the "Dioxin Prep System" and composed of a multi-layer silica gel column and a dual-layer carbon cartridge connected in series. It has been shown to shorten considerably sample preparation time while maintaining high accuracy for performing PCDD/Fs analysis and it has been applied to a range of environmental samples such as stack emissions, fly ashes and waste waters[4,5,6].

Before the Dioxin Prep System became commercially available in the UK, Corus UK and Hall Analytical Laboratories were invited to evaluate it alongside their existing dioxin analytical procedure. In this paper, PCDD/Fs results obtained from blanks and QC materials are presented using Dioxin Prep System and they are compared with those obtained using the existing method in our laboratories.

Materials and Methods

Blanks and quality control (QC) materials were analysed both by Corus UK and Hall Analytical Laboratories to evaluate the efficiency of the clean-up using Supelco's multi-layer silica gel column and dual-layer carbon cartridge connected in series. Quantitation of 2,3,7,8 substituted PCDD/Fs congeners was by isotope dilution using the US EPA method 23 internal standard and recovery standard solutions (Cambridge Isotope Laboratories, LGC Promochem, UK). Samples were extracted by accelerated solvent extraction (150°C for 12 min, 2000 psi) using a Dionex ASE 200. As shown in Fig. 1, the Supelco multi-layer silica gel column contained 7 layers of treated silica which met the requirements of Japanese Industrial Standard Methods K-0311 and K-0312. The dual-layer carbon column was composed of two 100 mg carbon layers, Carboxen 1016 (surface area 75 m^2/g) and Carboxen 1000 (surface area 1200 m^2/g). Prior to clean-up, multi-layer silica gel and dual-layer carbon columns were pre-conditioned separately using 200 ml of *n*-hexane and 50 ml toluene followed by 100 ml *n*-hexane, respectively. Extracts were applied to the Supelco combination columns and eluted with 200 ml *n*-hexane. Multi-layer silica columns were disconnected and replaced by empty silica columns to perform an additional clean-up step using

30 ml n-hexane / DCM (97/3 ; v/v) in order to remove potential interferences. Finally, dual-layer carbon cartridges were back-eluted with 80 ml toluene to obtain PCDD/F fractions.

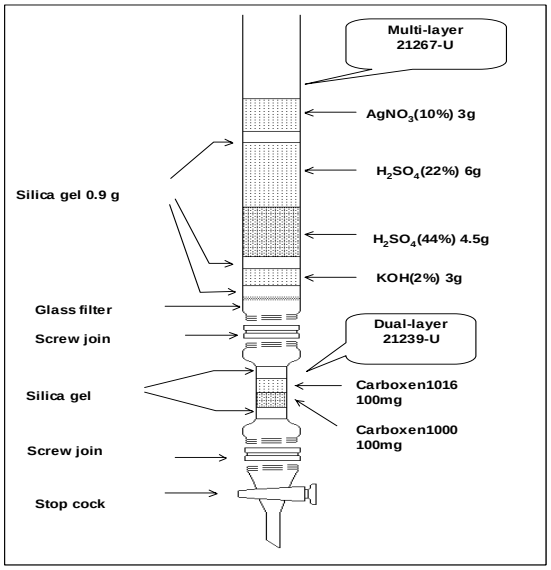

Figure 1. Schematic of the Dioxin Prep System (multi-layer silica gel column and Dual-Layer carbon column connected in series) for rapid clean-up of PCDD/F extracts

Elution steps were all performed under vacuum (100-400 mm Hg ; 3ml/min) using a vacuum manifold. Analysis of cleaned-up extracts for PCDD/Fs was conducted by HRGC/HRMS using a Hewlett-Packard 6890 gas chromatograph equipped with a 60 m DB5-MS column and coupled to a Micromass Autospec Ultima high resolution mass spectrometer. Analyte solution (1 µl) was injected in splitless mode, and the injector was maintained at 280°C. The temperature programme was: hold at 120°C for 4 min, 15°C/min to 220°C, 1.5°C/min to 240°C, hold 2 min, 4°C/min to 310°C, hold 5 min. For all analyses, the GC/MS interface and ion source temperatures were held at 280°C. The MS was operated at 10,000 resolution in the positive ion mode at 39eV energy with perfluorokerosene as the mass range calibrant. All data were analysed using proprietary software Mass Lynx version 4.0 (Micromass, Manchester, UK).

Results and Discussion

Recoveries of $^{13}C_{12}$ labeled PCDD/F standards. The first step in the evaluation of the Dioxin Prep System consisted of analysing blank samples spiked with $^{13}C_{12}$-labeled PCDD/Fs. After extraction and clean-up using the Dioxin Prep System, mean recoveries of $^{13}C_{12}$-labeled internal standards, see Fig. 2, ranged from 66 to 90%, and were well within the acceptance criteria of the method US EPA 23, while the relative standard deviation (RSD % ; N=3) ranged from 10 to 20 %.

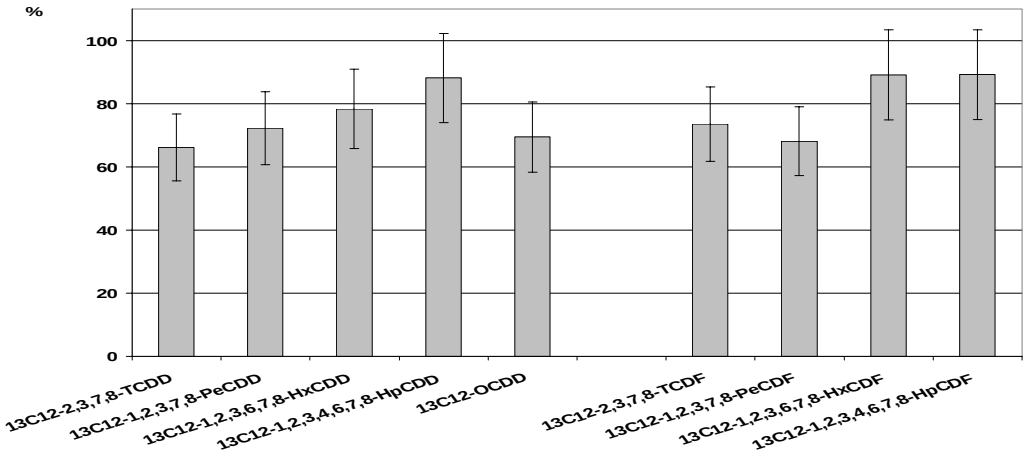

Figure 2. Internal standard recoveries obtained after analysis of blank samples cleaned-up using Supelco Dioxin Prep System (multi-layer silica gel column and Dual-layer carbon column connected in series)

Interferences of HxCBs with PeCDDs. Using the Dioxin Prep System, a single fraction containing PCBs and PCDD/Fs is collected after back-elution of the dual-layer carbon column. After the analysis of a fraction from a blank sample spiked with both $^{13}C_{12}$ labeled PCDD/Fs and WHO-12 PCBs, interferences were observed from HxCBs in the PeCDD channel. For instance, the analysis of standard solutions containing both native and labeled PCDD/Fs and PCBs showed that native and $^{13}C_{12}$-HxCBs 156, 157 and 169 were detected in the PeCDDs function (Fig.3a.), due to the fact that the molecular ion of an HxCB was very close to the [M + 4] ion of a PeCDD [native HxCB : M = 357.8444 ; $^{13}C_{12}$HxCB : M=369.8847 ; native PeCDD : M + 4 = 357. 8517 ; $^{13}C_{12}$ PeCDD : M + 4 = 369.8919]. As PCB 169 and 1,2,3,7,8-PeCDD were not well separated, some problems were experienced in the quantitation of the dioxin congener. As shown in Figure 3b, this interference was successfully eliminated by monitoring M and [M + 2] ions of PeCDDs instead of their [M + 2] and [M + 4] ions.

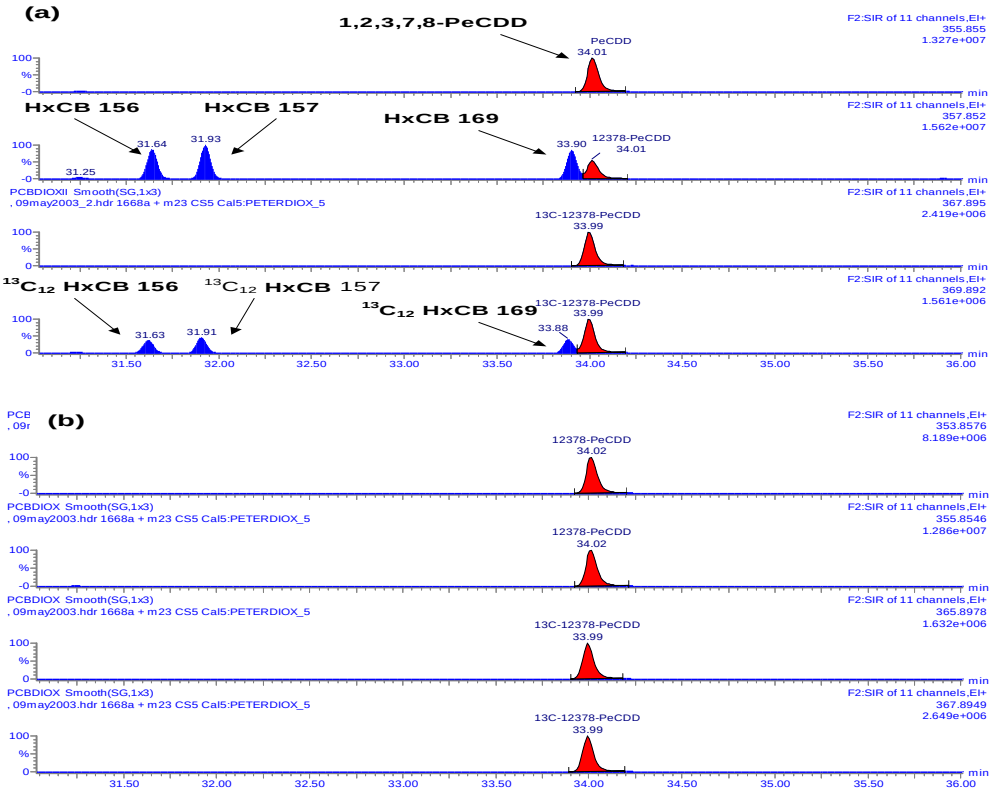

Figure 3. Analysis of standard solutions of native and $^{13}C_{12}$ PCBs and PCDD/Fs : (a) interferences caused by the molecular ion of HxCBs on the PeCDD detection channel and (b) masses monitored to avoid interferences between HxCBs and PeCDDs

Analysis of a QC material. An internal QC material (waste dust from an iron making process) was analysed. For this particular QC material, figure 4 shows the results obtained by Corus UK and Hall Analytical Laboratories using the Dioxin Prep System and compares it to the mean values of the QC data obtained using the existing dioxin method (N = 59 replicate analysis ; RSD % ranged

from 8 to 25%). Both laboratories obtained results well in agreement with the QC data showing the efficiency of the clean-up which enables accurate analysis of PCDD/Fs.

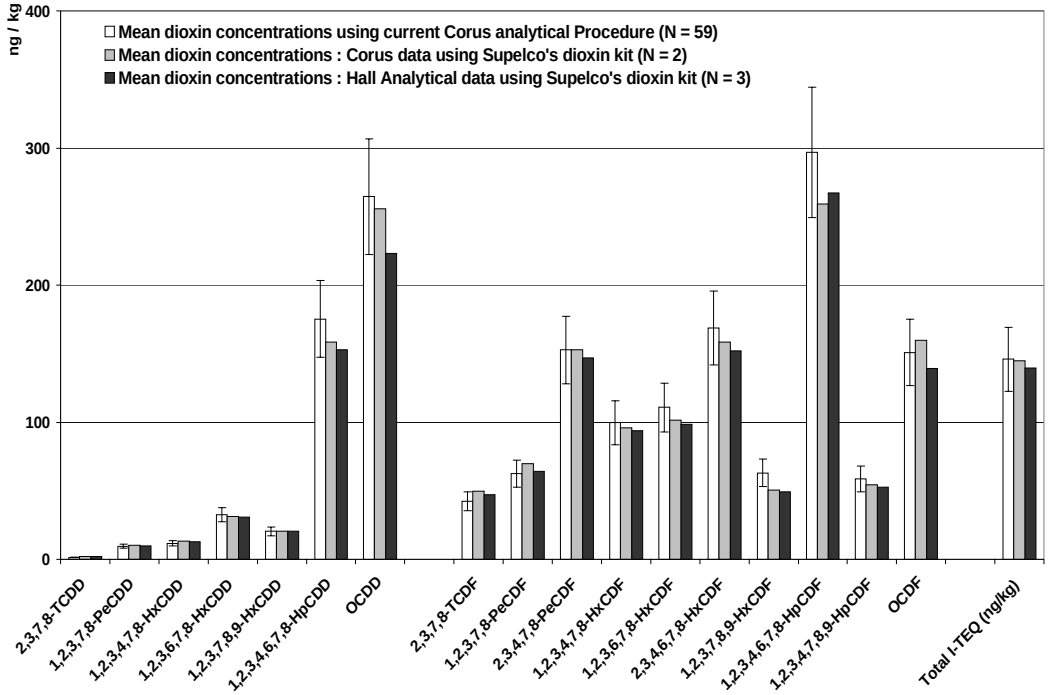

Figure 4. Analysis of a QC material by Corus UK and Hall Analytical Laboratories using Supelco Dioxin Prep System. Dioxin results are compared with QC data from the replicate analysis of N = 59 samples using the existing Corus analytical procedure

Conclusions

Both laboratories involved in this study found that the use of a multi-layer silica gel column connected to a dual-layer reversible carbon column (Supelco Dioxin Prep System) led to PCDD/Fs results for a QC material very similar to those obtained with their current analytical procedure with acceptable internal standards recoveries. Consequently, the Dioxin Prep System provides the opportunity to perform a more rapid clean-up step than using the previous analytical procedure [2 days of sample preparation (including extraction and clean-up) before HRGC/HRMS analysis of PCDD/F fractions vs. 3 days of sample pre-treatment].

References

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