VALIDATION OF AN LC-LC-GC METHOD FOR ENVIRONMENTAL MONITORING OF PLANAR PCBs AND DIOXINS

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Introduction

The congener-specific analysis of persistent organic pollutants in general, and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in particular is a very tedious and costly task. This makes it difficult to find resources for extensive studies of the environmental occurrence, distribution and fate of these com-pounds. Large-scale environmental monitoring programmes are particularly expensive, as they require regular, usually yearly, analyses of large numbers of samples. There are three common solutions to this problem (i) to exclude the PCDD/Fs, non- and mono-ortho PCBs from the programme, (ii) to reduce the analysis frequency or (iii) to combine several samples into a composite material, which is analysed instead of the individual samples. All of these common solutions have distinct disadvantages. A much better solution is to continue to analyse a relatively large number of samples, but try to develop simpler and more cost-effective methods of analysis. One approach is to determine concentrations of selected representatives of a class of compounds, so-called indicator com-pounds by a cheaper, more automated, analytical technique, and to estimate the levels of the other compounds on the basis of their usual ratios to the concentra-tions of the indicator compounds. We have adopted this approach and developed an on-line liquid chromatography- liquid chromatography- gas chromatography electron capture detection (LC-LC-GC-ECD) technique for PCDD/F and planar PCB analysis[1]. This method is now validated and the results are presented in this paper.

Methods and Materials

Herring from three Swedish locations, Fladen (on the west coast), Utklippan (on the south coast) and Harufjärden (at the northern end of the east coast), and Guillemot eggs from Stora Karlsö (on the east coast) were included in the study. These samples were analysed for the seventeen 2,3,7,8-substituted PCDD/Fs and the PCBs 77, 105, 118, 126, 156, 157, and 169 using our traditional GC-high resolution mass spectrometry (HRMS) method [2]. In addition, four congeners, viz. 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-PentaCDF), PCB77, PCB126, and PCB157, were analysed using the LC-LC-GC-ECD method[1]. Here, two columns that separates by different mechanisms were utilised to obtain enough selectivity, viz. silica and PYE (2-(1-pyrenyl)ethyldimethylsilylated silica), and n-pentane was selected as the mobile phase. Following injection, the appropriate fraction of eluent from the silica column is heart-cut transferred to the PYE column, which is eluted in the forward direction until 15 seconds before the first indicator is expected to elute. The PYE column is then back-flushed via the silica column, and the resulting back-flush peak is transferred to the GC using a loop interface. The GC is operated under concurrent solvent vaporisation (CSV) conditions to concentrate the large volume of solvent entering the GC.

Further, the GC is equipped with an early vapour exit to shorten the analysis time and to protect the detector. Finally, the four indicator congeners were quantified using a multi-level calibration and the remaining sixteen PCDD/Fs, three mono-*ortho* PCBs, and PCB 169 were estimated using their usual ratios to the concentrations of 2,3,4,7,8-PentaCDF, PCB157, and PCB126, respectively.

Results and Discussion

Seven samples from each location were analysed in parallel with GC-HRMS and LC-LC-GC-ECD, and the results from the GC-HRMS analyses were used to calculate calibration factors, i.e. the relative abundances of indicators and other congeners. Next, congener-specific data for the LC-LC-GC-ECD method were obtained by applying these factors.

Generally, the results of the two methods compare well. The concentration ranges overlap for all congeners and sampling locations. In Figure 1 the average, maxim-um and minimum concentrations of all detected congeners, in herring muscle samples from Harufjärden, are compared for the two methods. Only minor diffe-rences in the concentration ranges are observed, except for TCDF and OCDD, which however are known to exhibit deviant behaviour. There are most probably different reasons for these deviations. TCDF is calculated from 2,3,4,7,8-PentaCDF in the LC-LC-GC-ECD approach, and TCDF and 2,3,4,7,8-PentaCDF do not exhibit a perfect correlation. OCDD on the other hand, is late eluting in GC and therefore more difficult to accurately analyse than the other congeners – especially using polar GC phases, which is the case in the GC-HRMS method.

The differences in average concentrations are also minor, c.f. Figures 1 and 2. The PCDD/Fs compare well, once again with TCDF and OCDD as exceptions, as do the non-ortho PCBs. However, the LC-LC-GC-ECD technique underestimates the mono-ortho PCBs somewhat.

Generally, the deviation between the indicator congener concentration estimates, obtained by the LC-LC-GC-ECD and GC-HRMS techniques is less than ± 30 per cent. This might seem high, but is actually in agreement with typical inter-laboratory variance in most inter-calibration exercises for this type of trace level contaminants. Further, it is much less than the biological variance among the same samples. Thus, it was concluded that the indicator method could be used as a substitute for the traditional GC-HRMS method.

Since 1996 the indicator technique has been used in the Swedish national environmental monitoring programme for the analysis of PCDD/Fs, mono- and non-ortho PCBs in herring muscle and guillemot eggs.

References:

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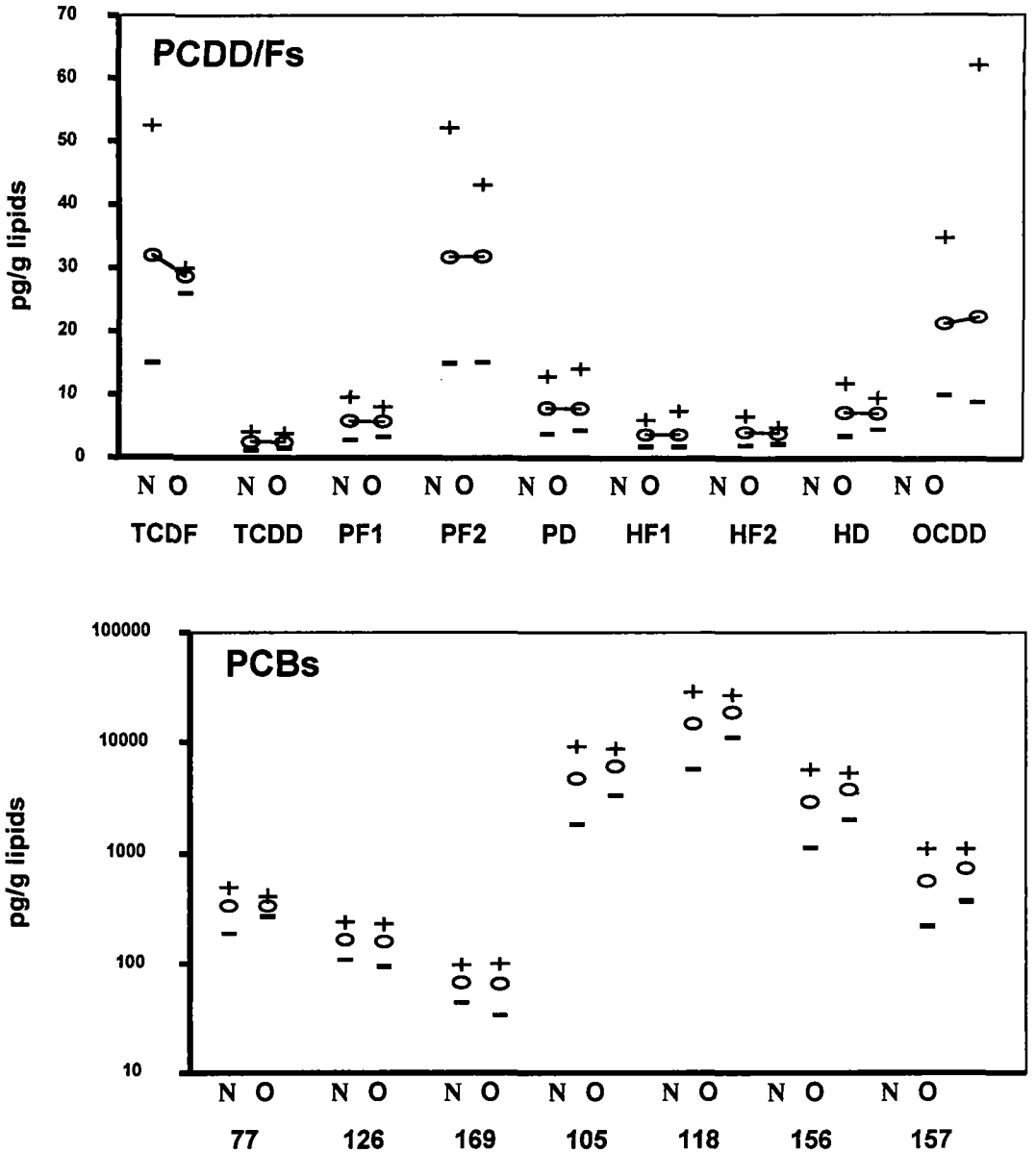

Figure 1: Comparison of average (O), maximum (+) and minimum (–) levels of PCBs and PCDD/Fs in herring from Harufjärden, as determined by LC-LC-GC-ECD (N) and GC-HRMS (O). TCDD= 2378DF, PF1= 12378DF, PF2= 23478DF, PD= 12378DD, HF1= 123478DF, HF2= 123789DF and HD=123678DD.

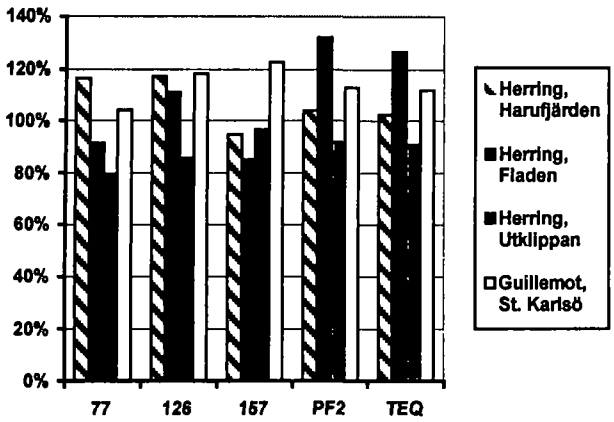

Figure 2: Relative average concentrations, LC-LC-GC vs. GC-HRMS, of indicator congeners and total dioxin toxic equivalency (TEQ) in herring muscle and guillemot eggs.