INTRODUCTION

Chlorobiphenyls (CBs) are persistent organic pollutants (POPs) listed on the Oslo and Paris Commission (OSPAR) List of Chemicals for Priority Action due to concern about their persistence, toxicity and potential to bioaccumulate in marine life. Twenty of the 209 possible CB congeners can attain a planar configuration due to the absence of ortho-chlorine substitution of the biphenyl rings (Figure 1). These congeners are commonly known as planar or non-ortho CBs. Although planar CBs are found at lower concentrations in the marine environment compared to ortho CBs they have a greater effect on the P-450 enzyme system and are therefore considerably more toxic than other CB congeners. Stereocchemistry they are similar to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and therefore elicit similar toxic and biological responses to dioxins.

There is a need for good quality certified reference materials (CRMs) to serve laboratories working in the field of organic contaminant analysis in the aquatic environment. However, there is a lack of biota and sediment CRMs for the analysis of dioxins, furans and non-ortho CBs. Table 1 lists the current CRMs available for non-ortho CBs in biota. During this study a candidate CRM (chub) prepared for the EC Institute for Reference Materials and Measurements (IRM) was analysed by twelve laboratories for non-ortho CBs (77, 81, 126 and 169; Table 2). The aim of the study was to establish the suitability of this material as a CRM for the analysis of planar CBs. This poster is an FRS perspective of a study coordinated and managed by RIVO (Netherlands Institute of Fisheries Research, Ijmuiden).

METHOD

The twelve participating laboratories used a variety of extraction and clean-up methods. Most laboratories used Soxhlet extractions. Sulphuric acid or gel permeation was generally used to remove the lipid. The majority of laboratories utilised HPLC to separate the ortho and non-ortho CBs. Quantification was by gas chromatography (GC)-mass spectrometry (MS) in electron ionisation (EI) or chemical ionisation (CI) mode using 13C-labelled internal standards. The method employed by FRS is shown in Figure 2.

RESULTS

The mass spectra for the planar CBs are shown in Figure 3. In all cases the molecular ion was also the base ion. A single ion monitoring (SIM) method was developed using the base ion for quantification. The molecular ion minus two chlorines was used as the qualifier ion for all four planar CBs. Replicate chub CRMs were analysed for planar CBs using GC-MS in SIM mode. Good resolution of all non-ortho CBs was obtained on a 0.5% phenyl-95% dimethylpolysiloxane phase column (30 m x 0.25 mm; 0.25 µm film thickness) (Figure 4). The mean concentrations from the twelve labs for CB 77, CB 81, CB 126 and CB 169 were 184.3 ± 33.5 pg g⁻¹, 12.8 ± 2.4 pg g⁻¹, 18.8 ± 3.3 pg g⁻¹ and 1.7 ± 0.4 pg g⁻¹ respectively (Figure 5). The greater degree of uncertainty for CB 169 was due to the very low concentration of this congener in the chub matrix.

CONCLUSIONS

• The use of 13C-labelled non-ortho CBs was highly recommended to compensate for recovery losses. Spiking of samples for recovery should take place after the samples have been dried and before extraction.

• 13C-labelled standards should be checked for the presence of 14C CBs.

• GC-MS was the preferred method of analysis. The use of GC-ECG was found to lead to higher concentrations of CB169. This was found to be a result of co-eluting contaminants.

• Polychlorinated naphtalenes (PCNs) produce ions with mass-to-charge ratios (m/z) also found in 14C labelled CBs (especially 12C-C677 and 13C-CB81, m/z 232, 302 and 304). This can interfere with the analysis if separation is not achieved.

• A constant temperature (0-5°C) for the HPLC column, used to separate ortho and non-ortho CBs is important for optimum separation of CBs and for stable retention times. The mobile phase should also be cooled to 0-5°C.

• Homogeneity testing of CBs (especially 13C-CB119 and 13C-CB81, m/z 232, 302 and 304). This can interfere with the analysis if separation is not achieved.

• A constant temperature (0-5°C) for the HPLC column, used to separate ortho and non-ortho CBs is important for optimum separation of CBs and for stable retention times. The mobile phase should also be cooled to 0-5°C.

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