HRGC/HRMS ANALYSIS OF PCB CONGENERS: METHOD DEVELOPMENT AND ANALYSIS OF REFERENCE MATERIALS

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1.0 INTRODUCTION

As more chemical and toxicological data is accumulated, there is strong evidence to suggest that certain PCB congeners represent a greater risk than others to the environment and ultimately, human health. Certain PCBs have been assigned tentative TEFs (toxic equivalency factors) that are equal to, or higher than, those for some of the 2378-substituted PCDDs and PCDFs[1].

Where in the past, PCB data was expressed as a concentration of the commercial mixtures (eg Aroclor™, Clophen™), it is now more common to find isomer-specific PCB data in the scientific literature. These analyses were, for the most part, prompted by the toxicological significance of certain PCBs. In addition, it is now well-established that the composition of commercial mixtures changes over time (due to environmental degradation and selective bioaccumulation) and that there are other sources of PCBs that do not give typical Aroclor/Clophen patterns (eg. incineration).

It is highly probable that future regulations or guidelines will require analyses for individual PCB congeners. The EPA, in its reassessment of dioxin[2], has targeted 'dioxin-like' compounds which (at the very least) includes the coplanar PCBs.

In our laboratory, HRGC/HRMS methods have been developed for the analysis of the major PCB congeners in commercial mixtures including congener-group totals. The coplanar PCBs are isolated and analyzed separately by HRGC/HRMS.

These methods were tested on sediment and tissue reference materials for which total PCB content has been well-established.

2.0 EXPERIMENTAL

2.1 Preparation of Samples

The sediment and tissue samples were spiked with 13C-labelled PCB surrogates and processed using the procedures shown in Figures 1 and 2, respectively. Prior to HRGC/HRMS analysis, internal (injection) standards namely $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD were added to the cleaned-up extracts.

2.2 HRGC/HRMS Analysis

All sample extracts were analyzed using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) using a Hewlett Packard 5890 Series II GC and a VG 70SE magnetic sector HRMS. A J & W 60 m DB5 column was used for all analyses.

A CTC 200 autosampler was interfaced to the GC and 2 μL injections were made using a splitless injection. The autosampler, HRGC and HRMS were controlled using a Digital MX3100 model 38 VAX workstation using VG OPUS 3.1 operating software.

Retention windows were initially set using a first/last eluters mixture of mono- to decachlorinated PCBs. MS resolution of 10000 or greater was maintained daily.

The actual analyses involved an initial 4-point calibration that was required to be linear. The calibration solutions also contained the GC retention time window definers.

The ions monitored for PCB analysis included two quantitation ions, ions to confirm loss of 2Cl, ions to monitor contribution from higher chlorinated PCBs, and ions for the 13C-surrogates. The HRGC/HRMS analytical run was divided into 8 functions.

2.3 Identification/Quantitation of PCBs

The criteria used to determine if a GC/MS peak was a PCB congener was as follows:

i) There must be simultaneous response (± 2 scan units) for all monitored ions.

ii) The response must occur within the predetermined retention time window for the particular congener group.

iii) The sample peak (for the most abundant characteristic ion) must be at least 3 times the noise level.

iv) The ion intensity ratios must be within ±20% of their theoretical values as well as those for the corresponding components in the external standards.

v) There must be no significant response for the higher chlorinated PCBs whose fragmented ions can interfere in the analysis of the PCBs.

vi) The M-2Cl ion must be present for a PCB to be confirmed.

vii) The recoveries of the surrogates must be within 30% and 130%.

Once a peak has been determined to be a PCB, its concentration was determined by peak area comparison to separate injections of the calibration standards of native surrogate PCBs using internal standard methods.

A considerable amount of development using VG's quantitation package OPUSQUAN™ was also involved in this project.

3.0 RESULTS/DISCUSSION

- The HRGC/HRMS, as expected, exhibited good sensitivity to the PCBs and gave a linear calibration. The RSDs of the relative response factors were less than 10% for all congeners.

- The methods used to process the sediment and tissue samples gave instrument ready extracts that were free of significant amounts of coextractable compounds.

- The data obtained for the two matrices agreed very well with the reference values.

The analytical protocols used and the data obtained will be presented and further discussed at the symposium.

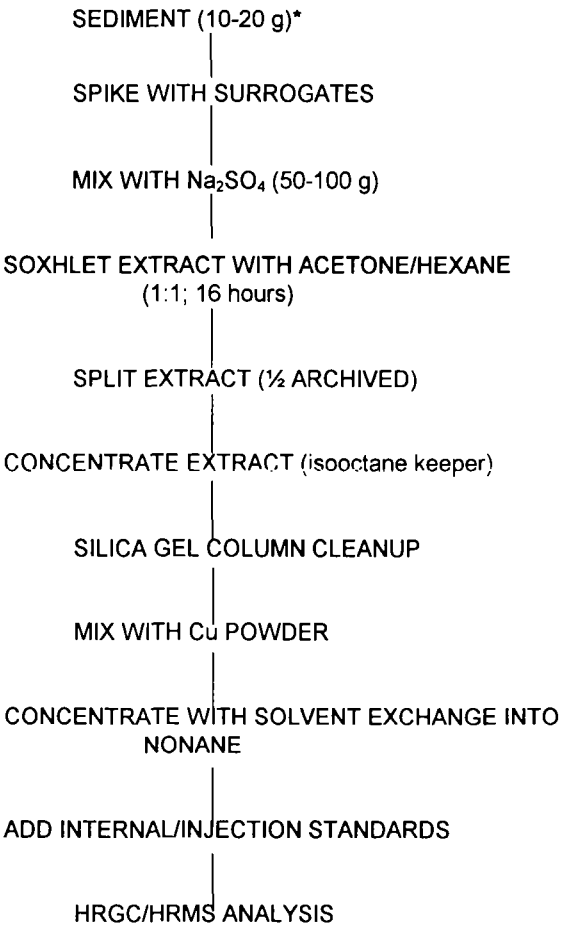
REF/QC

4.0 REFERENCES

1) Safe S.: Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). *Critical Reviews in Toxicology* 1990; 21: 51-88.

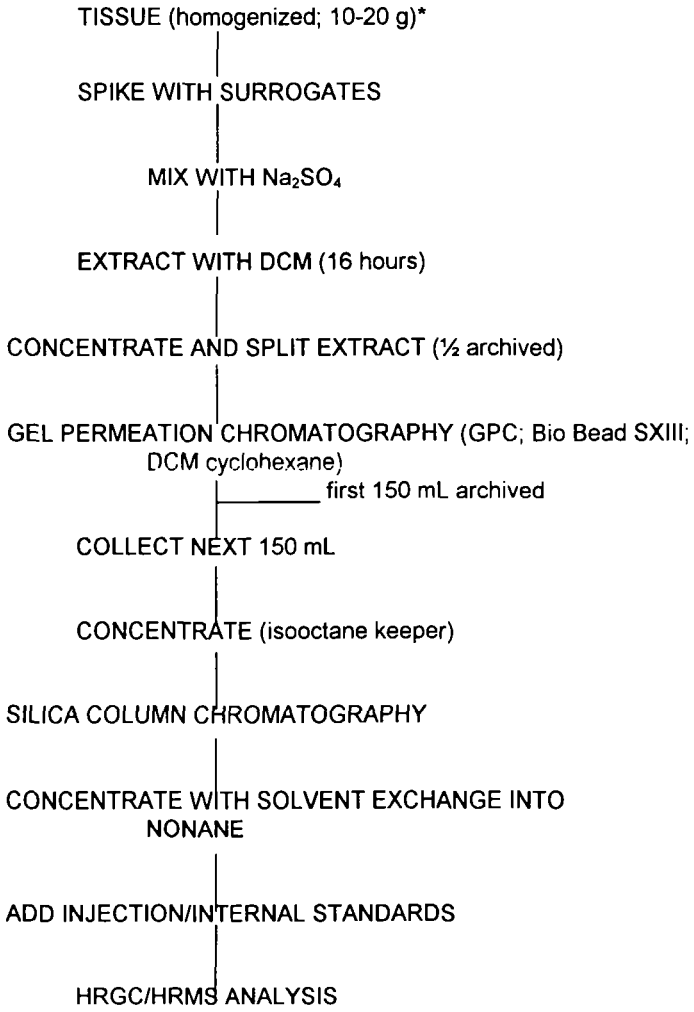
2) U.S. Environmental Protection Agency. *Health Assessment Document for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds,* Vol. III; external review draft; Office of Health and Enviromental Assessment. Office of Research and Development. U.S. Government Printing Office: Washington, D.C., August 1994; EPA/600/BP-92/001C

Figure 1: Preparation of Sediment Samples for PCB Analysis



* Wet Weight; Moisture content and dry weight determined separately

Figure 2: Preparation of Tissue Samples for PCB Analysis



* Wet Weight; Moisture content and dry weight determined separately