AN EPA METHOD FOR TOXIC PCBs IN VARIOUS MATRICES BY HRGC/HRMS

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1. Introduction

Many substances that persist in the environment possess the ability to bioaccumulate. Many of these substances are toxic either to their host organism, consumers of the host organism, or both, either due simply to their presence or in their accumulated concentrations. Concern over the health effects of bioaccumulated toxic chemicals in fish has focused attention on determining increasingly lower levels for these chemicals in water, where they exist in much smaller concentrations. Polychlorinated biphenyls (PCBs) possess bioconcentration factors for fish ranging from tens of thousands to approximately one million relative to their aquatic concentrations. Concern over the human health impact of PCBs in fish on Native Americans along estuaries in the Columbia River Basin has prompted the U.S. Environmental Protection Agency (EPA) to focus attention on determining PCB concentrations in fish and water matrices at levels below those normally measured.

Recent work has shown that specific congeners of the 209 PCBs are toxic. The World Health Organization-European Center for Environment and Health (WHO-ECEH) and the

International Programme on Chemical Safety (IPCS) has developed Toxic Equivalency Factors (TEFs) for 13 PCB congeners that satisfy the following criteria: 1) the congener shows a structural relationship to the polychlorinated dibenzo-p-dioxins and dibenzofurans, 2) the congener binds to the aryl hydrocarbon (Ah) receptor, 3) the congener elicits dioxin-specific biochemical and toxic response, and 4) the congener shows environmental persistence and bioaccumulates in the food chain [1]. The 13 toxic PCBs (IUPAC numbers 77, 105, 114, 118, 123, 126, 156, 157, 167, 169, 170, 180, and 189) consist of 3 non-*ortho* (co-planar), 8 mono-*ortho*, and 2 di-*ortho* substituted congeners.

This paper describes an analytical method developed by EPA for determination of the 13 toxic PCB congeners. The method uses technologies from the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. The extraction techniques and use of high resolution GC and high resolution MS has allows determination of these compounds at the parts per quadrillion level (pg/L) in water samples.

2. Objectives

While EPA currently employs analytical methods for the analysis of PCBs by GC/ECD and GC/MS for Aroclor classes [2] (i.e., Aroclor 1260), a method was needed for determination of the 13 individual toxic congeners in order to address the growing concern of bioaccumulative toxicity and the use of toxic equivalency factors for individual congener toxicities. Isotope dilution HRGC/HRMS was determined to be best suited for these PCB congeners, since this technique is highly specific for determining individual chemical compounds in low concentrations, and because the technique has been shown to be near-ideal for determination of the CDDs/CDFs [3]. Of particular importance in the determination of the toxic PCBs, and as is the case with the CDDs/CDFs, is identification of the sample extract clean-up techniques needed to separate the low levels of PCBs from interferences that could exist at concentrations orders of magnitude larger.

3. Method 1668

The use of isotope dilution for quantitation; the use of relative retention times, isotopic abundance ratios, and relative response factors for congener identification; and use of labeled compound recovery criteria for assessing method performance are techniques adopted from EPA Method 1613 that has been used for congener-specific determination of the individual 2,3,7,8-substituted, tetra- through octa-chlorinated CDDs/CDFs. Initially, the exact m/z's to be monitored for each PCB congener and its labeled analog were identified, and the theoretical abundance ratios were calculated for later identification of the individual congeners when samples are analyzed.

Extraction techniques include solid-phase (liquid-solid) for waters, Soxhlet/Dean-Stark (SDS) for solids, and Soxhlet for fish and other tissue. For multi-phase samples, the phases are separated prior to extraction. Cleanup procedures were optimized for separation of the toxic congener PCBs from sample matrix and chemical interferences and include gel permeation chromatography, high performance liquid chromatography, and Florisil, silica gel, and carbon columns. Method detection limits were established, with a target of approximately 10 pg/L (parts per quadrillion). A two-column GC column system (SPB-Octyl, DB-1) is used to provide congener-specific separation for all 209 PCB congeners and is based on the review of work and discussions with George Frame of General Electric Corp [4].

Method 1668 is performance-based; i.e., the analyst is permitted to modify the method to lower the costs of measurements and to improve method performance provided that equivalent or better performance is demonstrated. Method equivalency is demonstrated by (1) the determination of method detection limits at levels at least as low as those in Method 1668, (2) an initial demonstration of the ability of the laboratory and analyst to generate data of acceptable accuracy and precision within the limits given in Method 1668, (3) an on-going demonstrations of laboratory performance by analysis of a laboratory control sample with each analytical batch, (4) analysis of a blank with each analytical batch to assure freedom from contamination, and (5) recovery of labeled compounds spiked into each sample to measure method performance on that sample.

4. Performance Characteristics and Requirements

As with Method 1613, Method 1668 contains tables that provide the performance characteristics and requirements. These tables are as follows:

Table 1	List of analytes, labeled analogs, and labeled internal standards with CAS Registry numbers
Table 2	Relative retention times and references, quantitation references, method detection limits, and minimum levels
Table 3	Concentrations of stock and spiking solutions for native compounds, labeled analogs, cleanup standards, and internal standards
Table 4	Concentrations of native and labeled compounds, cleanup standards, and internal standards in calibration and verification solutions
Table 5	GC retention time window defining solution and isomer specificity test standard of the SPB-Octyl and DB-1 columns
Table 6	Acceptance criteria for performance tests when all toxic PCBs are determined
Table 6a	Acceptance criteria for performance tests when the co-planar PCBs only are

	determined
Table 7	Labeled compound recovery from samples when all toxic PCBs are determined
Table 7a	Labeled compound recovery from samples when the co-planar PCBs only are determined
Table 8	Descriptors, exact m/z's, m/z types, and elemental compositions of the PCBs
Table 9	Theoretical m/z abundance ratios and QC limits

Method 1668 also contains flowcharts for extraction and analysis of aqueous, solid, multi-phase, and tissue samples.

5. Conclusion

Method 1668 has been developed to provide a reliable means for determination of the identities and concentrations of the individual toxic PCB congeners at the parts per quadrillion level in water, and at the parts per trillion level in solid and tissue matrices. The total "dioxin-like" toxicity for each sample can be determined by application of the toxic equivalency factors for the individual PCB congeners, and this total toxicity can be compared with the toxicity resulting from determination of the CDDs/CDFs. With Method 1668 as a tool, studies such as the Columbia River Basin study willbe used to correlate water and bioaccumulative concentrations of the toxic PCB congeners to assess the extent of toxic PCB contamination in a large watershed. Method 1668 is available from the EPA Office of Science and Technology [5].

6. References

1) Ahlborg U.G., G.C. Becking, L.S. Birnbaum, A. Brouwer, H.J.G.M. Derks, M. Feeley, G. Golor, A. Hanberg, J.C. Larsen, A.K.D.Liem, S.H. Safe, C. Schlatter, F. Waern, M. Younes, E. Yrjanheikki (1994): Toxic Equivalency Factors for Dioxin-Like PCBs. Chemosphere, Vol. 28, 1049-1067.

2) Method 608, Organochlorine Pesticides and PCBs, and Method 625, Base/Neutrals and Acids, 40 CFR Part 136, July 1, 1993. Method 8080A, Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography (Revision 1, November, 1992) and Method 8081 Organochlorine Pesticides, Halowaxes and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique (Revision 0, November, 1992), SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.

3) Method 1613, Revision B, US EPA Office of Water, EPA 821-B-94-005, October, 1994.

4) Personal communication between George Frame and Dale Rushneck, 09 February 1995; "A Comprehensive, Multi-Center Study of PCB Elution on Capillary GC Columns," presented by G.M. Frame at the PittCon '95, 08 March 1995.
5) Requests for copies of Method 1668 should be directed to: Water Resource Center, Mail Code RC-4100, 401 M Street, SW, Washington, D.C. 20460.