CONF-9009205--1

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DE90 013666

PCB ANALYSIS: STATUS AND CHALLENGES*

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May 1990

*Work supported by the U.S. Department of Energy under Contract W-31-109-Eng-38.

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ABSTRACT: Present PCB analysis methods evolved from the old pesticide analysis methods using GC/ECD. These "classic" methods are still being improved upon and are heavily used. Newer methods using congener-specific high resolution GC/ECD and GC/MS have improved the specificity and information content of the analyses. Acceptable accuracy and precision with both classic and newer methods continue to be challenges to analysts.

INTRODUCTION: Polychlorinated biphenyls (PCBs) are a class of 209 chemical compounds with from one to ten chlorines substituted onto either of two benzene rings. Following their commercial use, many PCBs found their way into the environment, where they are quite stable. Beginning in the late 1960's, concern mounted about the environmental and human health implications of PCBs as (incorrect) information surfaced that they were carcinogenic. The U.S. EPA (many other governments have also banned PCBs in the past two decades) acted to severely restrict the use and disposal of PCBs beginning in 1976. We now find ourselves as a society with a "PCB problem" of removing PCBs from service and properly and economically disposing of these unwanted chemicals.

RESULTS AND DISCUSSION: The technical challenges of PCB analysis have pushed trace organic analysis techniques, such as gas chromatography and mass spectrometry, to the limits. The analytical chemistry challenges of PCBs center around the fact that PCBs were manufactured and used as complex mixtures of 20 to 60 congeners, but are regulated as a class. Thus the analyst must perform trace identification and quantitation of a complex mixture that may or may not resemble the original commercial product, but must usually report only a single number. The complexity of this analysis can generate large errors, yielding fairly uncertain results. Yet these results are used routinely to make multimillion dollar decisions.

Methods of PCB analysis grew out of the packed column gas chromatography/electron capture detector (GC/ECD) pesticide analyses of the 1960's because PCBs are similar compounds found in the same matrices by the same analysts.[1,2] However, unlike most of the chlorinated pesticides, PCBs are complex mixtures and the analytical challenge is thus significantly different. This difficulty has not always been acknowledged, and many standard methods do not give sufficient directions for qualitative and quantitative data interpretation. For example, the U.S. EPA methods for hazardous waste site cleanup [Superfund's Contract Laboratory Program (CLP) Methods[3]] and for hazardous waste characterization under the Resource Conservation and Recovery Act (RCRA)[4] are ambiguous on the criteria for identification and quantitation of PCBs. Many thousands of such analyses are conducted annually in the U.S. and there is substantial room for error because of the ambiguity in the written methods. To further complicate the issue, these and many other U.S. EPA methods require the analyst to report in terms of Aroclors. As we move further in time from when the PCBs first entered the environment, the mixture composition resembles the original Aroclor (or other commercial mixture) less and less. For example, I have conducted CLP analyses where PCBs appeared to be present but resembled no Aroclor and were therefore reported as "undetected" at sample quantitation limits in the 10,000-50,000 μg/kg range. Clearly, something is wrong where a method directs the analyst to ignore PCBs in the sample if they do not resemble the parent Aroclor.

One of the most widely used and still most accurate methods of PCB data reduction is the Webb-McCall method.[5] Each individual peak in a packed column GC/ECD chromatogram of an Aroclor is assigned a weight percentage, which is then used to calculate a response factor for the standard. That response factor is used in quantitating the corresponding peak in unknowns, and these quantities are summed for all peaks. Rules are given by Webb and McCall for dealing with multiple Aroclors. A key feature of the method is that it compensates for weathered or metabolized samples where the PCB pattern is skewed from the original Aroclor pattern.

Over the past decade or so, several PCB analysis methods have been developed to utilize the capabilities of more modern instrumental analysis techniques, specifically higher resolution gas chromatography (HRGC) using capillary columns and mass spectrometry (MS). The advantage of HRGC is the increased resolution for the PCB congeners. Although no single capillary can resolve all 209 PCBs, the number of peaks containing co-eluting PCBs and interferences can be reduced to a minimum[6]. The problem with HRGC analyses is data reduction. A typical environmental sample may contain 60 PCB congeners; qualitative interpretation (i.e., whether a peak can be identified as a PCB congener or a group of peaks as an Aroclor) is easier because of the higher precision of the retention times and the cleaner peaks with better separation. Quantitative interpretation of HRGC data is more complex than that for the old packed column analyses. More peaks must be quantitated, yielding more sources of error, and the individual congener standards are available only to a few researchers.[7]

PCB analyses are currently done by a number of methods, as shown on Table 1. This list is not comprehensive, but gives an idea of the diversity of methods.

Another area of evolution over the years has been quality control. Most early methods completely ignored QC instructions. More recently, extensive QC guidelines are prescribed in the methods and, quite often, additional written documents (standard operating procedures, quality assurance plans, etc.) are required for each analytical laboratory. This evolution from prescriptive methods to performance-based methods is welcome. In some cases, methods have incorporated measures to evaluate the performance on each individual sample. Examples are the three EPA By-Products Methods,[7] which use four ^{13}C-labeled PCBs as recovery surrogates, much like the ^{13}C-labeled 2,3,7,8-TCDD universally used in dioxin analyses. Many PCB analyses are used to make decisions on very expensive environmental cleanups, regulatory compliance, or other high-risk decisions. We cannot afford to take a "trust me" attitude about analytical data. All data must be backed by documentation that demonstrates the quality of the results.

CONCLUSION: PCB analyses have evolved over the past quarter century with many improvements in detection limits, discrimination against interferences, precision, and accuracy. Yet many challenges remain. In particular, we need to:

- Change the U.S. regulatory analyses to prevent "non-Aroclor" PCBs from going unreported.
- Incorporate more and better internal standards to improve precision.
- Incorporate sufficient quality controls and documentation requirements into methods to provide reliable and defensible data to our customers, but not make the entire process too cumbersome and wasteful.
- Develop technical improvements in extractions, cleanups, GC, and detection that will lead to better sensitivity, fewer interferences, and overall better data.

In addition, major improvements are needed in data-reduction capabilities in several areas:

- Qualitative identification of PCBs with GC/ECD data is still subjective and open to analyst prejudices.
- Quantitation based on Aroclor standards can be made to work as with the Webb-McCall method. Similar procedures have been proposed for HRGC/ECD data but have not been validated or incorporated into standard methods.
- Several HRGC/ECD and HRGC/MS methods rely on specific individual congeners. If, as is the case in some of the European countries, a set of key indicator congeners is used for the analysis and the results for only these congeners are presented, precision and accuracy problems are minimal, but we get informaion on only a fraction of the PCBs in the sample. If, as is the case with many other methods, selected calibration congeners are

used and results are extrapolated to all PCBs, the error introduced by this method is not well-characterized.

We analytical chemists need to educate our customers about the quality and usability of the PCB data we generate. This is especially important for PCBs because there are so many variables (209 results summed to yield one reported number) and artifacts of regulations which make the results open to misinterpretation. It is irresponsible for the analytical chemistry community to presume that our responsibility stops with delivery of the results. We need to communicate the complexities of the analytical results to engineers, environmental scientists, lawyers, toxicologists, corporate managers, and public.

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Table 1. Major Environmental Standard Procedures of Analysis for PCBs

Procedure Designat.	Matrix	Extraction	Cleanup[a]	Determination Method	Qual.	Quantitation Method	LOD	QC	Reference
D3534-80	Water	Hexane/ CH_2C1_2	(Florisil) (Silica Gel)	PGC/ECD[b]	No	Total area or Webb-McCall	0.1 µg/L	No	8
608	Water	CH_2Cl_2	(Florisil) (S Removal)	PGC/ECD	No	Area	0.04-0.15 µg/L	Yes	9
625	Water	CH_2Cl_2	None	PGC/EIMS (CGC)	Yes	Area	30-36 µg/L	Yes	10
680	Water, Soil Sediment	CH_2Cl_2	S Removal	HRGC/MS	Yes	Homolog	1-10 ng	Yes	11
CLP	Water	CH_2Cl_2	GPC Alumina (S Removal)	PGC/ECD	No	Sum Individual Peaks	0.5-1.0 µg/L	Yes	3
D3304-77	Air Water Soil Sediment	DI[c] Hexane H_2O/CH_3CN	(H_2SO_4) (Saponification) (Alumina)	PGC/ECD	No	Total Area	NS	Yes	12
8080	Solid Waste	CH_2Cl_2	(Florisil)	PGC/ECD	No	Area	1 µg/g	Yes	4
8250	Solid Waste	CH_2Cl_2	None	PGC/EIMS	No	NS[d]	1 µg/g	Yes	4
8270	Solid Waste	$CHCl_2$	None	HRGC/EIMS	No	NS	1 µg/g	Yes	4

Table 1. (Continued)

Procedure Designat.	Matrix	Extraction	Cleanup[a]	Determination Method	Qual.	Quantitation Method	LOD	QC	Reference
CLP	Soil/ Sediment	Hexane or CH_2Cl_2/ Acetone	GPC Alumina (S removal)	PGC/ECD	No	Sum Individual Peaks	80-160 µg/kg	Yes	3
EPA (ambient air)	Air near Hazardous Waste Sites Collected on PUF	Hexane/Ether	Alumina	PGC/ECD	No	Total Area or Peak Height	10-50 ng/m^3	No	13
NIOSH (P&CAM 244)	Air Collected on Florisil	Hexane	None	PGC/ECD	No	Peak Height or Area from Standard Curve or Webb-McCall	0.01 mg/m^3	No	14
NIOSH (P&CAM 253)	Air Collected on Florisil	Hexane	None	PGC/ECD Perchlorination	No	Peak Height or Area from Standard Curve	0.01 mg/m^3	No	15, 16
D3303-74	Capacitor Askarels	DI[b]	None	HRGC/FID	No	Total Area	2.8 x 10^{-8} mol/L	No	17
D4059-83	Mineral Oil	Dilute with Hexane or Isooctane	Florisil (H_2SO_4) (Florisil Column)	PGC/ECD (PGC/HECD)	Yes	Ind. Peaks or Webb-McCall	50 ppm	No	18

Table 1. (continued)

Procedure Designat.	Matrix	Extraction	Cleanup[a]	Determination Method	Qual.	Quantitation Method	LOD	QC	Reference
EPA (oil)	Transformer Fluids or Waste Oils	DI	(H_2SO_4) (Florisil) (Alumina) (Silica gel) (GPC), (CH_3CN)	PGC/HECD or /ECD or /EIMS (HRGC)	No	Total Area or Webb-McCall	1 mg/kg	Yes	19
EPA (by-products)	Products or Wastes	Several	Several	HRGC/EIMS	Yes	Ind. Peaks	NS	Yes	7

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a. Techniques in parentheses are described as optional in the procedure.

b. Or PGC with microcoulometric or electrolytic conductivity.

c. DI = Direct injection or dilution and injection.

d. NS = not specified