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Project Summary

EPA Method Study 28, PCBs in Oil

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The full report describes the experimental design and the results of the U.S. Environmental Protection Agency (USEPA) Method Study 28 for two analytical methods to detect polychlorinated biphenyls (PCBs) in oil. In this study, the methods were used to analyze for four PCB Aroclors (1016, 1242, 1254, and 1260), 2-chlorobiphenyl (2-MCB), and decachlorobiphenyl (DCB). The first method consists of diluting the oil in hexane and analyzing by gas chromatography using an electrolytic conductivity detector in the halogen mode. The second method consists of diluting the oil in hexane, cleaning/separating with sulfuric acid extraction or with column chromatography, and analyzing by gas chromatography using an electron capture detector. Four oil types were tested in this study: capacitor fluid, hydraulic fluid, transformer oil, and waste oil. Each oil was spiked with six concentration levels of PCBs that constituted three Youden pairs. Capacitor fluid was spiked with Aroclor 1016, hydraulic flulid with Aroclor 1242 and 2-MCB, transformer oil with Aroclor 1260 and DCB, and waste oil with Aroclor 1254.

Statistical analyses and conclusions presented in the full report are based on analytical data obtained by 18 participating laboratories and two volunteer laboratories. The two methods are assessed quantitatively with respect to their expected precision and accuracy. In addition, aspects of the methods, such as sample stability and methods detection limits, are discussed.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In 1976, polychlorinated biphenyls (PCBs) became regulated substances under the U.S. Toxic Substances Control Act (TSCA, PL 94-496). In support of Section 6 (e)(1) of TSCA, Final Rules Prescribing Requirements for Disposal and Marking of PCBs in PCB-Containing Materials, an interlaboratory study was conducted for two test procedures for the analyses of PCBs in oil. The PCBs studied were Aroclor 1016, Aroclor 1242, Aroclor 1254, Aroclor 1260, 2-MCB and DCB.

The interlaboratory study involved the analyses of four PCB-spiked oil types by 20 laboratories and was conducted between September 1981 and December 1981. The method evaluated in this study is described in the USEPA Draft Method "The Analysis of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils" (revised June 1981).

Procedure

The study was patterned after Youden's non-replicate plan for collaborative evaluation of analytical methods, in which samples are analyzed in pairs, each member of a pair having a slightly different concentration of the constituent of interest. The analyst is directed to conduct a single analysis and to report one value for each sample, as for a normal routine sample. Samples of three Youden pairs used in this study contained low, medium, and high concentrations of the PCBs, 2-MCB, and DCB, spiked into four different oil types and then analyzed.

Prior to the interlaboratory method study, participants were familiarized with both the study design and the analytical procedure through a preliminary study involving analyses of two oil samples spiked at mid-level concentrations following prescribed instructions. After resolving method interpretation and analytical problems, participating laboratories were supplied with the test materials required by the formal collaborative study and instructed to begin the analyses.

Statistical analyses of the data were performed using the Interlaboratory Method Validation Study computer program, which was developed at Battelle's Columbus Laboratories for USEPA. The program is designed to output the raw data in tabular form and compile summary statistics including:

- Number of data points
- True value
- Mean recovery
- Accuracy as percent relative error
- Overall standard deviation
- Overall percent relative standard deviation
- Single-analyst standard deviation
- Single-analyst percent relative standard deviation

The overall standard deviations indicate the dispersion expected among values generated from multiple laboratories. The single-analyst standard deviations indicate the dispersion expected among replicate determinations within a single laboratory.

Results and Discussion

The data collected during this interlaboratory study were statistically analyzed in order to establish the relationship between accuracy and the true concentration, and between precision and the mean recovery. Those relationships are summarized by the linear regression equations presented in Table 1.

The final rules under the U.S. Toxic Substances Control Act prescribe a concentration of 50 mg/kg of PCB in oil for disposal and marking. Therefore, this value (except for DCB) was substituted into the respective regression equations and the accuracy and precision compared for the HECD and ECD methods. Percentage recoveries for all PCBs/oils averaged approximately 84 percent for both detection systems. The overall and single-analyst standard deviation approximated 10.0 and 7.0 mg/kg, respectively, for both detection systems.

Percentage recoveries of DCB in transformer oil were unusually high for the HECD and ECD methods and were attributed to data submitted from four laboratories on three of the six ampules. Subsequent recalculation without their data resulted in the following regression equations:

$$\text{HECD } \bar{X} = 1.02\ C + 0.05$$
$$S = 0.39\ \bar{X} + 0.00$$
$$S_r = 0.12\ \bar{X} + 0.08$$
$$\text{ECD } \bar{X} = 1.01\ C + 0.00$$
$$S = 0.37\ \bar{X} + 0.03$$
$$S_r = 0.06\ \bar{X} + 0.08$$

Conclusions and Recommendations

Based upon the results of the interlaboratory study for PCBs in oils, it is concluded that:

- At a concentration level of 50 mg/kg, the HECD and ECD methods gave comparable results.
- Outlier tests rejected 19 percent of the data from 20 laboratories.
- The HECD and ECD methods in general gave a pronounced negative bias for recovery.
- The minimum detection level for the ECD method is consistently lower than for the HECD method.

Some laboratories had difficulty integrating the DCB peak area, especially at concentrations approximating 0.4 mg/kg. It is recommended that the oven temperature be optimized to provide the

Table 1. Summary of Accuracy and Precision Regression Equations

Oil/PCB	$\bar{X}$, mg/kg	S, mg/kg	S_r, mg/kg
Capacitor Fluid/1016 (33-492 mg/kg)			
HECD	$\bar{X} = 0.86T + 1.21$	$S = 0.23\bar{X} + 0.90$	$S_r = 0.09\bar{X} + 4.98$
ECD	$\bar{X} = 0.81T + 3.10$	$S = 0.35\bar{X} - 2.70$	$S_r = 0.24\bar{X} - 1.86$
Hydraulic Fluid 1242 (39-492 mg/kg)			
HECD	$\bar{X} = 0.89T - 4.28$	$S = 0.12\bar{X} + 2.50$	$S_r = 0.08\bar{X} + 3.29$
ECD	$\bar{X} = 0.92T - 5.87$	$S = 0.13\bar{X} + 5.45$	$S_r = 0.11\bar{X} - 0.67$
Hydraulic Fluid/2-MCB (41-1018 mg/kg)			
HECD	$\bar{X} = 0.97T - 13.00$	$S = 0.16\bar{X} + 1.74$	$S_r = 0.13\bar{X} - 0.40$
ECD	$\bar{X} = 0.88T - 5.35$	$S = 0.32\bar{X} + 2.42$	$S_r = 0.24\bar{X} + 0.73$
Transformer Oil/1260 (32-392 mg/kg)			
HECD	$\bar{X} = 1.02T - 2.62$	$S = 0.15\bar{X} + 5.97$	$S_r = 0.11\bar{X} + 3.50$
ECD	$\bar{X} = 1.04T - 4.46$	$S = 0.11\bar{X} + 2.14$	$S_r = 0.04\bar{X} + 1.89$
Transformer Oil/DCB (0.37-16.6 mg/kg)*			
HECD	$\bar{X} = 1.63T - 0.20$	$S = 0.74\bar{X} - 0.14$	$S_r = 0.12\bar{X} + 0.08$
ECD	$\bar{X} = 1.26T - 0.09$	$S = 0.55\bar{X} - 0.06$	$S_r = 0.39\bar{X} - 0.07$
Waste Oil/1254 (46-461 mg/kg)			
HECD	$\bar{X} = 0.84T - 2.00$	$S = 0.17\bar{X} + 6.28$	$S_r = 0.09\bar{X} + 5.59$
ECD	$\bar{X} = 0.95T - 7.02$	$S = 0.12\bar{X} + 3.29$	$S_r = 0.09\bar{X} + 2.07$

$\bar{X}$ = Mean Recovery.
S = Overall Method Precision.
S_r = Single-Analyst Method Precision.
T = True Value for the Concentration.
** = See recalculated regression equations in text.*

best peak geometry to assure the best accuracy and precision for the HECD and ECD methods.

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***Edward L. Berg** and **Robert L. Graves** are the EPA Project Officers (see below).*
The complete report, entitled "EPA Method Study 28, PCB's in Oil," (Order No. PB 85-115 178; Cost: $8.50, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officers can be contacted at:
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