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Project Summary

EPA Method Study 18 Method 608 — Organochlorine Pesticides and PCB's

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This report describes the results obtained and data analyses from an interlaboratory study of EPA Method 608 (Organochlorine Pesticides and PCB's). The method is designed to analyze for 16 single-compound pesticides, chlordane, toxaphene, and seven Aroclor formulations in water and wastewater. All were included in this study except endrin aldehyde, sufficient quantities of which could not be obtained. As tested here, the method utilizes three 60-mL extractions with dichloromethane, cleanup/separation on a Florisil column, and injection into a gas chromatograph equipped with an electron capture detector.

The study design required the analyst to dose six waters with eight analytical groups, each at six levels. The six dosing levels of each substance or combination represented three Youden pairs, one each at a low, an intermediate, and a high level. The six waters used were a laboratory pure water, a finished drinking water, and a surface water, collected by the participant, and three low-background industrial effluents (SIC's 2869, 2869 and 2621) provided by the prime contractor. A total of 22 laboratories participated in the study.

The method is assessed quantitatively with respect to the accuracy and precision that can be expected. In addition, results of method detection limit studies are included as are qualitative assessments of the method based upon comments by the participating laboratories.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 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

EPA first promulgated guidelines establishing test procedures for the analysis of pollutants in 1973, following the passage of the Federal Water Pollution Control Act in 1972 by Congress. Pursuant to the amendment and publication of these guidelines, EPA entered into a Settlement Agreement—the Consent Decree—which required the study and, if necessary, regulation of 65 "priority" pollutants and classes of pollutants of known or suspected toxicity to the biota. Subsequently, Congress passed the Clean Water Act of 1977, mandating the control of toxic pollutants discharged into ambient waters by industry.

In order to facilitate the implementation of the Clean Water Act, EPA selected 129 specific toxic pollutants, 113 organic and 16 inorganic, for initial study. The organic pollutants were divided into 12 categories based on their chemical structure. Analytical methods were developed by EPA for these 12 categories through in-house and contracted research. These analytical methods may eventually be required for the monitoring of 113 toxic pollutants in industrial wastewater effluents, as specified by the Clean Water Act of 1977.

As a logical subsequence to the work that produced proposed EPA Method 608 (Organochlorine Pesticides and PCB's), an interlaboratory study was conducted

to determine the precision and accuracy of the proposed method. This report describes the work performed, presents the data acquired, and gives the conclusions drawn from the collaborative effort.

Of the 25 priority pollutants named in Method 608, 24 were tested in this study. Endrin aldehyde, which is included in Method 608, was eliminated from this study because it could not be obtained in sufficient quantity for the study, except through a costly synthesis effort.

The objective of this interlaboratory study was to obtain information about the accuracy and precision associated with measurements generated by Method 608. This objective was met through the use of statistical analysis techniques designed to extract and summarize the relevant information about accuracy and precision from the data reported by the participating laboratories. The statistical techniques employed in the data reduction process are similar to the techniques suggested in the ASTM Standard Practice D2777-77.

The algorithms required to perform the statistical analyses have been integrated into a system of computer programs referred to as IMVS (Interlaboratory Method Validation Study). The analyses performed by IMVS include several tests for the rejection of outliers (laboratories and individual data points), summary statistics by concentration level for mean recovery (accuracy), overall and single-analyst standard deviation (precision), determination of the linear relationship between mean recovery and concentration level, determination of the linear relationship between the precision statistics and mean recovery, and a test for the effect of water type on accuracy and precision.

Procedure

The study design was based on Youden's original plan for collaborative evaluation of precision and accuracy for analytical methods. According to Youden's design, samples are analyzed in pairs where each sample of a pair has a slightly different concentration of the constituent. The analyst is directed to do a single analysis and report on value for each sample, as if for a normal, routine sample.

In this study, samples were prepared as concentrates in sealed glass ampules and shipped to the analyst with portions of final effluents from manufacturing plants from three relevant industries. Each participating laboratory was responsible for supplying laboratory pure water, a

finished drinking water and a surface water, thus giving a total of six water matrices involved in the study. The analyst was required to add an aliquot of each concentrate to a volume of water from each of the six waters and submit the spiked water to analysis. Three pairs of samples were used. One pair contained the substances at what was considered to be equivalent to a low level for the industrial effluents; a second pair contained the substances at an intermediate level; and the third pair contained the substances at a high level.

Before the formal study began, each participant was sent a pair of ampules (not one of the pairs used in the study) for a trial analysis by Method 608. After submitting data from these analyses to SwRI, all participants met in Cincinnati to discuss problems encountered during the trial run.

Results and Discussion

The accuracy of the method could generally be expressed as a linear function of the true concentration. The regression equations are shown in Table 1.

The precision of the method could generally be expressed as a linear function of the mean recovery. These regression equations are also shown in Table 1.

Recoveries at the midrange concentration were similar to those obtained during the developmental phase in many instances and lower in others, indicating satisfactory method performance. The recoveries ranged from 68 to 101% for single-compound pesticides, 73 to 86% for multiple-compound pesticides, and 69 to 101% for the PCB formulations in the first five matrices. Lower recoveries were obtained in the third industrial effluent due to emulsion formation. Eighty-six percent of the recoveries among the first five matrices exceeded 80% and 12.5 exceeded 90%.

At the midrange concentration, overall percent relative standard deviations of 12 to 45, 19 to 36, and 14 to 40% were obtained for the three above groupings of compounds among the first five matrices. The single-analyst percent relative standard deviations were from 11 to 33, 10 to 31, and 12 to 28%, respectively, under the same conditions. Poorer precision values were obtained for industrial effluent 3, as expected, due to the nature of the effluent.

Six water types were used in this study: laboratory pure, finished drinking, surface and three industrial effluents. The

only significant difference among the results obtained was in the recovery of the substances from the third industrial effluent. This effluent gave a large emulsion on extraction that resulted in lowered extraction efficiency. With one exception, there was no detectable difference in precision among the results from the six waters studied.

The principal problem area noted by the participants was related to the concentration of extracts with the Kuderna-Danish apparatus.

Conclusions and Recommendations

The participating laboratories in this study were able to obtain results with Method 608 that were comparable to those obtained during the single-laboratory evaluations conducted after method development. The accuracy and precision statements presented earlier apply only to the range of concentrations studied and should not be extrapolated beyond those limits.

Table 1. Accuracy and Precision Equations

Water type Range, µg/L	Aldrin 0.9444-5.60	alpha-BHC 0.470-3.96	beta-BHC 0.864-9.15	gamma-BHC 0.476-3.34	sigma-BHC 0.944-5.76	4,4'-DDD 2.46-22.3
Laboratory Pure						
Accuracy	X = 0.81c + 0.04	X = 0.84c + 0.03	X = 0.81c + 0.07	X = 0.82c - 0.05	X = 0.81c + 0.07	X = 0.84c + 0.30
Precision						
Overall	S = 0.20X - 0.01	S = 0.23X	S = 0.33X - 0.05	S = 0.22X + 0.04	S = 0.25X + 0.03	S = 0.27X + 0.14
Single analyst	SR = 0.16X - 0.04	SR = 0.13X + 0.04	SR = 0.22X - 0.02	SR = 0.12X + 0.06	SR = 0.18X + 0.09	SR = 0.20X - 0.18
Finished Drinking						
Accuracy	X = 0.81c + 0.04	X = 0.83c + 0.06	X = 0.85c + 0.17	X = 0.79c - 0.02	X = 0.81c + 0.03	X = 0.85c + 0.32
Precision						
Overall	S = 0.18X + 0.11	S = 0.21X	S = 0.27X - 0.01	S = 0.19X + 0.08	S = 0.32X - 0.05	S = 0.24X - 0.16
Single analyst	SR = 0.09X + 0.13	SR = 0.09X + 0.06	SR = 0.09X + 0.22	SR = 0.08X + 0.13	SR = 0.14X + 0.09	SR = 0.13X + 0.14
Surface						
Accuracy	X = 0.82c + 0.05	X = 0.83c + 0.06	X = 0.81c + 0.12	X = 0.83c - 0.03	X = 0.82c + 0.01	X = 0.88c + 0.09
Precision						
Overall	S = 0.15X + 0.14	S = 0.21X + 0.01	S = 0.27X - 0.04	S = 0.15X + 0.09	S = 0.31X + 0.04	S = 0.22X - 0.05
Single analyst	SR = 0.11X + 0.10	SR = 0.20X - 0.02	SR = 0.17X	SR = 0.04X + 0.15	SR = 0.16X + 0.11	SR = 0.14X + 0.32
Ind. Effluent 1						
Accuracy	X = 0.76c + 0.06	X = 0.78c + 0.17	X = 0.79c + 0.15	X = 0.81c + 0.04	X = 0.75c + 0.08	X = 0.96c + 0.06
Precision						
Overall	S = 0.22X + 0.03	S = 0.28X + 0.05	S = 0.25X - 0.03	S = 0.05X + 0.15	S = 0.35X - 0.03	S = 0.22X - 0.08
Single analyst	SR = 0.14X + 0.06	SR = 0.25X	SR = 0.17X + 0.01	SR = 0.07X + 0.10	SR = 0.20X + 0.05	SR = 0.20X + 0.01
Ind. Effluent 2						
Accuracy	X = 0.75c - 0.03	X = 0.83c + 0.04	X = 0.85c - 0.06	X = 0.83c - 0.07	X = 0.85c - 0.01	X = 0.83c + 0.26
Precision						
Overall	S = 0.28X	S = 0.19X + 0.01	S = 0.27X	S = 0.13X + 0.06	S = 0.25X + 0.03	S = 0.18X + 0.13
Single Analyst	SR = 0.24X - 0.07	SR = 0.14X + 0.03	SR = 0.17X + 0.01	SR = 0.06X + 0.07	SR = 0.15X + 0.10	SR = 0.06X + 0.56
Ind. Effluent 3						
Accuracy	X = 0.34c - 0.07	X = 0.63c	X = 0.66c	X = 0.63c - 0.03	X = 0.66c - 0.03	X = 0.55c - 0.13
Precision						
Overall	S = 0.63X + 0.02	S = 0.31X + 0.02	S = 0.26X - 0.01	S = 0.28X + 0.03	S = 0.31X + 0.09	S = 0.42X + 0.13
Single analyst	SR = 0.37X + 0.01	SR = 0.11X + 0.07	SR = 0.11X + 0.12	SR = 0.19X + 0.05	SR = 0.22X + 0.06	SR = 0.23X + 0.24

Table 1. (Continued)

| Water type Range, µg/L	4,4'-DDE 1.31-9.84	4,4'-DDT 3.64-22.2	Dieldrin 1.32-12.3	Endosulfan I 1.26-13.4	Endosulfan II 2.27-14.0	Endosulfan sulfate 3.86-29.7
Laboratory Pure						
Accuracy	X = 0.85c + 0.14	X = 0.93c - 0.13	X = 0.90c + 0.02	X = 0.97c + 0.04	X = 0.93c + 0.34	X = 0.89c - 0.37
Precision						
Overall	S = 0.28X - 0.09	S = 0.31X - 0.21	S = 0.16X + 0.16	S = 0.18X + 0.08	S = 0.47X - 0.20	S = 0.24X + 0.35
Single analyst	SR = 0.13X + 0.06	SR = 0.17X + 0.39	SR = 0.12X + 0.19	SR = 0.10X + 0.07	SR = 0.41X - 0.65	SR = 0.13X + 0.33
Finished Drinking						
Accuracy	X = 0.81c + 0.17	X = 0.89c + 0.31	X = 0.89c - 0.08	X = 0.90c + 0.02	X = 0.88c + 0.10	X = 0.87c + 0.11
Precision						
Overall	S = 0.20X + 0.07	S = 0.32X - 0.01	S = 0.15X + 0.24	S = 0.16X	S = 0.28X + 0.37	S = 0.26X + 0.02
Single analyst	SR = 0.10X + 0.23	SR = 0.13X + 0.73	SR = 0.13X + 0.14	SR = 0.14X - 0.06	SR = 0.17X + 0.30	SR = 0.15X + 0.06
Surface						
Accuracy	X = 0.84c + 0.10	X = 0.95c - 0.09	X = 0.85c + 0.01	X = 0.90c + 0.38	X = 0.86c + 0.03	X = 0.87c - 0.57
Precision						
Overall	S = 0.22X - 0.07	S = 0.29X - 0.34	S = 0.26X - 0.03	S = 0.23X + 0.18	S = 0.24X + 0.23	S = 0.22X + 0.19
Single analyst	SR = 0.13X + 0.01	SR = 0.15X + 0.13	SR = 0.24X - 0.14	SR = 0.15X	SR = 0.23X + 0.11	SR = 0.11X + 0.39
Ind. Effluent 1						
Accuracy	X = 0.89c + 0.05	X = 0.92c + 0.04	X = 0.86c + 0.12	X = **0.93c** + 0.12	X = 0.97c + 0.32	X = 0.91c - 0.46
Precision						
Overall	S = 0.23X - 0.09	S = 0.28X - 0.11	S = 0.15X + 0.06	S = 0.12X + 0.02	S = 0.39X - 0.03	S = 0.39X + 0.28
Single analyst	SR = 0.23X - 0.08	SR = 0.26X - 0.11	SR = 0.18X - 0.10	SR = 0.12X - 0.02	SR = 0.05X + 0.94	SR = 0.24X + 1.04
Ind. Effluent 2						
Accuracy	X = 0.74c + 0.11	X = 0.76c + 0.04	X = 0.90c - 0.08	X = 0.89c - 0.01	X = 0.84c + 0.45	X = 0.81c - 0.17
Precision						
Overall	S = 0.23X	S = 0.25X + 0.16	S = 0.13X + 0.16	S = 0.18X + 0.04	S = 0.24X + 0.61	S = 0.32X - 0.14
Single analyst	SR = 0.19X + 0.12	SR = 0.13X + 0.47	SR = 0.12X + 0.15	SR = 0.11X + 0.07	SR = 0.02X + 0.94	SR = 0.27X - 0.16
Ind. Effluent 3						
Accuracy	X = 0.52c - 0.13	X = 0.55c - 0.64	X = 0.55c	X = 0.57c + 0.05	X = 0.66c + 0.16	X = 0.60c + 0.39
Precision						
Overall	S = 0.46X + 0.08	S = 0.55X + 0.16	S = 0.39X + 0.03	S = 0.46X + 0.06	S = 0.69X - 0.22	S = 0.36X + 0.42
Single analyst	SR = 0.25X + 0.12	SR = 0.28X + 0.29	SR = 0.27X - 0.03	SR = 0.16X + 0.30	SR = 0.14X + 0.26	SR = 0.18X + 0.31

Table 1. *(Continued)*

Water type Range, µg/L	Endrin 2.15-22.6	Heptachlor 0.446-3.22	Heptachlor epoxide 0.872-6.62	Chlordane 8.49-53.0	Toxaphene 47.0-403	Aroclor 1016 10.2-88.3
Laboratory Pure						
Accuracy	X = 0.89c - 0.04	X = 0.69c + 0.04	X = 0.89c + 0.10	X = 0.82c - 0.04	X = 0.80c + 1.74	X = 0.81c + 0.50
Precision						
Overall	S = 0.24X + 0.25	S = 0.16X + 0.08	S = 0.25X - 0.08	S = 0.18X + 0.18	S = 0.20X + 0.22	S = 0.15X + 0.45
Single analyst	SR = 0.20X + 0.25	SR = 0.06X + 0.13	SR = 0.18X - 0.11	SR = 0.13X + 0.13	SR = 0.09X + 3.20	SR = 0.13X + 0.15
Finished Drinking						
Accuracy	X = 0.86c + 0.31	X = 0.79c - 0.02	X = 0.83c + 0.09	X = 0.79c - 0.37	X = 0.84c + 0.72	X = 0.87c - 0.39
Precision						
Overall	S = 0.21X + 0.12	S = 0.24X + 0.06	S = 0.24X - 0.05	S = 0.27X + 0.22	S = 0.20X + 1.55	S = 0.15X + 0.18
Single analyst	SR = 0.17X + 0.17	SR = 0.14X + 0.07	SR = 0.14X + 0.07	SR = 0.17X + 0.42	SR = 0.10X + 3.96	SR = 0.10X + 0.77
Surface						
Accuracy	X = 0.89c + 0.45	X = 0.75c + 0.02	X = 0.84c + 0.11	X = 0.82c - 0.61	X = 0.79c + 2.03	X = 0.80c + 0.90
Precision						
Overall	S = 0.31X + 0.33	S = 0.24X + 0.04	S = 0.20X + 0.01	S = 0.18X + 0.18	S = 0.24X - 0.30	S = 0.14X + 0.98
Single analyst	SR = 0.27X + 0.21	SR = 0.16X + 0.03	SR = 0.12X + 0.02	SR = 0.11X + 0.19	SR = 0.20X - 0.53	SR = 0.10X + 0.77
Ind. Effluent 1						
Accuracy	X = 0.97c + 0.15	X = 0.66c + 0.03	X = 0.83c + 0.11	X = 0.82c - 0.43	X = 0.80c - 0.44	X = 0.81c + 0.99
Precision						
Overall	S = 0.32X + 0.03	S = 0.21X + 0.08	S = 0.19X - 0.04	S = 0.40X - 1.14	S = 0.21X + 2.34	S = 0.11X + 1.69
Single analyst	SR = 0.24X + 0.31	SR = 0.14X + 0.08	SR = 0.15X + 0.01	SR = 0.28X - 0.85	SR = 0.15X - 1.92	SR = 0.12X + 0.43
Ind. Effluent 2						
Accuracy	X = 0.94c	X = 0.58c + 0.08	X = 0.87c + 0.08	X = 0.74c + 0.13	X = 0.71c + 4.74	X = 0.75c + 1.10
Precision						
Overall	S = 0.28X - 0.01	S = 0.30X + 0.11	S = 0.18X + 0.03	S = 0.27X - 0.66	S = 0.21X + 7.45	S = 0.19X + 0.28
Single Analyst	SR = 0.23X - 0.18	SR = 0.22X + 0.07	SR = 0.15X + 0.08	SR = 0.17X - 0.48	SR = 0.15X - 1.92	SR = 0.20X - 0.17
Ind. Effluent 3						
Accuracy	X = 0.55c + 0.13	X = 0.28c - 0.01	X = 0.54c	X = 0.34c - 0.20	X = 0.42c + 2.27	X = 0.50c + 0.78
Precision						
Overall	S = 0.49X	S = 0.93X - 0.03	S = 0.33X + 0.10	S = 0.42X + 0.23	S = 0.44X + 0.43	S = 0.48X - 0.40
Single analyst	SR = 0.29X + 0.04	SR = 0.57X + 0.02	SR = 0.18X + 0.14	SR = 0.34X - 0.20	SR = 0.23X + 3.04	SR = 0.36X - 0.94

Table 1. *(Continued)*

Water type Range, µg/L	Aroclor 1221 23.9-191	Aroclor 1232 24.8-185	Aroclor 1242 13.0-106	Aroclor 1248 16.4-154	Aroclor 1254 17.4-108	Aroclor 1260 36.8-254
Laboratory Pure						
Accuracy	X = 0.96c + 0.65	X = 0.91c + 10.79	X = 0.93c + 0.70	X = 0.97c + 1.06	X = 0.76c + 2.07	X = 0.66c + 3.76
Precision						
Overall	S = 0.35X - 0.62	S = 0.31X + 3.50	S = 0.21X + 1.52	S = 0.25X - 0.37	S = 0.17X + 3.62	S = 0.39X - 4.86
Single Analyst	SR = 0.29X - 0.76	SR = 0.21X - 1.93	SR = 0.11X + 1.40	SR = 0.17X + 0.41	SR = 0.15X + 1.66	SR = 0.22X - 2.37
Finished Drinking						
Accuracy	X = 0.84c + 1.56	X = 0.91c + 2.06	X = 1.00c - 1.09	X = 0.90c + 1.96	X = 0.83c + 1.28	X = 0.78c + 3.87
Precision						
Overall	S = 0.37X - 0.95	S = 0.42X - 3.01	S = 0.22X + 0.05	S = 0.20X + 3.66	S = 0.17X + 2.04	S = 0.34X - 2.36
Single analyst	SR = 0.31 X - 2.70	SR = 0.29X - 2.71	SR = 0.11X + 1.20	SR = 0.12X + 4.58	SR = 0.13X + 0.87	SR = 0.20X - 2.12
Surface						
Accuracy	X = 0.84c + 2.37	X = 0.99c + 2.27	X = 0.93c + 0.31	X = 0.86c + 1.72	X = 0.77c + 1.81	X = 0.84c + 3.10
Precision						
Overall	S = 0.40X - 0.18	S = 0.35X - 1.50	S = 0.28X + 0.55	S = 0.22X - 0.37	S = 0.17X + 3.12	S = 0.27X - 0.74
Single analyst	SR = 0.22X + 3.93	SR = 0.25X - 1.92	SR = 0.14X + 0.57	SR = 0.10X + 1.80	SR = 0.12X + 0.51	SR = 0.15X + 0.10
Ind. Effluent 1						
Accuracy	X = 0.84c + 6.78	X = 0.88c + 7.65	X = 0.99c + 0.89	X = 0.91c + 0.85	X = 0.88c - 1.41	X = 0.79c + 3.27
Precision						
Overall	S = 0.19X + 9.76	S = 0.35X - 1.27	S = 0.22X + 1.87	S = 0.18X + 1.22	S = 0.19X + 0.52	S = 0.25X + 2.53
Single analyst	SR = 0.07X + 9.70	SR = 0.30X - 5.27	SR = 0.04X + 2.54	SR = 0.11X + 1.78	SR = 0.10X + 1.66	SR = 0.11X + 2.50
Ind. Effluent 2						
Accuracy	X = 0.76c + 4.92	X = 0.91c + 1.94	X = 0.90c + 0.43	X = 0.82c + 3.72	X = 0.75c - 1.74	X = 0.80c - 1.84
Precision						
Overall	S = 0.37X - 0.39	S = 0.44X - 5.16	S = 0.17X + 1.83	S = 0.22X + 4.09	S = 0.23X - 0.44	S = 0.33X - 2.71
Single Analyst	SR = 0.24X + 2.57	SR = 0.25X - 2.45	SR = 0.09X + 1.65	SR = 0.05X + 5.60	SR = 0.17X - 1.04	SR = 0.14X + 0.14
Ind. Effluent 3						
Accuracy	X = 0.58c + 0.71	X = 0.57c - 0.03	X = 0.53c + 0.30	X = 0.52c + 0.19	X = 0.48c - 0.26	X = 0.56c - 0.24
Precision						
Overall	S = 0.57X - 1.78	S = 0.52X - 0.19	S = 0.33X + 1.92	S = 0.49X + 0.30	S = 0.38X + 1.12	S = 0.44X + 0.70
Single analyst	SR = 0.45X - 1.80	SR = 0.26X - 2.09	SR = 0.13X + 2.36	SR = 0.35X - 0.26	SR = 0.22X + 1.85	SR = 0.16X + 5.01

c - true concentration
X - mean concentration
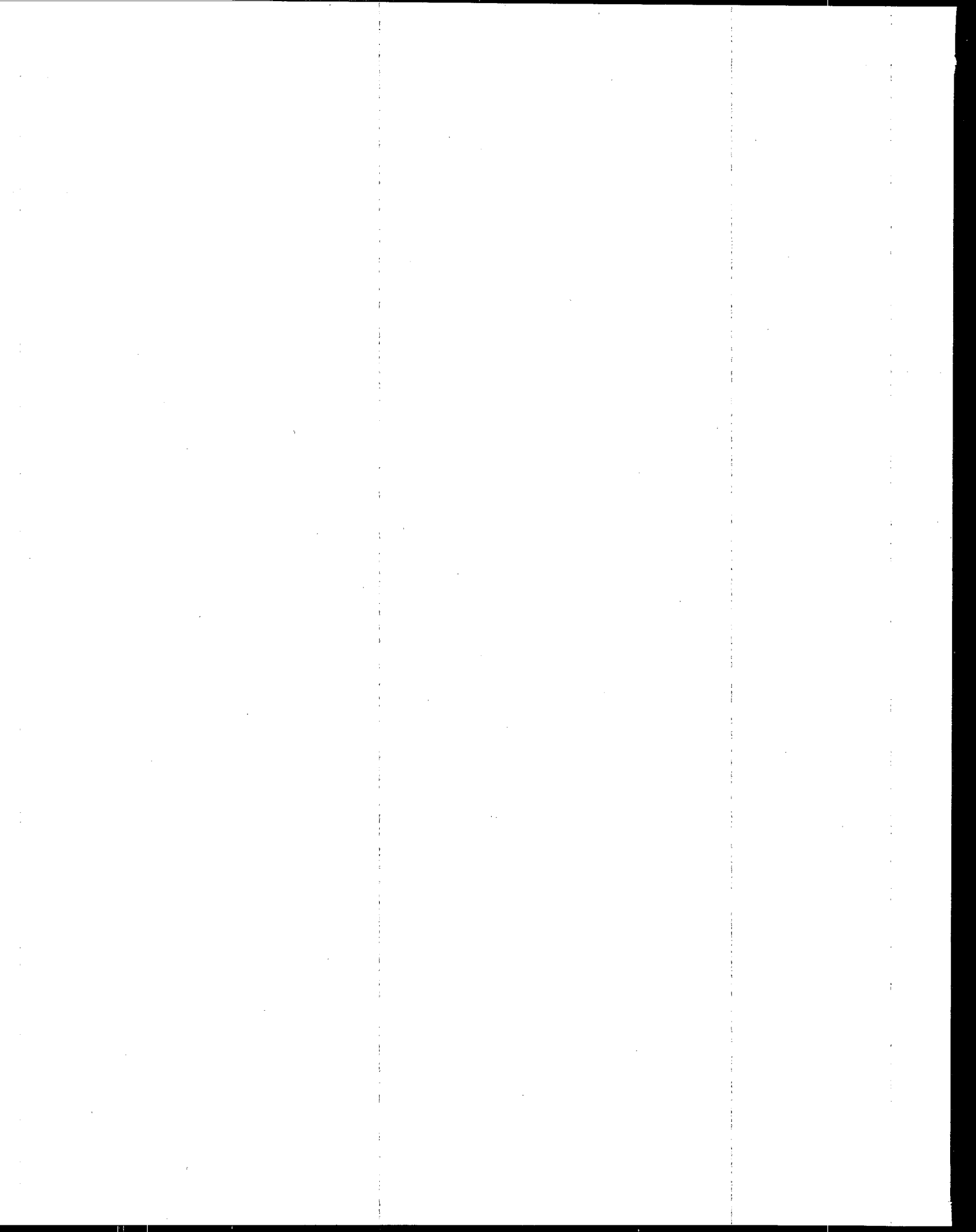
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   Southwest Research Institute, San Antonio, TX 78284.
Robert L. Graves and **Edward L. Berg** are the EPA Project Officers (see below).
The complete report, entitled "EPA Method Study 18, Method 608—Organo-
   chlorine Pesticides and PCB's," (Order No. PB 84-211 358; Cost: $17.50,
   subject to change) will be available only from:
      National Technical Information Service
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