



Project Summary

USEPA Method Study #39, Method 504, 1,2- Dibromoethane (EDB) and 1,2- Dibromo-3-Chloropropane (DBCP) in Water by Microextraction and Gas Chromatography

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An interlaboratory collaborative study was conducted to determine the precision and bias (recovery) of Method 504 for the analysis of two semivolatile organic compounds in groundwater. Method 504 is entitled "1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-Chloropropane (DBCP) in Water by Microextraction and Gas Chromatography" and includes instructions for quality control, sample preparation and analysis of samples by gas chromatography.

The study design was based upon Youden's non-replicate plan for collaborative tests of analytical methods. Each water type was spiked with three Youden sample pairs of the two semivolatile compounds and analyzed using method 504. The test waters included reagent water as a "control" and one ground water. The resulting data were analyzed using the USEPA computer program entitled "Interlaboratory Method Validation Study (IMVS)." The data analyses produced measures of precision and recovery for each compound in each water type and compared the performance of the method between water types.

The study was conducted under the auspices of the U.S. Environmental Protection Agency, Cincinnati, Ohio, under EPA Contract No. 68-03-3254. This report covers a period from June 1987 to December 1987. Analytical work was completed as of October 1987.

This Project Summary was developed by EPA's Environmental Monitoring Systems 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

The Office of Water (OW) of the U.S. Environmental Protection Agency (USEPA), gathers water quality data to provide information on water resources and drinking waters to monitor safe drinking water quality, establish maximum contaminant limits, and assure compliance or further regulations under the Safe Drinking Water Act (1986) and its amendments. The success of these activities depends upon the reliability of the data provided by the laboratories,

particularly when legal actions are contemplated.

EMSL-Cincinnati develops/selects analytical methods and provides quality assurance (QA) support to the Office of Drinking Water (ODW) as required by regulations. The QA program is designed to maximize the reliability and legal defensibility of water quality information collected by the Agency, the primary regulating authorities in the states, and by the laboratories performing analyses for public water supplies. The responsibility for providing QA support is assigned to the QA Branch of EMSL-Cincinnati. One QA Branch activity is to conduct interlaboratory method validation studies on ODW's analytical methods to obtain precision and bias statements for the analytical methods specified for regulated analytes.

The full report describes an inter-laboratory method validation study on Method 504 entitled "1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-Chloropropane (DBCP) in Water by Microextraction and Gas Chromatography." Ten commercial laboratories, with demonstrated experience in the analyses of drinking water, were selected, based on technical criteria, to participate in this study. The Bionetics Corporation, as primary contractor to the Quality Assurance Branch of EMSL-Cincinnati, was responsible for the collection and characterization of ground water used as a test water in the study and the subsequent spiking levels of the analytes. Additional activities included analyses of the samples to confirm the true values, preparation of user instructions and report forms, distribution of the samples, screening of returned data for gross errors, and drafting of the final report. Statistical evaluation of the raw data was performed using a series of computer programs entitled "Inter-laboratory Method Validation Studies" (IMVS).

Procedure

Study Design

The study design was based on Youden's original non-replicate design for collaborative evaluation of precision and recovery for analytical methods. Two similar yet different samples were prepared at each of three levels over the selected range of concentrations such that the concentration of the pairs varied between 5-20% of the mean of the pairs. Analysts were directed to do a single analysis and report one value for

each sample. Analyses in reagent water evaluated the proficiency of the method on a sample free of interferences; analyses in the other water were intended to reveal the effects of matrix interferences in the method.

Spiking solutions, standard solutions and quality control samples were heat-sealed in ampuls. From each ampul, containing 1.5 mL of solution, 35 μ L was used to spike 35 mL of matrix water. Ampul solutions were analyzed for true values against standards freshly prepared from neat materials prior to distribution. At the completion of the study the ampuls were again analyzed against freshly prepared standards to verify the stability of the study samples.

The ground water used for this study was acquired from a well at a Superfund hazardous waste site. The well was purged prior to sample collection. The water samples were preserved by adjusting the pH to 2.0 with 1:1 HCl then mixed thoroughly to ensure homogeneity, dispensed into glass bottles with Teflon lined lids and sealed in plastic bags for shipment to the participating laboratories.

Each of the ten participating laboratories received twelve ampuls (six concentrations for each of two waters) and instructions for spiking into the waters. Each laboratory also received four quality control sample ampuls and instructions plus the "in control" limits. Copies of the method, report forms, a questionnaire and approximately 1 liter of groundwater were provided to the laboratories.

Each participating laboratory was required to prepare full volume test samples using the six Youden spiking solutions spiked into their own reagent water and the ground water provided. For each water type a matrix blank and a quality control sample were also analyzed. The laboratories were instructed to analyze the samples using the exact written method, and to complete the analyses and report forms within a 60-day period from receipt of samples.

A questionnaire was sent to the participating laboratories requesting information on instrument operating conditions, type of instrumentation used, problems encountered with the method, and other variables associated with the conduct of the method.

Selection of Participating Laboratories

The Quality Assurance Branch was responsible for the selection of the

participating laboratories. As per the standard competitive bid process, an abstract of the scope of work was announced in the Commerce Business Daily. Over 100 laboratories were forwarded the request for proposal (RFP). The evaluation criteria for the technical proposal were:

- Suitability of the Project Management Plan – This includes the experience of the project manager in managing contracts of a similar nature as this contract, the suitability of the organizational plan in that all roles, responsibilities and authorities shall be clearly identified, and demonstrate the ability of the offeror to provide the required number of analyses within the period of performance given in the contract.
- Personnel Qualifications – The offeror must demonstrate the experience of all analysts involved in the method study.
- Suitability of Facilities and Instrumentation – The offeror must describe the facilities and instrumentation which will be made available for this contract.
- Suitability of Quality Assurance Plan – The offeror must describe what efforts are to be made to ensure the quality and timeliness of the data.

All responses were evaluated and ranked. Technically acceptable laboratories were sent performance evaluation (PE) samples for analysis. Each offeror was required to bid separately on each of eight different method validation studies. The offerors were instructed to analyze the samples utilizing the written method, and the same personnel and instrumentation as listed in their proposal for the formal study. The PE sample contained five purgeable volatile organics, four pesticides and three aldicarbs as unknowns. The offeror's data were evaluated against statistics generated by EMSL-QAB from past performance evaluation and method validation studies. Ten laboratories from the list of technically acceptable laboratories were chosen based on the competitive range of cost.

Results and Discussion

The objective of this study was to characterize the performance of Method 504 in terms of recovery, overall precision, single-analyst precision, and the effect of water types on both recovery and precision. Through the Interlaboratory Method Validation Study (IMVS) computer programs, statistical

Table 1. IMVS Study 504, Regression Equations for Recovery and Precision

Water Type	1,2-Dibromoethane	1,2-Dibromo-3-Chloropropane
<i>Applicable Conc. Range</i>	(0.05 - 6.68) µg/L	(0.05 - 6.40) µg/L
<i>Reagent Water</i>		
<i>Single-Analyst Precision</i>	SR = 0.41X + 0.004	SR = 0.065X + 0.000
<i>Overall Precision</i>	S = 0.075X + 0.008	S = 0.143X - 0.000
<i>Recovery</i>	X = 1.072C - 0.006	X = 0.987X - 0.000
<i>Ground Water</i>		
<i>Single-Analyst Precision</i>	SR = 0.046X + 0.002	SR = 0.076X - 0.000
<i>Overall Precision</i>	S = 0.102X + 0.006	S = 0.160X + 0.006
<i>Recovery</i>	X = 1.077C - 0.001	X = 0.972C + 0.007

X = Mean recovery

C = True value for the concentration

analyses of 240 analytical values provided estimates of recovery and precision expressed in regression equations presented in Table 1.

A detailed investigation of the number of outliers is a good measurement of the ruggedness of the method. In this study, 15% of the submitted data points were rejected as outliers. The laboratory ranking test, associated with systematic errors, represented 67% of the total rejected data while the individual outlier test accounted for the remaining 33%. One laboratory accounted for 41% of the total outliers while 7 laboratories had no outliers for 1,2-dibromoethane and 8 laboratories had no outliers for 1,2-dibromo-3-chloropropane. The ground water produced no apparent matrix effect on the number of outliers (7.1% outliers in reagent water and 7.9% outliers in ground water). The relatively low percentage of outlier data indicated that the method is rugged.

The recovery of the method was obtained by comparing the mean values from the study to the true value concentrations. Recoveries of 107% and 108% for reagent water and ground water were found for 1,2-dibromo-

ethane. For 1,2-dibromo-3-chloropropane recoveries of 99% and 97% were found for reagent water and ground water, respectively.

The overall standard deviation expressed as the percent relative standard deviation (%RSD) was 8% and 10% for 1,2-dibromoethane in reagent water and ground water respectively. The %RSD was 14% and 16% for 1,2-dibromo-3-chloropropane in reagent water and ground water, respectively.

The single-analyst standard deviation expressed as the percent relative standard deviation (%RSD-SA) was 4% and 5% for 1,2-dibromoethane in reagent water and ground water and 7% and 8% for 1,2-dibromo-3-chloropropane in reagent water and ground water, respectively.

The statistical comparisons of the data across water types indicated no matrix effects in the recovery or precision regression equations.

Conclusions and Recommendations

Method 504 is recommended for the analyses of 1,2-dibromoethane and

1,2-dibromo-3-chloropropane in water. The recovery, overall precision and single-analyst precision were acceptable. There was no significant difference in performance between the waters tested in this study.

Impurities contained in the extracting solvent can account for many analytical problems noted in this study. It is recommended that only the highest grade extraction solvent be obtained and tested prior to use for analyses.

Instances of sample contamination have been attributed to diffusion of volatile organics through the septum seal of unlined caps into the sample bottle during shipment and storage. It is recommended that Teflon-lined caps with septum seals be used.

The primary column (Durawax – DX3, 0.25 µm film, 30 m x 0.32 mm) is recommended for normal analyses, because 1,2-dibromoethane, at low concentrations, can be masked on the confirmation column by high levels of dibromochloromethane, a common chlorinated drinking water contaminant.

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The complete report, entitled "USEPA Method Study #39, Method 504, 1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-Chloropropane (DBCP) in Water by Microextraction and Gas Chromatography," (Order No. PB 89-119 580/AS; Cost: \$15.95, 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 Officer can be contacted at:
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