



Project Summary

EPA Method Study 23B, Method 501.2, Trihalomethanes by Liquid/Liquid Extraction

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The experimental design and results of an interlaboratory study for an analytical method to detect trihalomethanes in water are described herein. In EPA Method 501.2, trihalomethanes are extracted by liquid/liquid extraction using n-pentane (2 mL pentane/10 mL water) and subsequent direct analysis by gas chromatography using an electron capture detector. The six concentrations (three Youden pairs) of spiking solutions used in this study contained chloroform, bromodichloromethane, chlorodibromomethane, and bromoform. The two water types, distilled and drinking water, were supplied by the individual analytical laboratories. Statistical analyses and conclusions are based on analytical data obtained by twenty collaborating laboratories.

Participating laboratories were selected based upon technical evaluation of proposals and upon the analytical results of prestudy samples. The data obtained from the interlaboratory study were analyzed employing a series of computer programs known as the Interlaboratory Method Validation Study (IMVS) system, which was designed to implement ASTM procedure D2777. The statistical analyses included tests for the rejection of outliers, estimation of mean recovery (accuracy), estimation of single-analyst and overall precision, and tests for the effects of water type on accuracy and precision.

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

The analytical laboratories of the U.S. Environmental Protection Agency (EPA) gather water quality data to provide information on water resources, to assist research activities, and to evaluate pollution abatement activities. The success of these pollution control activities depends upon the reliability of the data provided by the laboratories, particularly when legal action is involved.

The Environmental Monitoring and Support Laboratory-Cincinnati (EMSL-Ci), of the EPA develops analytical methods and conducts quality assurance programs for the water laboratories. The quality assurance program of EMSL is designed to maximize the reliability and legal defensibility of all water quality information collected by EPA laboratories. The responsibility for these activities of EMSL is assigned to the Quality Assurance Branch (QAB). One of these activities is to conduct interlaboratory tests of the methods. This study reports the results of the interlaboratory study on Method 501.2 (Study 23B).

The method evaluated in the full report was prepared by the EMSL-Cincinnati staff at the request of the Office of Drinking Water, with cooperation from the Technical Support Division, Office of Drinking Water and the Municipal Environmental Research Laboratory. Additional comments and suggestions from the Health Effects Research Laboratory are gratefully acknowledged.

Procedure

The interlaboratory study of EPA Method 501.2 consisted of three distinct phases. Phase I involved the analysis of the prestudy samples by twenty participating laboratories. Two samples were analyzed for each of the four trihalomethanes, one in organic-free water and one in drinking water. Both waters were supplied by the individual participating laboratories. The objective of Phase I was to become familiar with the methodology employed and to identify any potential problems associated with the analytical methodology. Accuracy was not as important as being familiar with the methodology. A short report, including the data obtained and any potential problems encountered, was received from each subcontracting laboratory at the completion of Phase I.

Phase II consisted of a prestudy conference held at U.S. EPA, Cincinnati, Ohio. Each subcontracting laboratory sent at least one participant to the meeting. The analyst, or principal analyst, if more than one was involved, attended this meeting. This meeting, which was held after the data from the prestudy had been evaluated, was designed to examine the results of the prestudy and to discuss any problems encountered in the methodology.

Phase III of the interlaboratory study required the analysis of the study samples. In the case of Method 501.2, the analysis of the four trihalomethanes in both distilled water and drinking water was required at each of six concentrations (three Youden pairs). Again, the participating laboratories supplied the required water samples for these analyses. In addition, the participating laboratories analyzed their distilled and tap water blanks. Each participating laboratory then issued a report containing all data ob-

tained, copies of all chromatograms, and any comments.

The final step in the study was to conduct a statistical analysis of all data obtained. This analysis was conducted by Battelle Memorial Laboratories, Columbus, Ohio, under contract with the U.S. EPA.

Results and Discussion

Through statistical analyses of 960 analyzed values, estimates of accuracy and precision were made and expressed as regression equations, shown in Table 1.

The accuracy is obtained by comparing the mean recovery to the true values of the concentration. The accuracy, expressed as percent recovery, ranges from 98% to 103% in both water types. The accuracy of the method based on percent recovery is excellent.

The overall standard deviation of the analytical results is an indication of the precision associated with the measurement generated by a group of laboratories. The percent relative standard deviation (% RSD) ranges from 12% to 25% for both water types for the middle and high concentration levels (45 ppb to 174 ppb). The percent relative standard deviation ranges from 18% to 76% for the lowest concentration levels (1.7 ppb to 7.2 ppb) in both water types. The overall standard deviation is very good except at the very low concentration levels.

The single-analyst standard deviation indicates the precision associated within a single laboratory. The percent relative standard deviation for single analyst (% RSD-SA) for both water types ranges from 5% to 12% for the middle and high concentrations. The lowest concentration levels yield a range of 5% to 81%. The single analyst standard deviation is excellent except at the very low concentration levels.

Method 501.2 performed satisfactorily in the hands of twenty laboratories, who used various instruments and varied conditions.

The background levels in drinking water were as high as 65 ppb for chloroform and 20 ppb for bromodichloromethane. It is concluded that the low precision is probably due to subtracting a large blank value at low concentration levels.

The comparison on the effect of water types shows a statistically significant difference for bromodichloromethane. However, a practical significant difference does not exist.

Conclusions and Recommendations

Method 501.2 is recommended for the analysis of trihalomethanes in drinking water. The accuracy is excellent. The overall precision and single-analyst precision are very good except at very low concentrations.

For analytical laboratories located at high altitude, isooctane is the recommended extraction solvent.

Extraction solvents must be checked for contamination. Solvents such as n-hexane and cyclohexane were reported to contain impurities which have the same retention time as chloroform and bromoform. Contamination can come from impurities in the solvent or from impurities being absorbed from the laboratory atmosphere. Analysis of blanks is recommended on a daily basis.

Table 1. Regression Equations for Accuracy and Precision for Compounds

Water Type	Chloroform	Bromodichloromethane	Chlorodibromomethane	Bromoform
Distilled Water				
Single-analyst precision	$SR = 0.06X + 0.76$	$SR = 0.05X + 0.07$	$SR = 0.07X + 0.09$	$SR = 0.07X + 0.24$
Overall precision	$S = 0.17X + 0.65$	$S = 0.17X + 0.31$	$S = 0.16X + 0.47$	$S = 0.15X + 0.17$
Accuracy	$X = 1.01C + 0.14$	$S = 0.98C + 0.02$	$S = 1.02C + 0.07$	$X = 1.01C - 2.29$
Tap Water				
Single-analyst precision	$SR = 0.08X + 1.33$	$SR = 0.07X + 0.67$	$SR = 0.07X + 0.30$	$SR = 0.08X - 0.11$
Overall precision	$S = 0.26X + 0.60$	$S = 0.23X + 0.86$	$S = 0.13X + 0.50$	$S = 0.16X + 0.11$
Accuracy	$X = 1.03X - 0.37$	$X = 1.01C + 0.51$	$X = 1.00C - 0.05$	$X = 1.03C - 2.08$

X = mean recovery.

C = true value for the concentration.

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Raymond Wesselman is the EPA Project Officer (see below).

The complete report, entitled "EPA Method Study 23B, Method 501.2, Trihalomethanes by Liquid/Liquid Extraction," (Order No. PB 84-168 806; Cost: \$16.95, subject to change) will be available only from:

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