



Project Summary

EPA Method Study 23A, Method 501.1, Trihalomethanes by Purge and Trap

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The experimental design and the results of an interlaboratory study for an analytical method to detect trihalomethanes in water are described herein. In EPA Method 501.1, trihalomethanes are extracted by an inert gas which is bubbled through the aqueous sample. The vapors are then trapped on a short column containing a suitable sorbent. The trapped compounds are subsequently thermally desorbed onto the head of a gas chromatographic column. An electrolytic conductivity detector is used to measure the compounds. The spiking solutions contained chloroform, bromodichloromethane, chlorodibromomethane, and bromoform at six concentrations. 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 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 validation effort on Method 501.1 (Study 23A).

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 501.1 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 at the completion of Phase I from each subcontracting laboratory.

Phase II consisted of a prestudy conference held at the 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 analyst 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 501.1, 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 obtained, 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 concentrations. The accuracy, expressed as percent recovery, ranges from 92% to 108% in both water types. The accuracy of the method based on percent recovery is excellent. A slight high bias is seen in the tap water, but it is not statistically significant. The probable cause of this slight bias is background in the tap water.

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 18% to 32%. The overall standard deviation is considered to be good. Over the range of 0.8 µg/L to 550 µg/L, the best precision occurs at the middle Youden pair, which is near the drinking water standards.

The single-analyst standard deviation indicates the precision associated within a single laboratory. The percent relative standard deviation for single analyst (% RSD-SA) ranged from 10% to 23%; this

also is considered to be good. Again, slightly higher values (not statistically significant) are reported for the tap water, and the probable cause is background in the tap water.

A statistical comparison of the effect of the type of water was performed. It indicated no significant difference between water types.

Conclusions and Recommendations

Method 501.1 is acceptable for the analysis of trihalomethanes in drinking water. The accuracy is excellent, and the overall precision and single-analyst precision are considered good.

Care must be taken to eliminate any hot metallic (active) sites in both the gas chromatograph and the detector. These sites can cause breakdown of the compounds, especially bromoform.

Special care must be taken in handling samples and blanks to avoid contamination from the laboratory atmosphere. It is recommended that at least daily checks for contamination be made by the use of appropriate blanks.

Carry-over of the trihalomethane analytes from the analysis of high concentration samples to the next analysis was noted. It is recommended that the purge device be filled with distilled water and purged for ten minutes after the analysis of samples suspected of containing high concentrations of trihalomethanes.

Table 1. Regression Equations for Accuracy and Precision for Compounds 1 - 4

Water Type	Chloroform	Bromodichloromethane	Chlorodibromomethane	Bromoform
Range (µg/L)	0.86 - 550	0.88 - 550	0.84 - 550	4.8 - 550
Distilled water				
Single-analyst precision	SR = 0.10X + 0.13	SR = 0.15X - 0.05	SR = 0.16X + 0.06	SR = 0.19X - 0.25
Overall precision	S = 0.20X + 0.20	S = 0.23X + 0.15	S = 0.26X + 0.35	S = 0.28X + 0.63
Accuracy	X = 0.92C + 0.04	X = 0.95C - 0.04	X = 0.99C - 0.08	X = 1.03C - 1.48
Tap Water				
Single-analyst precision	SR = 0.11X + 0.03	SR = 0.15X + 0.18	SR = 0.18X + 0.13	SR = 0.23X - 0.05
Overall precision	S = 0.18X + 0.74	S = 0.22X + 0.38	S = 0.27X + 0.07	S = 0.32X + 0.47
Accuracy	X = 1.02C + 0.52	X = 1.02C + 0.08	X = 1.04C - 0.16	X = 1.08C - 1.75
Range (µg/L) ¹	0.26 - 550	0.88 - 550	0.84 - 550	4.84 - 550

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 23A, Method 501.1, Trihalomethanes by Purge and Trap," (Order No. PB 84-169 994; Cost: \$16.95, subject to change) will be available only from:

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The EPA Project Officer can be contacted at:

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