



Project Summary

Two Methods for Analyzing Trihalomethanes in Drinking Water by Purge and Trap and Liquid-Liquid Extraction Techniques

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The experimental design and the results of an interlaboratory study of two U.S. Environmental Protection Agency (USEPA) methods to detect trihalomethanes in drinking water are described herein. In USEPA 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. In USEPA Method 501.2, trihalomethanes are extracted by liquid/liquid extraction using *n*-pentane (2 mL pentane per 10 mL water) and subsequent direct analysis by gas chromatography using an electron capture detector. For both methods, 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 USEPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in two separate reports of the same title (see Project Report ordering information at back).

Introduction

The various analytical laboratories of USEPA 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-Cincinnati), of USEPA, develops analytical

methods and conducts quality assurance programs for the water laboratories. EMSL-Cincinnati's quality assurance program is designed to maximize the reliability and legal defensibility of all water quality information collected by USEPA laboratories. The responsibility for these activities is assigned to the Quality Assurance Branch (QAB) which conducts interlaboratory tests of the methods.

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

Procedure

The interlaboratory study of the two methods consisted of three distinct phases. Phase I involved the analysis of the prestudy samples by 20 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 study. 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 in Cincinnati, Ohio. Each subcontracting laboratory sent at least one analyst to the 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. For both methods, 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 which was conducted by Battelle

Memorial Laboratories, Columbus, Ohio, under contract to USEPA.

Results and Discussion

Through statistical analyses of 960 analyzed values per methods, estimates of accuracy and precision were made and expressed as regression equations. Table 1 represents those regression equations for Method 501.1 and Table 2 is for Method 501.2.

The accuracy is obtained by comparing the mean recovery to the true values of concentrations. The accuracy expressed as percent recovery for both water types ranges from 92% to 108% for Method 501.1 and from 98% to 103% for Method 501.2. The accuracy of the methods based on percent recovery is excellent. With Method 501.1, 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. For Method 501.1, 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 $\mu\text{g/L}$ to 550 $\mu\text{g/L}$, the best precision occurs at the middle Youden pair which is near the drinking water standards. For Method 501.2, the % RSD ranges from 12% to 25% for both water types for the middle and high concentration levels (45 ppb to 174 ppb). The % RSD 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 single-analyst percent relative standard deviation (% RSD-SA) in Method 501.1 ranged from 10% to 23%; this 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. For Method 501.2, the % 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. A statistical comparison of the effect of the type of water in Method 501.1 indicated no significant difference between water types.

The background levels in drinking water were as high as 65 ppb for chloroform and 20 ppb for bromodichloromethane. The low

precision is probably due to subtracting a large blank value at low concentration levels.

The comparison on the effect of water types for Method 501.2 shows a statistically significant difference for bromodichloromethane. However, a practical significant difference does not exist.

Conclusions and Recommendations

Method 501.1 is acceptable for the analysis of trihalomethanes in drinking water. The accuracy is excellent, while 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 be made for contamination 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 10 minutes after the analysis of samples suspected of containing high concentrations of trihalomethanes.

Method 501.2 is also 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 absorbed from the laboratory atmosphere. Analysis of blanks is recommended on a daily basis.

Table 1. Method 501.1 Regression Equations for Accuracy and Precision

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)	0.26 - 550	0.88 - 550	0.84 - 550	4.84 - 550

X = mean recovery.

C = true value for the concentration.

Table 2. Method 501.2 Regression Equations for Accuracy and Precision

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 consists of two volumes:

"EPA Method Study 23A, Method 501.1, Trihalomethanes by Purge and Trap" (Order No. PB 84-169 994; Cost \$13.00, subject to change).

"EPA Method Study 23B, Method 501.2, Trihalomethanes by Liquid/Liquid Extraction" (Order No. PB 84-168 806; Cost \$13.00, subject to change).

The above reports will be available only from:

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