



Project Summary

EPA Method Study 32: Method 450.1—Total Organic Halides (TOX)

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The full report describes the interlaboratory method study that was performed to evaluate Interim Method 450.1 for total organic halides (TOX). In the method, a measured volume of water is passed through two columns in series, each containing 50 mg of activated charcoal. Organic halides (OX) present in the water are adsorbed onto the charcoal which is washed to eliminate trapped inorganic halides. The contents of the columns are then pyrolyzed, converting the halides to titratable species that are measured microcoulometrically. In this study, three water matrices, reagent water, groundwater and surface water, were spiked at six concentrations with a solution containing a combination of four chlorinated compounds. These were lindane, bromoform, pentachlorophenol, and tetrachloroethene. A chlorinated drinking water diluted to four concentrations with reagent water was also analyzed.

Ten laboratories participated in the study. Data obtained were analyzed using a computerized statistical program package known as Interlaboratory Method Validation Study (IMVS), which is designed to implement the recommendations of ASTM Standard D-2777. The IMVS package includes outlier tests; estimation of mean recovery as a measure of bias; estimation of single-analyst and overall precision; and tests for effects of water type on these statistical estimates.

This report was submitted in fulfillment of Contract No. 68-03-3163 by James M. Montgomery, Consulting En-

gineers, Inc. It covers work performed from September 1982 to June 1985.

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

Several of the laboratories of the USEPA gather water quality data to provide information on water resources, to assist research, and to evaluate pollution abatement activities. The success of these pollution control activities depends on the reliability of data provided by the laboratories.

The Environmental Monitoring and Support Laboratory-Cincinnati (EMSL-Cincinnati) of USEPA develops or selects 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 method evaluated in this report was prepared by the EMSL-Cincinnati and Water Engineering Research Laboratory (WERL) staff at the request of the Office of Drinking Water, with coopera-

tion from its Technical Support Division.

Results and Discussion

With the use of the IMVS system, estimates of precision and bias were made and expressed as the regression equations (see Table 1). Of the 220 analytical values, 27 or 12.3 percent were rejected as outliers. The bias of the method was estimated by comparing mean recoveries to true TOX values at six concentration levels between 38.7 and 441.1 $\mu\text{g/L}$. The average recovery calculated from the regression equations was 86.5 percent, with the actual recoveries ranging from 83.5 percent to 117.2 percent. The highest recoveries occurred at the lowest concentration levels.

The overall standard deviation, S , was not significantly dependent on recovery \bar{X} , as indicated by slopes of regression equations for \bar{X} ranging from -0.0128 to 0.0374 . The intercepts ranged from 6.4 to 14.1 and closely approximated the actual S values obtained for the low, medium and high concentration ranges: 2.9 to 14.4 $\mu\text{g/L}$, 5.7 to 14.1 $\mu\text{g/L}$ and 10.4 to 15.4 $\mu\text{g/L}$, respectively. Percent relative standard deviations for low, medium and high Youden pair samples were 7.2 to 31.8 percent, 3.2 to 6.6 percent, and 3.0 to 4.4 percent, respectively.

The single-analyst precision, S_r , showed little dependence on recovery \bar{X} . The slopes of the regressions for S_r ranged from -0.0092 to 0.0033 , with intercepts ranging from 5.48 to 12.7. Single-analyst precision values actually obtained for low, middle and high concentrations ranged from 5.7 to 12.3, 4.5 to 9.3, and 9.4 to 12.0, respectively. Single-analyst relative standard deviations for low, middle and upper concentrations were 11.8 to 23.7 percent, 2.2 to 3.9 percent, and 2.5 to 3.4 percent, respectively.

No regression equation for TOX recovery from chlorinated drinking water was calculated due to the absence of a true concentration value for that sample type. Regressions calculated for overall S and S_r against mean analyzed value, \bar{X} , yielded an equation for S with a strongly negative intercept. The equation generated did not accurately predict the S values obtained from the study data and was considered invalid. The most probable cause for this was considered to be the use of four rather than six concentration levels for calculation of the regression. Individual S values for the four water samples ranged

Table 1. Regression Equations for Precision and Bias

Water Type	\bar{X}	S	S_r
Reagent	$\bar{X} = 0.807C + 14.1$	$S = -0.0128\bar{X} + 14.2$	$S_r = -0.0092\bar{X} + 12.7$
Surface	$\bar{X} = 0.894C + 7.14$	$S = 0.0374\bar{X} + 2.68$	$S_r = -0.0109\bar{X} + 6.14$
Ground	$\bar{X} = 0.896C + 6.38$	$S = 0.0280\bar{X} + 3.40$	$S_r = 0.0033\bar{X} + 5.48$
Chlorinated Drinking Water	--	$S = 0.0946\bar{X} - 9.22$	$S_r = 0.1037\bar{X} - 0.1014$

\bar{X} = Mean recovery (bias) as $\mu\text{g/L}$.

S = Overall precision as $\mu\text{g/L}$.

S_r = Single-analyst precision as $\mu\text{g/L}$.

C = True value as $\mu\text{g/L}$.

from 3.1 to 7.9 for TOX concentrations between 63.8 $\mu\text{g/L}$ and 83.6 $\mu\text{g/L}$. For TOX concentrations in the range of 137.8 to 178.5 $\mu\text{g/L}$, S values ranged from 12.7 to 29.6 $\mu\text{g/L}$. Single-analyst precision ranged from 4.5 at the low concentration range to 22.8 $\mu\text{g/L}$ for the higher concentration range.

Statistical comparisons of the effect of water type were performed. No significant effect of water type on bias or precision of Method 450.1 was observed.

Conclusions and Recommendations

Method 450.1 is recommended for the analysis of total organic halide (TOX) in drinking, ground and surface waters. The method bias and precision are acceptable and there are no significant matrix effects with the waters listed above. The "Interim" designation should be removed from the current title of the method.

- To ensure more consistent performance of the method, several ambiguous points that became apparent during Phase I of the study should be clarified.
- Additional research should be conducted on performances of the method when analyzing chlorinated drinking water supplies.
- In order to avoid TOX carryover from one sample to the next, the sample reservoir should be rinsed with two 100-mL volumes of distilled water before adding another sample.
- Users of the method must take precautions to avoid contamination of the samples and the analytical system, especially when analyzing samples expected to have low TOX concentrations. The potential for contamination from contact with the fingers can be greatly reduced by following the instructions found in Section 5.2.4 of the method.

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Terence M. Grady is the EPA Project Officer (see below).

The complete report, entitled "EPA Method Study 32: Method 450.1—Total Organic Halides (TOX)," (Order No. PB 86-136 538/AS; Cost: \$11.95, subject to change) will be available only from:

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