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Project Summary

EPA Method Study 24, Method 601 — Purgeable Halocarbons by the Purge Trap Method

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An interlaboratory method study to detect 28 halocarbons in water is described herein. In Method 601, the halocarbons are purged by an inert gas which is bubbled through the aqueous sample. The vapors are trapped in a short column containing a suitable sorbent. The trapped components are then thermally desorbed onto the head of a chromatographic column and measured by means of a halide-specific detector. In this study the 28 halocarbon compounds were divided into three separate mixes to minimize interferences from co-eluting peaks. The spiking solutions employed in the study contained the 29 halocarbons at six concentrations. Six water matrices were used in the study: a distilled, drinking, and surface water supplied by the cooperating laboratories; and three industrial wastewaters supplied by Monsanto Company. Statistical analyses and conclusions in this report are based on analytical data obtained by 20 collaborating laboratories.

Participating laboratories were selected based upon technical evaluation of proposals and upon the analytical results of prestudy samples. Data obtained from the interlaboratory study were analyzed employing EPA's computer programs known as the Interlaboratory Method Validation Study (IMVS) system, which are designed to implement the concepts recommended in ASTM Standard D 2777. The statistical analyses included rejection of outliers, estimation of mean recovery (accuracy), estimation of single-analyst and overall precisions, 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, particularly when legal action is involved, depends upon the reliability of the data provided by the laboratories.

Under provisions of the Clean Water Act, the EPA is required to promulgate guidelines establishing test procedures for the analysis of pollutants. The Clean Water Act Amendments of 1977 emphasize the control of toxic pollutants and declare the 65 "priority" pollutants and classes of pollutants to be toxic under Section 307(a) of the Act. This report is one of a series that investigates the analytical behavior of selected priority pollutants. The Environmental Monitoring and Support Laboratory (EMSL) Cincinnati develops analytical methods and conducts a quality assurance (QA) program for EPA water laboratories which is designed to

increase the reliability and legal defensibility of water quality information collection. The responsibility for QA is assigned to the Quality Assurance Branch (QAB), one of whose activities is to conduct interlaboratory tests of the methods. This study reports the results of the interlaboratory study on Method 601 (Study 24).

Procedure

The study consisted of three distinct phases. Phase I involved the analysis of two prestudy samples per analyte by the 20 participating laboratories in order that they become familiar with the methodology employed and to identify any potential problems associated with the analytical methodology. The purgeable halocarbons, were combined into three mixes to minimize interferences from coeluting chromatographic peaks. These mixes were supplied by Monsanto at two concentrations in sealed glass ampuls. The higher concentration mixes were spiked into drinking water supplied by the individual participating laboratories and the lower concentration mixes were spiked into a wastewater sample supplied by Monsanto. A short report, including the data obtained and any potential problems encountered, was sent to Monsanto by each participating laboratory at the completion of Phase I.

Phase II consisted of a prestudy conference held at EMSL-Cincinnati. 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 held after the data from the prestudy had been evaluated, examined the results of the prestudy and discussed problems encountered in the methodology.

Phase III consisted of the formal interlaboratory study. In the case of Method 601, the analyses of three mixes at each of six concentrations (three Youden pairs) was required in six different water matrices. In addition, the participating laboratories performed an analysis of all water blanks with no spiked compounds. Each participating laboratory then issued a report to Monsanto containing all data obtained, copies of representative chromatograms, and any comments.

The final step in the study was a statistical analysis of all data by Battelle Memorial Laboratories, Columbus, Ohio, under contract 68-03-2624 employing EPA's IMVS system.

Results and Discussions

The object of this study was to characterize the performance of Method 601 in terms of accuracy, overall precision, single-analyst precision and the effect of water types on accuracy and precision. Through statistical analyses of 26,160 analytical values, estimates of accuracy and precision were made and expressed as regression equations, which are shown in Tables 1 and 2. Table 1 presents the linear regression equations as originally calculated by EPA's IMVS system of computer programs. A detailed examination of the analytical data results in the revised equations presented in Table 2 for 10 of the 28 compounds. Of the 26,160 analytical values only 17% were rejected as outliers.

The accuracy of the method is obtained by comparing the mean recovery to the true values of concentration. For all but two of the 27 analytes, the average accuracy over all six waters ranged from 83% to 108%. The two exceptions were trans-1,3-dichloropropene at 76% and cis-1,3 dichloropropene at 56% which were found to be unstable.

The overall standard deviation indicates the precision associated with measurements generated by a group of laboratories. The percent relative standard deviation (%RSD) over six waters ranges from 16% to 29% for all but four of the 27 analytes. Exceptions include cis-1,3 dichloropropene at 40% bromomethane gas at 42%, trans-1,3-dichloropropene at 45%, and chloromethane gas at 50%.

The gases are expected to be less precise due to handling problems associated with both the sample and standard preparations. The average precision of all analytes in a given water was relatively independent of water type, ranging from 24% to 29% for the six water matrices. In

Table 1. Regression Equations for Accuracy and Precision

Water Type	Trichlorofluoromethane	Chloromethane	Vinyl Chloride	Trans-1,2-Dichloroethene
Applicable Conc. Range	(8.00 - 499.00)	(8.00 - 499.00)	(8.00 - 500.00)	(8.00 - 500.00)
Distilled Water				
Single-Analyst Precision	SR = 0.15X + 0.67	SR = 0.28X - 0.31	SR = 0.13X + 0.65	SR = 0.11X + 1.46
Overall Precision	S = 0.26X + 0.91	S = 0.52X + 1.31	S = 0.27X + 0.40	S = 0.17X + 1.46
Accuracy	X = 0.89C - 0.07	X = 0.77C + 0.18	X = 0.97C - 0.36	X = 0.97C - 0.16
Tap Water				
Single-Analyst Precision	SR = 0.22X - 0.03	SR = 0.28X + 0.27	SR = 0.14X - 0.17	SR = 0.16X + 0.29
Overall Precision	S = 0.30X + 0.64	S = 0.49X + 1.51	S = 0.32X + 0.07	S = 0.24X + 0.95
Accuracy	X = 0.92C - 1.21	X = 0.91C - 0.99	X = 1.06C - 1.86	X = 0.98C - 1.02
Surface Water				
Single-Analyst Precision	SR = 0.15X - 0.42	SR = 0.24X + 1.26	SR = 0.16X + 0.15	SR = 0.12X + 0.36
Overall Precision	S = 0.25X + 0.02	S = 0.55X + 0.45	S = 0.33X - 0.29	S = 0.21X + 0.59
Accuracy	X = 0.96C - 1.11	X = 0.99C - 2.07	X = 1.12C - 1.59	X = 1.03C - 0.95
Waste Water 1				
Single-Analyst Precision	SR = 0.18X + 0.46	SR = 0.22X + 2.27	SR = 0.12X + 1.00	SR = 0.13X + 0.27
Overall Precision	S = 0.31X + 0.20	S = 0.49X + 1.35	S = 0.22X + 1.06	S = 0.23X + 0.96
Accuracy	X = 0.96C - 0.86	X = 0.94C - 0.87	X = 1.13C - 2.63	X = 1.02C - 1.55
Waste Water 2				
Single-Analyst Precision	SR = 0.14X + 0.69	SR = 0.13X + 3.19	SR = 0.12X + 1.89	SR = 0.10X + 1.11
Overall Precision	S = 0.28X + 0.26	S = 0.58X + 1.11	S = 0.37X - 0.10	S = 0.15X + 1.47
Accuracy	X = 0.92C - 1.17	X = 0.81C - 0.16	X = 1.08C - 2.36	X = 1.00C - 0.30
Waste Water 3				
Single-Analyst Precision	SR = 0.16X + 1.12	SR = 0.19X + 4.99	SR = 0.09X + 2.04	SR = 0.14X + 1.20
Overall Precision	S = 0.29X + 0.75	S = 0.38X + 5.31	S = 0.21X + 1.36	S = 0.28X + 1.21
Accuracy	X = 0.96C - 1.57	X = 0.70C + 6.44	X = 1.14C - 1.05	X = 1.03C - 0.90

Table 1. *(Continued)*

Water Type	1,1,1-Trichloroethane	Trichloroethene[a]	Dibromochloromethane	2-Chloroethylvinyl Ether[a]
Applicable Conc. Range	(8.00 - 500.00)	(8.00 - 501.00)	(8.00 - 488.00)	(8.00 - 501.00)
Distilled Water				
Single-Analyst Precision	$SR = 0.15X + 0.04$	$SR = 0.13X - 0.03$	$SR = 0.11X + 1.10$	
Overall Precision	$S = 0.20X + 0.37$	$S = 0.23X + 0.30$	$S = 0.24X + 1.68$	
Accuracy	$X = 0.90C - 0.16$	$X = 1.32C - 2.52$	$X = 0.94C + 2.72$	
Tap Water				
Single-Analyst Precision	$SR = 0.14C - 0.33$	$SR = 0.13X + 0.23$	$SR = 0.10X + 1.55$	
Overall Precision	$S = 0.27X - 0.76$	$S = 0.32X - 0.57$	$S = 0.23X + 0.91$	
Accuracy	$X = 0.92C + 0.02$	$X = 1.40C - 3.26$	$X = 0.98C + 2.89$	
Surface Water				
Single-Analyst Precision	$SR = 0.14X - 0.17$	$SR = 0.13X - 0.39$	$SR = 0.12X + 1.22$	
Overall Precision	$S = 0.23X - 0.67$	$S = 0.37X - 0.90$	$S = 0.25X + 1.44$	
Accuracy	$X = 0.94C - 0.00$	$X = 1.46C - 4.16$	$X = 0.92C + 1.45$	
Waste Water 1				
Single-Analyst Precision	$SR = 0.15X + 1.65$	$SR = 0.10X + 2.22$	$SR = 0.05X + 3.74$	
Overall Precision	$S = 0.30X + 1.24$	$S = 0.27X + 1.41$	$S = 0.14X + 3.68$	
Accuracy	$X = 0.94C - 0.51$	$X = 1.35C - 2.49$	$X = 0.92C + 2.44$	
Waste Water 2				
Single-Analyst Precision	$SR = 0.10X + 2.01$	$SR = 0.16X - 0.41$	$SR = 0.10X + 2.99$	
Overall Precision	$S = 0.22X + 0.91$	$S = 0.25X + 0.50$	$S = 0.25X + 2.46$	
Accuracy	$X = 0.92C + 0.42$	$X = 1.41C - 3.14$	$X = 0.95C + 3.27$	
Waste Water 3				
Single-Analyst Precision	$SR = 0.18X + 2.93$	$SR = 0.15X + 0.83$	$SR = 0.13X + 0.49$	
Overall Precision	$S = 0.37X - 0.50$	$S = 0.28X + 0.47$	$S = 0.28X + 1.18$	
Accuracy	$X = 1.11C - 0.17$	$X = 1.40C - 2.32$	$X = 0.97C + 3.98$	

X = Mean Recovery
C = True Value for the Concentration
[a] = Revised equations presented in Table 2 herein.

Water Type	Tetrachloroethene	1,2-Dichlorobenzene[a]
Applicable Conc. Range	(8.00 - 500.00)	(8.00 - 501.00)
Distilled Water		
Single-Analyst Precision	$SR = 0.14X + 0.38$	$SR = 0.10X + 0.97$
Overall Precision	$S = 0.18X + 2.21$	$S = 0.13X + 6.13$
Accuracy	$X = 0.94C + 0.06$	$X = 0.93C + 1.70$
Tap Water		
Single-Analyst Precision	$SR = 0.17X + 0.96$	$SR = 0.12X + 2.02$
Overall Precision	$S = 0.25X + 0.58$	$S = 0.17X + 2.26$
Accuracy	$X = 0.96C + 0.35$	$X = 0.91C + 1.12$
Surface Water		
Single-Analyst Precision	$SR = 0.13X + 0.71$	$SR = 0.09X + 0.11$
Overall Precision	$S = 0.22X + 0.56$	$S = 0.19X + 0.38$
Accuracy	$X = 0.97C - 0.66$	$X = 0.90C - 0.28$
Waste Water 1		
Single-Analyst Precision	$SR = 0.22X + 2.54$	$SR = 0.14X + 0.66$
Overall Precision	$S = 0.35X + 2.33$	$S = 0.19X + 3.30$
Accuracy	$X = 0.85C + 0.03$	$X = 0.89C - 0.29$
Waste Water 2		
Single-Analyst Precision	$SR = 0.18X + 0.20$	$SR = 0.13X + 0.65$
Overall Precision	$S = 0.26X + 0.57$	$S = 0.18X + 1.26$
Accuracy	$X = 0.96C - 0.12$	$X = 0.91C - 0.47$
Waste Water 3		
Single-Analyst Precision	$SR = 0.13X + 1.03$	$SR = 0.10X + 0.72$
Overall Precision	$S = 0.26X + 1.13$	$S = 0.17X + 1.79$
Accuracy	$X = 0.96C + 1.24$	$X = 0.91C - 0.71$

X = Mean Recovery
C = True Value for the Concentration
[a] Revised equations presented in Table 2 herein.

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Table 1. (Continued)

Water Type	Bromomethane[b]	Chloroethane	1,1-Dichloroethene[a]	Chloroform
Applicable Conc. Range	(8.00 - 499.00)	(8.00 - 498.00)	(8.00 - 499.00)	(8.00 - 501.00)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.28X + 0.27$ $S = 0.36X + 0.94$ $X = 0.76C - 1.27$	$SR = 0.14X - 0.13$ $S = 0.17X + 0.63$ $X = 0.99C - 1.53$	$SR = 0.21X - 0.23$ $S = 0.29X - 0.40$ $X = 0.98C - 0.87$	$SR = 0.13X + 0.15$ $S = 0.19X - 0.02$ $X = 0.93C - 0.39$
Tap Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.24X + 0.12$ $S = 0.65X - 0.82$ $X = 1.03C - 3.70$	$SR = 0.07X + 0.65$ $S = 0.19X + 0.39$ $X = 1.08C - 1.97$	$SR = 0.12X + 0.13$ $S = 0.31X - 0.71$ $X = 1.03C - 1.16$	$SR = 0.05X + 5.58$ $S = 0.09X + 6.21$ $X = 0.90C + 3.44$
Surface Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.23X + 1.37$ $S = 0.45X + 1.29$ $X = 0.91C - 2.05$	$SR = 0.18X + 0.17$ $S = 0.22X + 1.70$ $X = 1.11C - 1.61$	$SR = 0.10X + 1.46$ $S = 0.21X + 1.24$ $X = 0.98C + 0.05$	$SR = 0.12X + 1.48$ $S = 0.20X + 0.50$ $X = 0.95C + 0.29$
Waste Water 1 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.11X + 1.66$ $S = 0.40X + 1.69$ $X = 0.79C + 0.03$	$SR = 0.08X + 0.45$ $S = 0.09X + 5.79$ $X = 1.01C + 0.61$	$SR = 0.19X - 0.81$ $S = 0.28X + 0.14$ $X = 0.93C - 0.07$	$SR = 0.13X + 0.47$ $S = 0.18X + 1.06$ $X = 0.90C + 0.49$
Waste Water 2 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.13X + 2.57$ $S = 0.40X + 0.69$ $X = 0.82C - 1.29$	$SR = 0.07X + 1.16$ $S = 0.22X + 0.87$ $X = 1.10C - 2.58$	$SR = 0.07X + 1.82$ $S = 0.32X + 0.34$ $X = 1.05C - 1.82$	$SR = 0.10X + 0.75$ $S = 0.17X + 0.11$ $X = 0.95C - 0.55$
Waste Water 3 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.12X + 0.62$ $S = 0.26X + 2.13$ $X = 0.69C + 0.48$	$SR = 0.10X + 1.02$ $S = 0.29X + 0.35$ $X = 1.09C - 1.50$	$SR = 0.14X - 0.58$ $S = 0.20X + 0.70$ $X = 1.02C - 0.82$	$SR = 0.07X + 2.98$ $S = 0.19X + 2.26$ $X = 0.95C + 0.29$

X = Mean Recovery
C = True Value for the Concentration
[a] = Revised equations presented in Table 2 herein.
[b] = Further comments contained in Section 6 of the full report.

Water Type	Carbon Tetrachloride	Trans-1,3-Dichloropropene[a]	1,1,2-Trichloroethane[a]	Bromoform
Applicable Conc. Range	(8.00 - 501.00)	(8.00 - 488.00)	(8.00 - 499.00)	(8.00 - 500.00)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.15X + 0.38$ $S = 0.20X + 0.39$ $X = 0.98C - 1.04$	$SR = 0.15X + 0.14$ $S = 0.40X + 0.26$ $X = 0.74C - 0.23$	$SR = 0.13X - 0.04$ $S = 0.19X + 0.67$ $X = 0.86C + 0.30$	$SR = 0.12X + 0.58$ $S = 0.21X + 2.41$ $X = 0.96C - 2.05$
Tap Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.10X + 1.57$ $S = 0.20X + 1.09$ $X = 1.00C - 2.20$	$SR = 0.14X + 0.64$ $S = 0.39X + 0.79$ $X = 0.69C + 0.26$	$SR = 0.06X + 0.99$ $S = 0.19X + 0.69$ $X = 0.84C + 0.83$	$SR = 0.10X + 0.20$ $S = 0.24X + 1.25$ $X = 1.02C - 1.81$
Surface Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.13X - 0.21$ $S = 0.20X - 0.30$ $X = 0.95C - 0.39$	$SR = 0.17X + 1.01$ $S = 0.39X + 0.73$ $X = 0.75C + 1.11$	$SR = 0.12X + 0.47$ $S = 0.22X + 0.80$ $X = 0.85C + 0.39$	$SR = 0.17X + 0.47$ $S = 0.20X + 1.41$ $X = 1.03C - 1.81$
Waste Water 1 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.10X + 0.90$ $S = 0.23X + 1.09$ $X = 0.92C - 2.02$	$SR = 0.28X + 1.14$ $S = 0.64X + 1.60$ $X = 0.72C + 0.25$	$SR = 0.17X + 0.15$ $S = 0.24X + 1.53$ $X = 0.78C + 0.03$	$SR = 0.18X + 0.27$ $S = 0.21X + 1.81$ $X = 0.91C - 0.39$
Waste Water 2 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.09X + 1.33$ $S = 0.21X + 0.47$ $X = 0.95C - 0.81$	$SR = 0.11X + 1.28$ $S = 0.37X + 0.91$ $X = 0.85C - 0.59$	$SR = 0.09X + 0.83$ $S = 0.19X + 0.79$ $X = 0.93C - 0.40$	$SR = 0.08X + 2.79$ $S = 0.22X + 2.82$ $X = 0.97C - 1.54$
Waste Water 3 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.10X + 1.10$ $S = 0.22X + 2.82$ $X = 1.02C - 1.62$	$SR = 0.20X - 0.55$ $S = 0.51X + 1.78$ $X = 0.78C + 1.36$	$SR = 0.08X + 1.52$ $S = 0.22X + 1.73$ $X = 0.92C - 0.15$	$SR = 0.17X + 1.77$ $S = 0.22X + 2.50$ $X = 1.01C - 1.00$

X = Mean Recovery
C = True Value for the Concentration
[a] = Revised equations presented in Table 2 herein.

Table 1. (Continued)

Water Type	Chlorobenzene[a]	1,4-Dichlorobenzene[a]
Applicable Conc. Range	(8.00 - 500.00)	(8.00 - 499.00)
Distilled Water		
Single-Analyst Precision	$SR = 0.15X - 0.02$	$SR = 0.14X - 0.03$
Overall Precision	$S = 0.18X + 1.21$	$S = 0.28X + 0.13$
Accuracy	$X = 1.00C - 1.23$	$X = 0.80C + 1.23$
Tap Water		
Single-Analyst Precision	$SR = 0.07X + 1.71$	$SR = 0.16X + 0.22$
Overall Precision	$S = 0.16X + 1.43$	$S = 0.20X + 0.74$
Accuracy	$X = 1.00C - 1.39$	$X = 0.81C + 0.60$
Surface Water		
Single-Analyst Precision	$SR = 0.12X + 0.99$	$SR = 0.09X + 0.87$
Overall Precision	$S = 0.18X + 0.72$	$S = 0.23X - 0.54$
Accuracy	$X = 0.98C - 0.54$	$X = 0.84C + 1.06$
Waste Water 1		
Single-Analyst Precision	$SR = 0.14X + 63.60$	$SR = 0.17X + 0.99$
Overall Precision	$S = 0.33X + 79.41$	$S = 0.27X + 0.93$
Accuracy	$X = 0.93C + 13.00$	$X = 0.82C + 1.57$
Waste Water 2		
Single-Analyst Precision	$SR = 0.12X + 0.48$	$SR = 0.11X + 0.95$
Overall Precision	$S = 0.21X + 0.99$	$S = 0.30X + 0.06$
Accuracy	$X = 0.93C - 1.44$	$X = 0.80C + 0.34$
Waste Water 3		
Single-Analyst Precision	$SR = 0.18X + 2.24$	$SR = 0.16X + 1.14$
Overall Precision	$S = 0.36X + 1.23$	$S = 0.37X + 0.03$
Accuracy	$X = 1.04C + 1.45$	$X = 0.94C - 1.26$

X = Mean Recovery
C = True Value for the Concentration
[a] = Revised equations presented in Table 2 herein.

Water Type	Methylene Chloride	1,1-Dichloroethane[b]	1,2-Dichloroethane[b]	Bromodichloromethane
Applicable Conc. Range	(8.00 - 501.00)	(8.00 - 499.00)	(8.00 - 500.00)	(8.00 - 501.00)
Distilled Water				
Single-Analyst Precision	$SR = 0.11X + 0.33$	$SR = 0.09X + 0.17$	$SR = 0.11X + 0.70$	$SR = 0.11X + 0.04$
Overall Precision	$S = 0.21X + 1.43$	$S = 0.14X + 0.94$	$S = 0.15X + 0.94$	$S = 0.20X + 1.00$
Accuracy	$X = 0.91C - 0.93$	$X = 0.95C - 1.08$	$X = 1.04C - 1.06$	$X = 1.12C - 1.02$
Tap Water				
Single-Analyst Precision	$SR = 0.08X + 1.04$	$SR = 0.09X + 0.47$	$SR = 0.06X + 1.69$	$SR = 0.13X + 1.41$
Overall Precision	$S = 0.17X + 2.43$	$S = 0.18X + 1.13$	$S = 0.18X + 1.21$	$S = 0.18X + 3.06$
Accuracy	$X = 0.97C - 1.50$	$X = 0.93C - 2.04$	$X = 1.03C - 0.41$	$X = 1.00C + 0.96$
Surface Water				
Single-Analyst Precision	$SR = 0.08X + 1.44$	$SR = 0.06X + 0.68$	$SR = 0.08X + 0.73$	$SR = 0.09X + 0.44$
Overall Precision	$S = 0.14X + 2.55$	$S = 0.14X + 1.07$	$S = 0.18X + 0.89$	$S = 0.17X + 1.14$
Accuracy	$X = 0.99C - 2.08$	$X = 0.97C - 1.72$	$X = 1.01C - 1.70$	$X = 1.12C - 1.63$
Waste Water 1				
Single-Analyst Precision	$SR = 0.09X + 0.97$	$SR = 0.13X + 0.70$	$SR = 0.18X + 7.48$	$SR = 0.10X + 1.09$
Overall Precision	$S = 0.18X + 1.50$	$S = 0.16X + 0.90$	$S = 0.28X + 9.59$	$S = 0.21X + 2.32$
Accuracy	$X = 1.00C - 1.76$	$X = 0.98C - 1.21$	$X = 0.86C + 11.31$	$X = 1.09C + 0.32$
Waste Water 2				
Single-Analyst Precision	$SR = 0.12X + 0.37$	$SR = 0.13X + 0.17$	$SR = 0.10X + 0.53$	$SR = 0.09X + 1.20$
Overall Precision	$S = 0.20X + 1.11$	$S = 0.16X + 0.95$	$S = 0.18X + 0.89$	$S = 0.22X + 1.02$
Accuracy	$X = 0.98C - 0.28$	$X = 0.96C - 0.32$	$X = 0.97C + 0.53$	$X = 1.09C - 0.47$
Waste Water 3				
Single-Analyst Precision	$SR = 0.14X + 1.41$	$SR = 0.12X + 0.24$	$SR = 0.25X + 14.54$	$SR = 0.12X + 2.33$
Overall Precision	$S = 0.19X + 1.91$	$S = 0.16X + 0.20$	$S = 0.71X + 4.18$	$S = 0.24X + 1.80$
Accuracy	$X = 0.95C - 0.31$	$X = 0.95C - 0.57$	$X = 0.39C + 50.00$	$X = 1.04C + 0.86$

X = Mean Recovery
C = True Value for the Concentration
[b] = Further comments contained in Section 6 of the full report.

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Table 1. (Continued)

Water Type	1,2-Dichloropropane	Cis-1,3-Dichloropropene[a]	1,2,2,2-Tetrachloroethane[a]	1,3-Dichlorobenzene
Applicable Conc. Range	(8.00 - 499.00)	(8.00 - 488.00)	(8.00 - 499.00)	(8.00 - 500.00)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.18X + 0.49$ $S = 0.28X + 1.17$ $X = 1.02C - 0.52$	$SR = 0.11X + 0.42$ $S = 0.38X - 0.26$ $X = 0.59C - 0.90$	$SR = 0.14X + 2.41$ $S = 0.23X + 2.79$ $X = 0.95C + 0.19$	$SR = 0.14X + 2.33$ $S = 0.26X + 2.34$ $X = 0.95C + 0.43$
Tap Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.19X - 0.61$ $S = 0.27X - 0.10$ $X = 0.98C + 1.19$	$SR = 0.17X - 0.04$ $S = 0.34X + 0.44$ $X = 0.60C - 1.07$	$SR = 0.09X + 1.42$ $S = 0.20X + 1.65$ $X = 0.92C - 0.60$	$SR = 0.15X + 0.64$ $S = 0.24X + 1.48$ $X = 0.91C - 0.13$
Surface Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.12X + 0.67$ $S = 0.21X + 0.94$ $X = 0.91C - 0.42$	$SR = 0.23X + 0.01$ $S = 0.49X + 0.26$ $X = 0.56C - 0.13$	$SR = 0.11X + 1.03$ $S = 0.26X + 0.44$ $X = 0.97C - 0.82$	$SR = 0.15X + 0.45$ $S = 0.23X + 0.69$ $X = 0.98C - 0.33$
Waste Water 1 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.17X + 2.88$ $S = 0.30X + 6.59$ $X = 0.87C + 4.67$	$SR = 0.19X + 1.94$ $S = 0.46X + 0.36$ $X = 0.61C - 0.70$	$SR = 0.19X + 9.29$ $S = 0.44X + 3.99$ $X = 0.84C + 7.12$	$SR = 0.21X + 0.37$ $S = 0.29X + 1.19$ $X = 0.94C - 0.06$
Waste Water 2 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.20X + 1.42$ $S = 0.30X + 1.63$ $X = 1.04C - 0.82$	$SR = 0.20X + 0.02$ $S = 0.37X + 1.77$ $X = 0.50C + 0.69$	$SR = 0.16X + 0.87$ $S = 0.30X + 1.26$ $X = 0.91C - 0.15$	$SR = 0.14X + 0.64$ $S = 0.20X + 1.60$ $X = 0.92C - 0.65$
Waste Water 3 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.21X + 2.19$ $S = 0.33X + 2.65$ $X = 1.10C + 1.47$	$SR = 0.18X + 1.64$ $S = 0.36X + 1.08$ $X = 0.53C + 1.35$	$SR = 0.15X + 2.33$ $S = 0.28X + 2.63$ $X = 1.00C + 0.98$	$SR = 0.13X + 1.98$ $S = 0.23X + 1.27$ $X = 0.93C - 0.89$

X = Mean Recovery
C = True Value for the Concentration
[a] = Revised equations presented in Table 2 herein.

Table 2. Revised Equations for Accuracy and Precision

Water Type	Trichloroethene	2-Chloroethylvinyl Ether	1,2-Dichlorobenzene
Applicable Conc. Range	(8.00 - 501.00)	(8.00 - 501.00)	(8.00 - 501.00)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.13X - 0.03$ $S = 0.23X + 0.30$ $X = 0.87C + 0.48$	$SR = 0.10X + 0.94$ $S = 0.29X + 1.65$ $X = 0.93C + 0.77$	$SR = 0.11X + 0.84$ $S = 0.15X + 5.90$ $X = 0.92C + 1.80$
Tap Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.13X + 0.23$ $S = 0.32X - 0.57$ $X = 0.92C - 0.10$	$SR = 0.19X - 1.03$ $S = 0.46X + 0.03$ $X = 0.72C + 1.00$	$SR = 0.12X + 2.02$ $S = 0.17X + 2.26$ $X = 0.91C + 1.12$
Surface Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.13X - 0.39$ $S = 0.37X - 0.90$ $X = 0.97C - 0.88$	$SR = 0.23X - 1.77$ $S = 0.43X - 0.33$ $X = 0.87C - 0.57$	$SR = 0.11X - 0.03$ $S = 0.21X + 0.22$ $X = 0.89C - 0.19$
Waste Water 1 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.10X + 2.22$ $S = 0.27X + 1.41$ $X = 0.90C + 0.57$	$SR = 0.12X - 0.40$ $S = 0.41X + 0.03$ $X = 1.01C - 0.19$	$SR = 0.14X + 0.66$ $S = 0.19X + 3.30$ $X = 0.89C - 0.29$
Waste Water 2 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.16X - 0.41$ $S = 0.25X + 0.50$ $X = 0.95C - 0.02$	$SR = 0.14X + 0.07$ $S = 0.39X + 0.23$ $X = 0.84C - 0.09$	$SR = 0.13X + 0.65$ $S = 0.18X + 1.26$ $X = 0.91C - 0.47$
Waste Water 3 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.15X + 0.83$ $S = 0.28X + 0.47$ $X = 1.11C + 0.86$	$SR = 0.18X + 0.28$ $S = 0.52X - 0.79$ $X = 0.88C - 0.19$	$SR = 0.10X + 0.72$ $S = 0.17X + 1.79$ $X = 0.91C - 0.71$

Table 2. (Continued)

Water Type	1,1-Dichloroethene	Trans-1,3-Dichloropropene	1,1,2-Trichloroethane
Applicable Conc. Range	(8.00 - 499.00)	(8.00 - 488.00)	(8.00 - 499.00)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.21X - 0.23$ $S = 0.29X - 0.40$ $X = 0.98C - 0.87$	$SR = 0.15X + 0.83$ $S = 0.40X + 0.56$ $X = 0.74C + 0.02$	$SR = 0.13X - 0.04$ $S = 0.18X + 1.18$ $X = 0.87C - 0.00$
Tap Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.12X + 0.13$ $S = 0.31X - 0.71$ $X = 1.03C - 1.16$	$SR = 0.14X + 0.64$ $S = 0.39X + 0.79$ $X = 0.69C + 0.26$	$SR = 0.06X + 0.99$ $S = 0.19X + 0.69$ $X = 0.84C + 0.83$
Surface Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.10X + 1.46$ $S = 0.21X + 1.24$ $X = 0.93C + 0.05$	$SR = 0.17X + 1.01$ $S = 0.39X + 0.73$ $X = 0.75C + 1.11$	$SR = 0.12X + 0.47$ $S = 0.22X + 0.80$ $X = 0.85C + 0.39$
Waste Water 1 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.19X - 0.80$ $S = 0.32X - 0.06$ $X = 0.93C - 0.06$	$SR = 0.28X + 1.14$ $S = 0.64X + 1.60$ $X = 0.72C + 0.25$	$SR = 0.17X + 0.15$ $S = 0.24X + 1.53$ $X = 0.78C + 0.03$
Waste Water 2 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.07X + 1.82$ $S = 0.32X + 0.34$ $X = 1.05C - 1.82$	$SR = 0.11X + 1.28$ $S = 0.40X + 0.74$ $X = 0.87C - 0.76$	$SR = 0.09X + 0.83$ $S = 0.19X + 0.79$ $X = 0.93C - 0.40$
Waste Water 3 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.14X - 0.58$ $S = 0.20X + 0.70$ $X = 1.02C - 0.82$	$SR = 0.20X - 0.55$ $S = 0.51X + 1.78$ $X = 0.78C + 1.36$	$SR = 0.08X + 1.52$ $S = 0.22X + 1.73$ $X = 0.92C - 0.15$

X = Mean Recovery
C = True Value for the Concentration

Table 2. (Continued)

Water Type	Chlorobenzene	1,4-Dichlorobenzene	Cis-1-3-Dichloropropene	1,1,2,2-Tetrachloroethane
Applicable Conc. Range	(8.00 - 500.00)	(8.00 - 499.00)	(8.00 - 488.00)	(8.00 - 499.00)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.15X - 0.02$ $S = 0.18X + 1.21$ $X = 1.00C - 1.23$	$SR = 0.10X - 0.61$ $S = 0.43X - 1.19$ $X = 0.96C - 0.28$	$SR = 0.11X + 0.42$ $S = 0.38X - 0.26$ $X = 0.59C - 0.90$	$SR = 0.14X + 2.41$ $S = 0.23X + 2.79$ $X = 0.95C + 0.19$
Tap Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.07X + 1.71$ $S = 0.16X + 1.43$ $X = 1.00C - 1.39$	$SR = 0.06X + 0.54$ $S = 0.26X + 0.21$ $X = 0.98C - 0.97$	$SR = 0.17X - 0.04$ $S = 0.34X + 0.44$ $X = 0.60C - 1.07$	$SR = 0.09X + 1.43$ $S = 0.21X + 1.53$ $X = 0.93C - 0.71$
Surface Water Single-Analyst Precision Overall Precision Accuracy	$SR = 0.12X + 1.04$ $S = 8.18X + 0.89$ $X = 0.98C - 0.41$	$SR = 0.05X + 0.73$ $S = 0.19X - 0.16$ $X = 0.95C + 0.03$	$SR = 0.23X + 0.01$ $S = 0.49X + 0.26$ $X = 0.56C - 0.13$	$SR = 0.11X + 1.03$ $S = 0.26X + 0.44$ $X = 0.97C - 0.82$
Waste Water 1 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.14X + 63.40$ $S = 0.33X + 79.41$ $X = 0.93C + 13.00$	$SR = 0.12X + 0.34$ $S = 0.39X - 0.16$ $X = 0.99C - 0.06$	$SR = 0.20X + 1.90$ $S = 0.48X + 0.24$ $X = 0.63C - 0.87$	$SR = 0.19X + 9.29$ $S = 0.30X + 3.99$ $X = 0.84C + 7.12$
Waste Water 2 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.12X + 0.48$ $S = 0.21X + 0.99$ $X = 0.93C - 1.44$	$SR = 0.07X + 0.73$ $S = 0.40X - 0.69$ $X = 0.96C - 1.10$	$SR = 0.20X + 0.02$ $S = 0.37X + 1.77$ $X = 0.50C + 0.69$	$SR = 0.16X + 0.87$ $S = 0.30X + 1.26$ $X = 0.91C - 0.15$
Waste Water 3 Single-Analyst Precision Overall Precision Accuracy	$SR = 0.18X + 2.24$ $S = 0.36X + 1.23$ $X = 1.04C + 1.45$	$SR = 0.09X + 0.95$ $S = 0.37X + 0.03$ $X = 1.08C - 2.55$	$SR = 0.18X + 1.64$ $S = 0.36X + 1.08$ $X = 0.53C + 1.35$	$SR = 0.15X + 2.33$ $S = 0.28X + 2.63$ $X = 1.00C + 0.98$

X = Mean Recovery
C = True Value for the Concentration

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all cases, as expected, the highest %RSD (poorest precision) occurred at the lowest Youden pair concentration. The precision is acceptable at all levels when the background interferences are minimal.

The single-analyst standard deviation indicates the precision associated with a single laboratory. The percent relative standard deviation for a single analyst (%RSD-SA), averaged overall the waters, ranged from 10% to 22% for the 27 analytes, while the average value of %RSD-SA for all analytes in a given water ranged from 12% to 15%. In all cases, the highest %RSD-SA (poorest precision) was associated with the lowest Youden pair concentration. The precision is acceptable at all levels where background interference is minimal.

Statistical comparisons of the effect of water type were performed on all analytes. These indicated a practical effect of water matrix on the accuracy or precision of Method 601 in the following cases:

Carbon tetrachloride in wastewater 1
Chlorobenzene in wastewater 1
1,4-Dichlorobenzene in wastewater 3, and
1,2-Dichloroethane in wastewater 3.

Conclusions and Recommendations

Method 601 is recommended for the analysis of purgeable halocarbons in municipal and industrial wastewaters. The accuracy and precision are acceptable, while the matrix effects are significant only at low concentration levels.

Care should be taken in the handling or packing of the chromatographic columns. Any type of mechanical shock may damage the fragile packing material and produce fines which result in plugged columns, decreased separation efficiency, and/or a contaminated detector furnace.

Metal columns are not recommended as they may be adversely affected by halogen compounds.

The proper size quartz combustion tube should be flamed prior to installation.

Care must be taken in obtaining laboratory pure ("organic-free") water. The use of an activated carbon column to purify distilled water is recommended. The waters should be capped tightly to prevent contamination from solvent vapors in the laboratory atmosphere.

The analyst should check the analytical curve for linearity. Several laboratories reported non-linearity above 200 ppt.

It is recommended that the purity of cis and trans-1,3-dichloropropene standard materials be checked. Some laboratories have observed impurities of 1,2 dichloropropane as a decomposition product.

Extra care should be observed in the preparation of gaseous standards due to potential losses of analyte. It is recommended that at least 10 mg of standard be weighed for the standard solution to allow three significant figures in the calculations. Premixed standards for gases are not recommended due to instability.

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