



## Project Summary

# EPA Method Study 25, Method 602, Purgeable Aromatics

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Described herein are the experimental design and the results of an interlaboratory study of an analytical method for detecting purgeable aromatics in water. EPA Method 602, Purgeable Aromatics, employs a purge-and-trap chromatographic technique for determining seven aromatic hydrocarbon analytes in water matrices. Three Youden pairs of spiking solutions were used and contained benzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, ethylbenzene, and toluene. Six water types were used: distilled water, drinking water, surface water, and three wastewater samples from industries employing or producing aromatic hydrocarbons. Twenty laboratories participated and supplied their individual distilled, drinking, and surface water samples. Monsanto Company supplied the three industrial wastewater samples. The statistical analyses and conclusions reached in this report are based on the analytical data obtained by the 20 participating 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 the concepts recommended in ASTM Procedure D 2777. 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 various 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 the Agency's 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 and suggests a suitable test procedure for their measurement. The priority pollutants to be analyzed by Method 602 covered by this report are the following purgeable aromatics:

- benzene
- chlorobenzene
- 1,2-dichlorobenzene
- 1,3-dichlorobenzene
- 1,4-dichlorobenzene
- ethylbenzene
- toluene

The Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-CI) of the EPA develops analytical methods and conducts a quality assurance program for the water laboratories. This

program 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 whose activities is to conduct interlaboratory tests of the methods. This report presents the results of interlaboratory study 25 on EPA Method 602, Purgeable Aromatics.

## Procedure

The study 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 seven purgeable aromatics; a medium concentration sample to be analyzed in drinking water supplied by the participating laboratories and a low level sample to be analyzed in a wastewater sample supplied by Monsanto Company. 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 familiarity with the methodology. A short report, including the data obtained and any potential problems encountered, was received by Monsanto

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

Phase II consisted of a prestudy conference held at EMSL-CI, 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, which was held after the data from the prestudy had been evaluated, and was designed to examine the results of the prestudy and to discuss any problems encountered in the methodology.

Phase III consisted of the formal interlaboratory study. Each of the seven aromatic purgeables were analyzed at six concentrations (three Youden pairs) in six different water matrices. The participating laboratories each supplied its own distilled water, drinking water and surface water. Monsanto Company supplied the three industrial wastewaters. In addition, the participating laboratories performed analyses of all water blanks with no spiked compounds. Each participating laboratory then issued a report to Monsanto Company 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 Columbus laboratories, Columbus, Ohio under contract 68-03-2624 employing a system of computer programs known as the Interlaboratory Method Validation Study (IMVS) system.

## Results and Discussion

The object of this study was to characterize the performance of EPA Method 602 in terms of accuracy, overall precision, single-analyst precision and the effect of water types on accuracy and precision. Through statistical analyses of 5,040 analytical values, estimates of accuracy and precision were made and expressed as regression equations, which are shown in Table 1.

The accuracy of the method is obtained by comparing the mean recovery to the true values of the concentration. Expressed as percent recovery it ranges from 88% to 97% in distilled, tap, and surface water. Excluding the values where large interferences entered into play, the accuracy in wastewaters ranges from 84% to 100%. Large interferences (background) existed in wastewater 5 for chlorobenzene and toluene. At the lowest concentration levels, recoveries exceeding 500% were reported. At the middle and high levels,

Table 1. Regression Equations for Accuracy and Precision

Water Type	Benzene	Chlorobenzene	1,2-Dichlorobenzene	1,3-Dichlorobenzene
<b>Distilled Water</b>				
Single-Analyst Precision	$SR = 0.09X + 0.59$	$SR = 0.09X + 0.23$	$SR = 0.17X - 0.04$	$SR = 0.15X - 0.10$
Overall Precision	$S = 0.21X + 0.56$	$S = 0.17X + 0.10$	$S = 0.22X + 0.53$	$S = 0.19X + 0.09$
Accuracy	$X = 0.92C + 0.57$	$X = 0.95C + 0.02$	$X = 0.93C + 0.52$	$X = 0.96C - 0.04$
<b>Tap Water</b>				
Single-analyst Precision	$SR = 0.11X - 0.06$	$SR = 0.10X + 0.12$	$SR = 0.10X + 0.42$	$SR = 0.08X + 0.33$
Overall Precision	$S = 0.22X + 1.11$	$S = 0.16X + 0.36$	$S = 0.18X + 0.28$	$S = 0.15X + 0.33$
Accuracy	$X = 0.97C + 0.05$	$X = 0.94C + 0.12$	$X = 0.91C + 0.44$	$X = 0.93C + 0.21$
<b>Surface Water</b>				
Single-Analyst Precision	$SR = 0.08X + 0.17$	$SR = 0.08X + 0.14$	$SR = 0.10X + 0.04$	$SR = 0.10X + 0.01$
Overall Precision	$S = 0.19X + 0.38$	$S = 0.19X + 0.20$	$S = 0.18X + 0.12$	$S = 0.18X + 0.80$
Accuracy	$X = 0.93C + 0.37$	$X = 0.92C - 0.14$	$X = 0.89C + 0.21$	$X = 0.93C + 0.40$
<b>Waste Water 1</b>				
Single-Analyst Precision	$SR = 0.13X + 0.56$	$SR = 0.08X + 3.02$	$SR = 0.11X + 0.93$	$SR = 0.15X + 0.46$
Overall Precision	$S = 0.26X + 0.69$	$S = 0.21X + 2.33$	$S = 0.25X + 0.37$	$S = 0.36X + 0.83$
Accuracy	$X = 0.91C + 0.06$	$X = 0.93C + 1.85$	$X = 0.90C + 0.38$	$X = 1.00C + 3.36$
<b>Waste Water 2</b>				
Single-Analyst Precision	$SR = 0.09X + 0.89$	$SR = 0.09X + 14.83$	$SR = 0.10X + 0.90$	$SR = 0.10X + 0.52$
Overall Precision	$S = 0.25X + 0.97$	$S = 0.31X + 11.81$	$S = 0.17X + 1.12$	$S = 0.19X + 0.79$
Accuracy	$X = 0.87C + 0.36$	$X = 0.63C + 19.77$	$X = 0.95C + 0.69$	$X = 0.92C + 0.50$
<b>Waste Water 3</b>				
Single-Analyst Precision	$SR = 0.10X + 0.43$	$SR = 0.10X + 0.43$	$SR = 0.15X + 0.14$	$SR = 0.12X + 0.29$
Overall Precision	$S = 0.25X + 0.58$	$S = 0.16X + 0.85$	$S = 0.18X + 0.51$	$S = 0.16X + 0.43$
Accuracy	$X = 0.93C + 0.50$	$X = 0.92C + 0.15$	$X = 0.88C - 0.39$	$X = 0.94C + 0.16$

average recoveries were 94% and 86%, respectively, for chlorobenzene and toluene.

The overall standard deviation indicates the precision associated with measurements generated by a group of laboratories. The percent relative standard deviation (%RSD) ranges from 9.9% to 39.8% for the middle and high Youden pairs. The low Youden pair ranges from 20.9% to 55% in distilled, tap, and surface water. The range in wastewater is 30.5% to 63.7% excluding chlorobenzene and toluene. In all cases, the highest %RSD (poorest precision) was at the lowest Youden pair.

The single-analyst standard deviation indicates the precision associated within a single laboratory. The percent relative standard deviation for a single-analyst (%RSD-SA) ranges from 6.1% to 31.8% for the middle and high Youden pair. The low Youden pair ranges from 9.0% to 33.7% for distilled, tap, and surface water. The range in wastewaters is 20.9% to 43.5%, excluding chlorobenzene and toluene. In all cases, the highest %RSD-SA (poorest precision) was at the lowest Youden pair.

A statistical comparison of the effect of water type was performed indicating a statistically significant difference for six of the analyte/water matrix combinations.

Of these six cases, a practical significant difference was established in only two cases; chlorobenzene and toluene in water 5.

### Conclusions and Recommendations

EPA Method 602 is recommended for the analysis of purgeable aromatics in municipal and industrial wastewaters. The accuracy and precision are acceptable, while the matrix effects are significant only at low concentration levels.

Because deposition of high-boiling compounds and column bleed onto the photoionization detector (PID) lamp window causes a continual loss of detector response, frequent cleaning of the lamp window is recommended. This may be alleviated by not exceeding the column temperature 90°C recommended in EPA Method 602. Venting of the column at higher temperature (e.g., 150°C) through the detector can lead to fouling of the detector window.

Potential carry-over problems from contaminated water can be lessened or eliminated by analyzing a blank sample prior to the next water sample.

Care must be taken in the preparation of laboratory pure water. Contamination

from solvents in the atmosphere is common.

Teflon is not recommended for gas lines. Methylene chloride permeates the Teflon, and naphthalene, which is used as a lubricant in the drawing of the Teflon, responds to the PID. Cooper or stainless steel gas lines are recommended.

Table 1. (continued)

Water Type	1,4-Dichlorobenzene	Ethylbenzene	Toluene
<i>Distilled Water</i>			
Single-Analyst Precision	$SR = 0.15X + 0.28$	$SR = 0.17X + 0.46$	$SR = 0.09X + 0.48$
Overall Precision	$S = 0.20X + 0.41$	$S = 0.26X + 0.23$	$S = 0.18X + 0.71$
Accuracy	$X = 0.93C - 0.09$	$X = 0.94C + 0.31$	$X = 0.94C + 0.65$
<i>Tap Water</i>			
Single-Analyst Precision	$SR = 0.09X + 0.39$	$SR = 0.10X + 0.18$	$SR = 0.10X + 0.18$
Overall Precision	$S = 0.15X + 0.39$	$S = 0.20X + 0.68$	$S = 0.21X + 0.16$
Accuracy	$X = 0.91C + 0.26$	$X = 0.97C + 0.41$	$X = 0.94C + 0.17$
<i>Surface Water</i>			
Single-Analyst Precision	$SR = 0.17X - 0.06$	$SR = 0.08X + 0.33$	$SR = 0.05X + 0.18$
Overall Precision	$S = 0.17X + 0.55$	$S = 0.71X + 0.36$	$S = 0.25X + 0.33$
Accuracy	$X = 0.88C + 0.27$	$X = 0.93C + 0.70$	$X = 0.93C + 0.02$
<i>Waste Water 1</i>			
Single-Analyst Precision	$SR = 0.07X + 0.85$	$SR = 0.12X + 0.38$	$SR = 0.11X + 1.05$
Overall Precision	$S = 0.18X + 0.59$	$S = 0.21X + 0.40$	$S = 0.24X + 0.67$
Accuracy	$X = 0.89C + 0.54$	$X = 0.94C + 0.38$	$X = 0.87C + 0.99$
<i>Waste Water 2</i>			
Single-Analyst Precision	$SR = 0.10X + 0.88$	$SR = 0.11X + 0.45$	$SR = 0.18X + 3.47$
Overall Precision	$S = 0.17X + 0.49$	$S = 0.25C + 0.53$	$S = 0.28X + 4.36$
Accuracy	$X = 0.93C + 0.33$	$X = 0.86C + 0.14$	$X = 0.71C + 8.63$
<i>Waste Water 3</i>			
Single-Analyst Precision	$SR = 0.09X + 0.34$	$SR = 0.13X + 0.52$	$SR = 0.10X + 1.20$
Overall Precision	$S = 0.15X + 0.33$	$S = 0.20X + 0.78$	$S = 0.21X + 1.55$
Accuracy	$X = 0.91C + 0.11$	$X = 0.69C + 0.73$	$X = 0.91C + 1.01$

X = Mean Recovery

C = True Value for the Concentration

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