⊕EPA

Project Summary

EPA Method Study 16 Method 606 — Phthalate Esters

John D. Millar, Richard E. Thomas, and Herbert J. Schattenberg

This report describes the results obtained and data analysis from an interlaboratory method study of EPA Method 606 (Phthalate Esters). The method is designed to analyze for six phthalate esters: dimethyl phthalate, diethyl phthalate, di-ni-butyl phthalate, benzylbutyl phthalate, bis-2-ethylhexyl phthalate, and di-n-octyl phthalate, in water and wastewater. As tested here, the method utilizes three 60-mL extractions with dichloromethane, cleanup/separation on a Florisil or alumina column, and injection into a gas chromatograph equipped with an electron capture detector.

The study design required the analyst to dose six waters with each of six mixtures of the six phthalates. The six dosing levels represented three Youden pairs, one each at a low, an intermediate, and a high level. The six waters used were a laboratory pure water, a finished drinking water, and a surface water, all collected by the participant, and three low-background industrial effluents provided by the prime contractor. A total of 16 laboratories participated in the study.

The method was studied to estimate the accuracy and precision that can be expected, including effects on accuracy and precision of analysis of different matrices. In addition, results of method detection limit and analytical curve studies and qualitative assessments of the method based upon comments by the participating laboratories are included.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 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

EPA first promulgated guidelines establishing test procedures for the analysis of pollutants in 1973, following the passage of the Federal Water Pollution Control Act in 1972 by Congress. Pursuant to the amendment and publication of these guidelines, EPA entered into a Settlement Agreement—the Consent Decree—which required the study and, if necessary, regulation of 65 "priority" pollutants and classes of pollutants of known or suspected toxicity to the biota. Subsequently, Congress passed the Clean Water Act of 1977, mandating the control of toxic pollutants discharged into ambient waters by industry.

In order to facilitate the implementation of the Clean Water Act, EPA selected, for initial study, 129 specific toxic pollutants, 113 organic and 16 inorganic. The organic pollutants were divided into 12 categories based on their chemical structure. Analytical methods were developed by EPA for these 12 categories through in-house and contracted research. These analytical methods may eventually be required for the monitoring of the 113 toxic pollutants in industrial wastewater effluents, as specified by the Clean Water Act of 1977.

As a logical subsequence to that work, an interlaboratory study was conducted to obtain accuracy and precision statements for Method 606 (Phthalate Esters) based upon multilaboratory data. This report describes the work performed, presents the data acquired, and gives the conclusions drawn from the collaborative effort.

The six compounds undergoing analysis in the interlaboratory study were dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), benzylbutyl phthalate (BBP), bis-2-ethylhexyl phthalate (2EHP), and di-n-octyl phthalate (DOP).

The objective of this interlaboratory study was to obtain information about the accuracy and precision associated with measurements generated by Method 606. This objective was met through the use of statistical analysis techniques designed to extract and summarize the relevant information about accuracy and precision from the data reported by the participating laboratories.

The algorithms required to perform the statistical analyses have been integrated into a system of computer programs referred to as IMVS (Interlaboratory Method Validation Study). The analyses performed by IMVS include several tests for the rejection of outliers (laboratories and individual data points), summary statistics by concentration level for mean recovery (accuracy), overall and single-analyst standard deviation (precision), determination of the linear relationship between mean recovery and concentration level, determination of the linear relationship between precision statistics and mean recovery, and a test for the effect of water type on accuracy and precision.

Procedure

The study design was based on Youden's original plan for collaborative evaluation of precision and accuracy for analytical methods. According to Youden's design, samples are analyzed in pairs where each sample of a pair has a slightly different concentration of the constituent. The analyst is directed to do a single analysis and report one value for each sample, as if for a normal, routine sample.

In this study, samples were prepared as concentrates in sealed glass ampules and shipped to the analyst with portions of final effluents from manufacturing plants from three relevant industries. Each participating laboratory was responsible for supplying laboratory pure water, a finished drinking water, and a surface water, thus giving a total of six water matrices involved in the study. The analyst was required to add an aliquot of each concentrate to a volume of water from each of the six waters and submit the spiked water to analysis. Three pairs of samples were used. One pair contained the substances at what was considered to be equivalent to a low level for the industrial effluents; a second pair contained the substances at an intermediate level; and the third pair contained the substances at a high level.

Before the formal study began, each participant was sent a pair of ampules (not one of the pairs used in the study) for a trial analysis by Method 606. After submitting data from these analyses to SwRI, all participants met in Cincinnati to discuss problems encountered during the trial run.

Results and Discussion

The accuracy of the method could generally be expressed as a linear function of the true concentration. The regression equations are shown in Table 1.

The precision of the method could generally be expressed as a linear function of the mean recovery, both as single-analyst and overall standard deviations. These regression equations are also shown in Table 1.

The percent recovery of the method differed from that obtained during the developmental phase, especially for DMP and DEP. Recoveries at the midrange of the concentrations studied ranged from 33 to 93%, with a median of 78.5. Twenty-nine of the thirty-six recoveries were at or above 70%.

There was considerable variability among the results, especially for DMP, DEP, and 2EHP. High relative standard deviations were determined for both 2EHP and DOP in laboratory pure water.

Six water types were used in this study: laboratory pure, finished drinking, surface, and three relatively interference-free industrial effluents. Differences in variability were noted for DEP and 2EHP and differences in mean recovery for DOP as a result of the comparison across water types. These differences were noted in comparison with the values obtained for laboratory pure water.

The principal problem for the collaborators was in attaining a consistent background and avoiding interferences, especially in the elution regions of DMP, DEP, and 2EHP. Other problem areas noted included Kuderna-Danish concentration, which some analysts believed to be the principal source of analyte losses.

There was a high rate of rejection of data due to missing results, values reported as below the laboratory's detection limit, and statistical outliers. Overall, almost 22% of the analyses were excluded from statistical treatment.

Conclusions and Recommendations

Based on the results of this study, Method 606 is a viable method for use in water and wastewater analysis. However, the problem of interferences, obtaining consistent blank values, and separation of components from other electron capture sensitive compounds can be formidable. The accuracy and precision statements presented earlier apply only to the range of concentrations studied and should not be extrapolated beyond those limits.

Table 1. Accuracy and Precision Equations

Water type Range, µg/L	Dimethyl phthalate 1.75-26.9	Diethyl phthalate 1.70-27.4	Di-n-butyl phthalate 2.48-34.9	Benzyl butyl phthalate 0.70-12.2	bis-2-Ethylhexyl phthalate 5.07-55.6	Di-n-octyl phthalate 8.49-52.1
Laboratory Pure						
Accuracy	$X = 0.73c + 0.17$	$X = 0.70c + 0.13$	$X = 0.79c + 0.17$	$X = 0.82c + 0.13$	$X = 0.53c + 2.02$	$X = 0.35c - 0.71$
Precision						
Overall	$S = 0.44X + 0.31$	$S = 0.45X + 0.11$	$S = 0.29X + 0.06$	$S = 0.25X + 0.07$	$S = 0.73X - 0.17$	$S = 0.62X + 0.34$
Single analyst	$SR = 0.26X + 0.14$	$SR = 0.27X + 0.05$	$SR = 0.23X + 0.20$	$SR = 0.26X + 0.04$	$SR = 0.80X - 2.54$	$SR = 0.38X + 0.71$
Finished Drinking						
Accuracy	$X = 0.85c - 0.08$	$X = 0.72c + 0.29$	$X = 0.75c + 0.35$	$X = 0.92c + 0.07$	$X = 0.74c + 1.72$	$X = 0.76c + 0.65$
Precision						
Overall	$S = 0.44X + 0.18$	$S = 0.40X + 0.06$	$S = 0.28X + 0.20$	$S = 0.37X - 0.01$	$S = 0.48X + 0.97$	$S = 0.43X + 1.45$
Single analyst	$SR = 0.30X + 0.30$	$SR = 0.28X + 0.05$	$SR = 0.20X + 0.36$	$SR = 0.32X - 0.03$	$SR = 0.36X + 0.46$	$SR = 0.20X + 5.44$
Surface						
Accuracy	$X = 0.72c + 0.44$	$X = 0.77c + 0.23$	$X = 0.78c + 0.40$	$X = 0.93c + 0.21$	$X = 0.50c + 7.12$	$X = 0.69c - 0.48$
Precision						
Overall	$S = 0.38X + 0.24$	$S = 0.42X + 0.46$	$S = 0.31X + 0.31$	$S = 0.30X + 0.07$	$S = 0.24X + 5.94$	$S = 0.40X - 0.11$
Single analyst	$SR = 0.35X - 0.03$	$SR = 0.26X + 0.15$	$SR = 0.31X - 0.06$	$SR = 0.32X - 0.10$	$SR = -0.01X + 9.71$	$SR = 0.26X - 0.64$
Ind. Effluent 1						
Accuracy	$X = 0.66c + 0.30$	$X = 0.86c + 0.36$	$X = 0.74c + 0.35$	$X = 0.79c + 0.07$	$X = 0.68c + 3.32$	$X = 0.64c - 0.31$
Precision						
Overall	$S = 0.41X + 0.03$	$S = 0.56X + 0.35$	$S = 0.32X + 0.24$	$S = 0.34X + 0.08$	$S = 0.41X + 4.42$	$S = 0.44X - 0.53$
Single analyst	$SR = 0.28X + 0.07$	$SR = 0.39X - 0.09$	$SR = 0.35X - 0.31$	$SR = 0.25X + 0.12$	$SR = 0.15X + 6.94$	$SR = 0.29X - 0.48$
Ind. Effluent 2						
Accuracy	$X = 0.73c - 0.23$	$X = 0.77c - 0.12$	$X = 0.84c + 0.07$	$X = 0.85c + 0.12$	$X = 0.81c + 2.73$	$X = 0.66c - 1.41$
Precision						
Overall	$S = 0.31X + 0.29$	$S = 0.48X + 0.28$	$S = 0.32X + 0.55$	$S = 0.23X + 0.17$	$S = 0.64X - 0.65$	$S = 0.36X + 0.90$
Single Analyst	$SR = 0.27X + 0.14$	$SR = 0.31X + 0.07$	$SR = 0.18X + 1.10$	$SR = 0.26X - 0.06$	$SR = 0.24X + 6.04$	$SR = 0.25X + 0.47$
Ind. Effluent 3						
Accuracy	$X = 0.69c + 0.22$	$X = 0.87c - 0.25$	$X = 0.78c + 0.10$	$X = 0.83c + 0.10$	$X = 0.47c + 11.52$	$X = 0.60c - 1.66$
Precision						
Overall	$S = 0.44X + 0.45$	$S = 0.66X + 0.03$	$S = 0.34X + 0.27$	$S = 0.28X + 0.06$	$S = -0.12X + 17.61$	$S = 0.37X + 1.02$
Single analyst	$SR = 0.26X + 0.59$	$SR = 0.49X - 0.30$	$SR = 0.28X - 0.13$	$SR = 0.27X$	$SR = -0.23X + 17.79$	$SR = 0.21X + 2.69$

c - actual concentration

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268
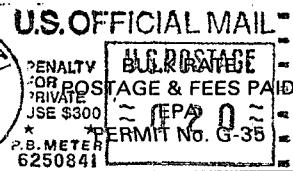
Official Business
Penalty for Private Use $300

EMSL0159000
MARY SULLIVAN
EMSL-CINCINNATI
QUALITY ASSURANCE BRANCH
26 W ST CLAIR
CINCINNATI OH 45268