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Project Summary

EPA Method Study 26, Method 613: 2,3,7,8-Tetrachlorodibenzo-p-Dioxin

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The experimental design and results of an interlaboratory study for an analytical method to detect 2,3,7,8-tetrachlorodibenzo-p-dioxin in water are described herein. In USEPA's Method 613, water containing an internal standard (labeled 2,3,7,8-TCDD) is extracted with methylene chloride, concentrated, exchanged to hexane, and then subjected to capillary column gas chromatography/mass spectrometric (GC/MS) analysis, which allows for separation and measurement of the 2,3,7,8-TCDD isomer in the extract. The method study consisted of the replicate analyses of a performance evaluation sample used primarily for determining laboratory competence for 2,3,7,8-TCDD specific analyses and subsequent analyses of six sample concentrations and a blank in six different waters (42 samples). Statistical analyses and conclusions in this report are based on analytical data obtained by eleven collaborating laboratories.

Participating laboratories were selected based upon technical evaluation of proposals and upon technical evaluation of proposals and upon the analytical results of prestudy samples. Data obtained from the interlaboratory study were analyzed employing USEPA series of computer programs known as the Interlaboratory Method Validation Study (IMVS) system, which was designed to implement the concepts recommended in ASTM Standard D-2777.

The statistical analyses included tests for the 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 (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, 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 USEPA 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 pollutant to be analyzed by Method 613 is 2,3,7,8-TCDD. The Environmental Monitoring and Support Laboratory—Cincinnati (EMSL) of the USEPA develops analytical methods and conducts a quality assurance (QA) program to maximize the reliability and legal defensibility of all water quality information collected by USEPA laboratories.

The responsibility for QA is assigned to the Quality Assurance Branch which conducts interlaboratory method validation studies. This study reports the results of the interlaboratory study on Method 613 (Study 26).

Procedure

Phase I included preliminary method study work conducted by Monsanto Research Corporation to (1) evaluate the original Method 613 as published in the December 3, 1979 *Federal Register;* (2) determine the method's minimum detection limit; and, (3) determine the storage stability of 2,3,7,8-TCDD/acetone solutions in ampuls over a 90-day period. As a result of the Phase I Study, Method 613 was revised to substantially alter the sample processing steps. These revisions are now included in the version of Method 613 as presented in test method manual, "Method for Organic Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, July 1982.

Phase II involved the selection of participating laboratories that could demonstrate satisfactory analytical results using their personnel and equipment. This selection was based partially on analysis of a performance evaluation sample of mixed tetrachlorodibenzo-p-dioxin isomers for 2,3,7,8-TCDD.

Phase III, the formal interlaboratory study, required analyses of 2,3,7,8-TCDD in six water types at each of six concentrations (three Youden pairs) in addition to the analysis of all water blanks with no spiked compound. Each participating laboratory then forwarded a report to Monsanto Research Corporation containing all data obtained, and a completed questionnaire covering specifics on the analyses including the source of distilled, tap and surface waters, instrumentation used, GC conditions, and specific problems encountered in the analyses.

The final step in the study was a statistical analysis of all data by Battelle Columbus Laboratories, Columbus, Ohio, under USEPA Contract No. 69-03-2624 employing USEPA's IMVS system of computer programs.

Results and Discussion

The objective of this study was to characterize the performance of Method 613 in terms of accuracy, overall precision, single-analyst precision, and the effects of water types on accuracy and precision. Through statistical analyses of 396 analytical values, estimates of accuracy and precision were made; these are expressed as regression equations in Table 1. The accuracy is obtained by comparing the mean recovery to the true values of the concentration. The average percent recovery is 91% with a range from 86% to 96%.

The overall relative standard deviation (RSD) indicates the precision associated with measurements generated by a group of laboratories. The average percent relative standard deviation is 21% with a range of 18% to 23%.

The relative single-analyst standard deviation (RSD-SA) indicates the precision associated within a single laboratory relative to the mean recovery. The average percent relative standard deviation for a single analyst is 16% with a range of 13% to 18%.

A statistical comparison of the effect of the water types indicated no statistically significant differences between water types.

Correct activation of the alumina column is critical. Overactivation causes adsorption which results in incomplete or no elution of TCDD from the column.

Some laboratories experienced poor recovery and poor precision on the labeled compounds. As a quality control measure, a second independent internal standard or surrogate should be used to detect possible error in known concentration, evaporated concentration, or incomplete dissolution of standards.

Six of the eleven laboratories experienced little or no difficulty with Method 613. In these cases, over 98% of the data points were retained (4 outliers out of 216 analyses). All data from one laboratory which used an incorrect internal standard were rejected. Of the remain-

Table 1. *Regression Equations for Accuracy and Precision 2,3,7,8-TCDD (Concentration Range 21-202 ppt)*

Water Type	*2,3,7,8-TCDD*
Distilled water	
Single-analyst precision	$SR = 0.13X + 1.29$
Overall precision	$S = 0.19X + 0.28$
Accuracy	$\bar{X} = 0.86C + 1.45$
Tap water	
Single-analyst precision	$SR = 0.01X + 7.78$
Overall precision	$S = 0.22X + 0.80$
Accuracy	$\bar{X} = 0.81C + 4.82$
Surface water	
Single-analyst precision	$SR = 0.09X + 2.25$
Overall precision	$S = 0.21X - 1.11$
Accuracy	$\bar{X} = 0.80C + 3.93$
Wastewater 1	
Single-analyst precision	$SR = 0.25X - 4.41$
Overall precision	$S = 0.28X - 4.63$
Accuracy	$\bar{X} = 0.94C + 1.03$
Wastewater 2	
Single-analyst precision	$SR = 0.06X + 2.71$
Overall precision	$S = 0.16X + 3.12$
Accuracy	$\bar{X} = 0.82C + 4.30$
Wastewater 3	
Single-analyst precision	$SR = 0.16X + 0.49$
Overall precision	$S = 0.20X + 0.01$
Accuracy	$\bar{X} = 0.78C + 4.26$

$\bar{X}$ = *mean recovery*
C = *true concentration*

ing four laboratories, 66% of the data were found to be outliers. In these cases, three problems were identified:

(1) difficulty with alumina cleanup (Laboratories 4 and 11).

(2) no recovery on $^{12}C_{13}$ internal standard (Laboratory 6).

(3) lack of sensitivity at low levels of TCDD (Laboratory 8).

Conclusions and Recommendations

Method 613 is recommended for the analyses of 2,3,7,8-TCDD in municipal and industrial wastewaters.

To increase sensitivity, place the end of the column as close to the ion source as possible.

The alumina column should be checked for proper activity. Overactivated alumina can cause adsorption of 2,3,7,8-TCDD which is not eluted or incompletely eluted by the solvent eluent.

Because some laboratories reported poor precision and experienced interferences with the labeled compounds, the use of a second internal standard or surrogate is recommended to detect errors in known concentration, evaporated concentrations or incomplete dissolution of standards.

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The complete report, entitled "EPA Method Study 26, Method 613, 2,3,7,8-Tetrachlorodibenzo-p-Dioxin," (Order No. PB 84-188 879; Cost: $11.50, subject to change) will be available only from:

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