



# Project Summary

## EPA Method Study 17, Method 607 — Nitrosamines

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

This report describes the results obtained and data analyses from an interlaboratory evaluation of EPA Method 607 (Nitrosamines). The method is designed to analyze for three nitrosamines, N-nitrosodimethylamine, N-nitrosodi-n-propylamine, and N-nitrosodiphenylamine, in water and wastewater. As tested here, the method utilized three 60-ml extractions with dichloromethane, cleanup/separation on an alumina column, and injection into a gas chromatograph equipped with a nitrogen-phosphorus detector.

The study design required the analyst to dose six waters with each of six mixtures of the three nitrosamines. 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 furnished by the prime contractor. A total of 17 laboratories participated in the study.

The method was studied to estimate the accuracy and precision that can be expected, including effects on the 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, 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

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 the work that produced proposed EPA Method 607 (nitrosamines), an interlaboratory study was conducted to test the validity of the proposed method. This report describes the work performed, presents the data acquired, and gives the conclusions drawn from the collaborative effort.

The three compounds undergoing analyses in the interlaboratory study were N-nitrosodimethylamine (NDMA), N-nitrosodi-n-propylamine (NDPrA), and N-nitrosodiphenylamine (NDPhA).

20  
11  
53  
59

The objective of this interlaboratory study was to obtain information about the accuracy and precision associated with measurements generated by Method 607. 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 statistical techniques employed in the data reduction process are similar to the techniques suggested in the ASTM Standard Practice D2777-77.

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 the 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 for a 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 607. 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 be expressed as a linear function of the true concentration. The regression equations for accuracy are shown in Table 1.

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

The percent recovery of the method was similar to that obtained during the developmental phase. The method has an extreme negative bias for NDMA, nearly quantitative recovery for NDPrA, and a moderate negative bias for NDPhA.

Percent recoveries at the midrange concentration were from 36 to 43% for NDMA, 84 to 102% for NDPrA, and 58 to 67% for NDPhA.

The precision of the method was about as expected for NDMA and NDPrA and higher than expected for NDPhA. The additional variability likely results from the column elution procedure.

Six water types were used in this study: laboratory pure, finished drinking, surface, and three relatively interference-free industrial effluents. No difference in method performance was attributable to the water type from which the analysis was performed.

Verifying the activity of the alumina and separating NDPhA from diphenylamine proved to be a difficult step in the analytical procedure and several laboratories were unable to achieve satisfactory separation.

Data rejected from the study due to missing results, values reported as below the laboratory's detection limit, and statistical outliers amounted to more than 19% of the total analyses.

## Conclusions and Recommendations

The participating laboratories in this study were able to obtain results with Method 607 that were comparable to those obtained during the single-laboratory evaluations conducted after method development. 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, ug/L	<i>N</i> -Nitrosodimethylamine 0.82-24.2	<i>N</i> -Nitrosodi- <i>n</i> -propylamine 1.22-26.7	<i>N</i> -Nitrosodiphenylamine 8.22-54.8
<b>Laboratory pure</b>			
Accuracy	$X = 0.370* + 0.06$	$X = 0.96C - 0.07$	$X = 0.64C + 0.52$
Precision			
Overall	$S = 0.25X + 0.11$	$S = 0.21X + 0.15$	$S = 0.46X - 0.47$
Single Analyst	$SR = 0.25X - 0.04$	$SR = 0.15X + 0.13$	$SR = 0.36X - 1.53$
<b>Finished Drinking</b>			
Accuracy	$X = 0.37C + 0.23$	$X = 0.84C - 0.02$	$X = 0.60C - 0.03$
Precision			
Overall	$S = 0.23X + 0.23$	$S = 0.28X + 0.05$	$S = 0.37X + 0.67$
Single analyst	$SR = 0.16X + 0.15$	$SR = 0.24X$	$SR = 0.23X + 0.81$
<b>Surface</b>			
Accuracy	$X = 0.42C + 0.14$	$X = 0.92C + 0.05$	$X = 0.62C - 0.56$
Precision			
Overall	$S = 0.34X + 0.17$	$S = 0.26X + 0.24$	$S = 0.32X + 1.03$
Single analyst	$SR = 0.29X + 0.15$	$SR = 0.16X + 0.24$	$SR = 0.23X + 0.24$
<b>Industrial Effluent 1</b>			
Accuracy	$X = 0.38C + 0.17$	$X = 1.00C + 0.21$	$X = 0.68C - 0.44$
Precision			
Overall	$S = 0.33X + 0.09$	$S = 0.26X + 0.39$	$S = 0.39X + 0.14$
Single analyst	$SR = 0.13X + 0.21$	$SR = 0.18X + 0.27$	$SR = 0.34X - 0.83$
<b>Industrial Effluent 2</b>			
Accuracy	$X = 0.35C + 0.13$	$X = 0.86C + 0.21$	$X = 0.58C + 0.15$
Precision			
Overall	$S = 0.33X + 0.09$	$S = 0.33X + 0.18$	$S = 0.42X + 0.66$
Single analyst	$SR = 0.25X + 0.03$	$SR = 0.26X - 0.04$	$SR = 0.22X + 0.65$
<b>Industrial Effluent 3</b>			
Accuracy	$X = 0.36C + 0.30$	$X = 0.94C + 0.14$	$X = 0.62C + 0.54$
Precision			
Overall	$S = 0.27X + 0.21$	$S = 0.37X + 0.25$	$S = 0.37X + 0.50$
Single analyst	$SR = 0.28X + 0.07$	$SR = 0.22X + 0.44$	$SR = 0.21X + 0.21$

\*C-true concentration  
X-mean concentration

John D. Millar, Richard E. Thomas, and Herbert J. Schattenberg are with the Southwest Research Institute, San Antonio, TX 78284.

Robert L. Graves and Edward L. Berg are the EPA Project Officers (see below). The complete report, entitled "EPA Method Study 17, Method 607—Nitrosamines," (Order No. PB 84-207 646; Cost: \$10.00, subject to change) will be available only from:

National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650

The EPA Project Officers can be contacted at:  
Environmental Monitoring and Support Laboratory  
U.S. Environmental Protection Agency  
Cincinnati, OH 45268

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