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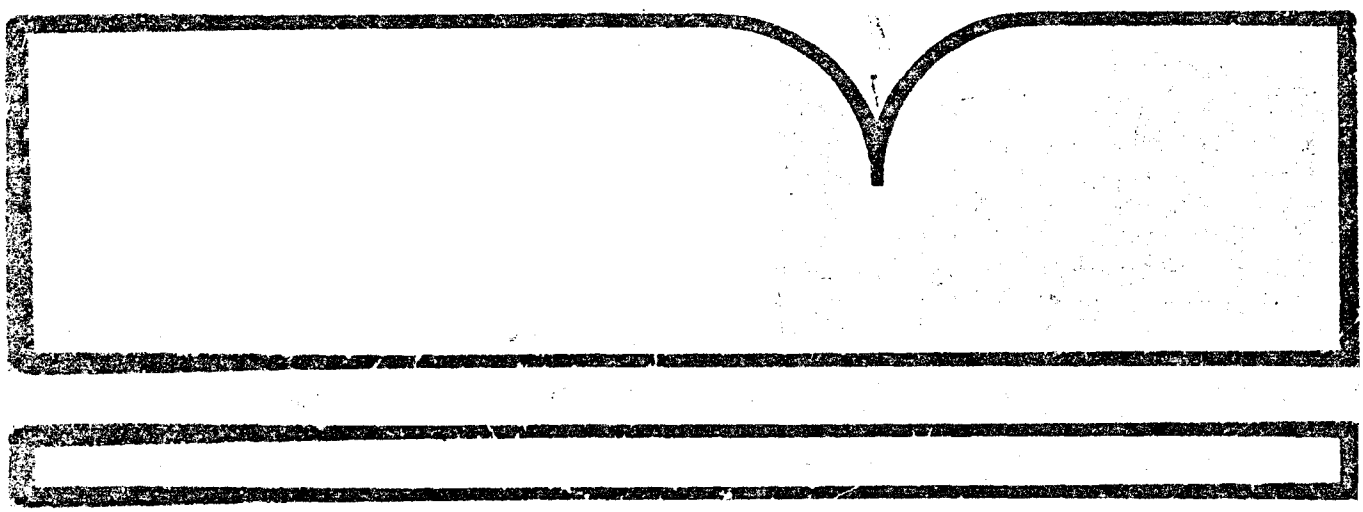
EPA (Environmental Protection Agency)
Method Study 17, Method 607 (Nitrosamines)

Southwest Research Inst., San Antonio, TX

Prepared for

Environmental Monitoring and Support Lab.
Cincinnati, OH

Jun 84



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EPA-600/4-84-051
June 1984

EPA METHOD STUDY 17
METHOD 607 (NITROSAMINES)

by

John D. Millar
Richard E. Thomas
Herbert J. Schattenberg
Southwest Research Institute
San Antonio, Texas 78284

Contract 68-03-2606

Robert L. Graves and Edward L. Berg, Project Officers

Quality Assurance Branch
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
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16. ABSTRACT

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.

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. 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.

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DISCLAIMER

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL)-Cincinnati, conducts research to:

- develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste,
- investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microorganisms in water,
- conduct studies to determine the responses of aquatic organisms to water quality,
- conduct an agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This publication reports the results of EPA's interlaboratory study 17 for the following priority pollutants, which are analyzed using EPA Method 607 (Nitrosamines):

N-nitrosodimethylamine
N-nitrosodi-n-propylamine
N-nitrosodiphenylamine

Federal agencies, states, municipalities, universities, private laboratories, and industry should find this evaluative study of assistance in monitoring and controlling pollution in the environment.

R. L. Booth
Director, EMSL-Cincinnati

ABSTRACT

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 report covers work accomplished over the period from September 1978 to December 1981 under EPA Contract 68-03-2606.

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TABLES

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We also acknowledge and thank James T. Ivy, Southwest Research Institute, for his valuable help in obtaining the industrial effluents that were used in this work.

SECTION 1

INTRODUCTION

EPA first promulgated guidelines [1] 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 [2], mandating the control of toxic pollutants discharged into ambient waters by industry.

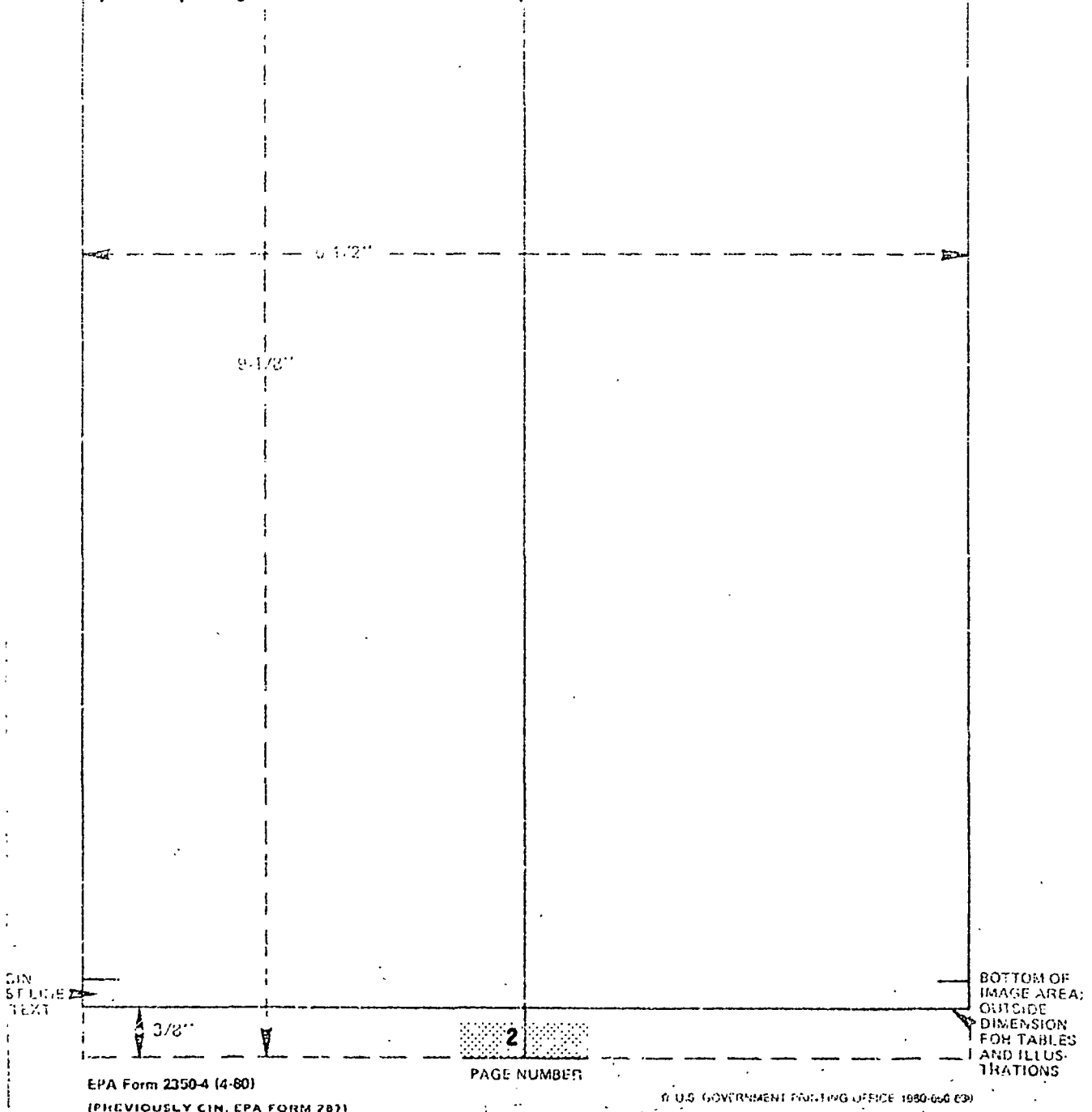
In order to facilitate the implementation of the Clean Water Act, EPA selected 129 specific toxic pollutants, 113 organic and 16 inorganic, for initial study. The organic pollutants were divided into 12 categories based on their chemical structure. Analytical methods were developed by EPA for these 12 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) [3], 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).

The laboratories participating in this study were the 17 lowest bidders from the list of qualifying laboratories that responded to the request for bids. Qualifications of the laboratories were established by review of information submitted on past experience and available equipment. Previous experience with the laboratories was also included in the

evaluation where applicable. The participants were selected to be typical of laboratories that would be using the methodology in its intended application. The number of participating laboratories was cut from 20 to 17 for budgetary reasons, and no volunteer laboratories could be acquired. The laboratories are identified by number in this report and no correlation between the identifying number and the order of laboratories in the list of participating laboratories should be presumed.



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TYPING GUIDE SHEET

TABLE 1. PARTICIPATING LABORATORIES

Analytical Development Corporation
1875 Willow Park Way
Monument, Colorado 80132

Analytical Research Laboratories
160 Taylor Street
Monrovia, California 91016

Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Biospherics, Inc.
4928 Wyaconda Road
Rockville, Maryland 20852

Camp, Dresser and McKee, Inc.
Environmental Sciences Division
6132 West Fond du Lac Avenue
Milwaukee, Wisconsin 53218

Environmental Research Group
117 North First
Ann Arbor, Michigan 48104

Environmental Science and Engineering, Inc.
P.O. Box ESE 32602
Newberry Road (5 mi west of 175)
Gainesville, Florida 32604

Radian Corporation
8500 Shoal Creek Boulevard
Austin, Texas 78766

Raltech Scientific Services, Inc.
3301 Kinsman Boulevard
P.O. Box 7545
Madison, Wisconsin 53707

Recra Research, Inc.
111 Wales Avenue
P.O. Box 448
Tonawanda, New York 14150

Southern Research Institute
2000 Ninth Avenue South
Birmingham, Alabama 35205

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

Technical Services, Inc.
103-7 Stockton Street
Jacksonville, Florida 32201

Texas Instruments, Inc.
13500 North Central Expressway
P.O. Box 225621
Dallas, Texas 75265

Versar, Inc.
6621 Electronic Drive
Springfield, Virginia 22151

West Coast Technical Service, Inc.
17605 Fabrica Way, Suite D
Cerritos, California 90701

Wilson Laboratories
528 North Ninth
Salina, Kansas 67401

SECTION 2

SUMMARY

As a result of the collaborative study conducted and the data analysis, the following conclusions can be drawn concerning EPA Method 607 (Nitrosamines).

- 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 2.
- 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 2.
- 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.

TABLE 2. ACCURACY AND PRECISION EQUATIONS

Water type Range, ug/L	N-Nitrosodimethylamine 0.84-24.2	N-Nitrosodi-n-propylamine 1.22-26.7	N-Nitrosodiphenylamine 8.22-54.8
Laboratory Pure			
Accuracy	X = 0.37C* + 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
Finished Drinking			
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
Surface			
Accuracy	X = 0.42C + 0.14	X = 0.92C + 0.05	X = 0.52C - 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
Industrial Effluent 1			
Accuracy	X = 0.38C + 0.17	X = 1.00C + 0.21	X = 0.63C - 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
Industrial Effluent 2			
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
Industrial Effluent 3			
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

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SECTION 3

DESCRIPTION OF STUDY

The study design was based on Youden's original plan [4] 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 along with portions of final effluents from manufacturing plants from three relevant industries. Each participating laboratory was responsible for supplying laboratory pure water, finished 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.

TEST DESIGN

A summary of the test design using Youden's nonreplicate technique for X and Y samples is given below:

1. Three Youden pairs were used for each parameter with the deviation from the mean of each pair being at least 5% but not more than 20%.
2. The three Youden pairs were spread over a usable and realistic range with the lowest level estimated to be near the detection limit in the industrial effluents with the highest background.
3. Analyses were performed in six waters. Therefore, each laboratory was to generate 36 data points for each compound.

Three of the waters were selected from relevant industries as determined from the information contained in a memorandum of December 29, 1978 from M. Dean Neptune, Analytical Programs, Effluent Guidelines Division to R. B. Schaffer, Director, Effluent Guidelines Division, through W. A. Telliard, Chief, Energy and Mining Branch.

4. Thirty-six concentrates in sealed glass ampules were shipped with approximately 12 liters (3 gallons) of each of the three industrial effluents to the 17 laboratories. The concentrations of substances in the ampules were unknown to the participants.

5. Each participant was supplied with a copy of Method 607 and supplementary instructions relative to spiking procedure, cleanup column to be used, GC column and detector to be used, and GC injection technique.

6. To commence an analysis, the analyst was instructed to open an ampule, add 1 mL of concentrate to 1 L of water, then analyze as per instructions.

7. Each sample was to be analyzed once.

8. 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, participants met in Cincinnati to discuss and resolve problems encountered during the trial run.

9. Fifty ampules of each concentrate prepared were supplied to the project officer.

PREPARATION OF SAMPLES, WASTEWATER SELECTION AND PROCUREMENT

The N-nitrosamines used to prepare sample concentrates were obtained from two commercial sources: Aldrich Chemical Company and Eastman Organic Chemicals. These compounds were compared to high purity compounds obtained from Ultra Scientific, Inc. (formerly RFR Corporation) and were found to be suitable for use as received.

The detailed protocol for concentrate and ampule production was reviewed and approved by the project officer before ampule production commenced. Salient points of the protocol are described in the following paragraph.

Sample concentrates were prepared by dissolving precisely-weighed (analytical balance) amounts in acetone in Class A volumetric flasks. Where dilutions were required, Class A volumetric glass pipettes were used to transfer the required volumes. All glassware had been fired overnight at approximately 400°C before use. The volumes transferred were never less than 4 mL. Solutions were put into brown, borosilicate glass ampules, chilled, heat-sealed, and wrapped in aluminum foil. The sealed ampules were stored in paperboard boxes at 4°C until shipped to participants. All weighing, pipetting, and filling operations were performed under subdued light in as short a time span as possible.

Before each concentrate was used to fill ampules, the concentrations of substances were compared with a standard that had been prepared from separate weighings of the substances. Two ampules taken at random from the ampules produced were checked against the same external standard mentioned immediately above. These verification checks served to prevent gross errors from being committed; the true values were assumed to be those established by the weighings of substances for concentrate preparation. It was rare to find a verification analysis which deviated more than 5% from the true value. The true values for all test substances are given in Table 3.

TABLE 3. TRUE CONCENTRATIONS IN STUDY SAMPLES
(1 mL concentrate in 1 L water; µg/L)

Compound	Lowest pair		Medium pair		Highest pair	
Ampule lot number	3	5	1	2	4	6
N-nitrosodimethylamine	0.837	1.008	6.696	8.064	20.088	24.192
N-nitrosodi-*n*-propylamine	1.484	1.217	10.388	8.519	26.71*	17.038*
N-nitrosodiphenylamine	8.216	10.956	16.432	21.912	41.080	54.780

* Slightly in excess of 20% deviation from the mean due to pipetting error. This exception approved by project officer.

Industrial effluents selected for the interlaboratory study were obtained from the following industrial categories:

Industrial effluent 1--rubber plant
Industrial effluent 2--textile plant
Industrial effluent 3--organics and plastics plant

Industrial effluents 1 and 2 presented no problems for the analyst. Industrial effluent 3 contained N-nitrosodimethylamine, or an artifact, at

a concentration in the low ppb range. Also in the third effluent was a peak eluting in the near vicinity of the N-nitrosodi-n-propylamine peak that could present some problem in peak measurements for this compound.

Each wastewater was collected in two 55-gallon untreated iron drums, treated for residual chlorine as required, shipped to SwRI, pooled, and reshipped to participants in 1-gallon glass containers obtained from Burdick and Jackson, Inc.

ANALYSIS AND REPORTING

In addition to admonitions to follow Method 607 procedure (Appendix B), supplementary instructions were sent to participants at the time the trial run ampules were shipped. Participants were advised how to dose the water and how to make injections of extract into the GC using the solvent-flush technique described by Burke [5]. Only N-P detectors were to be used. Only alumina cleanup columns were permitted; the substitution of Baker aluminum oxide, basic (T-0539) or Fisher Scientific alumina, basic (A-941) for the Woelm product (Super 1, basic, 04571) specified in the method was permissible. Also, the stipulation was made that all pertinent GC recorder charts were to be sent with the data submitted for the trial run and the formal tests to follow.

At the Cincinnati conference, trial run data were presented and a step-by-step discussion of the method was given. The most common errors (calculation, standards preparation, and improper expression of results) were pointed out. At the meeting, the following supplementary instructions were given:

1. Column 1, as given in Method 607, and N-P detectors will be used by all participants (earlier instructions as to the detector to be used were unclear to some).

2. Tap water and surface water samples should be tested for residual chlorine. If present, it should be removed by adding sodium thiosulfate as described in the method.

3. The N-nitrosamine ampules should be protected from light and kept at 4°C until used. Subcontractors were requested to use the ampules within a 30-day period, if possible, and to include the date of use of each ampule in their final report.

After the Cincinnati conference, a follow-up letter was sent to each participant requesting that the example data calculation sheets and data

summary sheets that were enclosed be used during the study. The same letter requested that the final report include information on the following:

1. method of quantitating;
2. sources of standards;
3. source of surface water and the nature of any possible contaminants;
4. suggestions as to how Method 607 could be improved.

DISTRIBUTION OF SAMPLES

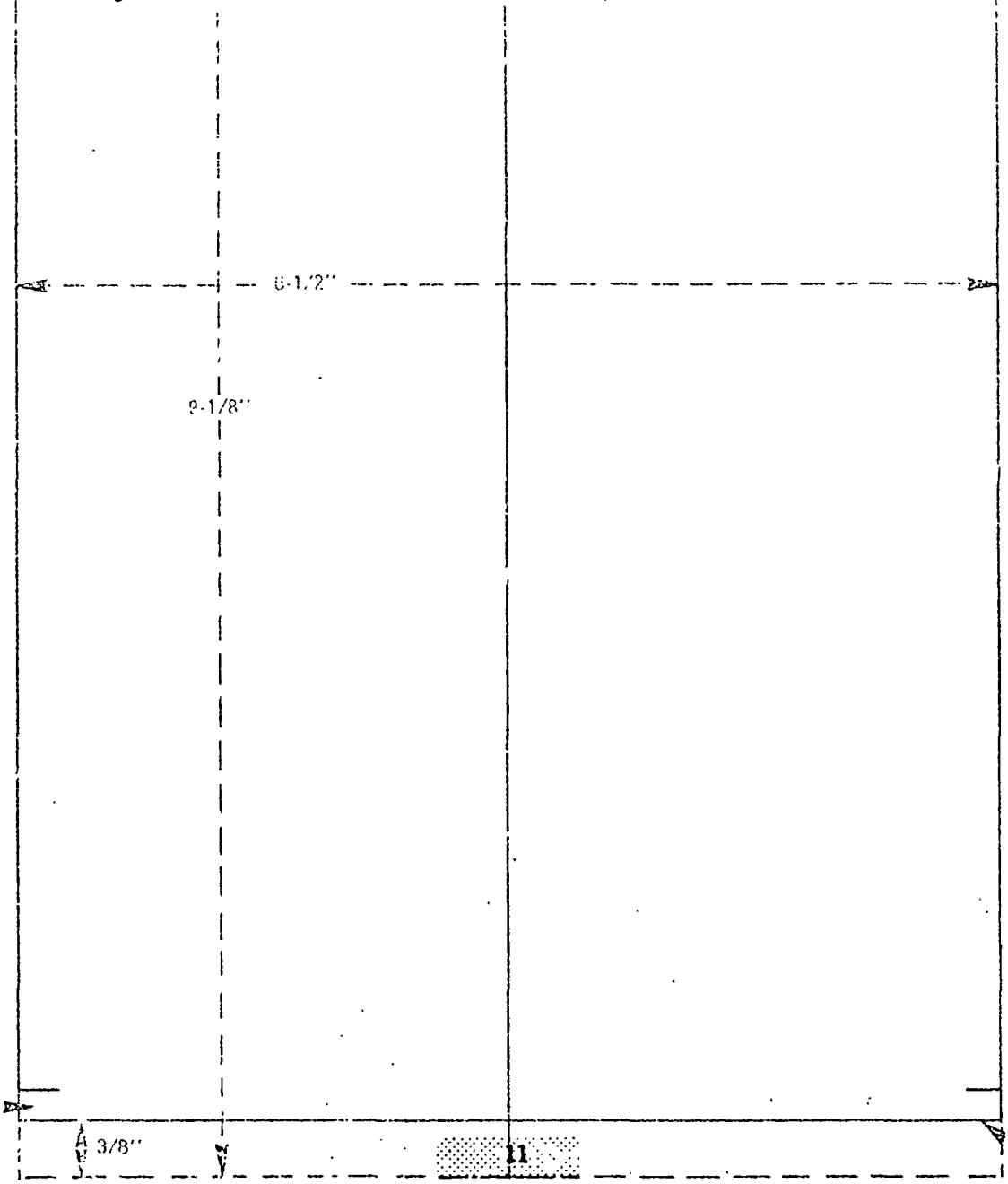
A single shipment of 36 ampules was made by overnight air express to all laboratories. No instance of ampule breakage during shipment was reported. However, some participants reported shortages or received empty, unbroken ampules and others accidentally broke ampules during the study. Replacement ampules were provided in these cases.

The water matrices were also shipped by overnight air express, each participant receiving approximately 12 liters (3 gallons) of each of the three industrial effluents. The time required to collect and distribute the effluents was about three weeks. No breakage in transit occurred. Several gallons were broken or otherwise made unusable through laboratory mishaps. Replacement shipments were made in these instances.

STABILITY OF SAMPLES

Since N-nitrosamine solutions, especially ones containing N-nitrosodiphenylamine, had exhibited measurable deterioration after storage of 30 to 45 days at 24°C, every effort was made to keep the period of time between solution preparation and date of use to a minimum. Extra precautions were taken by wrapping the ampules in aluminum foil immediately after preparation, advising participants to keep the ampules in the refrigerator until used, and asking that they be used within 30 days after delivery. Solutions and ampules were prepared and shipped within a period of one week. All laboratories, except one, reported that their ampules had been used within nine weeks from the time the solutions had been prepared at Southwest Research Institute. The time period required for this last laboratory to use the ampules was about 11 weeks. Samples from excess ampules held in storage at Southwest Research Institute in the dark at 4°C were analyzed at the end of four weeks and again at the end of nine weeks. No evidence of deterioration was found. Method 607 was followed in the analyses at the four- and nine-week points. At the nine-week point, an HPLC method was also used. The latter procedure can separate N-

nitrosodiphenylamine and diphenylamine (degradation product) on the analytical column, whereas Method 607 depends upon separation of these two compounds by liquid-solid chromatography before injection into the GC-NPD instrument. The absence of serious deterioration of N-nitrosodiphenylamine is considered to be unequivocal. Therefore, deterioration of the N-nitrosamines before use in the Method 607 study should not be a factor, assuming that all subcontractors stored the ampules at 4°C as instructed.



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SECTION 4

TREATMENT OF DATA

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 [6] 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.

A detailed description of each of the statistical analysis procedures is presented below.

PREPROCESSING

An initial review of the data was performed to determine if a systematic error was evident in the data that could be identified and legitimately corrected prior to data analysis. Chromatograms and supporting data were investigated to verify that the analyses were run under the proper conditions and that calculations were accurate and supportable. Where an anomaly existed, such as a series of results that were different from the true values by one or more orders of magnitude, the analyst was contacted, told that there was an apparent error, and asked to check his values. No indication was given as to the nature of the

inconsistency in order not to prejudice the results. If an error was found, the corrected values were used in the data analyses. If the analyst reported no error could be found, the data were allowed to stand as reported.

All analyses reported as less than a detection limit and results that the analysts noted as influenced by spillage or loss of sample were removed from the data set prior to insertion into the computer program. The data set thus prepared was utilized in the statistical analysis supplied by the sponsor.

REJECTION OF OUTLIERS

Spurious data points are always a part of any set of data collected during an interlaboratory test program. It is important to identify and remove these data points because they can lead to values of summary statistics which are not representative of the general behavior of the method. However, some erratic behavior in the data may be directly related to some facet of the method under the study. Therefore, spurious data points should not be removed indiscriminantly, and any points that are removed should be clearly identified since further investigation of the analytical conditions related to the outliers might be of value. Data rejected as outliers for this study as a result of any of the following tests for outliers have been identified by the symbol "*" in the raw data tables.

YOUDEN'S LABORATORY RANKING PROCEDURE

In some cases the analytical values reported by a specific laboratory are so consistently high or low that a large systematic error may be attributed to that laboratory. These data are not representative of the method and should be rejected. Youden's [4] ranking test for outlying laboratories was applied separately to data from each of the waters used in this study. Since six water types were used in this study, the laboratory ranking procedure was applied to these six different subsets of the data. Each laboratory ranking test was performed at the 5% level of significance.

The Youden laboratory ranking procedure requires a complete set of data from every laboratory within a given water type. Missing data from labortory i for water type j were replaced by the following procedure. Letting X_{ijk} denote the reported measurement from laboratory i for water type j and concentration level C_k, it is assumed that

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk}$$

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where β_j and γ_j are fixed parameters which determine the effect of water type j, L_i is the systematic error due to laboratory i and ε_{ijk} is the random within laboratory error. Taking natural logarithms, it follows that

$$\ln X_{ijk} = \ln \beta_j + \gamma_j \ln C_k + \ln L_i + \ln \varepsilon_{ijk}$$

which is a linear regression model with dependent variable $\ln X_{ijk}$ and independent variable $\ln C_k$. (Details and justification for this model are discussed in the section "Comparison of Accuracy and Precision Across Water Types.")

The natural logarithms of the individual laboratory's data were regressed against the natural logarithms of the true concentration levels for the six ampules in each water type. The predicted values $\widehat{\ln X_{ijk}}$ were obtained from the regression equation, and the missing values for X_{ijk} were estimated by $\hat{X}_{ijk} = \exp(\widehat{\ln X_{ijk}})$, where exp (c) denotes the constant e raised to the c power.

If the ranking test rejected a laboratory for a specific water type, then all of the laboratory data for that water type were rejected as outliers. The rejected values were excluded from all the remaining analyses. In addition, after completion of the laboratory ranking procedure, the predicted values created to fill in for the missing data were rejected and excluded from further analyses for all laboratories.

TESTS FOR INDIVIDUAL OUTLIERS

The data remaining after the laboratory ranking procedure were grouped by water type. For each water type, the data were broken down into six subsets defined by the six concentration levels (ampules) used in the study. For each subset of the data, all missing, zero, "less than" and "nondetect" data were rejected. Next, the test for individual outliers constructed by Thompson [7] and suggested in the ASTM Standard Practice D2777-77 was applied to the data using a 5% significance level. If an individual data point was rejected based on this test, it was removed from the subset, and the test was repeated using the remaining data in the subset. This process was continued until no additional data could be rejected.

STATISTICAL SUMMARIES

Several summary statistics were calculated using the data remaining for each concentration level after the outlier rejection tests were

performed. These summary statistics include: the number of retained data points, the mean recovery, accuracy as a percent relative error, the absolute overall standard deviation, the percent relative overall standard deviation, the absolute single-analyst standard deviation, and the percent relative single-analyst standard deviation. The basic formulas used to calculate these statistics are presented below where X_1, X_2, ..., X_n denote the values of the n retained data points for a specific concentration level.

Mean Recovery (X):

$$X = \frac{1}{n} \sum_{i=1}^{n} X_i$$

The conventional notation for mean recovery is $\bar{X}$; however the symbol X is used in this report to be consistent with the output from the computer program.

Accuracy as a % Relative Error:

$$\%RE = \frac{X - \text{True Value}}{\text{True Value}} \times 100$$

Overall Standard Deviation:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - X)^2}$$

and

Percent Relative Overall Standard Deviation:

$$\%RSD = \left(\frac{S}{X}\right) \times 100$$

The overall standard deviation S indicates the precision associated with measurements generated by a group of laboratories. This represents the broad variation in the data collected in an interlaboratory study. However, a measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This single-analyst precision, denoted by SR, was estimated for each Youden pair by

$$SR = \sqrt{\frac{1}{2(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2}$$

where m - the number of complete sets of Youden pair observations remaining after outliers have been removed,
D_i - the difference between the observations in the i^{th} Youden pair,
$\bar{D}$ - average of the D_i values.

The percent relative single-analyst standard deviation was calculated by

$$\%RSD\text{-}SR = \frac{SR}{X^*} \times 100$$

where X* is the average of the two mean recovery statistics corresponding to the two concentration levels defining the particular Youden pair.

These summary statistics provide detailed information on the accuracy and precision of the data obtained for each concentration level. One objective of the statistical analysis of the data is to summarize the information about accuracy and precision which is contained in the statistics.

A systematic relationship often exists between the mean recovery (X) and the true concentration level (C) of the analyte in the sample. In addition, there are often systematic relationships between the precision statistics (S and SR) and the mean recovery (X). Usually these systematic relationships can be adequately approximated by a linear relationship (i.e., by a straight line). Once these straight lines are established, they can be used to conveniently summarize the behavior of the method within a water type, and they can aid in comparing the behavior of the method across water types. In addition they can be used to obtain estimates of the accuracy and precision at any concentration level within the applicable range studied. They can also be used to predict the behavior of the method when used under similar conditions. These important relationships are discussed below.

STATEMENT OF METHOD ACCURACY

The accuracy of the method is characterized by the relationship of the mean recovery (X) to the true concentration (C) of the analyte in the water sample. In order to obtain a mathematical expression for this relationship, a regression line of the form

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$$X = a + b \cdot C \qquad (1)$$

was fitted to the data by regression techniques

The true concentration values often vary over a wide range. In such cases, the mean recovery statistics associated with the larger concentration values tend to dominate the fitted regression line producing relatively larger errors in the estimates of mean recovery at the lower concentration values. In order to eliminate this problem, a weighted least squares technique was used to fit the mean recovery data to the true concentration values. The weighted least square technique was performed by dividing both sides of Equation (1) by C resulting in Equation (2)

$$\frac{X}{C} = a \cdot \frac{1}{C} + b \qquad (2)$$

The X/C values were regressed against the 1/C values using ordinatory least squares to obtain estimates for the values of a and b. (This is equivalent to performing a weighted least squares with weights $w = 1/C^2$; see Reference 8, page 108 for details.) Equation (2) can easily be converted to the desired relationship given by Equation (1). The intercept (b) from Equation (2) becomes the slope (b) for Equation (1) and the slope (a) from Equation (2) becomes the intercept (a) for Equation (1). Equation (1) can be used to calculate the percent recovery over the applicable range of concentrations used in the study.

The percent recovery is given by

$$\text{Percent Recovery} = \left[\frac{a + b \cdot C}{C}\right] \times 100 = \left[\frac{a}{C} + b\right] \times 100 \qquad (3)$$

If the absolute value of the ratio (a/C) is small relative to the slope (b) for concentration in the low end of the range of concentration levels used in the study, then the percent recovery can be approximated by b x 100. For example, suppose the true concentration values range from 25 µg/L to 515 µg/L, the fitted line is given by $X = 0.20 + 0.85 \cdot C$. The percent recovery would be approximated by (0.85) x 100 = 85% over the specified range of 25 µg/L to 515 µg/L.

If the ratio (a/C) is not small relative to the slope (b), then the percent recovery depends upon the true concentration (C), and it must be evaluated at each concentration value within the specified range.

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STATEMENT OF METHOD PRECISION

The precision of the method is characterized by the relationships between precision statistics (S and SR) and mean recovery (X). In order to obtain a mathematical expression for these relationships, regression lines of the form

$$S = d + e \cdot X \quad (4)$$

and

$$SR = f + g \cdot X^* \quad (5)$$

were fitted to the data.

As discussed previously with respect to accuracy, the values of X and X* often vary over a wide range. In such cases the standard deviation statistics associated with the larger mean recovery values will dominate the regression lines. This will produce relatively larger errors in the estimates of S and SR at the lower mean recovery values. Therefore, a weighted least squares technique was also used to establish the values of the parameters d, e, f and g in Equations (4) and (5). The weighted least squares technique was performed by dividing both sides of Equation (4) by X* resulting in Equation (6)

$$\frac{S}{X} = d \cdot \frac{1}{X^*} + e \quad (6)$$

and by dividing both sides of Equation (5) by X* resulting in Equation (7)

$$\frac{SR}{X^*} = f \cdot \frac{1}{X^*} + g \quad (7)$$

The {S/X} values were regressed against the {1/X} values and the {SR/X*} values were regressed against the {1/X*} values using ordinary least squares to obtain estimates for the parameters d, e, f and g.

Equations (4) and (5) were obtained from Equations (6) and (7) in a manner similar to that discussed for mean recovery. The slope (d) for Equation (6) is the intercept (d) for Equation (4), and the intercept (e) for Equation (6) is the slope (e) for Equation (4). Similarly, the slope

(f) for Equation (7) is the intercept (f) for Equation (5), and the intercept (g) for Equation (7) is the slope (g) for Equation (5).

Given Equations (4) and (5), the percent relative overall standard deviation and the percent relative single-analyst standard deviation are

$$\%RSD = \left[\frac{d}{X} + e\right] \times 100 \qquad (8)$$

and

$$\%RSD\text{-}SA = \left[\frac{f}{X^*} + g\right] \times 100 \qquad (9)$$

respectively. If the absolute value of the ratio (d/X) is small relative to the slope (e), then the percent relative overall standard deviation can be approximated by (e x 100) over the applicable range of mean recovery values. Similarly if the ratio (f/X*) is small relative to the slope (g), then the percent relative single-analyst standard deviation can be approximated by (g x 100) over the applicable range of mean recovery values.

If the ratios (d/X and f/X*) are not small relative to the slopes (e) and (f), then the percent relative standard deviations depend upon the values of the mean recovery statistics X and X*, and they should be evaluated separately for each value of X and X*.

COMPARISON OF ACCURACY AND PRECISION ACROSS WATER TYPES

It is possible that the accuracy and precision of Method 607 depend upon the type of water being analyzed. The summary statistics X, S and SR are calculated separately for each concentration level within each water type. They can be compared across water types in order to obtain information about the effects of water type on accuracy and precision. However, the use of these summary statistics in this manner has several disadvantages. First, it is cumbersome since there are 36 mean recovery statistics (X) (six concentrations x six waters), 36 percent statistics (S) and 18 precision statistics (SR) calculated for each compound. Comparison of these statistics across concentration levels and across water types becomes unwieldly. Second, the statistical properties of this type of comparisons procedure are difficult to determine. Finally, due to variation associated with X, S and SR, comparisons based on these statistics can lead to inconsistent conclusions about the effect of water type. For example, distilled water may produce a significantly lower value

than surface water for the precision statistic S at a high concentration, but a significantly higher value for S at a low concentration.

An alternative approach, described in detail in Reference [9], has been developed to test for the effects of water type. This alternative approach is based on the concept of summarizing the average effect of water type across concentration levels rather than studying the local effects at each concentration level. If significant differences are established by this alternative technique, then the summary statistics can be used for further local analysis.

The test for the effect of water type is based on the following statistical model. If X_{ijk} denotes the measurement reported by laboratory i for water type j and ampule k, then

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \qquad \begin{matrix} i = 1,2,\ldots,n \\ j = 1,2,\ldots,6 \\ k = 1,2,\ldots,6 \end{matrix} \qquad (10)$$

The model components β_j and γ_j are fixed parameters which determine the effect of water type j on the behavior the observed measurements $\{X_{ijk}\}$. The parameter C_k is the true concentration level associated with ampule k. The model component L_i is a random factor which accounts for the systematic error associated with laboratory i. The model component ε_{ijk} is the random factor which accounts for the within laboratory error.

The model is designed to approximate the global behavior of the data. The multiplicative structure was chosen because of two important properties. First, it allows for a possible curvilinear relationship between the data $\{X_{ijk}\}$ and the true concentration level C_k through the use of the exponent γ_j on C_k. This makes the model more flexible in comparison to straight line models. Second, as will be seen below, there is an inherent increasing relationship between the variability in the data and the concentration level C_k in this model. This property is important because it is typical of interlaboratory data collected under conditions where the true concentration levels vary widely.

Accuracy is related directly to the mean recovery or expected value of the measurements $\{X_{ijk}\}$. The expected value for the data modeled by Equation (10) is

$$E(X_{ijk}) = \beta_j \cdot C_k^{\gamma_j} \cdot E(L_i \cdot \varepsilon_{ijk}) \qquad (11)$$

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Precision is related to the variability in the measurements $\{X_{ijk}\}$. The variance of the data modeled by Equation (10) is

$$\text{Var}(X_{ijk}) = \left[\beta_j C_k^{\gamma_j}\right]^2 \text{Var}(L_i \cdot \epsilon_{ijk}) \qquad (12)$$

which is an increasing function of C_k.

The effect of water type on the accuracy and precision of Method 607 is determined by the values of the parameters $\{\beta_j\}$ and $\{\gamma_j\}$ in Equations (11) and (12). If the $\{\beta_j\}$ and $\{\gamma_j\}$ vary with j (i.e., vary across water type), then the accuracy and precision of the method also vary across water type.

In order to determine if these parameters do vary across water type and to compare their values, they must be estimated from the laboratory data using regression techniques. Equation (10) represents the basic model. However, taking natural logarithms of both sides of Equation (10), the following straight line regression model is obtained,

$$\ln X_{ijk} = \ln \beta_j + \gamma_j \ln C_k + \ln L_i + \ln \epsilon_{ijk} \qquad (13)$$

which can be analyzed using standard linear model analysis techniques. The parameter $\ln \beta_j$ is the intercept and γ_j the slope of the regression line associated with water type j. It is assumed that $\ln L_i$ is normally distributed with mean 0 and variance σ_L^2 and that $\ln \epsilon_{ijk}$ is normally distributed with mean 0 and variance σ^2 and that the $\ln L_i$ and $\{\ln \epsilon_{ijk}\}$ terms are independent.

Based on Equation (13) the comparison of water types reduces to the comparison of straight lines. Distilled water is viewed as a control, and each of the remaining lines is compared directly to the line for distilled water.

Using the data on the log-log scale and regression techniques, the parameters $\ln \beta_j$ (and hence β_j) and γ_j can be estimated. The estimates are then used to test the null hypothesis that there is no effect due to water type. The formal null and alternative statistical hypotheses H_0 and H_A are given by

$$H_0: \ \ln \beta_j - \ln \beta_1 = 0 \text{ and } \gamma_j - \gamma_1 = 0 \text{ for } j = 2,3,4,5,6$$

versus

H_A: $\ln \beta_j - \ln \beta_1 \neq 0$ and/or $\gamma_j - \gamma_1 \neq 0$ for some $j = 2,3,4,5,6$

The test of null hypothesis H_0 against the alternative hypothesis H_A is based on an F-statistic derived from standard linear model theory. The probability of obtaining a value of an F-statistic as large as the value which was actually observed (F OBS), denoted by P(F > F OBS), is calculated under the assumption that H_0 is true. The null hypothesis H_0 is rejected in favor of H_A if P(F > F OBS) is less than 0.05.

If H_0 is rejected, then some linear combination of the differences $\ln \beta_j - \ln \beta_1$ and $\gamma_j - \gamma_1$ is statistically different from zero. However, this does not guarantee there will be a statistically significant direct effect attributable to any specific water type since the overall F test can be overly sensitive to minor systematic effects common to several water types. The effect due to water type is judged to be statistically significant only if one of the differences $\ln \beta_j - \ln \beta_1$ and/or $\gamma_j - \gamma_1$ is statistically different from zero. This is determined by checking the simultaneous 95% confidence intervals which are constructed for each of these differences. Each true difference can be stated to lie within its respective confidence interval with 95% confidence. If zero is contained within the confidence interval, then there is no evidence that the corresponding difference is significantly different from zero.

If at least one of the confidence intervals for the differences $\ln \beta_j - \ln \beta_1$ or $\gamma_j - \gamma_1$ fails to include zero, then the statistical significance of the effect due to water type has been established. However, establishment of a statistically significant effect due to water type does not necessarily mean that the effect is of practical importance. Practical importance is related to the size and interpretation of the difference.

The interpretation of the differences involves comparing the mean recovery and standard deviation of the $\{X_{ijk}\}$ data for each water type to the mean recovery and standard deviation obtained for distilled water. These comparisons are made on a relative basis. The mean recovery for water type j is given by Equation (11). The mean recovery for water type j is compared to that for distilled water (j=1) on a relative basis by

$$\frac{E(X_{ijk})}{E(X_{i1k})} = \frac{\beta_j \, C_k^{\gamma_j} \, E(L_i \cdot \varepsilon_{ijk})}{\beta_1 \, C_k^{\gamma_1} \, E(L_i \cdot \varepsilon_{i1k})} = \frac{\beta_j}{\beta_1} \, C_k^{\gamma_j - \gamma_1} \qquad (14)$$

[The ratio of the standard deviations would be equivalent to Equation (14) and therefore the interpretation of the effect on precision is the same as that for the effect on mean recovery.]

The ratio in Equation (14) is a measure of the relative difference in mean recovery between water type j and distilled water. It is composed of two parts (a) β_j/β_1, which is independent of the true concentration level (i.e., the constant bias) and (b) $C_k^{\gamma_j-\gamma_1}$ which depends upon the true concentration level (i.e., the concentration dependent bias). If $\gamma_j - \gamma_1$ is zero, then the relative difference in mean recovery is just β_j/β_1 which is independent of concentration level C_k. It can then be stated that the mean recovery of water type j is $(\beta_j/\beta_1) \times 100\%$ of the mean recovery for distilled water. If $\gamma_j - \gamma_1$ is not zero, then the mean recovery of water type j is $[(\beta_j/\beta_1) \cdot C_k^{\gamma_j-\gamma_1}) \times 100\%$ of that for distilled water and therefore depends upon the true concentration level C_k.

In order to illustrate these points consider the following example. Suppose that a significant F-value has been obtained and the confidence intervals for all the differences contain zero except for water type 5. For water type 5, the point estimate for $\ln \beta_5 - \ln \beta_1$ is -0.38 and the confidence interval for $\ln \beta_5 - \ln \beta_1$ is (-0.69, -0.07). The point estimate for $\gamma_5 - \gamma_1$ is 0.07, and the confidence interval for $\gamma_5 - \gamma_1$ is (-0.04, 0.18). In this case a statistically significant effect due to water type has been established which involves only water type 5. The practical significance of this effect is judged by considering Equation (14). The ratio of mean recoveries for water type 5 and distilled water is given by

$$\frac{E(X_{i5k})}{E(X_{i1k})} = \frac{\beta_5}{\beta_1} C_k^{\gamma_5-\gamma_1} \qquad (15)$$

and the ratio of the standard deviations is given by

$$\frac{Var(X_{ijk})}{Var(X_{i1k})} = \frac{\beta_5}{\beta_1} C_k^{\gamma_5-\gamma_1} \qquad (16)$$

Since the confidence interval for $\gamma_5 - \gamma_1$ contains zero this difference is assumed to be insignificant and is set to zero. Therefore, Equations (15) and (16) reduce to β_5/β_1. The point estimate for $\ln \beta_5 - \ln \beta^1$ was -0.38. Therefore, the point estimate for β_5/β_1 is 0.68, and the mean recovery for water type 5 is estimated to be 68% of the mean recovery for distilled water. Similarly the standard deviation for the data for water type 5 is

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estimated to be 68% of the standard deviation for distilled water. Since the 95% confidence interval for $\ln \beta_5 - \ln \beta_1$ was (-0.69, -0.07), any value in the interval (0.50, 0.93) is a reasonable estimate for β_5/β_1, and the mean recovery (standard deviation) for water type 5 can be claimed to be from 50% to 93% of the mean recovery (standard deviation) for distilled water. The practical significance of the effect due to water type 5 would depend upon the importance of a mean recovery (standard deviation) which is between 50% and 93% of the mean recovery (standard deviation) observed for distilled water.

The comparison of accuracy and precision across water types just discussed is based on the assumption that Equation (10) approximately models the data. It is clear that in practical monitoring programs of this type such models cannot model the data completely in every case. This analysis, therefore, is viewed as a screening procedure which identifies those cases where differences in water types are likely to be present. A more detailed, local analysis can then be pursued using the basic summary statistics for precision and accuracy.

SECTION 5

DISCUSSION AND CONCLUSIONS

The rejection rate for these data were similar to expectations for an interlaboratory method study. A total of 356 values were rejected, including missing data, data reported as less than some value, and statistical outliers rejected according to the criteria stated earlier. These represent 19.4% of all data requested.

The summary statistics obtained from the collaborative study data are presented in Tables 4 through 6 for the three nitrosamines studied. Discussion of the accuracy, precision and consistency across water types is presented separately in the following sections.

ACCURACY OF THE METHOD

The accuracy of the method is estimated by the linear regression of mean recovery versus true concentration presented earlier. The equations are valid only over the range of true values studied and should not be extrapolated beyond this range.

As an illustration of the accuracy that can be expected for the three nitrosamines under study, the midrange concentrations were inserted into the regression equations to estimate percent recoveries. These predicted recoveries at the midrange, shown in Table 7, provide a basis for comparing the recoveries across water types and among nitrosamines. Recoveries at other concentrations would vary due to the relative impact of the slope and intercept of the regression line upon the calculated result.

There is good consistency across water types for the nitrosamines, with recoveries ranging from 36 to 43% for NDMA, 84 to 102% for NDPrA, and 58 to 67% for NDPhA.

PRECISION OF THE METHOD

The precision of the method is estimated by calculating regression equations for the precision components versus the mean recovery. In each case, the regression model is assumed and both the overall standard

TABLE 4.

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***EPA METHOD VALIDATION STUDY - SRI NITROSAMINES*

STATISTICAL SUMMARY FOR N-NITROSODIMETHYLAMINE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
NUMBER OF DATA POINTS	14	14	14	16	12	13	14	15	14	14	13	13
TRUE VALUE UG/L	0.84	1.01	0.84	1.01	0.94	1.01	0.84	1.01	0.84	1.01	0.84	1.01
MEAN RECOVERY	.34	.47	.44	.74	.55	.46	.40	.67	.44	.45	.52	.78
ACCURACY AS % REL ERROR	-59.53	-52.92	-47.08	-26.10	-33.74	-54.23	-52.76	-33.03	-47.06	-55.33	-37.86	-22.60
OVERALL STD DEV (S)	.18	.26	.24	.68	.39	.32	.17	.49	.24	.24	.32	.52
OVERALL REL STD DEV, %	53.50	55.63	54.20	91.49	69.73	68.86	41.86	72.09	54.33	54.20	61.07	66.84
SINGLE STD DEV, (SR)	.07		.24		.29		.29		.16		.25	
ANALYST REL DEV, %	16.87		40.30		57.75		53.00		31.62		39.01	
MEDIUM YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
NUMBER OF DATA POINTS	14	13	14	13	12	13	15	13	13	13	13	15
TRUE VALUE UG/L	8.70	8.06	8.70	8.06	8.70	8.06	8.70	8.06	8.70	8.06	8.70	8.06
MEAN RECOVERY	2.74	3.09	2.60	3.11	2.88	3.93	2.73	2.95	2.42	2.80	2.25	3.39
ACCURACY AS % REL ERROR	-59.03	-61.73	-61.14	-61.40	-57.01	-51.23	-59.26	-63.46	-63.89	-65.27	-66.35	-57.93
OVERALL STD DEV (S)	.53	.73	.68	.70	.62	2.08	1.01	1.01	.84	1.00	.36	1.08
OVERALL REL STD DEV, %	19.43	23.78	26.19	22.59	21.60	52.89	36.99	34.34	34.84	35.86	16.13	31.77
SINGLE STD DEV, (SR)	.43		.60		1.23		.54		.41		.76	
ANALYST REL DEV, %	14.87		21.09		36.15		18.99		15.78		27.01	
HIGH YOUDEN PAIR	4	6	4	6	4	6	4	6	4	6	4	6
NUMBER OF DATA POINTS	13	15	15	15	14	14	14	14	14	13	14	16
TRUE VALUE UG/L	20.09	24.19	20.09	24.19	20.09	24.19	20.09	24.19	20.09	24.19	20.09	24.19
MEAN RECOVERY	6.80	9.03	8.00	9.14	8.45	10.14	7.65	9.42	7.37	8.07	7.71	8.85
ACCURACY AS % REL ERROR	-66.17	-64.32	-60.20	-62.21	-57.94	-58.09	-61.92	-61.06	-60.34	-66.64	-61.64	-63.40
OVERALL STD DEV (S)	1.49	3.70	1.49	2.49	3.09	3.79	1.95	3.07	2.35	3.33	2.01	3.93
OVERALL REL STD DEV, %	21.91	42.89	18.44	27.24	36.60	37.38	25.49	32.54	29.50	41.24	26.13	44.41
SINGLE STD DEV, (SR)	2.57		1.46		2.54		1.50		2.72		2.60	
ANALYST REL DEV, %	33.26		17.25		27.28		17.52		33.86		31.39	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 5.

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EPA METHOD VALIDATION STUDY - SRI NITROSAMINES

STATISTICAL SUMMARY FOR N-NITROSODI-N-PROPYLAMINE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	4	3	5	3	5	3	5	3	5	3	5
NUMBER OF DATA POINTS	13	13	12	11	13	15	14	13	14	15	13	12
TRUE VALUE UG/L	1.48	1.22	1.48	1.22	1.48	1.22	1.48	1.22	1.48	1.22	1.48	1.22
MEAN RECOVERY	1.23	1.18	1.12	1.09	1.39	1.19	2.04	1.19	1.44	1.27	1.76	1.13
ACCURACY AS % REL ERROR	-17.15	-2.90	-24.38	-11.49	-6.95	-3.23	37.34	-2.13	-2.84	4.05	18.28	-7.35
OVERALL STD DEV (S)	.45	.33	.41	.28	.31	.81	1.28	.59	.66	.62	1.17	.56
OVERALL REL STD DEV, %	36.27	29.04	36.79	26.09	36.90	92.11	62.95	49.92	45.59	48.74	66.50	49.37
SINGLE STD DEV, (SR)	.30		.26		.43		.56		.32		.75	
ANALYST REL DEV, %	24.72		23.30		33.85		34.68		23.96		51.68	

MEDIUM YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
NUMBER OF DATA POINTS	13	13	14	14	16	16	13	14	15	16	15	15
TRUE VALUE UG/L	10.39	8.52	10.39	8.52	10.39	8.52	10.39	8.52	10.39	8.52	10.39	8.52
MEAN RECOVERY	9.83	8.09	9.30	6.57	9.16	8.18	11.27	8.43	9.05	8.13	9.59	9.24
ACCURACY AS % REL ERROR	-5.42	-5.09	-10.46	-22.94	-11.83	-3.94	8.47	-1.05	-12.91	-4.52	-7.69	8.42
OVERALL STD DEV (S)	2.09	2.48	2.54	2.18	2.37	2.79	2.58	2.49	2.54	2.75	4.20	3.65
OVERALL REL STD DEV, %	21.31	30.73	27.29	33.16	25.91	34.09	22.87	29.59	28.11	33.75	43.76	39.56
SINGLE STD DEV, (SR)	1.81		2.66		1.89		1.88		1.80		3.11	
ANALYST REL DEV, %	20.25		33.53		21.80		19.04		20.90		33.04	

HIGH YOUDEN PAIR	4	6	4	6	4	6	4	6	4	6	4	6
NUMBER OF DATA POINTS	11	14	14	13	13	16	14	13	16	16	14	14
TRUE VALUE UG/L	26.71	17.04	26.71	17.04	26.71	17.04	26.71	17.04	26.71	17.04	26.71	17.04
MEAN RECOVERY	25.68	16.53	23.89	13.63	24.17	16.01	25.55	16.89	22.03	14.57	24.13	14.99
ACCURACY AS % REL ERROR	-3.87	-2.39	-10.57	-20.00	-9.51	-6.06	-4.33	-.86	-17.52	-14.47	-9.65	-12.03
OVERALL STD DEV (S)	2.32	4.41	4.49	4.52	4.49	5.59	7.59	4.40	9.40	4.98	7.91	5.16
OVERALL REL STD DEV, %	9.02	26.91	19.90	33.18	19.02	34.95	29.72	26.03	42.69	34.79	32.77	34.41
SINGLE STD DEV, (SR)	2.41		2.91		2.77		4.36		3.66		3.44	
ANALYST REL DEV, %	11.40		15.90		13.77		20.54		30.91		17.60	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 6.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY - SRI NITROSAMINES

STATISTICAL SUMMARY FOR N-NITROSODIPHENYLAMINE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
NUMBER OF DATA POINTS	14	13	13	13	11	13	12	12	13	15	13	14
TRUE VALUE UG/L	9.22	10.96	9.22	10.96	9.22	10.96	8.22	10.96	8.22	10.96	9.22	10.96
MEAN RECOVERY	5.84	7.94	4.93	6.04	4.25	6.38	5.20	7.07	4.99	6.62	5.56	6.97
ACCURACY AS % REL ERROR	-29.88	-35.79	-40.02	-44.86	-48.25	-41.80	-36.76	-35.51	-39.23	-39.53	-32.30	-36.41
OVERALL STD DEV (S)	2.14	2.64	2.74	3.85	2.39	3.06	2.23	3.06	3.12	3.49	2.68	3.07
OVERALL REL STD DEV, %	36.89	37.46	59.94	47.16	56.21	47.99	42.89	43.31	62.45	52.74	48.27	44.14
SINGLE ANALYST STD DEV, (SR)	.66		2.13		1.33		1.23		2.17		1.63	
SINGLE ANALYST REL DEV, %	10.26		38.82		25.09		20.01		37.43		26.04	
MEDIUM YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
NUMBER OF DATA POINTS	13	12	14	15	13	12	11	12	13	14	14	14
TRUE VALUE UG/L	16.43	21.91	16.43	21.91	16.43	21.91	16.43	21.91	16.43	21.91	16.43	21.91
MEAN RECOVERY	11.39	14.94	11.03	12.83	9.95	14.00	10.49	15.31	9.34	12.65	11.34	15.47
ACCURACY AS % REL ERROR	-30.94	-32.26	-32.91	-41.44	-39.43	-36.11	-36.42	-30.13	-43.15	-42.27	-31.01	-29.39
OVERALL STD DEV (S)	5.52	6.37	2.92	5.06	4.55	4.79	3.09	7.51	4.09	3.18	3.97	6.60
OVERALL REL STD DEV, %	48.66	42.91	34.63	39.41	45.76	33.60	29.61	49.07	43.75	25.17	35.04	42.64
SINGLE ANALYST STD DEV, (SR)	3.80		3.02		4.11		3.89		1.96		2.47	
SINGLE ANALYST REL DEV, %	29.02		25.30		34.35		29.92		17.83		18.40	
HIGH YOUDEN PAIR	4	6	4	6	4	6	4	6	4	6	4	6
NUMBER OF DATA POINTS	14	13	15	14	10	11	12	13	15	15	13	15
TRUE VALUE UG/L	41.08	54.78	41.08	54.78	41.08	54.78	41.08	54.78	41.08	54.78	41.08	54.78
MEAN RECOVERY	25.64	36.37	23.67	30.34	21.44	34.29	25.27	39.26	25.17	31.89	25.23	32.25
ACCURACY AS % REL ERROR	-35.15	-37.26	-37.91	-44.62	-47.91	-37.41	-38.49	-28.32	-38.72	-41.79	-35.59	-41.12
OVERALL STD DEV (S)	11.13	14.92	15.30	14.63	8.14	12.44	8.46	17.10	14.07	16.38	10.83	12.14
OVERALL REL STD DEV, %	41.95	41.42	40.11	47.57	37.98	36.29	33.48	43.56	55.89	51.38	42.93	37.65
SINGLE ANALYST STD DEV, (SR)	8.42		7.93		9.04		9.78		8.68		7.18	
SINGLE ANALYST REL DEV, %	27.60		28.30		18.10		30.30		30.42		24.98	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 7. ESTIMATED PERCENT RECOVERY FOR VARIOUS WATER TYPES AT MIDRANGE CONCENTRATION

Compound	Percent recovery in given water types						
	Midrange	Laboratory pure	Finished drinking	Surface	Industrial effluent 1	Industrial effluent 2	Industrial effluent 3
N-nitrosodimethylamine	12.52	37	39	43	39	36	38
N-nitrosodipropylamine	13.96	95	84	92	102	88	95
N-nitrosodiphenylamine	31.51	66	60	60	67	58	64

deviation (S) and single-analyst standard deviation (SR) are expressed in this manner. As was the case with the accuracy equation, these equations may only be said to be valid over the range of concentrations studied.

As was done with the accuracy equation, the precision of the method is illustrated by the calculation of percent relative standard deviations at the midrange concentration. Although the variability at any concentration over the range studied will depend upon the relative impact of the slope and intercept of the precision equations, these relative standard deviations, shown in Tables 8 and 9, allow a general evaluation of method performance.

COMPARISON ACROSS WATER TYPES

The summaries on the effects of water type on the results obtained are presented in Tables 10, 11, and 12. In none of the instances was the F-statistic significantly large to warrant rejection of the null hypothesis of equality. The conclusion is that the method performed in a comparable manner over the six waters used in this study. It should be remembered, however, that the industrial effluents selected for this study were chosen because of their relatively low background of interfering substances. Some differences can be expected to occur when analyzing a variety of effluents and the user should evaluate method performance with each matrix on which it is used.

METHOD EVALUATION

The accuracy of the method as determined from the collaborative study data compared favorably to the results obtained by SwRI in the developmental phase of the method [10]. In developmental studies in interference-free water, recoveries of 40, 98 and 80% were obtained for NDMA, NDPrA, and NDPhA, respectively, and in samples of five effluents, the average recoveries ranged from 25 to 38 for NDMA, 54 to 103 for NDPrA, and 46 to 89 for NDPhA. By comparison, the percent accuracy at midranges spanned 36 to 43 for NDMA, 84 to 102 for NDPrA, and 58 to 67 for NDPhA in the waters used in this study.

Method detection limit (MDL) was determined for each of the three compounds in interference-free water and in two industrial effluents, using a procedure specified by the Environmental Monitoring and Support Laboratory. In this procedure, at least seven sample replicates containing the compounds at concentrations near the estimated detection limit of each were analyzed by Method 607. The standard deviation of the replicate measurements was calculated and multiplied by the Student's t value

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TABLE 8. ESTIMATED OVERALL PERCENT RELATIVE STANDARD DEVIATION FOR VARIOUS WATER TYPES AT MIDRANGE CONCENTRATION

	Overall RSD for given water type						
Compound	Midrange	Laboratory pure	Finished drinking	Surface	Industrial effluent 1	Industrial effluent 2	Industrial effluent 3
N-nitrosodimethylamine	12.52	26	25	35	34	34	29
N-nitrosodipropylamine	13.96	22	28	28	29	34	39
N-nitrosodiphenylamine	31.51	45	39	35	39	44	39

TABLE 9. ESTIMATED SINGLE-ANALYST PERCENT RELATIVE STANDARD DEVIATION FOR VARIOUS WATER TYPES AT MIDRANGE CONCENTRATION

	Single-analyst RSD for given water type						
Compound	Midrange	Laboratory pure	Finished drinking	Surface	Industrial effluent 1	Industrial effluent 2	Industrial effluent 3
N-nitrosodimethylamine	12.52	25	17	30	15	25	29
N-nitrosodipropylamine	13.96	16	24	18	20	26	25
N-nitrosodiphenylamine	31.51	31	26	24	31	24	22

TABLE 10.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI NITROSAMINES*

EFFECT OF WATER TYPE ON N-NITROSODIMETHYLAMINE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE(GAMMA(1)) = .95634

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.1927	-.0437
3	.0588	.0166
4	.1669	-.0533
5	.0412	-.0428
6	.3387	-.1193

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	732.67159	732.67159		
REG(WATER/DISTILLED)	10	3.29595	.32959	1.53	.1270
ERROR	470	101.54278	.21605		
TOTAL	481	837.51027			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	.1927	(-.1409 , .5062)	-.0437	(-.1945 , .1072)
3	.0588	(-.2774 , .3950)	.0166	(-.1389 , .1721)
4	.1669	(-.1597 , .4905)	-.0533	(-.2052 , .0985)
5	.0412	(-.2853 , .3677)	-.0428	(-.1961 , .1104)
6	.3387	(.0073 , .6700)	-.1193	(-.2726 , .0340)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

TABLE 11.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY - SRI NITROSAMINES

EFFECT OF WATER TYPE ON N-NITROSODI-N-PROPYLAMINE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = 1.04130

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.0394	-.0298
3	.0321	-.0278
4	.1194	-.0363
5	.1295	-.1068
6	.1490	-.0774

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	646.87932	646.87932		
REG(WATER/DISTILLED)	10	1.94096	.19410	1.10	.3572
ERROR	472	82.99233	.17583		
TOTAL	483	731.80860			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL		SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL	
2	-.0394	(-.4069 ,	.3280)	-.0298	(-.1952 ,	.1356)
3	.0321	(-.3175 ,	.3817)	-.0278	(-.1873 ,	.1318)
4	.1194	(-.2360 ,	.4748)	-.0363	(-.1976 ,	.1250)
5	.1296	(-.2183 ,	.4775)	-.1068	(-.2639 ,	.0503)
6	.1490	(-.2122 ,	.5102)	-.0774	(-.2403 ,	.0854)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

TABLE 12.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY - SPI NITROSAMINES

EFFECT OF WATER TYPE ON N-NITROSODIPHENYLAMINE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .94289

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.2551	.0396
3	-.6813	.1901
4	-.3402	.0995
5	-.2833	.0417
6	-.1117	.0232

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	215.77398	215.77398		
REG(WATER/DISTILLED)	10	2.45695	.24570	1.19	.2937
ERROR	447	92.10445	.20605		
TOTAL	458	310.33539			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL		SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL	
2	-.2551	(-1.1794 ,	.6653)	.0396	(-.2609 ,	.3321)
3	-.6813	(-1.6432 ,	.2807)	.1901	(-.1230 ,	.5031)
4	-.3402	(-1.2841 ,	.6038)	.0995	(-.2057 ,	.4027)
5	-.2833	(-1.1929 ,	.6263)	.0417	(-.2913 ,	.3348)
6	-.1117	(-1.0279 ,	.8040)	.0232	(-.2723 ,	.3187)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

appropriate for a 99% confidence level with n-1 degrees of freedom (3.143 for seven replicates) to give the MDL value. The MDL values obtained are given in Table 13. Also shown in Table 13 for easy comparisons with the MDLs are the lowest concentrations used in the interlaboratory study.

TABLE 13. METHOD DETECTION LIMITS AND LOWEST CONCENTRATIONS USED IN STUDY

	Concentration, µg/L		
	NDMA	NDPrA	NDPhA
Interference-free water, MDL	0.149	0.462	0.807
Industrial effluent 1, MDL	0.099	0.359	0.757
Industrial effluent 3, MDL	0.121	0.741	1.57
Lowest conc. in study	0.837	1.217	8.216

In conjunction with the MDL determinations, analytical curves for the compounds were determined on duplicate samples at five concentration levels chosen in conference with the project officer. The analytical curve study showed that an essentially linear response was observed for N-nitrosodimethylamine up to concentrations of 148 µg/L and for N-nitrosodi-n-propylamine up to 466 µg/L; these concentrations are far above the highest concentrations used in this study. For N-nitrosodiphenylamine, a significant deviation from linearity was observed with an approximate one-third drop in response factor when the concentration went from 8 µg/L to 800 µg/L. However, the concentration span from the lowest Youden pair to the highest Youden pair in the interlaboratory study was only from 8 to 55 µg/L, a segment of the analytical curve where essentially linear response was observed.

The lowest spiking levels used in the study ranged from five to eight times the MDL values for NDMA and NDPhA and from two to three times the MDL values for NDPrA. The smaller difference between MDL and spiking level for NDPrA had no adverse effect on the assay of this substance, and study results for it and NDMA are about as expected. The results for NDPhA, although acceptable, are not as good as anticipated. The critical part of the procedure for NDPhA is its separation from the potentially interfering compound, diphenylamine (DPA) and NDMA, on the alumina cleanup column. To achieve the separation, the alumina activity must be within a narrow range that is presumably attained by adding 2 mL of water to 100 g of Woelm, Super 1 activity, basic alumina as received. Although this procedure was

found to work well in the laboratory at Southwest Research Institute, it did not work well for a number of the participants in the study. A further difficulty in this area developed when a temporary shortage of the Woelm product forced the substitution of alumina from other sources. Alumina from Fisher Scientific and Baker were recommended as substitutes with the amount of water added to be 1 mL per 100 g of alumina as received. Difficulties in attaining the desired separation were also reported when the Fisher and Baker products were used. Irrespective of the brand of alumina used, 8 of the 17 laboratories in the study reported separation difficulties which may have adversely affected their abilities to determine the amount of NDPhA in their samples. As a criterion for determining when the activity of the alumina was in the acceptable range, participants were instructed to adjust the percentage of water in the alumina until the amount of NDPrA (from a standard mixture applied to the alumina column) in the first fraction of eluate ranged from 10 to 33% of the amount added, with the balance to be found in the second fraction of eluate. A few participants had difficulty in preparing alumina with an activity that distributed the NDPrA as recommended, and one participant challenged the NDPrA distribution as a satisfactory index of activity.

Although 9 of the 17 participants were able to achieve satisfactory separations by following the method instructions, preparing alumina with an acceptable activity and maintaining that activity until used will always be a potentially troublesome part of the procedure because great care is required in preparation, the ambient humidity may vary widely during use, and individual work habits and skills may vary greatly. To reduce the difficulties experienced by eight of the laboratories, it might be advisable to modify the method by including the following suggestions:

1. Each freshly prepared batch of deactivated alumina will be tested before use on unknown samples for its ability to separate NDPhA and DPA, making sure at the same time that all of the NDMA is in the eluate fraction containing the DPA.
2. Condition alumina as received, before deactivating, in a thin layer overnight in an oven at a constant temperature within the range of 150 to 300°C.
3. Use a tightly closed container during preparation and storage; do not store the prepared alumina more than five days.
4. Protect from atmospheric exposure wherever possible during use.

Another major trouble spot that appeared during the study was the great variation in response of the N-P detector. This trouble is greatly reduced by venting the injected solvent, and all participants reporting difficulties with response were advised to install a vent in their GC system and to inject standards several times per day.

Several laboratories reported that they had great difficulty injecting the first fraction of eluate (30% ethyl ether/70% pentane) because of its low boiling point and suggested that it, too, should be solvent exchanged with methyl alcohol before analysis by GC.

Several participants complained that the temperatures given in the method for concentrating the fractions in a Kuderna-Danish apparatus were too low and therefore the times required to perform this step were too long.

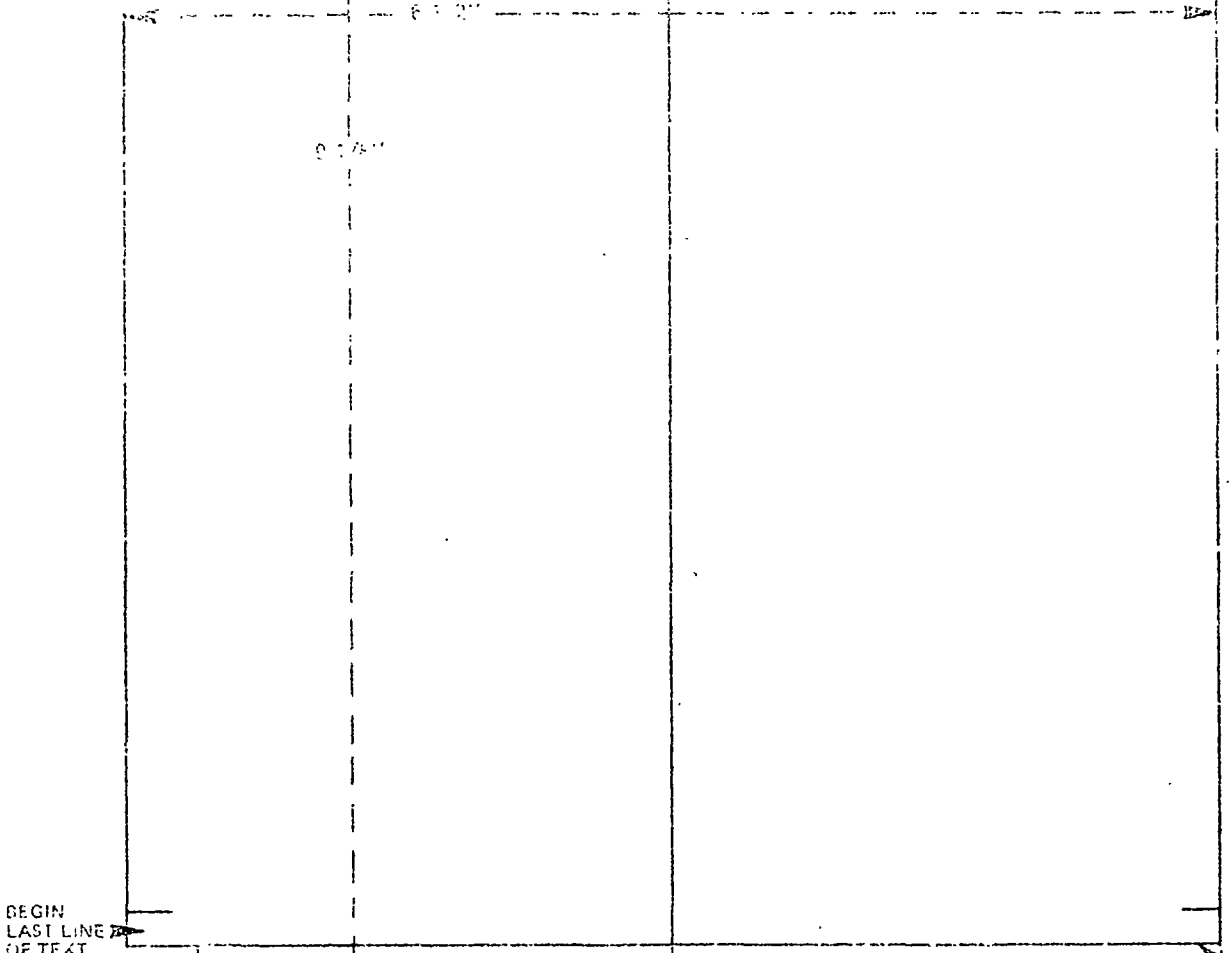

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TABLE A-1.

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OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY - SRI NITROSAMINES

RAW DATA FOR N-NITROSODIMETHYLAMINE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
TRUE VALUE UG/L	0.84	1.01	0.84	1.01	0.84	1.01	0.84	1.01	0.84	1.01	0.84	1.01
LABORATORY NUMBER												
701	1.05*	1.05	1.02	1.07	1.00	1.15	2.80*	1.73	1.00	1.50*	0.31	1.10
702	0.19	0.09*	0.38	0.21	1.44	0.41	0.24	0.21	0.29	0.21	0.62	0.41
703	0.69	0.61	0.39	0.46	0.28	0.01	0.56	1.20	0.44	0.48	0.17	0.44
704	0.45	0.42	0.31	0.31	0.21	0.21	0.40	0.47	0.45	0.34	0.80	0.97
705	0.70	0.99	0.72	0.92	0.59	0.99	0.99	0.95	0.59	0.96	0.71	1.02
706	0.36	0.46	0.43	0.50	0.43	0.68	0.45	0.93	0.37	0.45	0.43	0.45
707	12.00*	6.52*	*	2.14	33.00*	6.40*	26.60*	29.80*	5.16*	2.40*	42.90*	7.00*
708	0.28	0.37	0.34	0.36	0.30	0.36	0.27	0.36	0.28	0.44	*	0.39
709	0.11	0.09	0.13	0.69	0.81	0.50	0.31	0.49	0.16	0.29	1.05	1.66
710	0.28	0.33	0.31	0.36	0.23	0.38	0.25	0.27	0.33	0.26	0.43	*
711	0.21	0.30	0.34	0.43	0.28	0.33	0.34	0.30	0.29	0.38	0.49	0.58
712	0.50	0.59 <	0.30*	0.30*<	0.30*<	0.30*<	0.30*<	0.30*<	0.30*	0.51	0.30	0.46
713	0.30	0.49	0.30	0.39	0.30	0.50	0.40	0.50	0.30	0.40	0.30	*
714	0.20	0.30	0.40	0.60	*	*	0.20	0.30	0.20*	0.20*	0.10	0.20
715	2.40*	2.20*	2.10*	2.10	2.30*	1.80*	0.70	0.80	0.80	1.00	2.60*	1.90
716	0.27	0.29	0.29	0.34	*	0.28	0.22	1.61	0.22	0.36	9.11*	10.00*
717	0.25	0.49	0.81	0.25	0.83	0.20	0.67	0.41	0.68	0.22	1.10	0.56

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-1 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI NITROSAMINES*

RAW DATA FOR N-NITROSODIMETHYLAMINE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
TRUE VALUE UG/L	6.70	8.06	6.70	8.06	6.70	8.06	6.70	8.06	6.70	8.06	6.70	8.06
LABORATORY NUMBER												
701	3.16 <	0.20*	2.34	3.45	0.31*	0.88	0.38	1.42	0.57	1.02	2.00	1.98
702	2.33	1.99	1.90	1.44	2.33	2.81	2.51	2.64	2.09	2.51	2.68	3.16
703	2.65	3.25	2.79	3.45	2.92	4.34	3.27	3.91	*	2.79	2.44	2.39
704	2.21	2.39	2.63	2.66	2.02	2.23	3.02	2.90	2.32	3.50	2.87	4.02
705	3.57	4.32	3.35	4.32	3.68	4.09	3.30	4.73	3.33	4.34	3.64*	4.75
706	3.22	4.43	2.72	2.74	3.07	3.18	2.93	3.67	2.85	3.13	2.23	2.40
707	30.00*	38.40*	29.10*	20.00*	46.20*	60.10*	91.00*	47.70*	37.70*	18.70*	33.10*	65.50*
708	2.79	3.11	3.19	3.66	3.84	4.50	2.80	2.85	2.50	3.58	2.37	2.61
709	3.01	3.61	1.28	3.00	3.51	7.42	1.52	1.53	1.64	1.98	2.53	4.48
710	8.15*	10.70*	11.60*	15.50*	9.31*	13.60*	4.07	11.60*	6.40*	19.40*	10.50*	15.50*
711	2.19	2.92	2.63	3.55	3.19	3.94	2.06	2.86	2.89	3.75	1.97	2.95
712	3.72	3.10	1.97*	1.47*	1.15*	1.11*	0.69*	2.56*	2.31	2.71	1.72	1.86
713	2.30	2.90	2.30	2.90	2.70	3.60	3.80	3.90	3.10	3.80	4.60*	3.10
714	2.90	2.10	3.90	2.30	*	*	2.90	1.90	1.40*	1.90*	2.30	3.70
715	4.90*	3.80*	3.60	3.40	2.80	8.60	1.50	3.00	1.40	1.50	1.60	4.50
716	2.24	2.81	2.69	9.46*	1.88	2.34	3.96	*	3.63	7.90*	2.33	3.68
717	2.20	3.20	1.70	3.40	2.60	3.40	2.90	3.40	2.80	1.80	2.20	5.40

* = REJECTED

WATER LEGEND

1 = DISTILLED WATER
2 = TAP WATER
3 = SURFACE WATER
4 = WASTE WATER 1
5 = WASTE WATER 2
6 = WASTE WATER 3

TABLE A-1 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SOI NITROSAMINES*

RAW DATA FOR N-NITROSODIMETHYLAMINE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	4	6	4	5	4	5	4	6	4	6	4	6
TRUE VALUE UG/L	20.09	24.19	20.09	24.19	20.09	24.19	20.09	24.19	20.09	24.19	20.09	24.19
LABORATORY NUMBER												
701	*	7.12	7.19	8.25	2.09	4.14	7.43	9.13	69.70*	6.17	5.29	5.14
702	6.59	2.21	7.04	6.63	7.49	3.79	6.27	5.52	5.83	1.75	6.22	3.67
703	6.79	9.79	7.41	9.27	6.26	8.57	9.25	9.21	13.50	6.05	4.52	7.93
704	6.42	8.08	5.91	8.50	7.33	10.20	10.10	12.00	8.51 <	8.84*	9.24	13.10
705	9.50	15.90	9.80	15.00	6.89	14.90	7.68	13.80	7.09	14.40	8.34	12.30
706	6.73	5.91	8.46	13.10	9.21	10.67	9.72	10.30	8.53	8.27	8.29	10.40
707	63.40*	46.40*	64.00*	161.50*	53.10*	37.40*	134.70*	210.50*	148.60*	63.90*	218.70*	54.90*
708	6.69	1.41	9.47	9.99	9.64	9.43	9.25	6.39	7.98	10.20	10.50	2.58
709	4.74	7.95	4.44	6.78	7.44	9.74	4.03	4.66	4.90	6.58	5.56	12.10
710	6.17	12.90	7.19	8.02	6.03	13.40	7.89	9.10	7.48	8.66	6.04	8.57
711	7.36	9.88	9.59	10.80	8.51	13.70	8.18	9.39	9.10	10.10	5.18	8.93
712	9.45	10.83	7.61*	3.03*	3.82*	7.89*	5.80*	8.19*	4.92	3.85	2.88*	6.06
713	7.80	10.20	10.30	10.40	8.50	13.10	8.60	11.80	8.70	10.90	8.50	13.50
714	9.00	10.40	8.30	9.50	*	*	3.50	*	3.40*	5.30*	6.00	4.60
715	10.40*	15.00*	7.00	10.90	14.90	17.40	0.10	9.10	6.10	10.90	11.80	12.60
716	12.80*	9.86	8.66	10.20	14.00	7.41	16.60*	15.70	11.10	20.90*	17.10*	14.90
717	5.10	7.10	8.00	3.80	8.10	9.50	7.10	6.80	7.70	7.20	6.40	5.70

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
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5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-2

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI NITROSAMINES*

RAW DATA FOR N-NITROSODI-N-PROPYLAMINE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
TRUE VALUE UG/L	1.48	1.22	1.48	1.22	1.48	1.22	1.48	1.22	1.48	1.22	1.48	1.22
LABORATORY NUMBER												
701	0.89	0.55	0.97	9.69*	0.96	0.25	2.53	1.33	9.53*	1.90*	1.69	1.05
702	1.70	1.29	1.84	1.23	2.47	1.23	1.52	0.94	1.79	1.13	3.71	1.60
703	2.18*	1.62*	1.09*	1.68*	1.90*	2.17*	1.90	2.23	2.02	1.38	2.00*	2.46*
704	1.25	1.26	0.93	1.00	1.40	1.20	4.83*	2.32*	3.09	2.03	4.23*	4.07*
705	1.68	1.71	1.73*	1.59*	1.52	1.95	1.65	1.63	1.71	1.64	1.67	1.90
706	1.83	1.09	1.35	1.20	1.79	2.27	1.38	1.14	1.17	1.11	1.92	0.94
707	*	*	*	*	*	*	4.75	1.99	1.88	*	3.68	1.36
708	1.54	1.29	0.77	*	1.96	1.62	1.63	0.98	0.50	1.17	*	0.92
709	0.78*	0.64*	0.42	0.69	0.81	0.86	0.78*	0.66*	0.67	0.75	0.86	0.73
710	0.35	0.63	0.79	0.62	0.77	0.65	0.88	0.57	0.68	0.46	0.93	*
711	0.78	1.15	1.08	1.08	1.19	0.69	1.55	1.55	1.03	1.71	0.72	0.57
712	1.29	1.19	0.70*	1.47	1.18	0.80	1.14	1.00	0.80*	0.62	0.83	0.90
713	1.40	1.30	1.40	1.10	0.90	1.40	1.80	1.40	1.60	1.40	1.00	0.90
714	1.00	1.00	1.90	1.50	1.20	1.20	1.40	0.70	0.90	0.90	0.90	2.30
715	3.80*	2.30*	4.40*	3.10*	5.50*	2.10	5.10	4.10*	5.60*	2.80	3.70	5.10*
716	1.53	1.26	0.99	1.11	*	1.14	0.90*	0.56*	1.54	1.37	*	*
717	0.75	1.70	1.70	0.95	1.80	0.34	1.30	0.02	1.30	0.62	1.70	0.45

* = REJECTED

WATER LEGEND

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2 = TAP WATER
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5 = WASTE WATER 2
6 = WASTE WATER 3

TABLE A-2 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY - SRI NITROSAMINES

RAW DATA FOR N-NITROSODI-N-PROPYLAMINE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM VOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
TRUE VALUE UG/L	10.39	8.52	10.39	8.52	10.39	8.52	10.39	8.52	10.39	8.52	10.39	8.52
LABORATORY NUMBER												
701	12.10 *	0.40*	12.60	9.39	6.79	3.82	13.10	9.00	13.90*	10.60*	15.70	9.84
702	6.57	4.83	7.19	5.35	7.19	4.26	6.78	4.83	7.09	3.54	10.60	4.00
703	13.00*	11.80*	13.20*	9.46*	15.10*	14.30*	13.60	10.50	*	8.61	11.50*	13.70*
704	10.50	5.99	9.41	8.15	10.90	8.68	13.10*	8.46*	11.30	11.40	15.20*	12.10*
705	12.40	12.50	12.50*	13.60*	12.80	13.50	11.50	13.50	11.10	12.90	12.20	13.60
706	8.63	8.74	5.85	7.83	11.30	8.97	10.20	7.74	9.64	7.57	8.92	7.27
707	29.10*	9.37	4.46*	0.98*	6.73	11.70	11.90	6.92	5.19	3.26	6.81	12.70
708	10.20	8.26	8.02	6.45	11.30	8.89	9.48	7.34	5.83	6.66	9.34	7.81
709	5.47*	5.29*	5.73	4.43	5.43	5.01	6.00*	5.86*	7.17	5.30	6.85	3.87
710	10.00	19.10	8.59	7.59	7.89	12.60	10.90	11.10	10.30	9.86	5.77	10.60
711	7.44	6.69	9.82	8.40	10.90	8.10	8.82	6.88	10.10	10.70	6.87	5.92
712	12.09	6.05	8.30	6.10	6.67	5.14	3.70*	7.40	8.77	9.00	6.35	4.33
713	9.30	8.90	9.70	7.70	10.90	8.90	15.10	10.50	12.60	10.00	11.10	11.00
714	8.30	5.60	9.10	6.70	11.10	8.10	10.70	6.20	5.80	6.90	18.50	16.00
715	16.10*	10.00*	9.40	8.70	9.60	8.70	8.80	9.30	7.60	10.00	9.63	9.60
716	12.80	9.00	11.10	3.60	6.45	7.68	3.58*	*	9.72	8.64	10.90	10.20
717	7.40	7.90	19.90	1.60	11.60	7.50	19.60	8.80	13.30	5.70	10.30	11.80

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
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5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-2 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI NITROSAMINES*

RAW DATA FOR N-NITROSODI-N-PROPYLAMINE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	4	6	4	6	4	6	4	6	4	6	4	6
TRUE VALUE UG/L	26.71	17.04	26.71	17.04	26.71	17.04	26.71	17.04	26.71	17.04	26.71	17.04
LABORATORY NUMBER												
701	*	17.80	29.00	20.50	20.30	12.50	40.30	21.40	110.00*	25.00*	37.30	17.30
702	22.30	13.20	19.00	11.90	20.00	19.00	20.50	14.50	23.90	13.80	26.60	16.50
703	31.40*	19.50*	31.20*	22.10*	34.50*	26.90*	33.00	18.30	37.90	14.30	35.60*	24.10*
704	24.30	16.70	23.70	18.00	13.80*	21.10	39.20*	24.80*	24.40	15.20	27.40*	26.10*
705	27.40	23.90	31.30*	23.70*	33.00	23.60	31.60	21.90	28.20	22.70	34.50	21.20
706	23.20	22.60	19.90	12.20	27.80	16.80	27.80	16.30	25.20	14.00	30.30	21.40
707	28.60	22.30	1.81*	1.99*	2.79*	4.30	15.90	22.90	7.35	2.71	7.85	2.37
708	28.70	16.60	22.70	10.20	27.00	17.60	28.80	14.10	26.00	18.30	19.20	14.80
709	14.30*	11.50*	19.20	10.90	19.40	12.40	17.30*	4.01*	14.50	10.10	17.40	13.30
710	10.30*	7.81	15.90	4.69	16.60	6.80	13.40	6.89	14.40	9.55	17.60	9.54
711	23.90	13.90	27.80	16.00	22.10	18.00	23.10	14.00	29.50	16.30	21.40	15.00
712	25.63	15.23	28.21	4.00*	11.81*	15.20	21.24	15.00	14.85	10.18	13.50*	10.23
713	27.20	18.70	29.70	17.90	25.50	26.30	32.30	21.10	32.00	18.30	25.60	21.40
714	23.70	16.30	23.20	16.40	21.20	17.70	16.10	*	2.00	15.90	16.73	14.50
715	29.00*	17.20*	22.70	15.90	27.30	19.90	26.10	17.70	18.10	17.10	28.80	16.20
716	27.70	16.40	24.70	15.00	26.20	15.20	10.60*	7.83*	26.30	21.90	28.73	*
717	16.40*	11.40	29.20	7.60	27.80	13.70	27.40	13.50	27.90	12.40	25.90	16.10

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-3

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI NITROSAMINES*

RAW DATA FOR N-NITROSODIPHENYLAMINE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
TRUE VALUE UG/L	8.22	10.95	8.22	10.95	8.22	10.96	8.22	10.96	8.22	10.96	8.22	10.96
LABORATORY NUMBER												
701	9.04	66.80*<	3.00*<	3.00*<	3.00*	13.60 <	3.00*	12.60 <	3.00*	4.90	17.90*<	4.00*
702	4.63	5.21	3.31	3.95	3.31	5.21	4.36	5.73	3.31	4.38	5.27	3.13
703	6.80	7.63	5.95	9.41	10.50*	12.90*	3.11	8.38	8.39	14.60	6.72	9.41
704	6.17	8.42	5.71	8.00	5.92	7.17	4.18	7.94	3.87	6.34	6.51	8.05
705	10.60*	12.80*	9.15*	12.10*	9.50*	13.00*	10.70*	12.00*	9.95*	12.80*	11.00*	12.30*
706	8.10	9.10	7.47	9.90	6.56	5.99	5.54	6.80	4.57	8.44	5.93	8.06
707	*	*	*	*	*	*	*	*	*	*	*	*
708	7.94	11.80	3.65	*	11.10*	14.40*	9.60*	14.00*	5.87	13.30	*	11.10
709	5.31	6.33	4.94	5.53	5.48	7.29	6.05	5.86	6.72	8.74	10.30	8.44
710	1.83	2.29	1.06	1.47	2.51	2.40	2.33	2.66	7.32	3.43	0.64	0.94
711	3.29	4.02	3.74	4.53	4.21	4.28	3.98	3.58	4.29	6.41	3.95	5.29
712	6.09	8.00 <	1.00*	7.50	5.38	6.92	6.00	8.33 <	1.00*	2.67	7.93	5.96
713	7.10	9.20	6.29	8.90	8.50	9.90	2.50	3.00	2.00	4.80	2.90	5.10
714	6.70	7.60	2.40	8.40	0.90	7.00	7.40	10.30	0.60	4.60	4.30	10.90
715	19.60*	17.60*	7.10	3.30	3.40	7.20	9.00	9.60	9.30	6.50	6.80	8.30
716	2.31	3.66	1.57	2.04	*	2.84	1.18*	2.76*	2.38	3.06	2.44	3.56
717	6.50	8.20	11.00	5.60	0.70	3.10	8.30	0.00*	11.00	7.30	8.60	10.40

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-3 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI NITROSAMINES*

RAW DATA FOR N-NITROSODIPHENYLAMINE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
TRUE VALUE UG/L	16.43	21.91	16.43	21.91	16.43	21.91	16.43	21.91	16.43	21.91	16.43	21.91
LABORATORY NUMBER												
701	< 3.00*<	3.00*<	3.00*	11.90	11.90 <	3.00*<	3.00*	28.80 <	13.20*	16.80 <	11.40*	4.94
702	6.36	7.29	3.82	5.28	6.57	14.10	6.15	6.28	7.14	11.20	7.38	10.70
703	8.43	22.20	15.30	13.60	19.90*	26.90*	10.60	14.90	*	25.90*	8.51	15.90
704	14.70	19.90	10.10	15.80	11.70	15.00	8.73	14.90	7.22	13.90	12.60	15.50
705	18.30*	30.80*	19.60*	30.50*	18.10*	31.30*	17.90*	29.60*	20.40*	31.10*	20.80*	29.60*
706	17.10	11.50	17.40	12.30	11.70	17.60	11.20	14.40	10.80	18.30	10.80	15.20
707	*	*	*	*	*	*	*	*	*	*	*	*
708	13.50	16.00	10.50	10.50	18.70*	27.30*	15.30*	21.00*	10.50	14.30	16.80	20.40
709	8.34	14.80	11.40	16.10	11.80	15.00	9.94	19.80	10.80	13.80	12.20	17.10
710	20.20	27.10	19.30	16.80	17.60	10.50	13.70	29.90	16.20	18.40	18.60	25.40
711	6.96	7.71	8.51	12.50	9.90	14.40	8.40	8.20	7.48	12.20	7.83	11.40
712	17.14	10.87	10.45	5.91	8.85	9.46	4.74*	11.05	5.36	11.67	7.59	15.52
713	14.80	18.30	13.35	15.40	15.80	22.20	6.30	9.00	9.10	12.00	7.40	6.70
714	13.20	15.80	12.90	16.30	1.70	20.10	13.30	11.50	5.80	7.90	14.60	26.60
715	34.00*	26.40*	9.60	10.60	13.20	14.10	11.70	15.10	18.50	14.60	16.70	22.30
716	4.30	6.66	4.57	3.03	3.26	7.44	2.32*	*	5.00	7.82	10.00	8.96
717	2.50	0.00*	11.20	21.40	6.00	8.10	15.90	0.00*	7.40	10.50	7.70	0.00*

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-3 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI NITROSAMINES*

RAW DATA FOR N-NITROSODIPHENYLAMINE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	4	5	4	6	4	6	4	6	4	6	4	6
TRUE VALUE UG/L	41.08	54.78	41.08	54.78	41.08	54.78	41.08	54.78	41.08	54.78	41.08	54.78
LABORATORY NUMBER												
701	10.10 <	3.00*	22.80	3.47 <	4.00*<	4.00*	61.20*	74.20	51.10	44.60 <	4.00*	25.20
702	20.90	19.70	13.90	23.70	19.70	28.20	19.70	25.40	11.30	23.00	13.30	36.30
703	36.00	54.20	36.80	49.70	33.60*	73.40*	30.20	47.50	51.80	48.40	40.60	52.80
704	32.80	49.70	33.50	44.00	*	43.80	32.00	47.20	22.00	35.10	25.90	28.90
705	54.00*	78.50*	54.40*	76.50*	55.00*	75.80*	55.20*	73.10*	56.30*	78.90*	55.60*	73.40*
706	38.40	25.20	36.80	31.90	26.70	24.10	18.30	42.50	20.50	38.80	30.30	43.00
707	*	*	*	*	*	*	*	*	*	*	*	*
708	42.40	38.10	36.00	38.60	46.30*	60.50*	50.10*	53.00*	42.80	67.30	33.20	14.80
709	31.00	25.30	19.50	42.70	33.20	42.70	39.90	13.10	31.30	41.10	39.40	42.50
710	7.89	14.10	9.93	13.30	7.59	15.00	10.70	19.60	13.20	17.30	7.35	16.30
711	25.40	25.40	26.50	26.30	24.70	44.10	16.00	27.00	25.60	31.10	23.10	27.70
712	34.80	44.80	33.64	12.50*	18.46*	36.54	26.33	31.33	12.00	3.33	19.31*	38.62
713	33.90	47.30	36.10	43.90	30.20	51.20	22.30	32.60	25.10	35.00	14.70	30.50
714	29.70	45.40	18.30	36.70	26.00	40.90	24.90	46.90	12.20	29.80	20.60	18.50
715	49.90*	54.80*	30.90	39.00	15.90	24.80	35.90	62.10	21.60	37.70	37.00	46.70
716	11.20	10.00	7.88	8.03	12.10	18.80	6.33*	9.56*	10.40	19.80	13.80	18.40
717	18.50	47.40	26.90	22.80	18.30	0.00*	27.00	42.00	29.70	7.00	28.80	43.70

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

APPENDIX B
NITROSAMINES
METHOD 607

1. Scope and Application

1.1 This method covers the determination of certain nitrosamines. The following parameters may be determined by this method:

Parameter	STORET No.
N-nitrosodimethylamine	34438
N-nitrosodiphenylamine	34433
N-nitrosodi-n-propylamine	34428

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

1.5 The analyst must understand that nitrosamines are known carcinogens. Utmost care must be exercised in the handling of materials

which are known or believed to contain nitrosamines.

2. Summary of Method

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Depending upon the nitrosamines being measured, a column cleanup procedure may be required. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general clean-up techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table 1.

.3.3 It is necessary to remove diphenylamine from the sample extract

prior to gas chromatography because it will interfere with the determination of N-nitrosodiphenylamine. Removal is achieved if the sample is processed completely through one of the clean-up procedures detailed in the method.

4. Apparatus and Materials

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle - amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps - Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment - Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnels - 2000 ml and 250 ml, with Teflon stopcock.

4.3 Drying column - 20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube - 10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask - 500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column - three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column - two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips - solvent extracted, approximately 10/40 mesh.

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.6 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including nitrogen-phosphorus or reductive Hall detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic column - Pyrex (approximately 300 mm long x 10 mm ID) with coarse fritted disc at bottom and Teflon stopcock (Kontes K-420540-0213 or equivalent).

4.8 Chromatographic column - Pyrex (approximately 400 mm long x 22 mm ID) with coarse fritted disc at bottom and Teflon stopcock (Kontes K-420540-0234 or equivalent).

5. Reagents

5.1 Preservatives:

5.1.1 Sodium hydroxide - (ACS) 10 N in distilled water.

5.1.2 Sulfuric acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.1.3 Sodium thiosulfate - (ACS) Granular.

5.2 Methylene chloride - Pesticide quality or equivalent.

5.3 Sodium Sulfate - (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards - Prepare stock standard solutions at a concentration of 1.00 ug/ul by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Methyl alcohol, pentane, acetone - Pesticide quality or equivalent.

5.6 Diethyl Ether - Nanograde, redistilled in glass if necessary.

5.6.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523.)

5.6.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.7 Florisil - PR grade (60/100 mesh); purchase activated at 1250°F and store in dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 hours at 130°C in a foil covered glass container.

5.8 Alumina - Activity Super I, Basic, W200 series (ICN Life Sciences Group, No. 404571).

5.9 Hydrochloric acid, 10%-(ACS) Add one volume of conc. HCl to nine volumes distilled water.

6. Calibration

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 ug/l in the final extract, for example, prepare standards at 10 ug/l, 50 ug/l, 100 ug/l, 500 ug/l, etc. so that injections of 1-5 ul of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. Quality Control

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method

blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. Sample Collection, Preservation, and Handling

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they must be preserved as follows:

8.2.1 Add 35 mg of sodium thiosulfate per part per million of free chlorine per liter of sample.

8.2.2 Adjust the pH of the water sample to pH 7 to 10 using sodium hydroxide or sulfuric acid. Record the volume of acid or base added.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. Sample Extraction

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 7 to 10 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-ml separatory funnel.

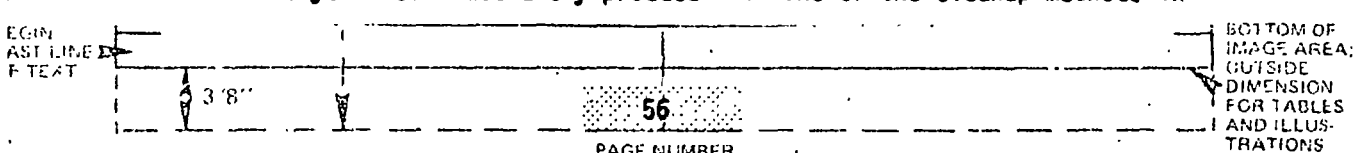
9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the 250-ml separatory funnel.

9.4 Perform a third extraction in the same manner. Add 10 ml of 10% HCl solution to the combined extracts and shake for 2 minutes. Allow the layers to separate. Drain the methylene chloride layer

through a drying column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the column with 20-30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1-2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. Because of the volatility of N-nitrosodimethylamine, K-D concentration must be carefully carried out. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 ml of methylene chloride. A 5-ml syringe is recommended for this operation. Unless the entire extract will be subjected to a cleanup operation (Section 10), adjust the extract volume to 10.0 ml with methylene chloride, add stopper, and refrigerate.

9.6 If the sample is being analyzed for N-nitrosodiphenylamine, the analyst must immediately proceed with one of the cleanup methods in



Section 10 to remove potential diphenylamine interference. Depending upon the sensitivity requirement for the analysis, the analyst may use the entire extract for this cleanup as described, or adjust the extract volume to 10.0 ml with methylene chloride and pipet a 2 ml aliquot onto the column in 10.2.2 or 10.3.3.

9.7 If N-nitrosodiphenylamine is of no interest, the analyst must choose between proceeding directly to Section II, or submitting the extract to a cleanup procedure before gas chromatography. A solvent exchange from methylene chloride to methyl alcohol is required for direct gas chromatography. Once the entire extract is in methyl alcohol it cannot be treated to either of the cleanup procedures in Section 10. Therefore, in the absence of previous experience with the sample matrix, the analyst should remove a 2.0 ml aliquot of the extract for gas chromatography and retain the remainder for cleanup if required later.

9.8 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. Cleanup and Separation

10.1 If the entire extract is to be cleaned up by one of the following procedures, it must be concentrated to 2.0 ml. To the concentrator tube in 9.5, add a clean boiling chip and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 ml methylene chloride to the top. Place the K-D apparatus on a steaming hot (60-65°C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical

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position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches about 0.5 ml, remove the K-D and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 ml of methylene chloride. Adjust the final volume to 2.0 ml and proceed with one of the following cleanup procedures.

10.2 Florisil Column Cleanup for Nitrosamines

10.2.1 Place 22g of activated Florisil in a 22 mm ID chromatographic column. After settling the Florisil by tapping the column, add about a 5 mm layer of anhydrous granular sodium sulfate to the top.

10.2.2 Preelute the column, after cooling, with 40 ml of 15% ethyl ether/85% pentane. Discard the eluate and just prior to exposure of the sodium sulfate layer to air, quantitatively transfer 2.0 ml of sample extract into the column by decantation using an additional 2 ml of pentane to complete the transfer.

10.2.3 Perform the first elution with 90 ml of 15% ethyl ether/85% pentane (V/V) and discard the eluate. This fraction will contain any diphenylamine.

10.2.4 Perform the second elution with 100 ml of 5% acetone/95% ethyl ether (V/V) and collect the eluate in a 500-ml K-D flask equipped with a 10-ml concentrator tube. This

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fraction will contain all of the nitrosamines.

10.2.5 Add 15 ml of methanol to the collected eluate and concentrate as in 9.5 at 70-75°C, substituting pentane for methylene chloride.

10.2.6 Analyze by gas chromatography.

10.3 Alumina Column Cleanup for Nitrosamines

10.3.1 Place 100g of alumina, as it comes from the manufacturer, into a 500 ml reagent bottle and add 2 ml of distilled water, which is free of nitrosamines and interferences. Mix the alumina preparation thoroughly by shaking or rolling for 10 minutes and let it stand for at least 2 hours. The preparation should be homogeneous before use. Keep the bottle sealed tightly to ensure proper activity.

10.3.2 Place 12 grams of the alumina preparation into a 10 mm ID chromatographic column and tap the column to settle the alumina. Add 1-2 cm of anhydrous sodium sulfate to the top of the alumina.

10.3.3 Preelute the column with 10 ml of 30% ethyl ether/70% pentane (V/V). Discard the eluate (about 2 ml) and, just prior to exposure of the sodium sulfate layer the air, transfer 2.0 ml of sample extract onto the column by decantation using an additional 2 ml of pentane to complete the transfer.

10.3.4 Just prior to exposure of the sodium sulfate layer to the air, add 70 ml of 30% ethyl ether/70% pentane. Discard the first 10 ml of eluate but collect the rest of the eluate in

a 500-ml K-D flask equipped with a 10 ml concentrator tube. This fraction contains N-nitrosodiphenylamine and probably a small amount of N-nitrosodi-n-propylamine.

10.3.5 Next elute the column with 60 ml of 50% ethyl ether/50% pentane, collecting the eluate in a second K-D flask equipped with a 10 ml concentrator tube. Add 15 ml methyl alcohol to the K-D. This fraction will contain N-nitrosodimethylamine, most of the N-nitrosodi-n-propylamine and any diphenylamine.

10.3.6 Concentrate both fractions as in 9.5 substituting pentane for methylene chloride.

10.3.7 Analyze by gas chromatography.

11. Gas Chromatography

11.1 N-nitrosodiphenylamine completely reacts to form diphenylamine at normal operating temperatures of the GC injection port. Therefore, N-nitrosodiphenylamine is actually chromatographed and detected as diphenylamine. The determination of either of the compounds in the original sample would be uncertain without the use of one of the previous cleanup procedures which separate the two compounds.

11.2 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by the primary column are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of

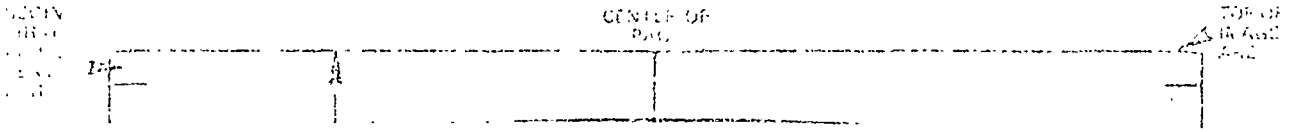
calibration standards.

11.3 If the extract has not been submitted to one of the cleanup procedures in Section 10, it is necessary to exchange the solvent from methylene chloride to methyl alcohol before the thermionic detector can be used. To a 1-10 ml volume of methylene chloride extract in a concentrrator tube, add 2 ml methyl alcohol, and a clean boiling chip. Attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 ml methylene chloride through the top. Place the K-D apparatus on a boiling water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position and insulate the apparatus as necessary to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches about 0.5 ml, remove the K-D and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 ml of methyl alcohol. Adjust the final volume to 2.0 ml.

11.4 Inject 2-5 ul of the sample extract using the solvent-flush technique. Smaller (1.0 ul) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 ul, and the resulting peak size, in area units.

11.5 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.6 If the peak area measurement is prevented by the presence of



interferences, further cleanup is required.

12. Calculations

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, ug/l} = \frac{(A)\ (B)\ (V_t)}{(V_1)\ \ (V_s)}$$

where A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_1 = volume of extract injected (ul)

V_t = Volume of total extract (ul)

V_s = Volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. Accuracy and Precision

The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratroy method study to determine the accuracy and precision of this test procedure.

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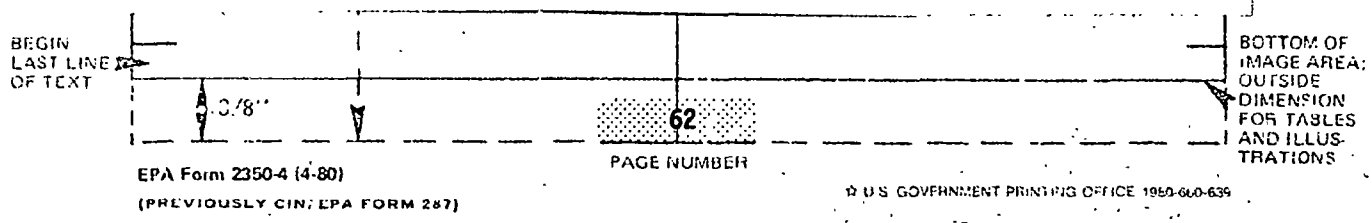

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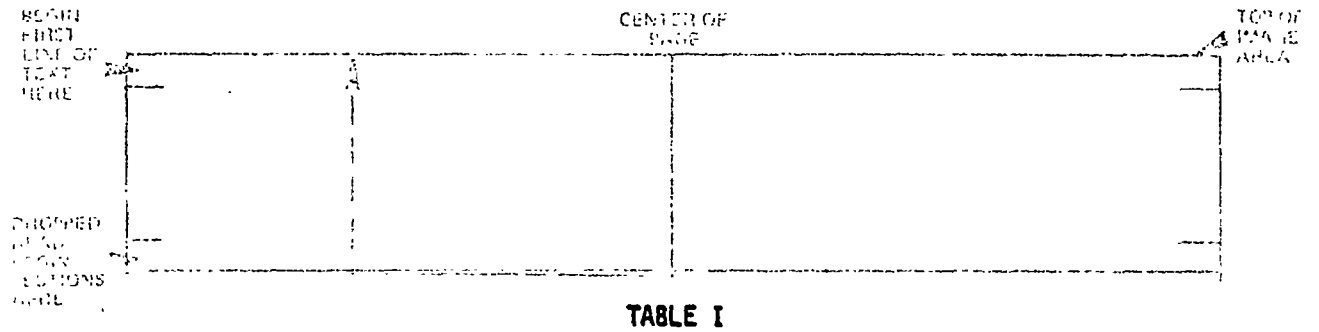


TABLE I

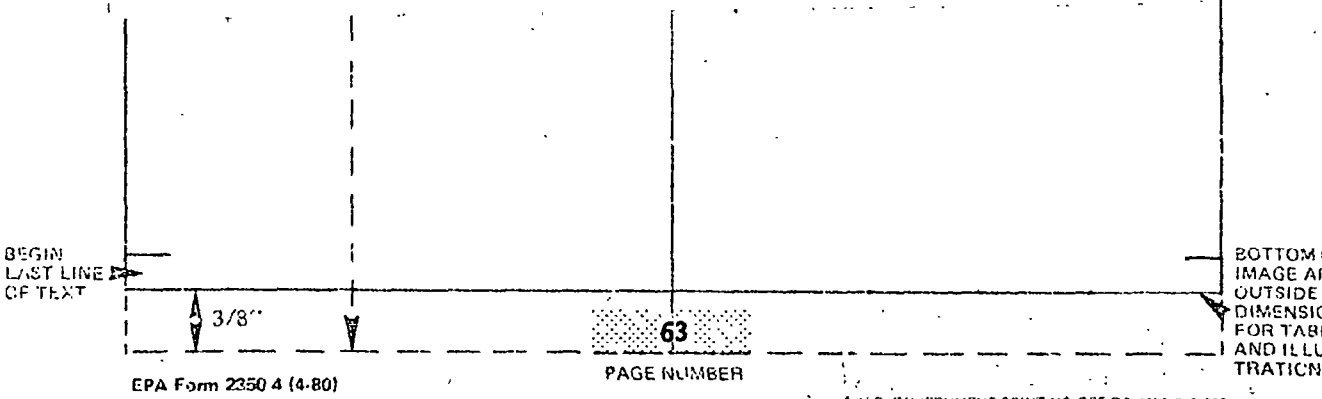
GAS CHROMATOGRAPHY OF NITROSAMINES

Nitrosamine	Retention Time (min.) Column 1	Column 2	Detection Limit (ug/l)
N-nitrosodidimethylamine	4.1	0.88	0.3
N-nitrosodi-n-dipropylamine	12.1	4.2	0.5
N-nitrosodidiphenylamine	12.8*	6.4**	1.0

Column 1 conditions: Chromosorb WAW 80/100 mesh coated with 10% Carbowax 20M/2% KOH packed in a 180 cm long x 4 mm ID glass column with helium carrier gas at 40 ml/min flow rate. Isothermal column temperature is 110°C except where * indicates 220°C.

Column 2 conditions: Supelcoport 100/120 mesh coated with 10% SP-2250 packed in a 180 cm long x 4 mm ID glass column with helium carrier gas at 40 ml/min flow rate. Isothermal column temperature is 120°C except where ** indicates 210°C.

Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters. A nitrogen-phosphorus detector was used to collect this data, but a Thermal Energy Analyzer exhibited equivalent sensitivity.



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FLOPPED DISK FIELD SECTIONS HERE

COLUMN: 10% CARBOWAX 20M + 2% KOH ON CHROMOSORB W-AW
TEMPERATURE: 110°
DETECTOR: PHOSPHORUS/NITROGEN

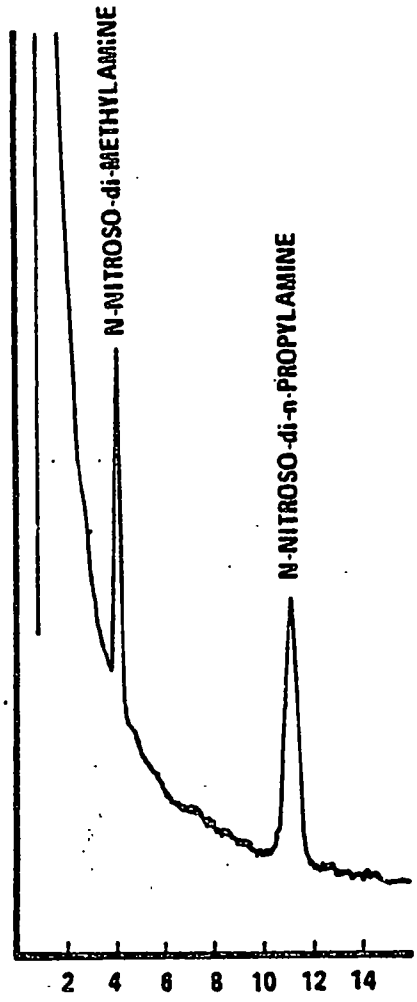

Figure 1. Gas chromatogram of nitrosamines

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DROPPED HEAD, MAIN SECTIONS ONLY

COLUMN: 10% CARBOWAX 20M + 2% KOH ON CHROMOSORB W-AW
TEMPERATURE: 220°C.
DETECTOR: PHOSPHORUS/NITROGEN

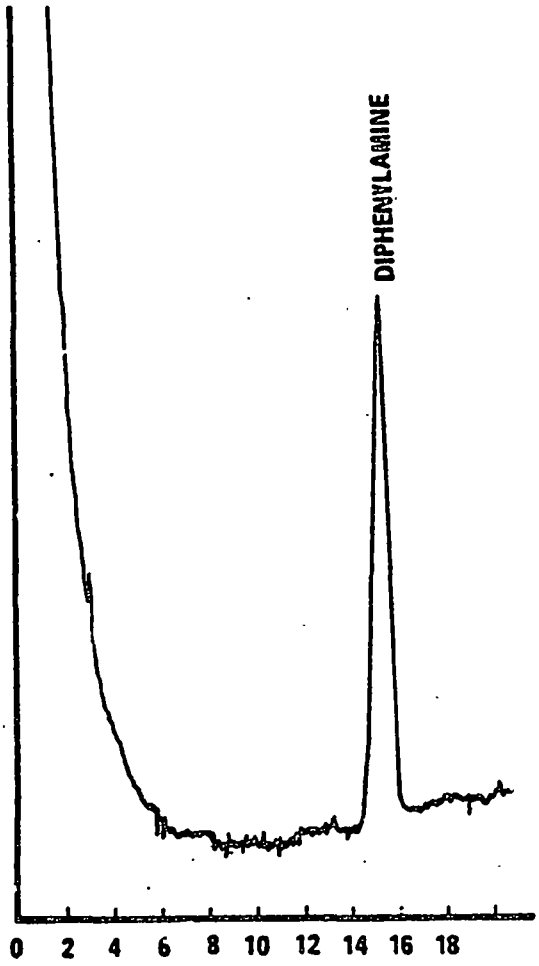

Figure 2. Gas chromatogram of N-nitrosodiphenylamine as diphenylamine

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