Designation: D 4983 – 89 (Reapproved 1996)

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Test Method for Cyclohexylamine, Morpholine, and Diethylaminoethanol in Water and Condensed Steam by Direct Aqueous Injection Gas Chromatography[1]

This standard is issued under the fixed designation D 4983; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the general considerations for the qualitative and quantitative determination of volatile amines such as cyclohexylamine, morpholine, and diethylaminoethanol in steam condensates and surface water by gas-liquid chromatography.[2,3]

1.2 This test method may be applied to water samples containing the amines in concentrations from 2 to 15 mg/L by direct injection of alkaline aqueous samples. Higher concentrations may be determined by appropriate dilution.

1.3 Although this test method is written for flame ionization detector, the basic technology is applicable to any highly sensitive nitrogen-specific detector provided water does not interfere with the measurement.

1.4 The test method may be extended to steam condensates containing low levels of these amines by adopting suitable concentration techniques such as steam distillation to bring the analyte concentration to an accurately quantifiable range.

1.5 The test method is applicable to other chromatographable amines by appropriately varying the chromatographic parameters. This must be validated by the individual analysts.

1.6 This test method has been used successfully with reagent-grade and boiler steam condensate waters. It is the user's responsibility to assure the validity of this test method for any untested matrices.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam [4]

D 1129 Terminology Relating to Water [4]

D 1193 Specification for Reagent Water [4]

D 2777 Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water [4]

D 2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography [5]

D 3370 Practices for Sampling Water from Closed Conduits [4]

E 355 Practice for Gas Chromatography Terms and Relationships [6]

3. Terminology

3.1 *Descriptions of Terms Specific to This Test Method:*

3.1.1 *vapor phase inhibitors*—a class of paraffinic, alicyclic, or heterocyclic, neutralizing amines that co-distill with steam and are carried throughout the distribution system in order to react with carbonic acid present in the system.

3.2 *Definitions*—For definitions of other terms used in this test method, refer to Terminology D 1129 and Practice E 355.

4. Summary of Test Method

4.1 The sample is preserved by adjusting the pH to 3.0 by addition of phosphate solutions. Prior to analysis the pH is raised to >10.0. After centrifugation, the sample is analyzed by direct aqueous injection gas chromatography using an alkaline polyethylene glycol liquid phase and a flame-ionization detector.

4.2 When high levels of these amines (>15 mg/L) are found in water samples, positive identification of the component(s) is required by supplemental testing, such as the use of different gas chromatographic column packings; a nitrogen-specific detector, derivatization, mass spectrometry, or a combination of these techniques should also be used.

4.3 In this test method, the elution profile of the subject amines occurs in the order: morpholine, cyclohexylamine, and diethylaminoethanol. (Refer to the chromatogram in Fig. 1.)

5. Significance and Use

5.1 Vapor phase inhibitors such as morpholine, cyclohexylamine, and diethylaminoethanol are added to water to reduce corrosion in steam-generating and distribution systems by

---

[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

Current edition approved Nov. 10, 1989. Published March 1990.

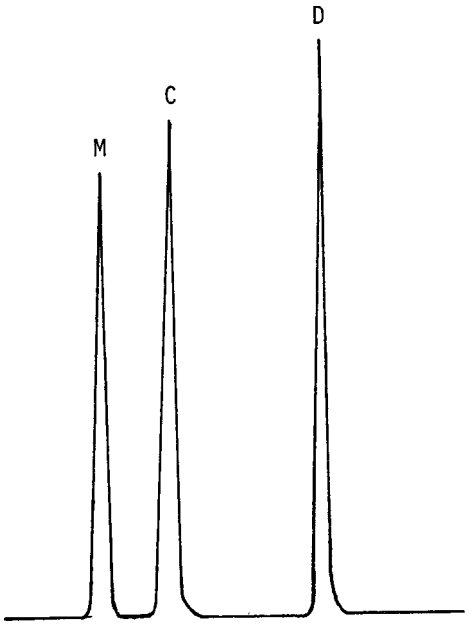
[2] Di Corcia, A., and Samperi, R., *Analytical Chemistry*, Vol 46, 1974, p. 977.

[3] (*a*) Supelco Inc. (Bellefonte, PA 16823) Bulletin 737B Copyright 1973. (*b*) Supelco Inc. (Bellefonte, PA 16823) Bulletin 738B Copyright 1976.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 11.02.

[6] *Annual Book of ASTM Standards*, Vol 14.02.



Conditions of Analysis:
Column: 1800 by 3.2-mm ID U-tube packed with Carbopack B (60 to 80 mesh) coated with 4.8 % PEG 20M + 0.4 % KOH
Column Temperature: 125 to 180°C programmed at 4°C/min with the initial hold of 5 min
Injection Port Temperature: 250°C
Detector Temperature: 260°C
Electrometer: 4 × 10; bucking range 10^{-10} A full scale
Sample Size: 5 µL
Carrier Gas: helium; flow rate: 15 mL/min

FIG. 1 Analysis of a Mixture of Morpholine (M), Cyclohexylamine (C), and Diethylaminoethanol (D) in an Aqueous Sample

neutralizing acids like carbonic acid. High concentrations of these amines must be avoided because, under these conditions, protective metallic oxide coatings on surfaces may slough off very rapidly, thereby affecting the corrosion inhibition occurring in the system. This test method is used to monitor the concentration of amines in steam condensates so that optimum level of these corrosion-inhibiting, neutralizing amines can be properly maintained.

5.2 In institutions such as hospitals, centrally generated steam is used for air humidification, medical supply sterilization and food preparations. Since volatile amines co-distill with steam and are carried throughout the distribution system, there is concern that these compounds, which have been shown to be toxic[7,8] to a variety of animal species, may prove to be hazardous, especially in critical areas such as operating rooms, nurseries, delivery rooms, and intensive care units. Further, there is also concern that morpholine-laden steam, when used in cooking, may react with the nitrite in the foodstuffs to form nitrosamines which are potent animal carcinogens. This test method may be used in such situations to monitor the levels of these amines in centrally generated steam.

6. Interferences

6.1 *Inorganic Cations Capable of Complexing with Amines*:

6.1.1 *Particulate Matter*—Usually oxides from metal surfaces and other solid impurities may remain in the sample as particulate or suspended matter and therefore must be removed without the loss of analyte. This is accomplished generally by centrifugation. This pretreatment is essential to prevent plugging of syringes. Acidification often facilitates dissolution of particulates. The pH should be lowered approximately to 3.0, and under this condition the amines of interest are generally unaffected.

6.1.2 Varying amounts of polyvalent metal ions, specifically ferric cations, present in the sample may likely chelate or complex with the amines. This prevents quantitative elution of the amines from the column. Prior to the analytical step, since the sample may have a pH greater than 10.0, the ferric hydroxide formed will entrap varying amounts of the amines. This will cause irreproducible results, produce nonuniform injection by fouling the microsyringe, and contaminate the glass liner of the injection port of the gas chromatograph. Therefore, after sampling, sufficient volumes of phosphate solution (8.7.1) and phosphoric acid solution (8.7.2) must be added to the sample in order to lower the pH to between 3 and 4 (pH test paper). The sample is then centrifuged to pelletize the insoluble particulates before preservation.

6.2 *Identical Retention Times*:

6.2.1 *Neutral and Basic Organic Compounds*—With any given gas chromatographic column and operating parameters, one or more components may have identical retention times under the sample elution conditions. Thus, a chromatographic peak is only presumptive evidence of a single component. Confirmation requires periodic analysis of boiler-feed water or condensed steam before amine formulations are added for background information. In addition, analysis using other gas chromatographic packings with varying physical and chemical properties may be used to confirm the identity of the peaks. When high levels of amines (>15 mg/L) are found, the components should be characterized and quantified by GC-MS either in their native forms or as their trifluoroacetyl [9] or pentafluoropropionyl [10] derivatives.

6.3 *Acidic Organic Compounds*—Before analysis when the sample is brought approximately to pH >10, components such as organic and inorganic acids, phenolic compounds, etc., are converted to their respective salts. The solution containing these salts is then flash-evaporated onto the inner walls of the glass liner in the injection port. If the salt build-up is very high, the amines may be irreversibly adsorbed or decomposed by the salts at high temperatures.

NOTE 1—Glass liners in the injection port are recommended. These inserts are easy to clean or replace, and minimize cleanup difficulties, repacking of columns, and loss of costly packings.

6.4 *Ghosting*—Ghosting is evidenced by an interference

[7] Environmental Health Directorate Report No. 79-EHD-39, October 1979, Information Services, Dept. of National Health and Welfare, Brooke Claxton Bldg., Ottawa, Canada, K1A OL2.

[8] Malaiyandi, M., Thomas, G. H., and Meek, M. E., *Journal of Environmental Science*, Health, Part A, Vol 14, 1979, and the references thereof.

[9] Gehrke, C. W., Kuo, K. C., Zumwalt, R. W., and Waalkes, T. P.," Polyamines in Normal and Neoplastic Growth,'' edited by D. H. Russell, Raven Press, New York, 1973, pp. 343–353.

[10] Rattenburg, J. M., Lax, P. M., Blau, K., and Sander, M., *Clinica Chimica Acta*, Vol 95, 1979, pp. 61–67.

peak that occurs at the same retention time as that of the component of interest or was carried from previous analyses, or both. Ghost peaks may persist because of organic sorption in the gas chromatographic train. Repeated injections with 5 µL of water between every sample and standard run will usually eliminate ghosting problems. This should be done while maintaining the detector at its maximum sensitivity. If interferences persist, it is necessary to repeat 5-µL water injections after increasing the injection port temperature and also to leave the cleaned injector at that temperature overnight or to change the glass inserts in the injection port.

6.5 *Delayed Elution*—High-boiling contaminants in the sample may unpredictably elute several chromatograms later and therefore act as interferences. This is particularly true with boiler waters that are fed with reclaimed, industrial waste waters. A combination of repeated water injections at elevated column temperature (maximum 210°C) and leaving the column overnight at this temperature may eliminate this problem. Back flush valves should be used if this problem is frequently encountered.

7. Apparatus

7.1 *General*:

7.1.1 *Bottles*, amber-colored, 125-mL, made of borosilicate glass for sample collection. These bottles are treated in sequence with approximately 10 % (w/v) aqueous NaOH solution, aqueous hydrochloric acid (1 + 1, v/v), rinsed several times with reagent water, and stoppered with TFE-fluorocarbon-laminated silicone septa and screw caps.

7.1.2 *Centrifuge Tubes*, 10 and 40-mL heavy-duty, graduated centrifuge tubes made of borosilicate glass. These tubes are cleaned using the same procedure as described for cleaning amber-colored bottles. The 15-mL polyethylene centrifuge tubes should be cleaned twice with water.

7.1.3 *Centrifuge*, bench top model with a maximum of 3000 r/min.

7.1.4 *Pipet*, 10-mL.

7.1.5 *Microsyringe*, 10 and 500-µL.

7.1.6 *Volumetric Flasks*, glass-stoppered, 100- and 1000-mL.

7.2 *Gas Chromatographic Equipment*:

7.2.1 *Analytical Gas Chromatograph*—A gas chromatograph provided with a temperature programmable column oven (50 to 250°C). A unit equipped for temperature programming will facilitate elution of high-boiling volatile amines.

7.2.2 *Injection Port Glass Inserts*—A 2-mm inside diameter glass liner, loosely packed with a 10-mm wad of silanized, ammonium hydroxide-washed glass wool at the tip facing the packing. Since aqueous alkaline samples are analyzed, solid materials will, in time, accumulate in the glass liner which can be replaced and cleaned for future use. This device prolongs the life of the costly chromatographic packing in the column.

7.3 *Gas Chromatographic Column*:

7.3.1 *Column Material and Dimensions*—The column should be constructed of borosilicate glass. Recommended dimensions are 1800 by 2 mm inside diameter. However, the column portion inserted into the injection port should be 150 by 4 mm inside diameter. The chromatographic packing in the 2-mm inside diameter tubing is retained by using silanized, ammonium hydroxide-washed glass wool.

7.3.2 *Column Preparation*—A properly prepared column is important to a precise chromatographic analysis. The column packings may preferably be obtained from commercial sources. Pack coiled glass columns with a gentle uniform vibration or tapping of the column starting from the silanized, glass wool-plugged detector end and slowly moving up to the injection end where the packing is poured. Rotate the column in the same direction every time. Carry out this operation along the full length of the column. Repeat vibration or tapping operation several times and terminate when no more than 2 mm of the level of the packing is lowered. When a U-tube column is used, charge the packing into the column with a mild vacuum at the silanized glass wool-plugged detector end of the column. Increase the suction periodically such that the packing is held firmly and coherently in the upright portion of the column. As in the previous case, use gentle vibration or tapping during packing of the column. When the column is packed, plug loosely the injection end with silanized glass wool. A U-tube column is recommended for easy packing.

NOTE 2—Care should be exercised so as not to crush the packing material by vibration; at the same time, the packing should not be so compact as to cause unnecessary back pressure and not so loose as to create voids during use at high temperatures.

NOTE 3—At the injection end, the glass wool is fitted into the 2-mm portion of the column to a length of 5 mm and with a loose wad occupying about 5 mm of the 4-mm inside diameter portion of the column. The packing is done in such a way so that the injection needle should never touch the packing.

7.3.3 *Column Conditioning*—Proper thermal conditioning is essential to eliminate column bleed so as to obtain acceptable gas chromatographic analyses. Connect the column in the oven only when the instrument is in operation, and connect the detector to an auxiliary carrier gas line with a gas flow of 25 mL/min. Condition the column for 1-h periods at 100, 125, 150, and 175°C and then hold for 4 h at 210°C, ensuring a carrier gas flow of 25 mL/min and the injection port temperature at 250°C. Raise the oven temperature to 220°C and leave at this temperature for 24 h. Attach the conditioned column to the detector and lower the oven temperature to 180°C until the instrument is ready for use.

NOTE 4—During operation, the column oven temperature should never exceed 210°C after conditioning.

7.4 *Recorder*—A 1-mV, full-scale response, strip chart recorder is recommended to obtain a permanent chromatogram; chart speeds should be adjustable between 5 and 20 mm/min. Determine the amount of analyte present in the sample by comparing the peak areas for the sample with those of appropriate standard.

NOTE 5—The peak areas are measured using an electronic integrating system or any suitable alternative device.

7.5 *Operating Conditions*—The recommended operating parameters of the gas chromatograph for the separation and quantification of volatile amines are as follows:

Carrier gas—helium at a flow rate of 15 to 40 mL/min
Initial oven temperature—125°C
Temperature programming 125 to 180°C at 4°C/min after initial hold of 5 min
Injection port temperature—250°C

Detector temperature—260°C
Sample size—5 µL.
Electrometer—8×10^{-12} A full scale (AFS).
If the GC is provided with an electrometer of 10^{-10} AFS, use µg/µL standards for calibration.

7.6 *Sampling Equipment*—The equipment for sampling steam and water is described in Practices D 3370. In most instances a single port-nozzle valve is recommended.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. These reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available. [11]

8.2 *Purity of Water*—Except as otherwise indicated, references to water shall be understood to mean water conforming to Specification D 1193, Type II. Additionally, the water shall be free of the interferences described in Section 6 and free of carbon dioxide.

8.3 *Amine Standards*, purity 99 %.

8.3.1 *Cyclohexylamine Solution, Standard* (1 mL = 0.1 mg of cyclohexylamine)—Prepare a stock solution by weighing 100 mg of cyclohexylamine in a weighing bottle, transferring the material to about 800 mL of water containing 8 mL of phosphate solution (8.7.1) and 2.0 mL of phosphoric acid solution (8.7.2), and diluting the solution to 1 L with water. Prepare four standard solutions by diluting appropriate volumes of the stock solution to 100 mL with water as in 11.1.

8.3.2 *Morpholine Solution, Standard* (1 mL = 0.1 mg of morpholine)—As described in 8.3.1, prepare the stock and standard solutions using morpholine instead of cyclohexylamine.

8.3.3 *Diethylaminoethanol Solution, Standard* (1 mL = 0.1 mg of diethylaminoethanol)—As described in 8.3.1, prepare the stock and standard solutions using diethylaminoethanol instead of cyclohexylamine.

8.4 *Ammonium Hydroxide Solution* (1 + 1)—Mix 1 volume of ammonium hydroxide (sp gr 0.90) with 1 volume of water.

8.5 *Barium Hydroxide Solution, Carbonate-Free*—Dissolve 10.5 g of barium hydroxide crystals ($Ba(OH)_2 \cdot 8H_2O$) in 100 mL of boiling water, cool, and store in a polyethylene bottle.

NOTE 6—Carbon dioxide-free water may be obtained by boiling for about 30 min and then cooling using an Ascarite tube before use.

8.6 *Gas Chromatographic Materials*:

8.6.1 *Column Packing*—Graphitized carbon (60 to 80 mesh) coated with 4.8 % polyethylene glycol 20M + 0.4 % KOH. [12]

8.6.2 *Glass Wool*, silanized, washed with ammonium hydroxide (1 + 1) and rinsed sequentially with water and acetone and then dried at 100°C.

8.6.3 *Carrier Gas*—Ultra-high-purity helium gas containing less than 1 ppm of carbon dioxide and oxygen.

8.6.4 *Hydrogen and Air*—For use with flame ionization detector, high-purity, filtered hydrogen and filtered air are recommended.

8.7 *Phosphate Solutions*:

8.7.1 *Phosphate Solution* (approximately 1 *M*)—Dissolve 33.8 g of potassium dihydrogen phosphate (KH_2PO_4) in 250 mL of water.

8.7.2 *Phosphoric Acid Solution* (1 + 1)—Dilute 1 volume of orthophosphoric acid (85 %) with 1 volume of water.

8.8 *Potassium Hydroxide Solution, Carbonate-Free*—(approximately 12 *M*)—Dissolve 168.5 g of potassium hydroxide pellets in water, dilute to 250 mL, and store in a polyethylene bottle. Prior to analysis, pour 10 mL of the alkali solution in a 15-mL polyethylene centrifuge tube and add 1 mL of barium hydroxide solution (8.5). After shaking, centrifuge at 3000 r/min to pelletize the barium carbonate. Use the resulting clear supernatant alkaline solution in the analyses.

9. Sampling and Preservation

9.1 Collect the water samples in accordance with Practice D 1066, Practices D 3370, and Practice D 2908, as applicable.

9.2 *Sampling Procedure for Steam*—Prior to sampling condensed steam, open the valve leading to the sample nozzle for a maximum rate of flow of steam, during which time the cooling water surrounding the condensing coil is drained. This will remove any material that might have previously deposited in the lines. When the actual sampling is carried out, cool the condensing coil with running cold water. After rinsing the bottle twice with approximately 10 mL of condensed water, collect 115 ± 5 mL of the sample in amber glass bottles. Immediately after the samples are collected, treat with approximately 1 mL of phosphate solution (8.7.1) followed by the addition of a few drops of phosphoric acid solution (8.7.2) to bring the pH approximately to 3. Stopper the containers tightly with TFE-fluorocarbon-laminated silicone septa [13] and with screw caps. Centrifuge the samples using 40-mL heavy-duty borosilicate glass centrifuge tubes at 3000 r/min for about 15 min to pelletize the particulates. Transfer 10-mL aliquots of the supernatant liquid into rinsed 1 0-mL centrifuge tubes.

9.3 Store the samples and standards at 4 to 6°C at all times prior to analysis.

10. Preparation of Gas Chromatograph

10.1 Before using the column, inject fifteen 5.0-µL volumes of ammonium hydroxide solution (1 + 1) followed by fifteen 5-µL volumes of CO_2-free water in quick succession at the conditioning temperature. After 10 min reduce the oven temperature to the operating temperature and immediately replace the septum with an unused, preconditioned one.

NOTE 7—Ammonium hydroxide solution and water injections at 220°C must be carried out when the column has been left unused for a few days or when the column behaves erratically in its resolution and in quantification of the components.

[11] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[12] Carbowax 20M-coated Carbopack B, available from Supelco Inc., Bellefonte, PA 16823, has been found suitable for this application.

[13] 12722 Septa available from Pierce Chemical Co., P.O. Box 117, Rockford, IL 61105, have been found suitable for this application.

10.2 Adjust the hydrogen flow to the detector to about 25 mL/min, and provide sufficient air flow to ignite the gas. Adjust the hydrogen and air flows as specified in the instrument manual to obtain maximum sensitivity of the detector and to maintain a steady flame during the injection of the 5.0-µL aqueous sample.

10.3 Lower the oven temperature to 125°C and adjust the carrier gas flow rate to between 15 and 40 mL/min to obtain proper resolution of the components in reasonable time. When the recorder baseline is no longer drifting, the column is ready for use.

10.4 When a series of analyses are completed for the day, raise the oven temperature to 200°C and leave overnight with the hydrogen and air turned off.

10.5 When the amine analysis is completed and the column is to be stored, bring the column to ambient temperature. After disconnecting the column, cap the ends.

11. Calibration and Standardization

11.1 *Working Standards*—Prepare standards of individual compounds and the working standards on the previous day before analysis. Determine their retention times using individual standards. For calibration purposes, prepare solutions of three amines in the concentration range between 1 and 15 mg/L in 100-mL volumetric flasks (8.3.1). Pipet 10-mL aliquots of the amine working standard solutions into 10-mL borosilicate glass centrifuge tubes. After capping with TFE-fluorocarbon-laminated septa and aluminum sealing caps, add 100 to 300 µL of carbonate-free potassium hydroxide solution (8.8) to bring to pH >10. Shake vigorously and centrifuge at 3000 r/min for 15 min.

NOTE 8—The microsyringe used for transferring the alkaline solution must be immediately rinsed twice with hydrochloric acid (1 + 1) and several times with water.

11.2 With the column at an equilibrated condition, inject 5 µL of the working standard amine solution. After a 5-min initial hold, program the oven temperature from 125 to 180°C at 4°C/min. Adjust the attenuation in all cases to keep the peak height on-scale. Rinse the syringe once with hydrochloric acid (1 + 1) and rinse several times with CO_2-free water to remove acid from the syringe.

11.3 When an analysis is complete, inject two 5.0-µL volumes of CO_2-free water at 180°C prior to bringing the column oven temperature down to 125°C for the next analysis.

11.4 Measure the peak area for each amine standard in the particular standards. This may be done accurately using an electronic integrator. Repeat analysis of standard solutions until no more than ±5 % error (relative error) in the area is noted for each component in three consecutive runs. Construct working curves for individual amines using peak area vs concentration, if necessary.

NOTE 9—Measurement using areas is preferable to peak heights because tail broadening causes errors in measurement due to asymmetry.

12. Procedure

12.1 Bring the stored samples (9.3) to room temperature and raise their pH to >10.0 as in 11.1 with 100 to 300 µL of carbonate-free potassium hydroxide solution (8.8). Shake vigorously and centrifuge at 3000 r/min for 15 min. With the column at operating conditions (7.5), inject 5.0 µL of sample onto the column.

12.2 Determine the retention times of amines in question.

12.3 If necessary, choose the volume of injection or the attenuation, preferably the former, to keep the highest peak on-scale for the major component in the sample.

12.4 Perform determinations at identical column conditions to standards. Inject 5.0 µL of CO_2-free water as in 11.3 between each analysis and intersperse an appropriate working standard between runs of each sample.

12.5 Measure the peak areas obtained for each individual amine.

13. Calculation

13.1 If there are two or more amines present in the sample, use the appropriate working standard value in the calculation. Label each peak area of the amine in the sample corresponding to the one in the standard.

13.2 If the level of any specific amine is high, confirmation of its identity by means of gas chromatography/mass spectrometry is recommended.

13.3 Calculate the amount of amine present as follows:

$$\text{Amine, mg/L} = (A_1/A_2) \times C \times (V_2/V_1)$$

where:

A_1 = area of sample,
A_2 = area of standard,
C = concentration of standard injected, mg/L,
V_1 = volume of sample, and
V_2 = volume of standard.

14. Precision and Bias [14]

14.1 The results may be reported in milligrams per litre or in other units as desired; the units must, however, be clearly noted in the report. The results reported herein follow Practice D 2777 as closely as possible. For morpholine and cyclohexylamine, nearly 80 data points were obtained, whereas for diethylaminoethanol, 60 data points were received.

14.1.1 Morpholine, cyclohexylamine, and diethylaminoethanol recovery studies from aqueous samples at levels ranging from 0.0 to 3.0 mg/L were performed by six laboratories using six different known levels of the three analytes. There were two to five replicate observations made by each laboratory by analyte combinations.

14.1.2 Although six laboratories furnished complete sets of data, only five laboratories produced usable data. Efforts to obtain more laboratory participation in the round-robin study failed. On January 13, 1988, the Technical Operations Subcommittee on the recommendation of the Results Advisor approved an exception to the Practice D 2777 – 86 requirement of six laboratories. This action was upheld by the executive subcommittee. Within five years, data from a sixth laboratory should be obtained and the precision and bias will be recalculated.

[14] Supporting data for the precision and bias statements are available from ASTM Headquarters, 100 Barr Harbor Dr., West Conshohocken, PA 19428. Request RR: D-19-1137.

NOTE 10—Among the six laboratories, one was an outlier for all three analytes and it provided very little information on the use of the procedure.

Two sample mixtures contained the same amounts of analytes except that 50 ppm or iron salts were added to one of the sample mixtures to verify the influence of iron salts on the recovery and precision and bias. The iron salts were added to the sample mixture prior to sub-sampling into containers before shipping the sample to participating laboratories.

It is noteworthy that when iron salts were present in the matrix, the overall precision and bias varied. It is therefore the user's responsibility to estimate the validity of the test method and hence the precision and bias. Further, it should be pointed out that this test method has been successfully employed to monitor amines in steam condensates from boilers in health care facilities with good reproducibility (see [7] and [8]).

14.1.3 The precision statements derived from the interlaboratory study are based on the results from spiked deionized, distilled water prepared, and sub-sampled in the laboratory.

14.2 *Precision:* The overall and single operator precision for morpholine, cyclohexylamine, and diethylaminoethanol were found to vary as shown in Table 1.

14.3 *Bias:* The recoveries of known amounts of morpholine, cyclohexylamine and diethylaminoethanol are shown in Table 1. The bias is mainly negative for all three analytes studied. Figs. 2-4 show a linear relationship between the amount of analyte recovered versus the amount added.

TABLE 1 Precision and Bias of Test Method D 4983

Sample Number	Amount Added, mg/L	Amount Found, mg/L	S_o, mg/L	S_o,%	S_t, mg/L	S_t, %	Bias, mg/L	Bias,%	Statistically Significant at 95 % Confidence Level
Morpholine:									
1	0.500	0.456	0.038	7.6	0.062	12.4	−0.044	−8.8	yes
2	1.001	0.977	0.047	4.7	0.063	6.3	− 0.024	−2.4	no
3	1.501	1.339	0.187	12.5	0.173	11.5	− 0.162	− 10.8	yes
4	2.001	1.964	0.100	5.0	0.176	8.8	− 0.037	−1.8	no
5	2.001 [A]	1.951	0.108	5.4	0.107	5.3	−0.050	−2.5	no
6	3.002	2.825	0.128	4.3	0.206	6.9	− 0.177	−5.9	yes
Cyclohexylamine:									
1	0.501	0.449	0.068	13.6	0.097	19.4	−0.052	−10.4	no
2	1.001	1.004	0.049	4.9	0.086	8.6	0.003	0.3	no
3	1.502	1.447	0.056	3.7	0.089	5.9	− 0.055	−3.7	yes
4	2.002	1.917	0.080	4.0	0.158	7.9	− 0.085	−4.2	no
5	3.004	2.737	0.256	8.5	0.400	13.3	− 0.267	−8.9	yes
6	3.004 [A]	2.722	0.100	3.3	0.280	9.3	−0.282	−9.4	yes
Diethylaminoethanol:									
1	0.500 [A]	0.476	0.021	4.2	0.045	9.0	−0.024	−4.8	no
2	0.500	0.492	0.037	7.4	0.051	10.2	−0.008	−1.6	no
3	1.000	0.985	0.042	4.2	0.107	10.7	− 0.015	−1.5	no
4	1.500	1.483	0.049	3.3	0.069	4.6	− 0.017	−1.1	no
5	2.000	2.026	0.089	4.5	0.133	6.7	0.026	1.3	no
6	3.000	2.879	0.233	7.8	0.310	10.3	−0.121	−4.0	no

[A] Sample of amine mixtures contains 50 ppm of iron salts.

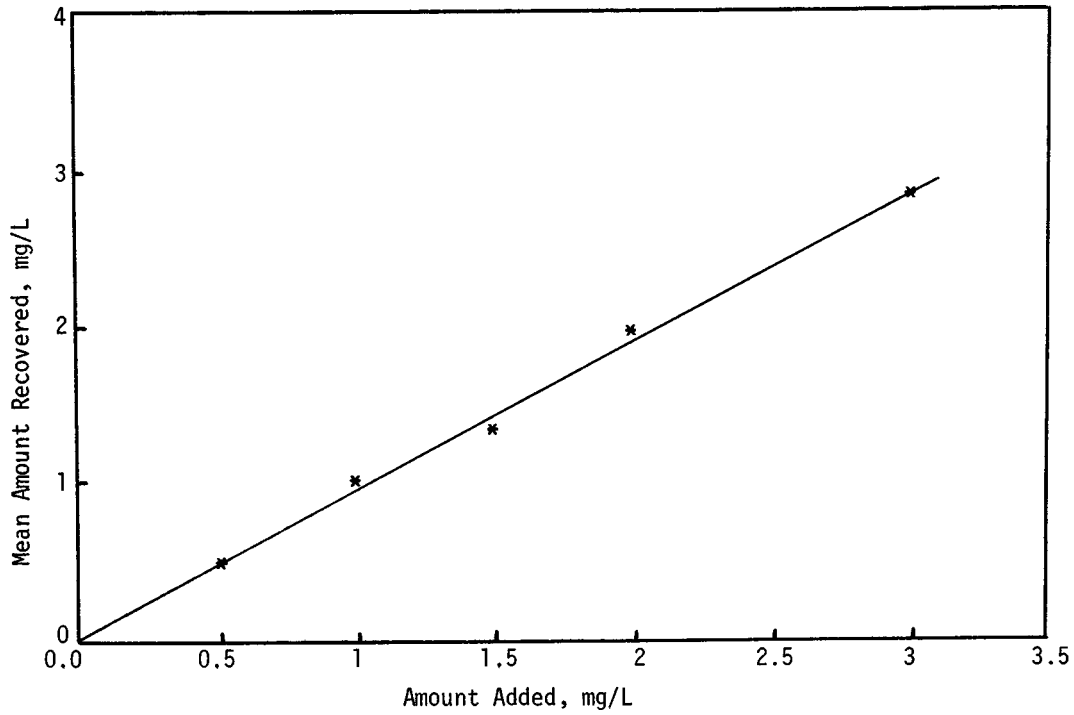


FIG. 2 Morpholine Mean Recovery Versus Amount Added

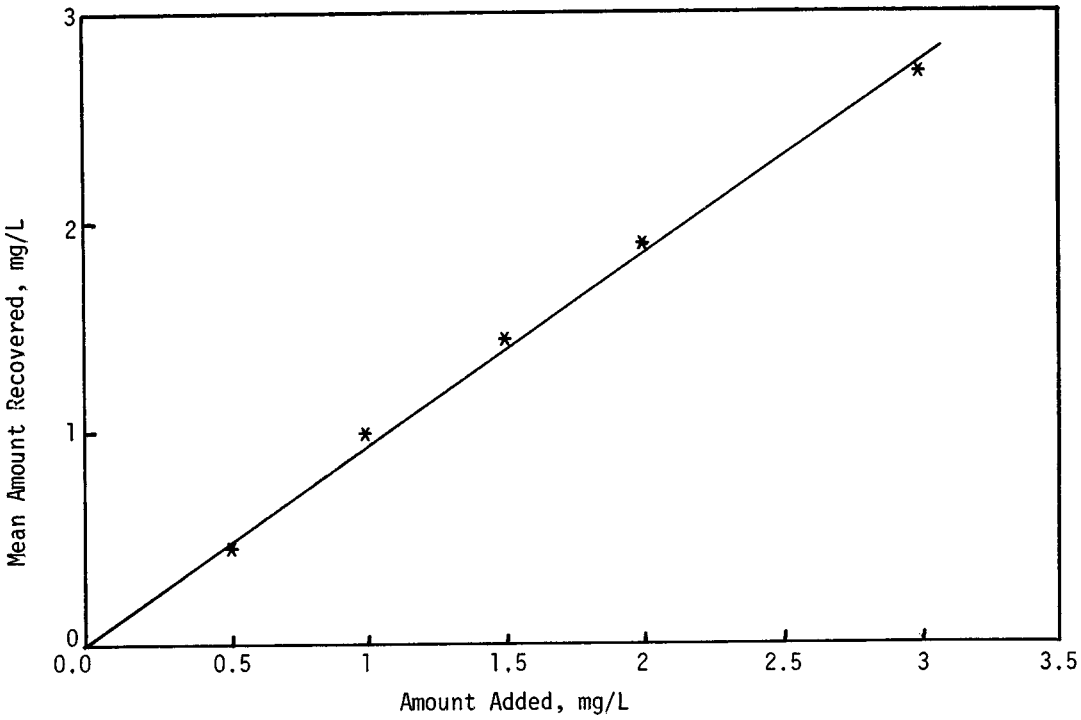


FIG. 3 Cyclohexylamine Mean Recovery Versus Amount Added

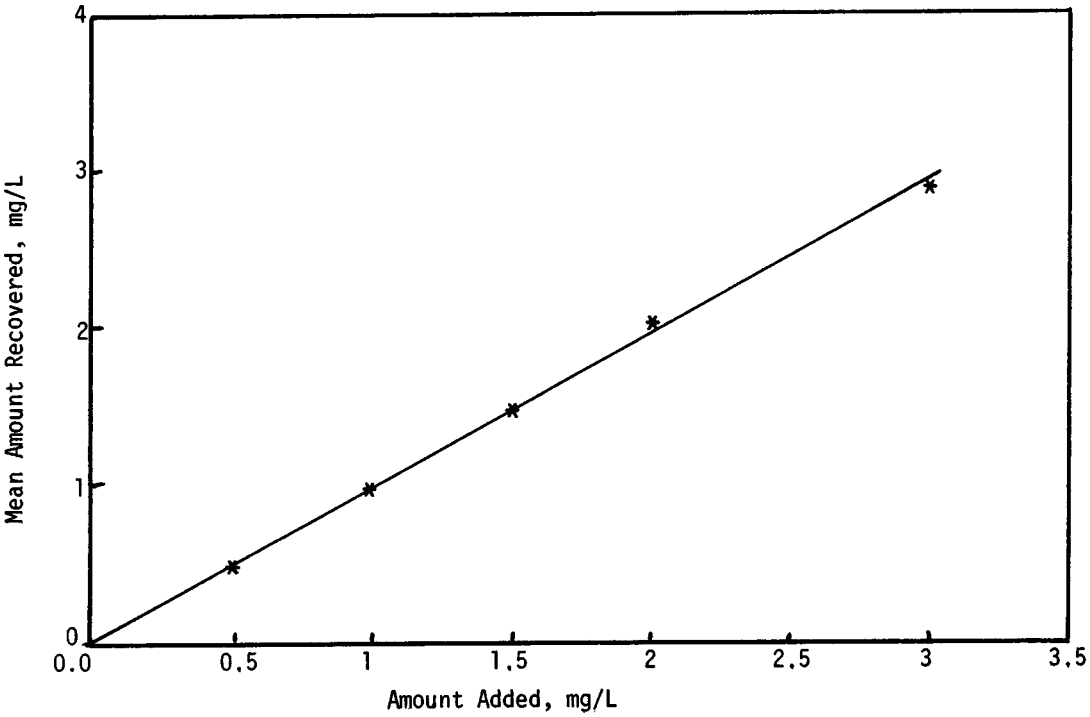


FIG. 4 Diethylaminoethanol Mean Recovery Versus Amount Added