



Standard Test Method for Cyclohexylamine, Morpholine, and Diethylaminoethanol in Water and Condensed Steam by Direct Aqueous Injection Gas Chromatography¹

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 Steam⁴

D 1129 Terminology Relating to Water⁴

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.

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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.

D 1193 Specification for Reagent Water⁴

D 2777 Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water⁴

D 2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography⁵

D 3370 Practices for Sampling Water from Closed Conduits⁴

E 355 Practice for Gas Chromatography Terms and Relationships⁶

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.

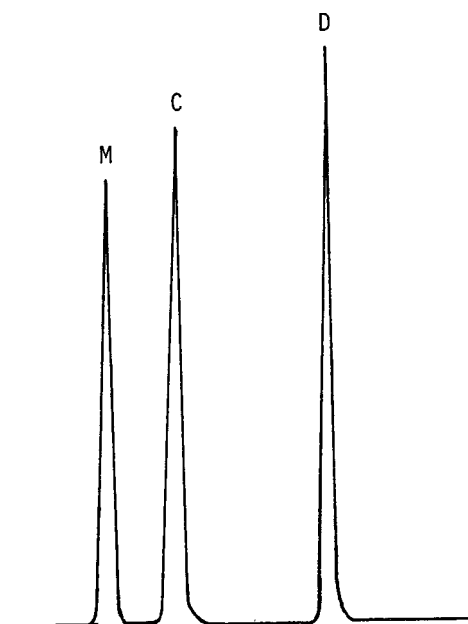
4.3 In this test method, the elution profile of the subject amines occurs in the order: morpholine, cyclohexylamine, and diethylaminoethanol. (Refer to the chromatogram in Fig. 1.)

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

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^{-10} A full scale
 Sample Size: 5 μ L
 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 trifluoroacetyl⁹ or pentafluoropropionyl¹⁰ 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 0L2.

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 μ L 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- μ L 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- μ L.

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