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An American National Standard

Standard Practice for Measuring Volatile Organic Matter in Water by Aqueous- Injection Gas Chromatography¹

This standard is issued under the fixed designation D 2908; 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 practice covers general guidance applicable to certain test methods for the qualitative and quantitative determination of specific organic compounds, or classes of compounds, in water by direct aqueous injection gas chromatography (1, 2, 3, 4).²

1.2 Volatile organic compounds at aqueous concentrations greater than about 1 mg/L can generally be determined by direct aqueous injection gas chromatography.

1.3 *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 1129 Terminology Relating to Water³
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits³
- D 1193 Specification for Reagent Water³
- D 2580 Test Method for Phenols in Water by Gas-Liquid Chromatography⁴
- D 3370 Practices for Sampling Water from Closed Conduits³
- E 260 Practice for Packed Column Gas Chromatography⁵
- E 355 Practice for Gas Chromatography Terms and Relationships⁵

3. Terminology

3.1 **Definitions**—The following terms in this practice are defined in accordance with Terminology D 1129.

¹ This practice is under the jurisdiction of ASTM Committee D19 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 The boldface numbers in parentheses refer to the list of references at the end of this practice.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 11.02.

⁵ *Annual Book of ASTM Standards*, Vol 14.02.

3.1.1 “ghosting” or *memory peaks*—an interference, showing as a peak, which appears at the same elution time as the organic component of previous analysis.

3.1.2 *internal standard*—a material present in or added to samples in known amount to serve as a reference measurement.

3.1.3 *noise*—an extraneous electronic signal which affects baseline stability.

3.1.4 *retention time*—the time that elapses from the introduction of the sample until the peak maximum is reached.

3.1.5 *relative retention ratio*—the retention time of the unknown component divided by the retention time of the internal standard.

3.2 For definitions of other chromatographic terms used in this practice, refer to Practice E 355.

4. Summary of Practice

4.1 This practice defines the applicability of various columns and conditions for the separation of naturally occurring or synthetic organics or both, in an aqueous medium for subsequent detection with a flame ionization detector. After vaporization, the aqueous sample is carried through the column by an inert carrier gas. The sample components are partitioned between the carrier gas and a stationary liquid phase on an inert solid support. The column effluent is burned in an air-hydrogen flame. The ions released from combustion of the organic components induce an increase in standing current which is measured. Although this method is written for hydrogen flame detection, the basic technology is applicable to other detectors if water does not interfere.

4.2 The elution times are characteristic of the various organic components present in the sample, while the peak areas are proportional to the quantities of the components. A discussion of gas chromatography is presented in Practice E 260.

5. Significance and Use

5.1 This practice is useful in identifying the major organic constituents in wastewater for support of effective in-plant or pollution control programs. Currently, the most practical means for tentatively identifying and measuring a range of volatile organic compounds is gas-liquid chromatography. Positive



identification requires supplemental testing (for example, multiple columns, speciality detectors, spectroscopy, or a combination of these techniques).

6. Interferences

6.1 Particulate Matter—Particulate or suspended matter should be removed by centrifugation or membrane filtration if components of interest are not altered. This pretreatment will prevent both plugging of syringes and formation of condensation nuclei. Acidification will often facilitate the dissolving of particulate matter, but the operator must determine that pH adjustment does not alter the components to be determined.

6.2 Identical Retention Times—With any given column and operating conditions, one or more components may elute at identical retention times. Thus a chromatographic peak is only presumptive evidence of a single component. Confirmation requires analyses with other columns with varying physical and chemical properties, or spectrometric confirmation of the isolated peak, or both.

6.3 Acidification—Detection of certain groups of components will be enhanced if the sample is made neutral or slightly acidic. This may minimize the formation of nonvolatile salts in cases such as the analysis of volatile organic acids and bases and certain chlorophenols.

6.4 Ghosting—Ghosting is evidenced by an interference peak that occurs at the same time as that for a component from a previous analysis but usually with less intensity. Ghosting occurs because of organic holdup in the injection port. Repeated Type I water washing with 5- μ L injections between sample runs will usually eliminate ghosting problems. The baseline is checked at maximum sensitivity to assure that the interference has been eliminated. In addition to water injections, increasing the injection port temperature for a period of time will often facilitate the elimination of ghosting problems.

6.4.1 Delayed Elution—Highly polar or high boiling components may unpredictably elute several chromatograms later and therefore act as an interference. This is particularly true with complex industrial waste samples. A combination of repeated water injections and elevated column temperature will eliminate this problem. Back flush valves should be used if this problem is encountered often.

7. Apparatus

7.1 Gas System:

7.1.1 Gas Regulators—High-quality pressure regulators should be used to ensure a steady flow of gas to the instrument. If temperature programming is used, differential flow controllers should be installed in the carrier gas line to prevent a decrease in flow as the pressure drop across the column increases due to the increasing temperature. An unsteady flow will create an unstable baseline.

7.1.2 Gas Transport Tubing—New tubing should be washed with a detergent solution, rinsed with Type I cold water, and solvent rinsed to remove residual organic preservatives or lubricants. Ethanol is an effective solvent. The tubing is then dried by flushing with nitrogen. Drying can be accelerated by installing the tubing in a gas chromatograph (GC) oven and flowing nitrogen or other inert gas through it, while heating the oven to 50°C.

7.1.3 Gas Leaks—The gas system should be pressure checked daily for leaks. To check for leaks, shut off the detector and pressurize the gas system to approximately 103 kPa (15 psi) above the normal operating pressure. Then shut off the tank valve and observe the level of the pressure gauge. If the preset pressure holds for 10 min, the system can be considered leak-free. If the pressure drops, a leak is indicated and should be located and eliminated before proceeding further. A soap solution may be used for determining the source of leaks, but care must be exercised to avoid getting the solution inside the tubing or instrument since it will cause a long lasting, serious source of interference. Leaks may also occur between the instrument gas inlet valve and flame tip. This may be checked by removing the flame tip, replacing it with a closed fitting and rechecking for pressure stability as previously noted.

7.1.4 Gas Flow—The gas flow can be determined with a bubble flow meter. A micro-rotameter in the gas inlet line is also helpful. It should be recalibrated after each readjustment of the gas operating pressure.

7.2 Injection Port—The injection port usually is insulated from the chromatographic oven and equipped with a separate heater that will maintain a constant temperature. The temperature of the injection port should be adjusted to approximately 50°C above the highest boiling sample component. This will help minimize the elution time, as well as reduce peak tailing. Should thermal decomposition of components be a problem, the injection port temperature should be reduced appropriately. Cleanliness of the injection port in some cases can be maintained at a tolerable level by periodically raising the temperature 25°C above the normal operating level. Use of disposable glass inserts or periodic cleaning with chromic acid can be practiced with some designs. When using samples larger than 5 μ L, blowback into the carrier gas supply should be prevented through use of a preheated capillary or other special design. When using 3.175-mm (0.125-in.) columns, samples larger than 5 μ L may extinguish the flame depending on column length, carrier gas flow, and injection temperature.

7.2.1 Septum—Organics eluting from the septum in the injection port have been found to be a source of an unsteady baseline when operating at high sensitivity. Septa should be preconditioned. Insertion of a new septum in the injection port at the end of the day for heating overnight will usually eliminate these residuals. A separate oven operating at a temperature similar to that of the injection port can also be used to process the septa. The septa should be changed at least once a day to minimize gas leaks and sample blowback. Septa with TFE-fluorocarbon backings minimize organic bleeding and can be used safely for longer periods.

7.2.2 On-Column Injection—While injection into the heated chamber for flash vaporization is the most common injection set-up, some analyses (for example, organic acids) are better performed with on-column injection to reduce ghosting and peak tailing and to prevent decomposition of thermally degradable compounds. This capability should be built into the injection system. When using on-column injection a shorter column life may occur due to solid build up in the injection end of the column.

