Designation: D2908 – 91 (Reapproved 2011)

Standard Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography[1]

This standard is issued under the fixed designation D2908; 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:*[3]

D1129 Terminology Relating to Water

D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[4]

D1193 Specification for Reagent Water

D3370 Practices for Sampling Water from Closed Conduits

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 *Definitions:*

3.1.1 The following terms in this practice are defined in accordance with Terminology D1129.

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

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

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

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

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

3.2 For definitions of other chromatographic terms used in this practice, refer to Practice E355.

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 E260.

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

[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.

Current edition approved May 1, 2011. Published June 2011. Originally approved in 1970. Last previous edition approved in 2005 as D2908 – 91 (2005). DOI: 10.1520/D2908-91R11.

[2] The boldface numbers in parentheses refer to the list of references at the end of this practice.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] The last approved version of this historical standard is referenced on www.astm.org.

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-µL 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 µL, 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 µL 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.

7.3 *Column Oven*—The column ovens usually are insulated separately from the injection port and the detector. The oven should be equipped with a proportional heater and a squirrel-cage blower to assure maximum temperature reproducibility and uniformity throughout the oven. Reproducibility of oven temperature should be within 0.5°C.

7.3.1 *Temperature Programming*—Temperature programming is desirable when the analysis involves the resolution of organics with widely varying boiling points. The column oven should be equipped with temperature programming between – 15 and 350°C (or range of the method) with selectability of several programming rates between 1 and 20°/min provided. The actual column temperature will lag somewhat behind the oven temperature at the faster programming rates. Baseline drift will often occur because of increased higher temperatures experienced during temperature programming. This depends on the stability of the substrate and operating temperature range. Temperatures that approach the maximum limit of the liquid phase limit the operating range. Utilization of dual matching columns and a differential electrometer can minimize the effect of drift; however, the drift is reproducible and does not interfere with the analysis in most cases.

7.4 *Detector*—The combination of high sensitivity and a wide linear range makes the flame ionization detector (FID) the usual choice in trace aqueous analysis. The flame ionization detector is relatively insensitive to water vapor and to moderate temperature changes if other operating parameters remain unchanged. If temperature programming is used, the detector should be isolated from the oven and heated separately to ensure uniform detector temperature. The detector temperature should be set near the upper limit of the programmed temperature to prevent condensation. The detector should also be shielded from air currents which could affect the burning characteristics of the flame. Sporadic spiking in the baseline indicates detector contamination; cleaning, preferably with diluted hydrochloric acid (HCl, 5 + 95), and an ultrasonic wash with water is necessary. Chromic acid also can be used if extreme care is taken to keep exposure times short and if followed by thorough rinsing. Baseline noise may also be caused by dirty or corroded electrical contacts at switches due to high impedance feedback.

7.5 *Recorder*—A strip-chart recorder is recommended to obtain a permanent chromatogram. Chart speeds should be adjustable between 15 and 90 in./h.

7.6 *Power Supply*—A 105- to 125-V, a-c source of 60-Hz frequency supplying 20-A service is required as a main power supply for most gas chromatographic systems. If voltage fluctuations affect baseline stability, a voltage regulating transformer may be required in addition to the one incorporated within the chromatographic instrument.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all instances for gas purification, sample stabilization, and other applications. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. [5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.1.1 All chemicals used for internal standards shall be of highest known purity.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I of Specification D1193.

8.3 *Carrier Gas System*—Only gases of the highest purity obtainable should be used in a chromatographic system designated for trace-organic monitoring in water. The common carrier gases used with a flame ionization detector (FID) are helium and nitrogen. Trace contaminants in even the highest purity gases can often affect baseline stability and introduce noise. Absorption columns of molecular sieves (14 by 30-mesh) and anhydrous calcium sulfate ($CaSO_4$, 8 mesh) in series between the gas supply tank and the instrument will minimize the effect of trace impurities. These preconditioning columns, to remain effective, must be cleaned by back flushing them with a clean gas (nitrogen, helium) at approximately 200°C, or they must be replaced at regular intervals. Use of catalytic purifiers is also effective **(4).**

8.4 *Column:*

8.4.1 *Column Tubing*—For most organic analyses in aqueous systems, stainless steel is the most desirable column tubing material. However, when analyzing organics that are reactive with stainless steel. Fused silica capillary columns have been demonstrated as having equal, if not better, performance in all cases. Columns of 0.25, 0.32, and 0.53 mm inside diameter are readily available from most suppliers of fused silica. With a flame ionization detector, maximum resolution with packed columns is achieved with long, small-diameter (3.175-mm (0.125-in.) and smaller) tubing. New tubing should be washed as described in 7.1.2.

8.4.2 *Solid Support*—Maximum column efficiency is obtained with an inert, small, uniform-size support. The lower limit of particle size will be determined by the allowable pressure drop across a column of given diameter and length. Elimination of fines will reduce the pressure drop and allow the use of smaller particles; the commonly used size is 80/100 mesh. Supports, which are not inert, may cause varying

[5] *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.