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

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 Water[3]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[3]
D 1193 Specification for Reagent Water[3]
D 2580 Test Method for Phenols in Water by Gas-Liquid Chromatography[4]
D 3370 Practices for Sampling Water from Closed Conduits[3]
E 260 Practice for Packed Column Gas Chromatography[5]
E 355 Practice for Gas Chromatography Terms and Relationships[5]

3. Terminology

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

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

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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.

still further. However, silanization can decrease column life. DMCS treatment is particularly useful when low liquid loads are used. Treatment with specific chemicals that approximate the properties of the sample being analyzed has also proven successful. For example, terephthalic acid treatment of Carbowax 20M[7] reduces organic acid and phenolic tailing. Use of fluorocarbon supports can significantly reduce tailing. For low boiling materials, porous polymer beads formed by the polymerization of monomers such as styrene with divinyl benzene as a crosslinker are finding more application in trace analysis. Since there is no liquid phase, there is minimal column bleed during temperature programming. In addition, elimination of the conventional solid support removes the adsorptive sites which normally cause tailing. Caution must also be taken not to exceed the recommended maximum temperature limit of the fluorocarbon supports or of the porous polymer beads being used.

8.4.3 *Liquid Phases*—Maximum resolution and minimum baseline noise and drift are achieved with a relatively lightly loaded column (less than 5 %) containing a stable substrate of low volatility. However, analysis of aqueous samples with light column loading produces shorter column life and a greater tendency for a shift in retention times and delayed elution as the column ages. Accelerated aging will occur if the maximum temperature limit of the liquid phase is exceeded or approached repeatedly. Liquid phases should be selected to permit operation at a temperature below the maximum allowable if at all possible. Selection of liquid phases should be based on the properties of the sample to be analyzed. In general, polar substrates will resolve polar compounds by order of relative volatility and polarity. Polar liquid phases will resolve nonpolar compounds by structural type. Nonpolar substrates will separate nonpolar compounds by volatility and polar compounds by structural type. For examples of applicable liquid phases for a particular application, consult published methods for specific organic classes.

8.4.4 *Column Conditioning*—All new columns should be pre-conditioned to drive off the residual contaminants which would foul the detector and cause severe baseline noise. New columns can be conditioned by attaching one end to the inlet port of the oven and allowing 20 to 30 mL/min of carrier gas to pass through the column either at 30°C above the expected maximum operating temperature or at the maximum temperature limit of the liquid phase, whichever is lower. The effluent end of the column should be vented. The column should not be attached to the detector during conditioning since eluting organics may foul the detector. Occasional 5-μL injections of water during the conditioning period will facilitate elution of the extraneous organics. The required conditioning period depends on the type of liquid phases and extraneous organics, but conditioning for about 12 h is adequate in most cases. A longer conditioning period may be necessary if peak tailing persists with polar compounds. The weight of column packing should be noted to allow preparation of identical replacement column, when needed.

8.5 *Detector Gases*—Hydrogen and air of the highest initial purity which have been further purified as described in 8.3, are fed to the detector. Hydrogen can also be used which is produced from the electrolytic decomposition of water.

8.6 *Glassware*—All glassware that will come into direct contact with the sample should be heated in an oven to 300°C (overnight if possible) as a final cleanup step. This will serve to remove any source of organic contamination from prior work.

9. Sampling

9.1 *Sample Collection*—Collect all samples in accordance with Specification D 1192 and Practices D 3370, as applicable. Additionally, sample containers and sample size and storage shall be as specified in 9.2-9.4 to.

9.2 *Sample Containers*—Care should be taken to collect a representative sample in a clean, completely full glass bottle. The screw cap should be lined with aluminum foil or TFE-fluorocarbon to reduce the sorption of insoluble organics.

9.3 *Sample Size*—The sample size must be small to prevent overloading of the 3.175-mm (0.125-in.) columns generally used. For most aqueous analyses, a sample size of 2 to 5 μL is generally optimum. If the components of interest are of relatively high concentration, a 1-μL sample is to be used. At low concentrations, a sample approaching 10 μL can be used to increase the detectable limit although the measurement accuracy is slightly decreased since a 10-μL syringe is used. For the best accuracy, select a syringe with a capacity 50 % greater then the size of the sample to be injected.

9.4 *Sample Storage*—Storage time of samples should be kept to a minimum. If storage cannot be avoided, the bacterial action should be minimized by refrigeration, by pH adjustment to about 2.0 (if organics are not acid degradable), or by the addition of 1 mL of saturated mercuric chloride ($HgCl_2$) solution to each liter of sample. Selection of a preservation procedure is dependent on the analysis being made.

10. Preparation of Apparatus

10.1 *Column*—Select the appropriate column and install in the chromatographic oven. If the column is new, it should be preconditioned according to the directions in 8.4.4. The column should then be attached to the detector and the system checked for leaks according to 7.1.3. The column temperature requirements should be set according to the requirements outlined in the specific method being used.

10.2 *Gases*—With a flame ionization detector the gases require adjustment in the ratio of about 1 part carrier gas to 1 part hydrogen to 10 parts air. A typical flow for the carrier gas when using 3.175-mm (0.125-in.) tubing is 25 mL/min. Refer to the specific method being used for flow requirements.

10.3 *Electrometer and Recorder*—Adjust the electrometer and recorder as specified on the instrument instructions so that the pen is zeroed and the attenuation steps are linear. Based on the organic content of the sample to be analyzed, adjust the electrometer attenuation to give as near mid-scale deflections of the recorder pen as is practical.

10.4 *Baseline Stability*—Before proceeding with the analysis, check the stability of the recorder baseline with the pen at zero and the attenuation at the level to be used for the analysis. If sporadic peaks occur, further column conditioning may be necessary. The recorder, electrometer, flow controllers, and flame detectors should also be checked as a possible source of the sporadic peaks.

10.5 *Column Storage*—When columns are not in use, their ends should be capped. The need for reconditioning prior to their reuse at a later time will be indicated by making calibration runs with a known concentration of standards. Reconditioning is generally minimal if the column was adequately purged prior to storage.

11. Calibration and Standardization

11.1 *Qualitative*:

11.1.1 The basic method of tentative compound identification is by matching the retention times of known standards suspected to be present with retention times of unknown compounds under identical operating conditions. The absolute retention time is measured in minutes from the time of injection to the peak maximum. Since retention time may vary significantly with concentration of the particular organic compounds, identification is done more positively by spiking the sample with the suspected constituent and noting an increase in peak height. In some instances more than one compound may elute at the same time and therefore have identical retention times. This condition can often be recognized by a poorly shaped peak (that is, double apex or shoulder). When this occurs, additional column(s) with different physical and chemical properties will be required to separate the combined peaks. An alternative, which is frequently preferable, is to trap the peaks and identify them spectrometrically (see 12.7).

11.1.2 Relative retention times are developed by the insertion of a common noninterfering organic into each standard as well as into the unknown. The absolute retention time of the common organic is then divided into the absolute retention time of each organic being analyzed. Utilization of relative retention times improves qualitative accuracy by balancing out numerous chromatographic variations from run to run, for example, slight variations in column temperature, programming rate, carrier gas flow, and sample size as well as column aging.

11.1.3 Based on the type and concentration of compounds expected in the sample to be tested, prepare similar standards in reagent water.

11.1.4 At least three relative retention times with a single column should be determined for each organic standard and the average used for qualitative analysis of the unknown sample. Relative retention times should be verified periodically.

11.1.5 One- and two-column identifications are not usually sufficient for positive identification. A third column or spectrometric analysis of the trapped peak will be required for an unequivocal identification.

11.2 *Quantitative*:

11.2.1 The quantitative measurement of each component is determined from the area under the individual chromatographic peaks. Peak areas can be determined more efficiently by mechanical or electronic integrators. If the peaks are symmetrical and sharp with minimum tailing, peak height can be used for estimating quantitative response for expediency in routine monitoring type analysis. The height is measured from the peak maximum to the baseline. If the peak occurs in an area of baseline drift, approximate the actual base of the peak for measuring purposes. Measuring the peak width at one half the peak height and multiplying it by the peak height will approximate the peak area. The error increases as the peak width becomes smaller or as peak tailing increases.

11.2.2 Insertion of an internal standard is useful for quantitative analysis. When response is calculated relative to an internal standard, compensation is provided for the inadvertent changes in chromatographic conditions. Selection of the internal standard should be based on its separation from other peaks, stability, and if possible on mid-chromatogram elution and structural similarity to the components being analyzed. The internal standard should be applied at approximately the expected average concentration of the organic constituents. When temperature programming is used, two internal standards may be needed, one for low-boiling and one for high-boiling constituents.

11.2.3 Mass response ratios are determined by the injection of standards containing the same concentration of both the internal standard and the individual components suspected to be in the samples to be tested. For accurate quantitative work triplicate injections should be made on a conditioned column with the average being used for further calculations. All chemicals used should be of the highest known purity, so that the appropriate correction may be made when calculating the final response factors. Response factors should be rechecked periodically.

11.2.4 The linearity of the response factors should be verified by varying the concentration of the individual components over the concentration range of interest while holding the internal standard concentration constant. These ratios when plotted against concentration should yield a straight line that passes through zero. Chromatographic operating conditions should always be recorded on the graph. The final peak areas of heights are adjusted according to the electrometer attenuation setting used for calibration.

12. Procedure

12.1 *Injection Practice*—Use a firm, relatively fast injection technique so that the sample can be injected either into the middle of the injection port for flash vaporization, or approximately 2 in. (51 mm) down the column for on-column injection in a slug-like condition. Slow injections may cause poor resolution and spreading. Use the same rhythm each time. Wash the syringe several times between injections with acetone, then rinse with water, and air dry by attaching to a vacuum line. Flush the syringe at least two times with the sample to be analyzed. Remove the bubbles by pumping the syringe plunger followed by a slow drawup of the sample. When injecting large samples at high inlet pressure (for example, 50 psi (345 kPa)), hold the plunger so as to prevent its blowout caused by the pressure buildup in the injection port; special syringes are needed for high-pressure work.

12.1.1 *Sample Injection*—Use direct aqueous injection whenever possible to prevent both the loss of some components and the introduction of extraneous peaks that may result from concentration techniques. However, when analyses are in the part per billion range, concentration techniques will be required. Carbon adsorption, gas stripping, solvent extraction, and freezeout have been shown to increase component concentration to detectable levels **(1, 5, 6).**

12.2 Establish operating conditions identical to those used for calibration and standardization. If changes are required because of sample peculiarities, repeat calibration and standardization using the new conditions. If an internal standard is used, minor changes in operating conditions are tolerable.

12.3 Inject sample prior to insertion of internal standard to assist in either the selection of the internal standard, or to assure that the internal standard selection is well resolved from component peaks in the sample. An open position in the chromatogram is selected for this purpose.

12.4 Add the internal standard(s) into the sample at a concentration approximating the components to be analyzed and repeat the analysis.

12.5 Refer to the specific method for suggested sample size; 3 to 5µ L are often used.

12.6 Determine the absolute retention times of the individual components in the sample. Calculate relative retention times using the retention time of the internal standard in the denominator. Refer to the previously developed listing for relative retention times of known compounds on specific columns; if absolute retention times are used, run standards several times during the test series. Repeat on additional columns as necessary to increase qualitative accuracy.

12.7 Trap individual peaks for confirmatory analysis. Mass spectrometric analysis of trapped components is often most informative; however, infrared spectrographic analysis, thin-layer chromatography, and microcoulometry or other specialized detectors (for example, flame photometric detector, modified flame halogen detector) are also useful.

12.8 Adjust attenuation to keep all peaks on scale and preferably near 50 % of full scale. After component identifications have been completed, triplicate determinations should be made at identical instrument conditions for quantitative analysis. Water washes are usually injected between samples to eliminate ghosting.

12.9 Measure peak areas or height (symmetrical, non-tailing peaks required) and average the results.

13. Calculation

13.1 Tentative identification of individual components is based primarily on relative retention times. Report confirmative identifications based on additional columns and on spectrometric analysis of trapped fractions.

13.2 Use the following formula to convert peak area to concentration, measured in milligrams per litre:

Concentration of *EC*, mg/L

$$= \frac{\text{peak area } EC}{\text{peak area } IS} \times \frac{\text{concentration } IS \text{ (mg/L)}}{\text{mass response ratio}}$$

where:
EC = eluted component, mg/L, and
IS = internal standard, mg/L.

To determine mass response ratio, divide the response of the eluted component by the response of the internal standard at the same concentration.

14. Keywords

14.1 aqueous; gas chromatography; organic; volatile

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