Designation: D3695 – 95 (Reapproved 2013)

Standard Test Method for
Volatile Alcohols in Water by Direct Aqueous-Injection Gas Chromatography[1]

This standard is issued under the fixed designation D3695; 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 a wide range of alcohols with various structures and boiling points that can be separated and detected quantitatively in water and waste water at a minimum detection limit of approximately 1 mg/L by aqueous-injection gas-liquid chromatography.[2] This test method can also be used to detect other volatile organic compounds qualitatively. Organic acids, amines, and high boiling, highly polar compounds are not readily detectable under this set of conditions. For analysis of organics with similar functionalities, refer to other test methods in Volumes 11.01 and 11.02 of the *Annual Book of ASTM Standards*.

1.2 This test method utilizes the procedures and precautions as described in Practice D2908. Utilize the procedures and precautions as described therein.

1.3 This test method has been used successfully with reagent grade Type II and natural chlorinated tap waters. It is the user's responsibility to assure the validity of this test method for any untested matrices.

1.4 *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
D1193 Specification for Reagent Water
D2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data (Withdrawn 2002)[4]
E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129 and Practice E355.

4. Summary of Test Method

4.1 An aliquot of an aqueous sample is directly injected into a gas chromatograph by means of a microlitre syringe. The organic compounds in the sample are separated and eluted from a chromatographic column into a flame ionization detector. The compounds are identified by relative retention time or Kovats Index, and measured by direct comparison with corresponding standard responses.

5. Significance and Use

5.1 The major organic constituents in industrial waste water need to be identified 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.

6. Interferences

6.1 Since the specified column and conditions are applicable to numerous organics, the possibility of one or more components having identical retention times is always present. Therefore, the analyst must determine the qualitative identity of the components of each peak by spectrometric techniques or a multi-column approach, or both, so that proper quantitation for those compounds of interest may be made. Refer to Table 1 for relative retention data.

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[1] This test method 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] Sugar, J. W., and Conway, R. A., "Gas-Liquid Chromatographic Techniques for Petrochemical Waste Water Analysis,'' *Journal of the Water Pollution Control Federation*, Vol 40, 1968, pp. 1622–1631.

[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.

TABLE 1 Kovats Index and Relative Retention Data for Typical Components[A]

Component	Kovats Index (Ix)	Relative Retention[B]
Diethyl ether	580	0.17
n-Hexane	600	0.19
Isopropyl ether	600	0.19
Ethylene oxide	700	0.20
Acetaldehyde	700	0.20
Vinyl ethyl ether	700	0.20
n-Heptane	700	0.20
Propylene oxide	737	0.22
Vinyl isobutyl ether	796	0.26
Acetone	796	0.26
n-Butyl chloride	796	0.26
Cyclohexene	808	0.27
Acrolein	820	0.28
Methyl acetate	820	0.28
Vinyl *n*-butyl ether	833	0.29
Octene-1	842	0.30
n-Butyraldehyde	865	0.32
Vinyl acetate	887	0.34
Isopropyl acetate	887	0.34
Methyl ethyl ketone	908	0.36
Ethyl acetate	912	0.37
Methanol	916	0.38
Isopropanol	935	0.39
Dioxolane	943	0.40
Benzene	962	0.42
Ethyl acrylate	978	0.44
Isopropenyl acetate	983	0.45
Methyl *n*-propyl ketone	983	0.45
Methyl vinyl acetate	992	0.46
Ethanol	1000	0.47
Acrylonitrile	1007	0.48
Propyl acetate	1007	0.48
2-Methylpentaldehyde	1026	0.51
n-Butyl ether	1026	0.51
Methyl isobutyl ketone	1035	0.52
Isobutyl acetate	1035	0.52
2-Ethylbutyraldehyde	1042	0.53
Acetonitrile	1050	0.54
1,2-Dichloropropane	1056	0.55
sec-Butyl alcohol	1056	0.55
Propylene dichloride	1065	0.57
2,3-Pentanedione	1080	0.60
Toluene	1080	0.60
n-Butyl acetate	1080	0.60
Ethylene dichloride	1092	0.62
n-Propanol	1100	0.63
Crotonaldehyde	1110	0.65
Paraldehyde	1118	0.66
1,4-Dioxane	1118	0.66
Isobutanol	1137	0.70
Mesityl oxide	1137	0.70
n-Methylmorpholene	1142	0.72
Methyl amyl acetate	1150	0.73
2-Pentanol	1157	0.74
primary-Amyl acetate (Isomers)	1157–1185	0.74–0.82
p-Xylene	1160	0.75
Ethyl benzene	1160	0.75
Ethylidene acetone	1170	0.77
Methyl isoamyl ketone	1173	0.78
n-Butanol	1185	0.82
n-Butyl acrylate	1190	0.83
Methyl amyl alcohol	1190	0.83
Diisobutyl ketone	1202	0.85
2-Ethylhexyl aldehyde	1210	0.87
Epichlorohydrin	1216	0.88
2-Picoline	1222	0.91
n-Ethylmorpholine	1226	0.92
Styrene monomer	1240	0.95
1,2-Trichlorethane	1244	0.96
Amyl alcohol	1260	1.00
Cyclohexanone	1260	1.00
1,3-Triethoxybutane	1260	1.00
Diethyl benzene	1275	1.04
2-Ethyl-1-butanol	1295	1.10
3-Picoline	1300	1.12
4-Picoline	1303	1.14
Diisobutyl carbinol	1308	1.15
1-Hexanol	1312	1.16
2-Ethylhexyl acetate	1322	1.20
n-Hexyl ether	1325	1.21
Diacetone alcohol	1330	1.23
Ethylene chlorohydrin	1338	1.25
2-Octanal	1341	1.26
1,3-Trichloropropane	1352	1.30
2-Methyl-5-ethyl pyridine	1354	1.31
Cyclohexanol	1354	1.31
Ethyl acetoacetate	1356	1.32
Iso-octanol (Isomers)	1362–1386	1.35–1.45
Dichloro isopropyl ether	1362	1.35
2-Ethyl-1-hexanol	1364	1.36
2-Ethylhexyl acrylate	1376	1.40
Dichloroethyl ether	1384	1.44
Tetralin	1388	1.45
Glycol diacetate	1392	1.46
n-Octanol	1402	1.51
Isophorone	1420	1.59
Styrene oxide	1423	1.60
Ethylene glycol	1430	1.63
Acetophenone	1435	1.65
Diethyl succinate	1441	1.67
Methyl acetoacetate	1443	1.69
Diethyl maleate	1460	1.79
n-Decyl alcohol	1483	1.85
Methylbenzyl alcohol	1486	1.86
2-(2-Butoxy) ethoxyethyl acetate	1486	1.86

[A] *Gas Chromatographic Data Compilation,* ASTM AMD 25A-51, ASTM, 1971.

[B] Relative to amyl alcohol.

7. Apparatus

7.1 *Gas Chromatograph and Accessory Equipment,* described in Practice D2908, Sections 7.1 through 7.6, is used for this analysis.

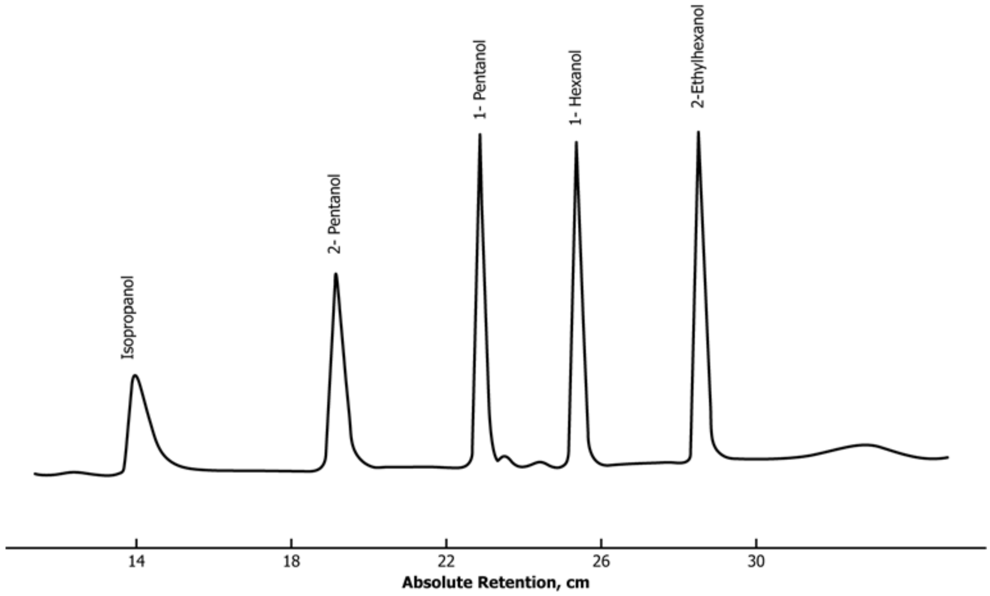

FIG. 1 Chromatogram

7.2 *Column,* Carbowax 20 M (trademark)[5] (5%) on 80/100 Acid Washed Chromosorb W (trademark),[6] 6.1-m (20-ft), 3.2-mm (1⁄8-in.) in outside diameter, 0.508-mm (0.020-in.) wall thickness, stainless steel.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used. 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.[7] 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.

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

8.3 *Calibration and Standardization* —Prepare a stock solution of the materials of interest by weighing a known amount of each, 1.00 g or less, diluting with water to 1 L, and mixing. Subsequent dilutions should be prepared as deemed necessary.

9. Sampling

9.1 Collect the sample in accordance with Section 9 of Practice D2908.

10. Procedure

10.1 Use the procedures described in Practice D2908.

11. Typical Chromatogram

11.1 *Instrument Parameters:*

Column	Carbowax 20 M (5 %), 80/100 AW Chromasorb W, 6.1-m (20-ft), 3.2-mm (1⁄8-in.) in outside diameter, stainless steel
Detector	flame ionization
Temperatures	injection port–165 to 260°C detector–250°C column–50 to 250°C at 8°C/min
Gases	carrier–He at 45 mL/min
Sample Size	10 µL
Recorder	chart speed 1.3 cm/min (0.5 in./min); full-scale response, 1 mV (23.3 cm)

11.2 See the chromatogram in Fig. 1 for relative retention times and separation of compounds used in the round-robin testing.

12. Precision and Bias[8]

12.1 Six laboratories determined the precision and bias of the procedure performing triplicate analyses at three levels in both natural and reagent water (see Table 2 and Table 3).

12.2 The precision and bias data presented in 12.1 and 12.2 were based on an interlaboratory collaborative study with samples containing alcohols only. The precision and bias of this procedure for the other compounds covered by the procedure may vary from these data.

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[5] The sole source of supply of the apparatus known to the committee at this time is Union Carbide Corp. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[6] The sole source of supply of the apparatus known to the committee at this time is Johns-Manville Products Co. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[7] *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.

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1045.

TABLE 2 Determination of Bias

Compound	Amount Added, mg/L	Amount Found, mg/L	± % Bias	± % Bias	Statistically Significant (95 % Confidence Level)
Reagent Water:					
Isopropanol	204	179	−25.2	−12.3	yes
	102	85.5	−16.4	−16.0	yes
	41	33	−8.0	−19.5	yes
2-Pentanol	197	196	−1.0	−0.5	no
	98	97	−1.0	−1.0	no
	39	37	−2.0	−5.0	no
1-Pentanol	197	195	−2.0	−1.0	no
	98	94.5	−3.5	−3.6	no
	39	36.8	−2.2	−5.6	yes
1-Hexanol	199	201	+ 2.0	+ 1.0	no
	99	93	−6.0	−6.0	no
	40	36.8	−3.2	−8.0	no
2-Ethylhexanol	84	85.3	+ 1.3	+ 1.5	no
	42	41.2	−0.8	−1.9	no
	17	16.1	−0.9	−5.3	no
Natural Water:					
Isopropanol	204	188	−16	−7.8	no
	102	90	−12	−11.8	yes
	51	43.5	−7.5	−14.7	yes
2-Pentanol	196	195	−1.0	−0.5	no
	98	95	−3.0	−3.0	no
	49	47.3	−1.7	−3.5	no
1-Pentanol	197	206	+ 9.3	+ 4.7	no
	98	103	+ 5.0	+ 6.1	no
	49	48.2	−0.8	−0.2	no
1-Hexanol	199	208	+ 8.8	+ 4.4	no
	99	99	0.0	0.0	no
	50	49.8	−0.2	−0.4	no
2-Ethylhexanol	84	83.6	−0.4	−0.5	no
	42	40.3	−1.7	−4.0	no
	21	20.1	−0.9	−4.3	no

TABLE 3 Precision [A]

	Reagent Water	Natural Water
Isopropanol	$S_T = 0.16X - 0.60$	$S_T = 0.19X - 2.4$
	$S_O = 0.06X - 0.7$	$S_T = 0.004X - 1.7$
2-Pentanol	$S_T = 0.04X - 0.007$	$S_T = 0.011X + 0.48$
	$S_O = 0.009X + 0.25$	$S_O = 0.006X - 0.11$
1-Pentanol	$S_T = 0.013X + 0.62$	$S_T = 0.031X + 0.26$
	$S_O = 0.004X + 0.41$	$S_O = 0.006X - 0.003$
1-Hexanol	$S_T = 0.024X + 0.77$	$S_T = 0.020X + 0.62$
	$S_O = 0.003 + 0.62$	$S_O = 0.003X + 0.21$
2-Ethyl hexanol	$S_T = 0.03X + 1.25$	$S_T = 0.028X + 0.39$
	$S_O = 0.01X + 0.25$	$S_O = 0.002X + 0.14$

[A] S_T = overall precision, mg/L, S_O = single-operator precision, mg/L, and X = concentration of organic determined, mg/L.

13. Quality Assurance/Quality Control (QA/QC)

13.1 Before this test method is applied to the analysis of samples of unknown alcohol concentrations, the analyst must establish quality control by the procedures recommended in Practice D4210 and Guide D3856.

13.2 A duplicate sample and known standard must be analyzed each day that an analysis is performed. The duplicate and standard shall meet the limits as established by the control chart before a determination is considered satisfactory.

13.3 A blank and a spiked sample shall be analyzed each day that an analysis is performed. Spiking shall be in accordance with that outlined in 11.11 of Guide D3856. The blank shall be low enough that it will not unduly influence the data.

13.4 One sample must be analyzed in duplicate with each group of 10 or less samples. The results must meet the criteria established in Table 2 and Table 3 of this test method before the data for that batch or set of 10 samples is acceptable.

13.5 Other QA/QC portions of this test method have not been completely established at this time. Analysts performing this test method will be required to measure their performance against the performance level achieved by the interlaboratory studies of this test method.

13.6 It is the intention of Subcommittee D19.06 to incorporate formal QA/QC procedures into this test method at such time as they have passed the consensus process and have been officially accepted by the Society.

14. Keywords

14.1 alcohols; aqueous-injection; gas chromatography; volatile alcohols

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