Designation: D 3695 – 95

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

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

This standard is issued under the fixed designation D 3695; 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 D 2908. 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:*

D 1129 Terminology Relating to Water [3]

D 1193 Specification for Reagent Water [3]

D 2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography [4]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water [3]

D 4210 Practice for Intralaboratory Quality Control Procedures and Discussion on Reporting Low Level Data [3]

E 355 Practice for Gas Chromatography Terms and Relationships [5]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129 and Practice E 355.

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.

7. Apparatus

7.1 *Gas Chromatograph and Accessory Equipment*, described in Practice D 2908, Sections 7.1 through 7.6, is used for this analysis.

7.2 *Column: Carbowax 20 M*[6] *(5%) on 80/100 Acid Washed Chromosorb W,* [7] 6.1-m (20-ft), 3.2-mm (⅛-in.) in outside diameter, 0.508-mm (0.020-in.) wall thickness, stainless steel.

[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.

Current edition approved Feb. 15, 1995. Published April 1995. Originally published as D 3695 – 78. Last previous edition D 3695 – 88.

[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] *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.

[6] Carbowax is a trademark of Union Carbide Corp.

[7] Chromosorb W is a trademark of Johns-Manville Products Co.

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.

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