Designation: D 3371 – 95

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Nitriles in Aqueous Solution by Gas-Liquid Chromatography [1]

1. Scope

1.1 This test method covers nitriles that can be separated and detected quantitatively at a limit of approximately 1 mg/L by aqueous injection on a selected gas-liquid chromatographic column.

1.2 This test method utilizes the procedures and precautions as described in Practice D 2908.

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[2]

D 2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography[3]

3. Terminology

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

4. Significance and Use

4.1 Nitriles at concentrations of a few milligrams per litre are potentially toxic to aquatic life. Nitriles in waste water discharges should be detected and controlled.

4.2 Gas-liquid chromatography (GLC) can detect and determine mixtures of nitriles at levels where wet chemical procedures are not applicable.

5. Special Comments

5.1 It is recommended that samples that cannot be analyzed immediately, be quick frozen for preservation. Samples should be neutralized to pH 7 at the time of collection to minimize hydrolysis of the nitrile groups.

5.2 Samples of nitriles to be employed as standards should be considered to be unstable. Storage in a freezer is recommended.

5.3 It is not always practical to translate operating conditions directly from one GLC instrument to another. An operator should optimize his instrument to a particular procedure, for example, injection and detection temperature, flow rates, etc.

6. Typical Chromatograms

6.1 The following instrument parameters were used to obtain the typical chromatograms (See Fig. 1 and Fig. 2).

6.1.1 *Column*—⅛ in. outside diameter stainless steel, 8 ft long packed with a porous styrene divinylbenzene polymer.

NOTE 1—"Chromosorb" 101, 50/60 mesh, was used for the typical chromatograms.

6.1.2 *Detector*, flame ionization.

6.1.3 *Temperatures*:

Injection port	240°C
Detector	240°C
Oven, isothermal	130°C
Oven, programmed at 10°C/min	110°C to max of 200°C

6.1.4 *Carrier Gas*, helium at 25 mL/min.

6.1.5 *Sample Size*:

isothermal 5 µL

programmed 3 µL

6.1.6 *Recorder*, ¾ in./min chart speed and 1 mV full-scale response.

6.2 *Kovats Index Values:*[4]

Compounds	Relative Retention	Kovats Index
Acetonitrile	1.00	470
Acrylonitrile	1.25	512
Proprionitrile	1.67	570
Methoxyacetonitrile	2.21	635 [5]
Butyronitrile	2.50	678
Isovaleronitrile	3.04	740 [5]
Valeronitrile	3.38	783
Hexanenitrile	4.25	905 [5]
Benzonitrile	5.42	990

7. Precision and Bias

7.1 An interlaboratory study was conducted in 1972 with participation from four laboratories and seven operators.

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[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D 19.06 on Methods for Analysis for Organic Substances in Water.

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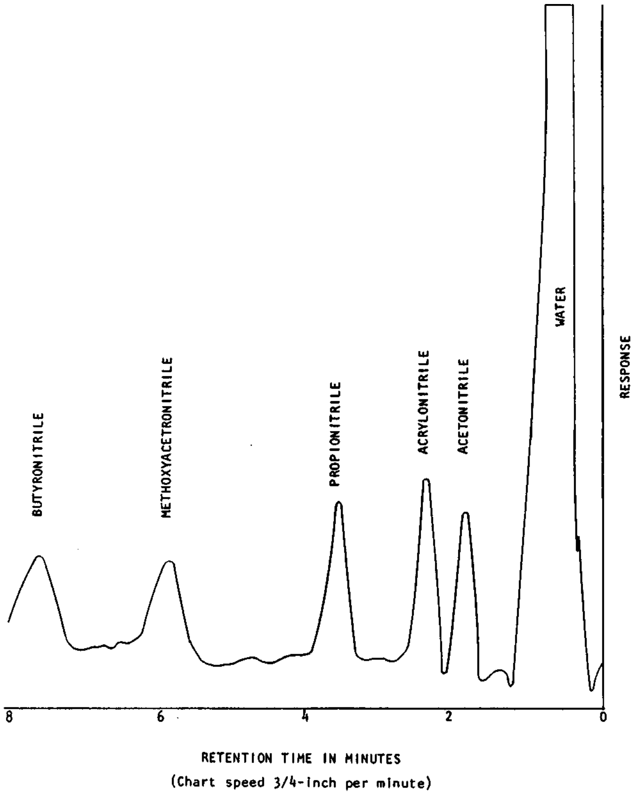
[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

[4] *Gas Chromatographic Data Compilation, ASTM AMD25A*, 1967.

[5] Kovats index values estimated from relative retention data because standard compound was not readily available.



Column Packing - Chromosorb 101, 50/60 mesh
Carrier Gas - Helium at 25 mL/min
Temperature - Isothermal operation of the column at 130°C
Sample Size - 5 microlitres containing 10 mg/L of each nitrile

FIG. 1 Isothermal Chromatographic Analysis of Nitriles in Aqueous Solution

Triplicate analyses of three concentrations in distilled water were contributed by all operators; see Table 1 for statistics from distilled water data. Three operators also did triplicate recoveries of three concentrations spiked into a river water of their choice; see Table 2 for the statistics from the river water recovery data.

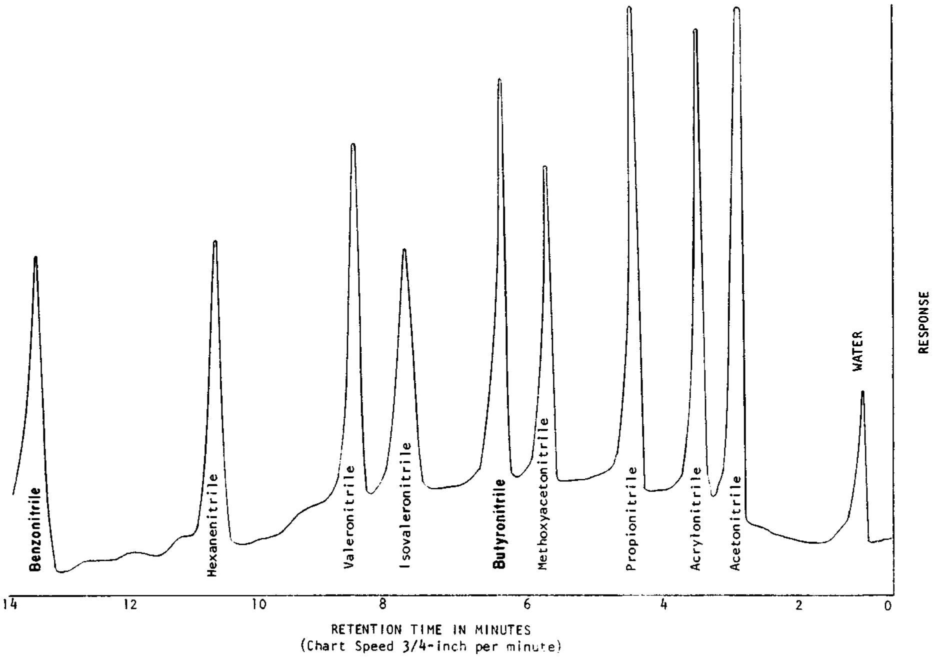
7.2 The precision of this test method within the range from 10 to 60 mg of standards/L in distilled water may be expressed as follows:

Compound	
Acetonitrile	$S_t = 0.182x + 0.194$
	$S_o = 0.023x + 0.038$
Proprionitrile	$S_t = 0.100x - 0.817$
	$S_o = 0.020x + 0.348$
Methoxyacetonitrile	$S_t = 0.260x + 0.263$
	$S_o = 0.026x + 0.671$
Butyronitrile	$S_t = 0.107x - 0.457$
	$S_o = 0.036x + 0.202$

where:
S_t = overall precision,
S_o = single operator precision, and
x = concentration of the specification compound, mg/L.

8. Keywords

8.1 flame ionization; gas-liquid chromatography; GLC; isothermal chromatographic analysis; Kovats index



Column Packing - Chromosorb 101, 50/60 mesh
Carrier Gas - Helium at 25 mL/min
Temperature - Programmed operation at 10°C/min from 110°C to a maximum of 200°C
Sample Size - 3 microlitres containing 1 500 mg/L of each nitrile

FIG. 2 Proposed Temperature Chromatographic Analysis of Nitriles in Aqueous Solution

TABLE 1 Recovery for Reagent Water

Compound	Amount Added, mg/L	Amount Found, mg/L	*n*	S_o	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Acetonitrile	60	50.7	21	1.37	11.0	−9.3	−15.5	yes
	30	24.4	21	1.10	5.90	−5.6	−18.7	yes
	10	8.42	21	0.57	1.86	−1.58	−15.8	yes
Proprionitrile	60	56.6	15	1.54	5.20	−3.4	−5.7	yes
	30	28.8	15	0.96	1.35	−1.2	−4.0	yes
	10	9.66	15	0.54	0.56	−0.34	−3.4	yes
Methoxyacetonitrile	60	62.8	18	2.21	15.6	2.8	4.7	no
	30	31.6	18	1.48	8.65	1.6	5.3	no
	10	9.88	18	0.91	2.50	−0.12	−1.2	no
Butyronitrile	60	57.9	21	2.43	6.08	−2.1	−3.5	no
	30	28.9	21	1.12	2.48	−1.1	−3.7	no
	10	9.31	21	0.66	0.78	−0.69	−6.9	yes

TABLE 2 Recovery for River Water

Compound	Amount Added, mg/L	Amount Found, mg/L	n	S_o	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Acetonitrile	60	38.7	9	2.83	17.4	−21.3	−35.5	yes
	30	16.3	9	1.59	9.94	−13.7	−45.7	yes
	10	4.32	9	1.12	4.58	−5.68	−56.8	yes
Proprionitrile	60	57.8	9	1.25	3.11	−2.2	−3.7	no
	30	29.6	9	0.64	2.67	−0.4	−1.3	no
	10	9.77	9	0.24	0.45	−0.23	−2.3	no
Methoxyacetonitrile	60	85.4	9	1.63	21.7	25.4	42.3	yes
	30	44.4	9	1.83	12.65	14.4	46.7	yes
	10	14.3	9	0.88	5.36	4.3	43.0	yes
Butyronitrile	60	62.5	9	1.68	5.73	2.5	4.2	yes
	30	29.9	9	0.76	1.38	−0.1	−0.3	yes
	10	9.75	9	0.64	0.90	−0.25	−2.5	yes