Designation: D7845 – 17

Standard Test Method for Determination of Chemical Species in Marine Fuel Oil by Multidimensional Gas Chromatography/Mass Spectrometry[1]

This standard is issued under the fixed designation D7845; 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 the quantitative determination of a variety of chemical species in marine fuel oil (bunker fuel oil) by gas chromatography/mass spectrometry. By using the same conditions and by selecting required mass spectral selected ions, the test method may be used for the determination of other species than those for which precision statements and limits of detection have been established.

1.2 An example list of chemical species for which a limit of quantification has been determined by means of this test method is given in Table 1.

1.3 Other refinery hydrocarbon fractions and their mixtures may be tested using the same test method conditions. However, the precision of this test method reflects the compounds in Table 1.

1.4 Results are reported to the nearest 1.0 mg⁄kg.

1.5 The values stated in SI units are to be regarded as standard.

1.5.1 *Exception*—Non-SI values are given for psig.

1.6 *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:*[2]

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

2.2 *Other Standards:*

ISO 8217:2010 Petroleum Products—Fuels (Class F)—Specifications of Marine Fuels[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *direct or open split interface, n*—any GC/MS interface used to maintain atmospheric pressure at capillary column outlet.

3.1.2 *reconstructed ion chromatogram (RIC), n*—a limited mass chromatogram representing the intensities of ion mass spectrometric currents for only those ions having particular mass to charge ratios used in this test method to selectively extract and identify components in the presence of a complex hydrocarbon matrix.

3.1.3 *total ion chromatogram (TIC), n*—mass spectrometer computer output representing either the summed intensities of all scanned ion currents or a sample of the current in the ion beam for each spectrum scan plotted against the corresponding spectrum number.

3.1.4 *wall coated open tubular (WCOT), n*—a type of capillary column prepared by coating or bonding the inside wall of the capillary with a thin film of stationary phase.

4. Summary of Test Method

4.1 A suitable internal standard, ethylbenzene d-10 is added to the sample, which is then introduced into a gas chromatograph equipped with two columns configured with a Deans switching system between the two columns. The sample first passes through the polydimethylsiloxane (WCOT) pre-column which then performs a separation of the light hydrocarbon fraction and eliminates the high boiling hydrocarbon fraction to vent. The compounds of interest and internal standard are transferred to the high resolution polydimethylsiloxane (WCOT) analytical column for chromatographic separation.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0M on Mass Spectroscopy.

Current edition approved Jan. 15, 2017. Published February 2017. Originally approved in 2013. Last previous edition approved in 2016 as D7845 – 16. DOI: 10.1520/D7845-17.

[2] 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.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

*A Summary of Changes section appears at the end of this standard

TABLE 1 Component Table

	Limit of Quantitation mg/kg
n-butyl alcohol	10
Cyclohexanol	10
n-butyl ether	10
n-butyl acrylate	10
Styrene	10
alpha-pinene	10
Phenol	20
alpha-methyl styrene	10
beta-pinene	10
4-methyl styrene	10
trans-B-methyl styrene	10
3-methyl styrene	10
2-methyl styrene	10
Dicyclopentadiene	10
Limonene	10
Indene	20
1-phenyl ethanol	20
para, alpha-Dimethyl styrene	20
2,5 dimethyl styrene	20
2,4 dimethyl styrene	20
2-phenyl ethanol (phenylethanol)	20
2-Ethyl Phenol	50
2,4 Dimethyl Phenol	20
4-Ethyl Phenol (co elutes with 3-ethylphenol)	20
2-Phenoxy-1-propanol	50
2-Phenoxy ethanol	50
4-isopropylphenol	50
1-Phenoxy-2-Propanol	20
Styrene Glycol	50

An auxiliary carrier gas is used to elute higher boiling hydrocarbons from the pre-column in back flush mode in order to prepare for the next analysis cycle. The resulting chromatogram is then processed by mass spectral analysis based on selected or extracted ion monitoring.

5. Significance and Use

5.1 The test method allows the quantitation of chemical species at low levels in marine fuel oils and cutter stocks. A great many types and concentrations of chemical species are found in marine fuel oils. A root cause relationship between the presence of such species or their concentration in fuels and any failure modes allegedly induced by the use of these fuels has not been established. This test method is necessary to establish test conditions required for future ISO 8217:2010 as defined in section 5.5 and Annex B item (d). Additional compounds may be determined by using the same conditions and by selecting required mass spectral selected ions, accordingly.

6. Apparatus

6.1 *Gas Chromatography:*

6.1.1 *Gas Chromatograph*—Any gas chromatograph equipped with a flame ionization detector (FID) and having sensitivity of 0.01 mg⁄kg. The gas chromatograph must be capable of linear temperature control from 50 °C to 320 °C for the capillary column oven. The gas chromatograph must be capable of controlling multiple valve events. Carrier gas flow controllers and or electronic pressure control modules shall be capable of precise control where the required flow rates are low. Pressure control devices and gauges shall be capable of precise control for the typical pressures required. The temperature program rate must repeat to within 0.1 °C and provide retention time repeatability of 0.05 min throughout the temperature program.

6.1.2 *Pre-Column Column*—WCOT Column, 25 m long by 0.53 mm inside diameter fused silica WCOT column with a 1.0 micron film thickness of polydimethyl siloxane or any column with suitable chromatographic resolution.

6.1.3 *Analytical Column*—WCOT Column, 100 m by 0.25 mm inside diameter fused silica WCOT column with a 0.5 micron film thickness of polydimethyl siloxane or any column with suitable chromatographic resolution.

6.1.4 *Purged Packed Injector*—An injection port that allows controlled injection of the sample at a temperature sufficient to pass the high boiling point fraction to the pre-column or any gas chromatographic injector system to perform the same function.

6.1.4.1 The injection port liner shall be replaced to remove non-volatile materials.

6.1.5 *Electronic Pressure Control*—Electronic pneumatic control of carrier gas flows. It can be flow or pressure programmed to speed up elution of components.

6.1.6 *Low-Volume Connector and Tees*—A special union or tee for connecting two lengths of tubing 1.6 mm inside diameter and smaller; sometimes referred to as a zero dead-volume union, tee, or an active splitting device.

6.1.7 *Pre-Column*—A polydimethylsiloxane WCOT column used to isolate the light hydrocarbons to include methane to n-hexadecane from the higher boiling portion of the sample for transfer to the analytical column for further separation and quantification.

6.1.8 *Deans Switching Backflush Configuration*[4] (Fig. 1)—A column backflush configuration utilizing dynamic pressure differential which provides suitable means to remove the heavier hydrocarbon fraction from the pre-column or any similar configuration that allows for controlled chromatographic separation of components of interest and heavier hydrocarbon fraction. An alternative Deans switching backflush configuration is shown on Fig. 2.

6.2 *Mass Spectrometry:*

6.2.1 *Mass Spectrometer,* capable of producing electron ionization spectra at 70 electron volts or higher, and capable of scanning the range of the specified quantitation masses or (m/e). The mass scan range shall cover the masses of interest for quantitation and should yield at least 5 scans across the peak width at half peak width for a 1 mg⁄kg to 3 mg/kg ethylbenzene d10 peak and cover the masses of interest for quantitation. A scan range set for specific ions is defined in Table 2.

6.2.1.1 The mass spectrometer shall be capable of being interfaced to a gas chromatograph and WCOT columns. The interface shall be at a high enough temperature to prevent condensation of components boiling up to 350 °C. Usually, 20 °C above the final column temperature is adequate. Direct column interface to the mass spectrometer may be used. An open split interface with computer controlled programmable flow controller(s) may also be used, to maintain all components

[4] Deans, D. R., *Chromatographia*, Vol 1, 18-22, 1968.

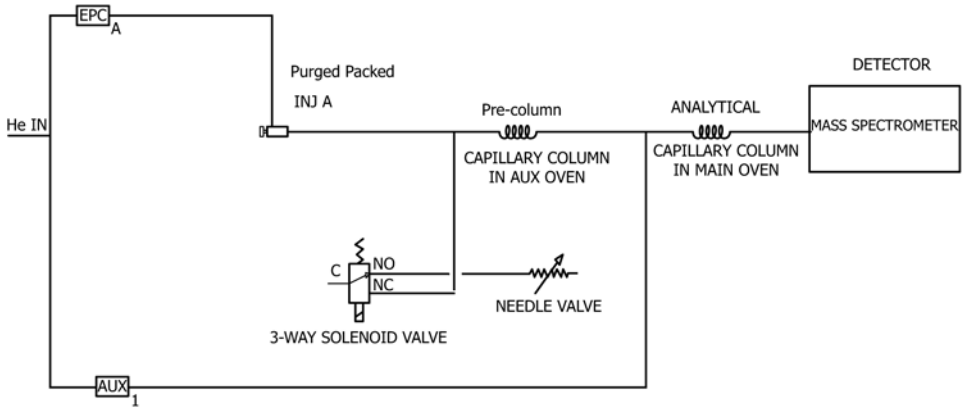

FIG. 1 Deans Switching Backflush, Configuration A

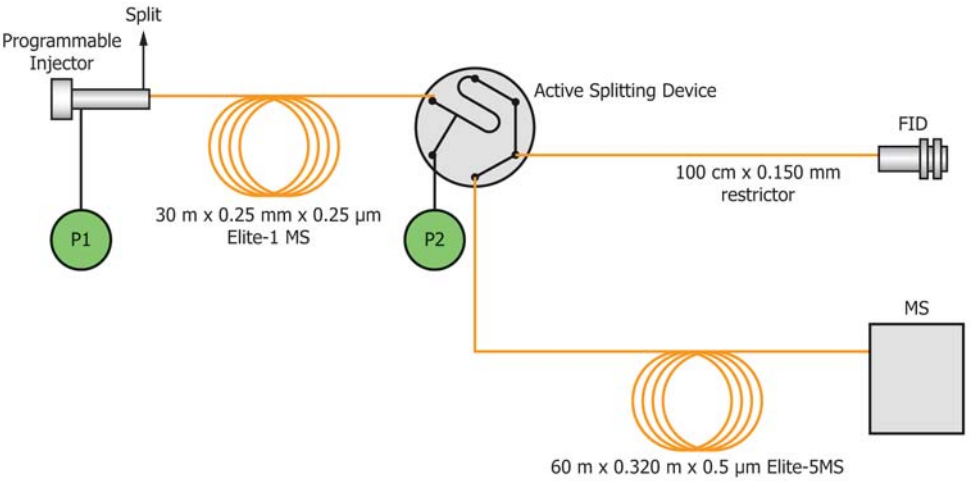

FIG. 2 Deans Switching Backflush, Configuration B

within the linearity of the mass spectrometer and at the same time maintain detectability of lower concentration chemical components.

6.2.1.2 Acquistion mode selected ion monitoring (SIM) extracted ion mode or full scan mode using the quantitative and qualitative ions referenced in Table 2. Additional compounds may be added by selecting and collecting data in full scan mode.

6.2.1.3 Tuning shall be performed for low mass resolution using perfluorotributylamine mass fragment ions at m/z 69, 131, and 219 amu. The mass spectrometer is tuned either automatically or manually for optimum performance.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents 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.

7.2 *Carrier Gas*—Helium and hydrogen have been used successfully. The recommended minimum purity of the carrier gas used is 99.999 mol %. Additional purification using commercially available scrubbing reagents may be necessary to remove trace oxygen, which may deteriorate the performance of the GC WCOT.

[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 *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 2 Mass Spectrometer Compound Quantitation Ions (Retention Time Data Based on Configuration A)

Retention Time	Compound	CAS #	Quantifying	Qualifier 1	Qualifier 2	Qualifier 3
21.55	Ethylbenzene-d10	25837-05-2	116	115		
13.55	n-butyl alcohol	71-36-3	56	74		
22.58	Cyclohexanol	108-93-0	82	100	44	
22.61	n-butyl ether	142-96-1	87	101	130	
22.78	n-butyl acrylate	141-32-2	55	128	73	
23.23	Styrene	100-42-5	104			
26.03	alpha-pinene	80-56-8	93	136	121	
26.66	Phenol	108-95-2	94	66		
27.79	alpha-methyl styrene	98-83-9	118	103		
28.21	beta-pinene	19902-08-0	93	136	121	
28.46	4-methyl styrene	622-97-9	117	118	116	103
28.57	trans-B-methyl styrene	873-66-5	117	118	103	77
28.66	3-methyl styrene	100-80-1	117	118	116	103
29.95	2-methyl styrene	611-15-4	117	118	103	77
30.11	Dicyclopentadiene	77-73-6	66	132		
30.43	Limonene	5989-27-5	68	93	136	121
31.11	Indene	95-13-6	116	115	63	89
31.16	1-phenyl ethanol	98-85-1	107	122	79	
32.93	para, alpha-Dimethyl styrene	1195-32-0	132	117	102	
33.29	2,5 dimethyl styrene	2039-89-6	132	117	77	
33.47	2,4 dimethyl styrene	2234-20-0	132	117	77	
33.57	2-phenyl ethanol (phenylethanol)	60-12-8	122	103	77	
34.05	2-Ethyl Phenol	90-00-6	107	122	77	
34.55	2,4 Dimethyl Phenol	105-67-9	122	107	77	
35.13	4-Ethyl Phenol (co elutes with 3-ethylphenol)	123-07-9	107	122	77	
	3-ethylphenol (co elution)	620-17-7				
35.86	2-Phenoxy-1-propanol	4169-04-4	94	152	121	
37.43	2-Phenoxy ethanol	122-99-6	94	138	77	
37.51	4-isopropylphenol	99-89-8	121	136	94	77
38.53	1-Phenoxy-2-Propanol	770-35-4	94	152	108	77
40.53	Styrene Glycol	93-56-1	107	138	79	

7.3 *Calibration Standard*—This standard shall be prepared by adding the chemicals to include those in Table 1 prepared from high (99+ %) purity reagent grade materials.

7.4 *Standards for Calibration and Identification*—Chemical compounds used to prepare standards should be 99 % or greater purity (see Table 1). If reagents of high purity are not available, an accurate assay of the reagent shall be performed using a properly calibrated GC or other techniques. The concentration of the impurities that overlap the other calibration components shall be known and used to correct the concentration of the calibration components. The use of only high purity reagents is strongly recommended because of the error that may be introduced from impurity corrections. Standards are used for calibration as well as for establishing the identification by retention time in conjunction with mass spectral match.

7.5 *n-hexadecane*—99+ % purity or better.

7.6 *Dilution Solvents*—Reagent grade toluene, 99.9 % (or suitable dilution solvent).

7.7 *Internal Standards*—Deuterated analog of ethylbenzene, as specified, shall be used as internal standard because of the similar chromatographic characteristics as the components analyzed.

8. Preparation of Apparatus

8.1 *Assembly*—Configure the GC system in a multidimensional configuration as described in Table 3 and Table 4. Connect the WCOT columns to the chromatographic system, including the multidimensional switching device, using low volume connectors and inert narrow bore tubing. It is important to minimize the volume of the chromatographic system that comes in contact with the sample; otherwise, peak broadening will occur.

8.2 This section provides details to establish the configurations described in Fig. 1. For other column configurations, adjust backflush and or cut times, accordingly.

8.3 It is essential that the appropriate backflush time be determined to prevent heavy contaminants from reaching the analytical column and potentially interfering with the determination of compounds of interest.

8.4 *Setting the Backflush Time for Configuration A*—The pre-column connected to the analytical column and the mass spectrometer as shown in Fig. 1 inject the calibration standard and record the chromatogram. Identify the peaks. The retention time data are used to set the valve on time to assure the compound peaks are not backflushed. The retention times should be incorporated into the software timed events before continuing with sample analysis. Assure all of the compounds of interest are present and high boiling hydrocarbons are backflushed consistently. Assure the retention time data is repeatable. If retention time shifts are encountered check for leaks to include replacing septum and that all column and valve connections are leak free.

8.4.1 The procedure used is as follows:

8.4.1.1 Prepare a timing standard containing all of the compounds of interest.

8.4.1.2 Inject the timing standard into the GC in the foreflush position with no backflush.

TABLE 3 Operating Conditions Configuration A

Gas Chromatograph:			
Inlet Type:	Purged Packed		
Inlet Temperature:	325 °C		
Oven temperature program:	70 °C for 2 min then 2.5 °C/min to 100 °C for 0 min then 4.5 °C/min to 185 °C for 0 min then 65 °C/min to 322 °C for 20 min		
Run Time:	54.997 min		
Columns:	25 m, 0.53 mm ID, 1.0 µm film polydimethylsiloxane (pre-column); 100 m, 0.25 mm ID, 0.5 µm film polydimethylsiloxane (analytical column)		
Carrier gas:	Helium		
Carrier gas:	Purged Packed Inlet Pre-column: 38 psi (262 kPa)		
Carrier gas:	Analytical Column - Auxiliary Pressure Module 1 set at 37 psi (255.1 kPa)		
Auxiliary Oven Temperature:	325 °C		
Valve 1 Timing:	Valve on at 3.5 min		
Needle Valve 1 Flow Setting:	7 mL/min		
GC-MS Interface:	Direct or open split interface		
GC-MS Interface Temperature:	350 °C		
Mass Spectrometer:			
Detector:	Quadrupole mass spectrometer		
MS Data Acquisition Mode:	Selected Ion Mode		
Ionization Voltage:	(eV) 70, fixed operating condition		
Mass Scan Range:	m/z 35-200		
Scan Rate (scan/s):	> 1		
Resolution Setting:	Low		
Ions/Dwell In Group	(Mass, Dwell)	(Mass, Dwell)	(Mass, Dwell)
	(41.00, 50)	(44.00, 50)	(51.00, 50)
	(55.00, 50)	(56.00, 50)	(63.00, 50)
	(66.00, 50)	(68.00, 50)	(73.00, 50)
	(74.00, 50)	(77.00, 50)	(79.00, 50)
	(82.00, 50)	(87.00, 50)	(89.00, 50)
	(91.00, 50)	(93.00, 50)	(94.00, 50)
	(98.00, 50)	(100.00, 50)	(101.00, 50)
	(103.00, 50)	(104.00, 50)	(105.00, 50)
	(107.00, 50)	(108.00, 50)	(116.00, 50)
	(117.00, 50)	(118.00, 50)	(121.00, 50)
	(122.00, 50)	(128.00, 50)	(130.00, 50)
	(132.00, 50)	(136.00, 50)	(138.00, 50)
	(152.00, 50)		
MS Source Temperature:	250 °C		
MS Quad Temperature:	200 °C		

TABLE 4 Operating Conditions Configuration B

Gas Chromatograph:	
Inlet Type:	Programmable split/splitless
Inlet Temperature:	200 °C for 14 min, then 200 °C/min to 400 °C, hold until end of run
Oven temperature program:	50 °C for 2 min then 7 °C/min to 200 °C for 0 min
Run Time:	24 min
Columns:	30 m, 0.25 mm ID, 0.25 µm film polydimethylsiloxane (pre-column); 60 m, 0.32 mm ID, 0.5 µm film 5% phenyl/polydimethylsiloxane (analytical column)
Bypass restrictor	2 m × 0.150 µm deactivated fused silica tubing
Carrier gas:	Helium
Carrier gas:	PSS Inlet Pre-column: 38 psig (261 kPa) for 14 min then 2 psig (13.78 kPa) for the remainder of the run
Carrier gas:	Split flow rate 25 mL/min for duration of run
Carrier gas:	Analytical Column - Auxiliary Pressure Module set at 15 psig (103.4 kPa) for the entire run
Mid-point monitor detector:	Flame ionization
Mass Spectrometer:	
GC-MS Interface:	Direct
GC-MS Interface Temperature:	250 °C
Detector:	Quadrupole mass spectrometer
MS Data Acquisition Mode:	Full scan with extracted ion quantification
Ionization Voltage:	(eV) 70 fixed operating condition
Mass Scan Range:	m/z 35-200
Scan Rate (scan/s):	> 1
MS Source Temperature:	250 °C

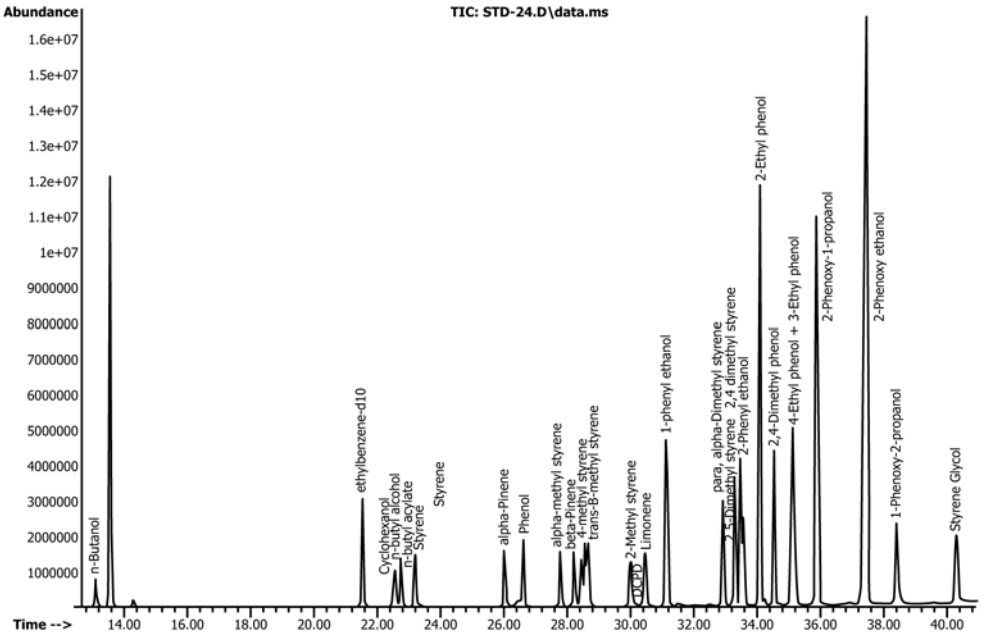

FIG. 3 TIC Chromatogram using Configuration A

8.4.1.3 Analyze the resulting chromatogram and determine the retention time of each of the compound peaks. See Figs. 3-5.

8.4.1.4 Starting at an arbitrary backflush time (4 min is a good starting point) reinject the sample and analyze the chromatogram for the presence of the compound peaks including C16.

8.4.1.5 Reduce the backflush time in 30 s increments and repeat until little or no C16 is visible. There should not be any significant decrease in the highest boiling compound peak area. Record this time as the backflush time. Conversely, if none of the peaks are visible, increase the backflush time in 30 s increments and repeat step (4) until the highest boiling compound peak area is entirely foreflushed into the analytical column.

8.5 *Setting the Backflush Time for Configuration B*—The elution of peaks from the precolumn is monitored by the flame ionization detector. The required backflush time may be established by locating the styrene glycol peak in a chromatogram of the calibration standard and setting the backflush point just after this.

8.5.1 The procedure used is as follows:

8.5.1.1 Prepare a timing standard containing all of the compounds of interest at a nominal concentration of 500 ppm.

8.5.1.2 Inject the timing standard into the GC in the foreflush position with no backflush.

8.5.1.3 Monitor the pre-column chromatogram on the FID and wait until the n-hexadecane solvent has eluted.

8.5.1.4 Analyze the resulting FID chromatogram and determine the retention time of the last eluting analyte, styrene glycol. See Fig. 6.

8.5.1.5 Enter a timed event into the analytical method to reduce the pressure at the injector to 2 psig (13.78 kPa) by a timed event at a time 0.5 min to 1.0 min later than the retention time of styrene glycol as shown in Fig. 2.

8.5.1.6 Check operation of the new method by re-injecting the timing mix and confirm that no peaks elute after styrene glycol from both columns.

NOTE 1—Backflush time is dependent upon specific instrument operating conditions, such as flow rate and temperature.

8.6 Replacement of the inlet septum should be performed at least every 10 to 20 injections to reduce the possibility of leaks. Liner replacement should be performed regularly if system performance degrades. The injection port septum purge line should be inspected and cleaned as necessary after 150 injections or when the performance deteriorates based on quality control sample performance data.

9. Calibration

9.1 *Preparation of Calibration Standards*—Prepare multicomponent calibration standards using the compounds referenced in Table 5 in toluene based on Test Method D4307.

9.2 Prepare a solution of 1 mg⁄kg of styrene and verify that it is detected with a signal to noise ratio of at least 5 at mass 104.

9.3 Each component in Table 1 shall be calibrated using a minimum of 5 point calibration curve in the range of approximately 10 mg⁄kg to 500 mg⁄kg (or as outlined in Table 5), accordingly.

9.4 In addition to the calibration standards, an instrument check standard shall be prepared from a different stock source and used to verify calibration. The composition of the calibration check standard shall contain the same compounds noted in Table 1. The linear working range of the mass spectrometer is established using the multipoint calibration standards established in step 1 of the calibration section. Samples containing compounds exceeding the calibration shall be diluted and retested to assure the concentration is within the calibrated range.

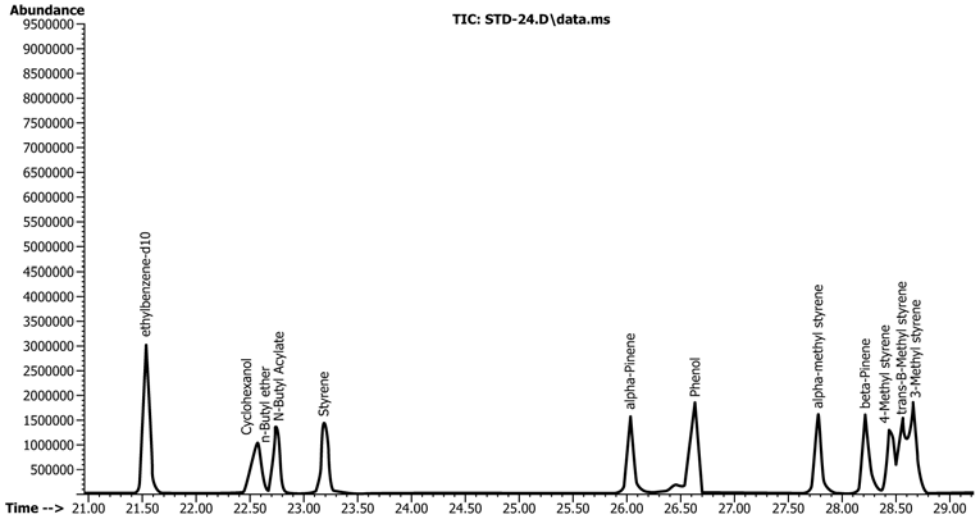

FIG. 4 TIC Chromatogram using Configuration A (21 min – 29 min window)

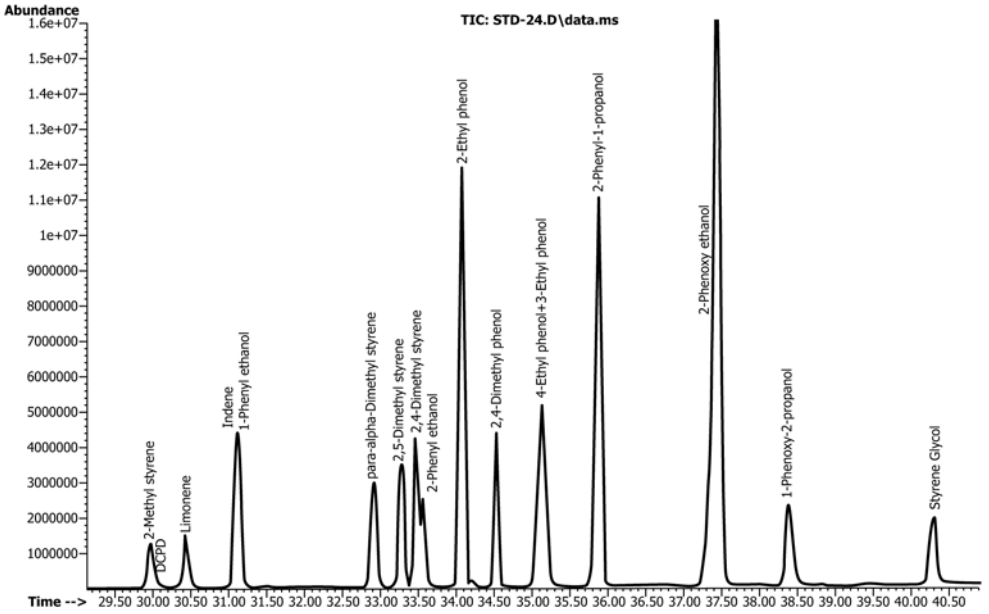

FIG. 5 Chromatogram using Configuration A (29 min – 41 min window)

9.5 Calibration verification shall be performed by analyzing the calibration check standard prior to and after each set of 5 samples thereby bracketing each set of 5 samples. If the calibration check standard is outside the established SQC control limits, immediately cease sample analyses and initiate an investigation and corrective action.

9.6 Check the correlation r^2 value for each chemical compound calibration. The value r^2 should be at least 0.90 or better (in most cases r^2 values of 0.99 or better can be obtained). Most modern commercial GCMS software is capable of performing this verification.

9.7 *Preparation of Internal Standard*—Prepare a stock internal standard solution containing 1000 mg⁄kg of ethylbenzene d10 in toluene. Accurately weigh 0.05 g of ethylbenzene d10 into 50 g of toluene and correct for the purity of ethylbenzene d10. Store this 1000 mg⁄kg internal standard in a refrigerator at 4 °C when not in use within one month.

9.8 Test each calibration standard using the instrument parameters. Record the data in such a manner that retention times and peak area response for each component are obtained. Peak identification is performed by using mass spectral software to identify each compound with the corresponding target quantitative and qualifier ions.

10. Quality Control Reference Material

10.1 After the calibration has been completed, prepare a quality control reference containing all compounds in Table 1. Analyze the reference material as described in Sections 11 through 13. The individual compound values obtained shall agree within ±10 % relative of the values in the prepared

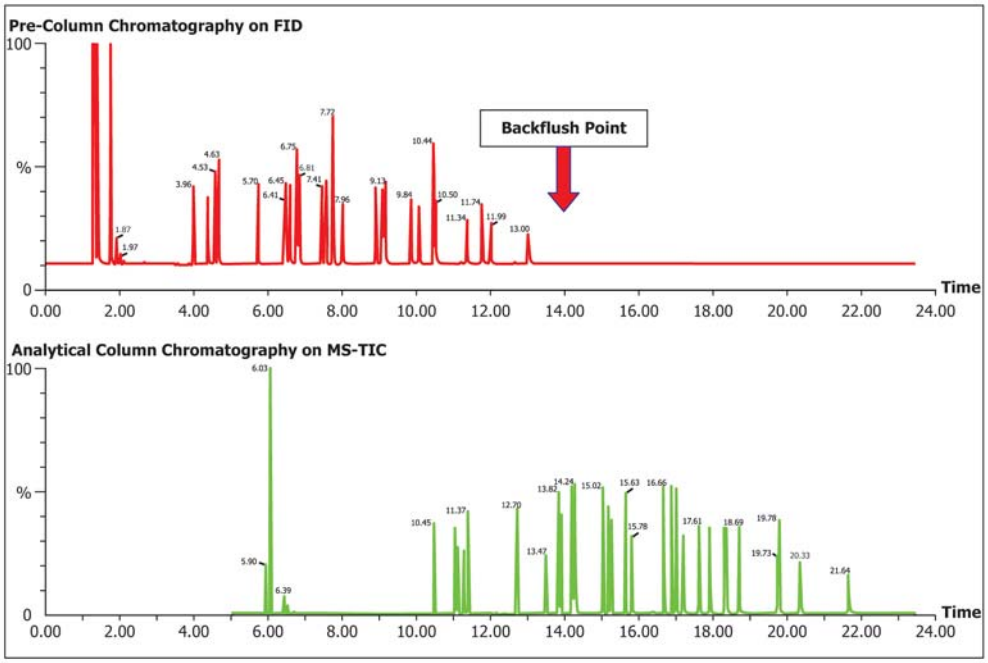

FIG. 6 Precolumn Chromatogram from FID and Analytical Column TIC Chromatogram from MS using Configuration B

TABLE 5 Preparation of Calibration Standards

Compound	Level 1 Weight %	Level 2 Weight %	Level 3 Weight %	Level 4 Weight %	Level 5 Weight %
Ethylbenzene d-10	0.0500	0.0500	0.0500	0.0500	0.0500
n-butyl alcohol	0.0010	0.0025	0.0075	0.0150	0.0300
Cyclohexanol	0.0010	0.0025	0.0075	0.0150	0.0300
n-butyl ether	0.0010	0.0025	0.0075	0.0150	0.0300
n-butyl acrylate	0.0010	0.0025	0.0075	0.0150	0.0300
Styrene	0.0010	0.0025	0.0075	0.0150	0.0300
alpha-pinene	0.0010	0.0025	0.0075	0.0150	0.0300
Phenol	0.0020	0.0040	0.0120	0.0240	0.0480
alpha-methyl styrene	0.0010	0.0025	0.0075	0.0150	0.0300
beta-pinene	0.0010	0.0025	0.0075	0.0150	0.0300
3-methyl styrene	0.0010	0.0025	0.0075	0.0150	0.0300
trans-beta-methyl styrene	0.0010	0.0025	0.0075	0.0150	0.0300
4-methyl styrene	0.0010	0.0025	0.0075	0.0150	0.0300
2-methyl styrene	0.0010	0.0025	0.0075	0.0150	0.0300
DCPD	0.0010	0.0025	0.0075	0.0150	0.0300
Limonene	0.0010	0.0025	0.0075	0.0150	0.0300
Indene	0.0020	0.0040	0.0120	0.0240	0.0480
1-phenyl ethanol	0.0020	0.0040	0.0120	0.0240	0.0480
para, alpha-dimethyl styrene	0.0020	0.0040	0.0120	0.0240	0.0480
2,5 dimethyl styrene	0.0020	0.0040	0.0120	0.0240	0.0480
2,4 dimethyl styrene	0.0020	0.0040	0.0120	0.0240	0.0480
2-phenyl Ethanol	0.0020	0.0040	0.0120	0.0240	0.0480
2-ethyl Phenol	0.0050	0.0100	0.0250	0.0500	0.1000
2,4 Dimethyl Phenol	0.0020	0.0040	0.0120	0.0240	0.0480
4-Ethyl Phenol + 3-Ethyl Phenol	0.0020	0.0040	0.0120	0.0240	0.0480
2-Phenyoxy -1-Propanol	0.0050	0.0100	0.0250	0.0500	0.1000
2-Phenoxy ethanol	0.0050	0.0100	0.0250	0.0500	0.1000
4-isopropylphenol	0.0050	0.0100	0.0250	0.0500	0.1000
1-Phenoxy-2-Propanol	0.0050	0.0100	0.0250	0.0500	0.1000
Styrene Glycol	0.0020	0.0040	0.0120	0.0240	0.0480

reference material. If the individual values are outside the specified range, verify calibration and instrumental parameters, and backflush timing.

10.2 If the linear least squares calibration does not yield results that meet the criteria, verify the calibration, calibration materials and instrument set up before testing samples.

10.3 Analyze the quality control reference materials before every batch of samples. It is recommended that the samples are bracketed by the reference materials in the form of calibration verification standards. If the reference material calibration does not meet the specifications in 10.1, the samples analyzed immediately preceding the reference material are considered suspect and should be rerun. Calibration shall be verified to assure consistent results due to mass spectrometer drift and tuning setting changes caused by mass spectral tuning.

10.4 When quality control/quality assurance (QC/QA) protocols are already established in the testing facility, they can be used, provided they include procedures to monitor the reliability of the test results. Refer to Appendix X1for additional information.

11. Procedure

11.1 Prepare each sample by adding 5 g of sample to a scintillation vial and record the weight. Then add 5 g of the 1000 mg⁄kg internal standard solution prepared in 9.7 and record the weight. The final internal standard concentration shall be approximately 500 mg⁄kg and is calculated using the weights obtained in this section. The sample weight and internal standard weights are used by the GC/MS chromatography software.

11.2 Ensure that the GC/MS operating conditions are identical to those used for calibration, the system is properly calibrated, and that all of the criteria in Sections 9 and 10 are met.

11.3 Transfer a sufficient quantity of the sample containing the appropriate internal standards from Section 11 to fill a GC autosampler vial and seal with a leak free septum cap.

11.4 Place the sample vial on the autosampler and start the analysis.

11.5 Software is available on commercial GC/MS systems for performing the mass spectral analysis.

12. Calculation

12.1 *Mass Concentration of Chemical Components:*

12.1.1 *Calibrated Components (*Table 1*)*—Identify the various aromatic components in Table 2 from their retention times and mass spectrum. To identify a compound, obtain a RIC for the primary ion (molecular ion used for quantitation) and the two other major secondary ions listed in Table 2. The criteria below shall be met for a qualitative identification:

12.1.1.1 SIM ions referenced in Table 2 with corresponding retention times are used for identification of each compound, accordingly. The quantitative ions are used to establish the calibration data. Qualifier ions are used to positively identify each compound when present at the same retention time and in the same relative ratios to known reference materials tested on the same mass spectrometer.

12.1.1.2 The characteristic ions for the compound shall be found to maximize in the same or within one spectrum or scan of each other. Ions for the compound shall agree within ±30 %, ±50 % and ±100 % relative for ions with a relative intensities of >50 %, 20 to 50 % and <20 %, respectively, when compared to the relative ion intensity ratios obtained for a calibration standard containing the compound at approximately the same concentration.

12.1.1.3 The retention time at the maximum intensity scan must be within ±15 s of the retention time of the authentic compound from the calibration analyses.

12.1.2 Calculations are performed using suitable commercially available GC/MS software.

13. Precision and Bias

13.1 It is not feasible to provide a complete precision statement covering repeatability and reproducibility for this test method at this time since a sufficient quantity of repeat tests and samples under the required ASTM protocol are not available. This information is being determined and will be available on or before May 31, 2018.

13.2 The temporary repeatability standard deviation was determined to be as shown in Table 6. These values were determined by selecting one standard containing the chemical species given in Table 1 in n-hexadecane, which was analyzed 2 times within a short time by a single operator in one laboratory. The repeatability standard deviation was calculated using the root-mean-square method.

13.3 *Bias*—Since there is no accepted reference material for determining the bias for the procedure in this test method for measuring the chemical species noted in Table 1, no statement on bias is being made.

14. Keywords

14.1 bunker fuel oil; gas chromatography; GC/MS; marine fuel oil; mass spectrometry

TABLE 6 Repeatability Estimates for Chemical Compounds

Compound	Result 1	Result 2	Average	Std Dev, Repeatability Condition	Repeatability Limit
n-Butanol	28.9	26.80	27.8	1.45	4.059
Cyclohexanol	28.0	31.99	30.0	2.81	7.860
n-Butylether	26.2	30.00	28.1	2.66	7.444
N-Butyl Acrylate	73.4	68.80	71.1	3.25	9.108
Styrene	41.2	43.36	42.3	1.54	4.316
alpha-Pinene	32.9	29.35	31.1	2.52	7.048
Phenol	51.2	58.99	55.1	5.49	15.364
alpha-methylstyrene	29.0	33.00	31.0	2.82	7.900
beta-Pinene	30.8	35.00	32.9	2.99	8.375
4-Methylstyrene	27.0	24.53	25.8	1.75	4.890
trans-B-Methyl styrene	38.9	45.01	41.9	4.33	12.137
3-Methylstyrene	35.0	32.00	33.5	2.12	5.940
2-Methylstyrene	32.9	24.21	28.6	6.15	17.225
DCPD	69.8	59.61	64.7	7.21	20.175
Limonene	30.3	23.58	26.9	4.73	13.246
Indene	56.2	52.30	54.2	2.72	7.623
1-Phenyl ethanol	48.9	42.75	45.8	4.33	12.117
para-alpha-Dimethylstyrene	58.3	47.20	52.7	7.81	21.878
2,5-Dimethylstyrene	59.2	49.36	54.3	6.92	19.383
2,4-Dimethystyrene	61.0	47.06	54.0	9.88	27.659
2-Phenylethanol	63.5	48.95	56.2	10.27	28.768
2-Ethylphenol	148.1	127.25	137.7	14.76	41.320
2,4-Dimethylphenol	63.3	51.50	57.4	8.31	23.264
4-Ethylphenol + 3-Ethylphenol	116.0	86.47	101.2	20.89	58.486
2-Phenyl-1-propanol	139.4	115.25	127.3	17.10	47.874
2-Phenoxyethanol	126.5	101.98	114.2	17.33	48.527
4-Isopropylphenol	142.5	121.80	132.2	14.67	41.063
1-Phenoxy-2-propanol	48.2	37.31	42.7	7.67	21.462
Styrene Glycol	56.3	43.66	50.0	8.96	25.085

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL PROTOCOL

X1.1 Monitor and control the stability and precision of the instrument by regularly analyzing a quality control (QC) sample.

X1.1.1 The type of QC sample used should be similar to the samples routinely analyzed by the instrument. An ample supply of QC material should be available for the intended period of quality control, and must be homogeneous and stable under the anticipated storage conditions.

X1.1.2 The frequency of QC testing is dependent on the criticality of the analysis, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each day of testing. The QC testing frequency should be increased if a large number of samples are routinely analyzed. However, when the testing process is demonstrated to be in statistical control, the QC testing frequency may be reduced.

X1.2 Record the QC sample results and analyze by control charts or other statistically equivalent techniques to immediately ascertain the statistical control status of the measurement process. See Practice D6299 and MNL 7A[6] for further guidance on QC and control charting techniques.

X1.2.1 Prior to using a QC sample control chart for assessing whether the measurement process is in statistical control, the user of the test method must have accumulated at least 15 suitable measurements and calculated an average value and control limits for the QC sample.

X1.2.2 Any QC sample result outside of control limits should trigger an investigation for root cause(s). The result of this investigation may indicate the need for instrument recalibration and other remedial action.

X1.2.3 Compare the site repeatability estimated from the QC sample with the published precision of this test method.

[6] MNL 7A, *Manual on Presentation of Data and Control Chart Analysis*, 7th Edition, ASTM International, 2002. Out of print.

SUMMARY OF CHANGES

Subcommittee D02.04 has identified the location of selected changes to this standard since the last issue (D7845 – 16) that may impact the use of this standard. (Approved Jan. 15, 2017.)

(1) Revised Table 4.

Subcommittee D02.04 has identified the location of selected changes to this standard since the last issue (D7845 – 13) that may impact the use of this standard. (Approved April 1, 2016.)

(1) Revised Table 1, Table 2, and Table 5.