



# Standard Test Method for Determination of Chemical Species in Marine Fuel Oil by Multidimensional Gas Chromatography – Mass Spectrometry<sup>1</sup>

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 ( $\epsilon$ ) 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. No other units of measurement are included in this standard.

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:*<sup>2</sup>

[D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards](#)

[D6299 Practice for Applying Statistical Quality Assurance](#)

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0M on Mass Spectroscopy.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[and Control Charting Techniques to Evaluate Analytical Measurement System Performance](#)

## 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. 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.

**TABLE 1 Component Table**

	Limit of Quantitation mg/kg
n-butyl alcohol	10
Cyclohexanol	10
n-butyl ether	10
n-butyl acylate	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

## 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 method is necessary to establish test conditions required for future ISO 8217:2010 Petroleum products- Fuels (class F)-Specifications of marine fuel oils 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 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*<sup>3</sup> (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 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 within the linearity of the mass spectrometer and at the same time maintain detectability of lower concentration chemical components.

<sup>3</sup> Deans, David R., *Chromatographia*, Vol 1, 18-22, 1968.

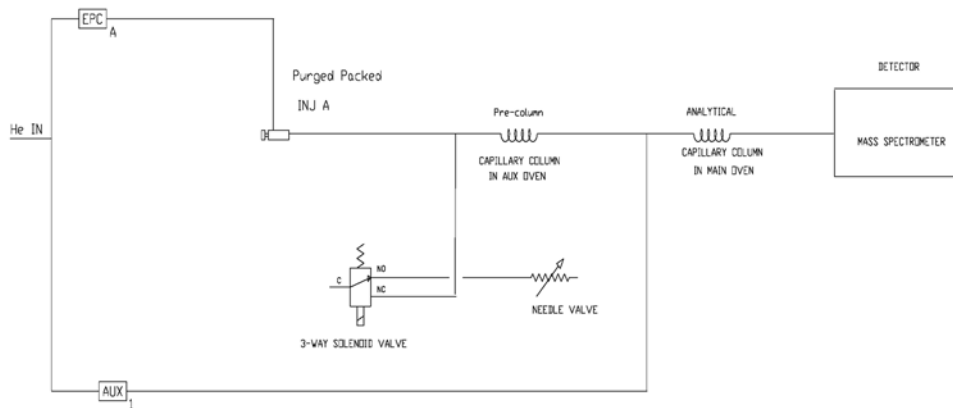


FIG. 1 Deans Switching Backflush, Configuration A

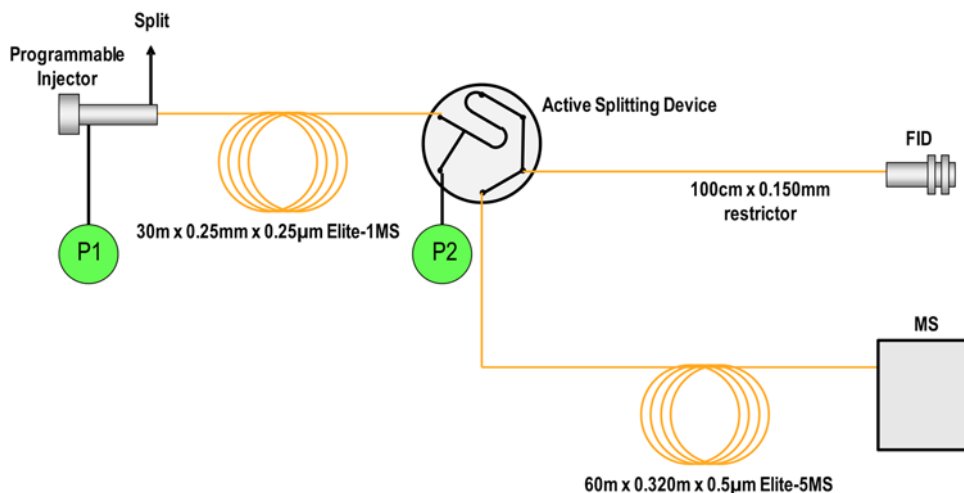


FIG. 2 Deans Switching Backflush, Configuration B

6.2.1.2 Acquisition 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.<sup>4</sup> Other grades may be used,

<sup>4</sup> 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.

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.

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