



Standard Test Method for Purity of Methyl Ethyl Ketone By Gas Chromatography¹

This standard is issued under the fixed designation D 2804; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope *

1.1 This test method covers the determination of the purity of methyl ethyl ketone by gas chromatography. Impurities including water, acidity, and nonvolatile matter are measured by appropriate ASTM procedures and the results are used to normalize the chromatographic value.

1.2 For purposes of determining conformance of an observed value or a calculated value using this test method to relevant specifications, test result(s) shall be rounded off “to the nearest unit” in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

1.3 For hazard information and guidance, see the supplier’s Material Safety Data Sheet.

2. Referenced Documents

2.1 ASTM Standards:

D 1353 Test Method for Nonvolatile Matter in Volatile Solvents for Use in Paint, Varnish, Lacquer, and Related Products²

D 1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)²

D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer and Related Products²

D 2593 Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography³

D 4626 Practice for Calculation of Gas Chromatographic Response Factor⁴

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁵

E 180 Practice for Determining the Precision of ASTM

Methods for Analysis and Testing of Industrial and Specialty Chemicals⁶

3. Summary of Test Method

3.1 A representative specimen is introduced into a gas-chromatographic column. The methyl ethyl ketone is separated from other impurities such as hydrocarbons, alcohols, acetone, di-sec-butyl ether, and ethyl acetate as the components are transported through the column by an inert carrier gas. The separated components are measured in the effluent by a detector and recorded as a chromatogram. The chromatogram is interpreted by applying component-attenuation and detector-response factors to the peak areas, and the relative concentration is determined by relating individual peak response to the total peak response. Water, acidity, and nonvolatiles are measured by the procedures listed in 3.2, and the results are used to normalize the results obtained by gas chromatography.

3.2 The appropriate ASTM test methods are:

3.2.1 *Water*—Test Method D 1364.

3.2.2 *Acidity*—Test Method D 1613.

3.2.3 *Nonvolatile Matter*—Test Method D 1353.

4. Significance and Use

4.1 This test method provides a measurement of commonly found impurities in commercially available methyl ethyl ketone. The measurement of these impurities and the results thereof can individually or when totaled and subtracted from 100 (assay) be used for specification purposes.

5. Apparatus

5.1 *Chromatograph*—Any gas chromatograph having either a thermal-conductivity or flame ionization detector provided the system has sufficient sensitivity and stability to obtain for 0.01 weight % of impurity a recorder deflection of at least 2 mm at a signal-to-noise ratio of at least 5 to 1. The specimen size to be used in judging the sensitivity must be such that the column is not overloaded.

5.2 *Column*—Any column capable of resolving methyl ethyl ketone from the impurities that may be present. Possible impurities are paraffins, acetone, methanol, ethanol, propanol, isopropanol, *tert*-butanol, *sec*-butanol, di-*sec*-butyl ether, and

¹ This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.35 on Solvents, Plasticizers, and Chemical Intermediates.

Current edition approved July 10, 2002. Published September 2002. Originally published as D 2804 – 69. Last previous edition D 2804 – 98.

² *Annual Book of ASTM Standards*, Vol 06.04.

³ *Annual Book of ASTM Standards*, Vol 05.01.

⁴ *Annual Book of ASTM Standards*, Vol 05.02.

⁵ *Annual Book of ASTM Standards*, Vol 14.02..

⁶ *Annual Book of ASTM Standards*, Vol 15.05.

ethyl acetate. The peaks should be resolved, quantitatively in proportion to concentration, within a practical elapsed time. Columns that meet the requirements of this test method are listed in Table 1. Other columns may be used, provided the user establishes that a column gives the required separation and the precision requirements of Section 13 are met.

5.3 Specimen Introduction System—Any specimen system capable of introducing a representative specimen into the column may be used. Systems that have been used successfully to introduce 1 to 10- μ L of methyl ethyl ketone specimens include microlitre syringes, micropipets, and liquid sampling valves.

5.4 Recorder—An electronic integrator or a recording potentiometer with a full-scale deflection of 5 mV or less, full-scale response time of 2 s or less, and sufficient sensitivity to meet the requirements of 5.1.

6. Reagents and Materials

6.1 Carrier Gas, appropriate to the type of detector used. Helium or hydrogen may be employed with thermal conductivity detectors, and nitrogen, helium, or argon with ionization detectors. The minimum purity of any carrier should be 99.95 mol %.

6.1.1 Warning—If hydrogen is used, take special safety precaution to ensure that the system is free of leaks and that the effluent is vented properly.

6.2 Column Materials:

6.2.1 Liquid Phase—The materials successfully used in cooperative work as liquid phases are listed in Table 1 (see Note 1).

6.2.2 Solid Support—The support for use in the packed column is usually (PTFE)-fluorocarbon, crushed firebrick, or diatomaceous earth. Table 1 lists conditions used successfully

in cooperative work (see Note 1).

NOTE 1—See research report for additional information, available from ASTM International Headquarters. Request RR:D01-1107.

6.2.3 Tubing Material—Copper, stainless steel, nickel copper alloy, aluminum, and various plastic materials have been found to be satisfactory for column tubing. The material must be nonreactive with the substrate, sample, and carrier gas.

6.3 Standards for Calibration and Identification—Standard samples for all components present are needed for identification by retention time, and for calibration for quantitative measurements (Note 2).

NOTE 2—Mixtures of components may be used, provided there is no uncertainty as to the identity or concentration of compounds involved.

7. Preparation of Apparatus

7.1 Column Preparation—The method used to prepare the column is not critical provided that the finished column produces the required separation (Note 3). Partitioning liquids, supports, and loading levels used successfully in cooperative work are listed in Table 1. These may be obtained from most chromatography supply houses.

NOTE 3—A suitable method for column preparation is described in Test Method D 2593.

7.2 Chromatograph—Install the column in the chromatograph and establish the operating conditions required to give the desired separation. Relative component retention times, along with the typical retention time for methyl ethyl ketone are listed in Table 1. Allow sufficient time for the instrument to reach equilibrium as indicated by a stable recorder baseline.

TABLE 1 Columns and Conditions Used Successfully in Cooperative Work

	Case I	Case II	Case III	Case IV	Case V	Case VI
Column:	packed	packed	packed	packed	packed	capillary
Liquid phase	polyethylene glycol 1500	polyethylene glycol 400	polyethylene glycol 300	polyethylene glycol 200	polyethylene glycol 1500	polytrifluoro-propylsiloxane
Liquid phase, weight %	10	28	20	20	20	1.2 μ m film
Support type	TFE resin	Pink, diatomaceous earth	Pink, diatomaceous earth	White, diatomaceous earth	Pink, diatomaceous earth	none
Support mesh size	40/60	30/60	40/60	60/80	60/80	...
Length, ft (m)	12 (3.7)	18 (5.5)	10 (3.0)	10 (3.0)	20 (6.1)	32.8 (10.0)
Outside diameter, in. (mm)	0.25 (6.4)	0.25 (6.4)	0.25 (6.4)	0.125 (3.2)	0.25 (6.4)	0.028 (0.72)
Inside diameter, in. (mm)	0.21 (5.3)	0.21 (5.3)	0.21 (5.3)	0.085 (2.2)	0.21 (5.3)	0.021 (0.53)
Column temperature, °C	100	80	75	70	100	30
Carrier gas	helium	helium	helium	helium	helium	helium
Carrier flow rate, mL/min	60	80	35	60	50	3.7
Typical retention time, min	6.9	17.0	11.0	5.8	16.5	8.8
Relative retention time (methyl ethyl ketone = 1.00):						
Propyl ether	0.19	0.14	...	...	...	...
Octenes	0.54	0.21	...	0.34	...	0.65
sec-Butyl ether	0.78	0.45	...	0.47	1.21	...
Acetone	0.61	0.54	0.64	0.67	0.67	0.60
Ethyl acetate	0.81	...	0.82	0.78	0.85	0.78
Methyl ethyl ketone	1.00	1.00	1.00	1.00	1.00	1.00
tert-Butanol	1.00	1.12	1.27	1.71	1.03	0.39
Methanol	1.10	...	1.36	1.71	1.09	0.27
Isopropanol	1.20	1.32	...	2.03	2.12	0.34
Ethanol	1.30	...	1.73	2.21	1.27	0.31
sec-Butanol	2.12	2.26	2.73	3.50	1.94	0.53
n-Propanol	2.35	...	3.27	3.97	...	0.43

8. Calibration and Standardization

8.1 *Identification*—Select the conditions of column temperature and carrier-gas flow that will give the necessary component resolution. Determine the retention time for each component by injecting small amounts of the compound either separately or in mixtures.

8.2 *Standardization*—The area under the peak of the chromatogram is considered a quantitative measure of the amount of the corresponding compound. The relative area is proportional to the concentrations if the detector responds equally to all of the sample components. Differences in detector response may be corrected by use of relative response factors obtained by injecting and measuring the response to pure (99 weight % minimum) compounds or known blends. It is permissible to use the established response factors shown in Table 2 instead of standardization.

8.3 In using literature values, area response from thermal-conductivity detectors is corrected by multiplying each component area by the respective weight factor above.

NOTE 4—It must be recognized that the use of published response factors serves only as a rough estimate, due to differences in equipment geometry, condition, and types of detectors. It is preferable for each analyst to determine actual response factors on his own instrument. Refer to Practice D 4626 for calculation of gas chromatographic response factor.

NOTE 5—When thermal-conductivity detectors are used for the analysis of high-purity methyl ethyl ketone, the difference between area percent is within the precision of the method.

9. Procedure

9.1 Using a suitable method selected from 5.3, introduce sufficient representative liquid specimen into the chromatograph to ensure a minimum of 10 % recorder deflection for a 0.1 % concentration of impurity at the most sensitive-operating setting of the instrument.

9.2 Using the same conditions as for component identification and standardization, record the peaks of all compounds at attenuation settings that provide maximum peak heights.

TABLE 2 Thermal Conductivity Detector^{A, B}

	Thermal Mole Response	Weight Factor
Methyl ethyl ketone	98	0.74
Di- <i>n</i> -butyl ether	160	0.81
Di-isopropyl ether	130	0.79
Ethyl acetate	111	0.79
<i>sec</i> -Butanol	97	0.76
<i>tert</i> -Butanol	96	0.77
Acetone	86	0.68
Isopropanol	85	0.71
Propanol	83	0.72
Ethanol	72	0.64
Methanol	55	0.58

^A The data on the thermal conductivity response are based on data presented by Messner, A. E. et al, *Analytical Chemistry*, Vol 31, 1959, pp. 230–233, and Dietz, W. A., *Journal of Gas Chromatography*, Vol 5, No. 2, February 1967, pp 68–71 (see Note 4 of this test method).

^B For reference, hydrogen flame response data on all compounds except the ethers are presented in the above paper by W. A. Dietz.

10. Calculation

10.1 Measure the area of all peaks (Note 6) and multiply by the appropriate attenuation factor to express the peak areas on a common basis. If a flame ionization detector was used, apply the appropriate detector-response factors to correct for the difference in response to the components. Calculate the weight percent composition by dividing the individual corrected component areas by the total corrected area. Make corrections to account for the water, acidity, and nonvolatile matter as determined by the ASTM procedures given in 3.1.

NOTE 6—Peak areas may be determined by any method that meets the precision limits given in Section 12. Methods found to be acceptable include planimetry, integration, and triangulation (multiplying the peak height by the width at the half-height).

10.2 Calculate weight percent as follows:

$$\text{Methyl ethyl ketone, weight \%} = (A/B) \times (100 - C) \quad (1)$$

where:

A = corrected peak response,

B = sum of corrected peak responses, and

C = sum of water, acidity, and nonvolatile impurities.

11. Report

11.1 Report the following information: weight percent of methyl ethyl ketone and any impurities of interest to the nearest 0.01 %.

12. Precision and Bias

12.1 *Precision*—The precision statements are based upon an interlaboratory study in which one operator in six different laboratories analyzed in duplicate on two days two specimens of methyl ethyl ketone from different manufacturers. The results were analyzed in accordance with Practice E 180, and the within-laboratory standard deviation was found to be 0.007 % absolute with 12 degrees of freedom and the between-laboratories standard deviation 0.033 % absolute with five degrees of freedom. Based on these standard deviations the following criteria should be used for judging the acceptability at the 95 % confidence level, of results obtained on methyl ethyl ketone having a purity of 99 to 100 %:

12.1.1 *Repeatability*—Two results each the mean of two runs obtained by a single analyst on different days should be considered suspect if they differ by more than 0.02 % absolute.

12.1.2 *Reproducibility*—Two results each the mean of two runs obtained by analysts in different laboratories should be considered suspect if they differ by more than 0.12 % absolute.

12.2 *Bias*—Bias can not be determined for this test method because there is no accepted reference material.

13. Keywords

13.1 GC; methyl ethyl ketone; purity by gas chromatography

SUMMARY OF CHANGES

Committee D01.35 has identified the location of selected changes to this standard since the last issue (D 2804 - 98) that may impact the use of this standard.

(1) Added Practice E 29 to the Scope section.

(2) Added Practice E 29 to the Referenced Documents section.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).