**Designation: D 3329 – 99**

# Standard Test Method for
# Purity of Methyl Isobutyl Ketone by Gas Chromatography[1,2]

This standard is issued under the fixed designation D 3329; 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 isobutyl ketone (MIBK) by gas chromatography and in addition provides a means for measuring certain impurities such as methyl isobutyl carbinol which are of interest. Impurities such as water and acidity are measured by other appropriate ASTM procedures and the results are used to normalize the chromatographic value.

1.2 *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.*

1.3 For specific hazard information and guidance, see the supplier's Material Safety Data Sheet for the materials listed in this test method.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)[3]

D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products[3]

D 2593 Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography[4]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[5]

E 260 Practice for Packed Column Gas Chromatography[6]

## 3. Summary of Test Method

3.1 A representative specimen is introduced onto a gas-liquid partition column. Methyl isobutyl ketone is separated from impurities such as acetone, 2-propanol, pentanone, mesityl oxide, methyl isobutyl carbinol, and several unidentified compounds 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 concentrations are determined by relating the individual peak responses to the total peak response. Water and acidity are measured in accordance with Test Methods D 1364 and D 1613 and the results are used to normalize the values obtained by gas chromatography.

## 4. Significance and Use

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

## 5. Apparatus

5.1 *Chromatograph*—Any gas liquid chromatographic instrument having either a thermal conductivity or flame ionization detector provided the system has sufficient sensitivity and stability to obtain for 0.01 % 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 used in judging the sensitivity must be such that the column is not overloaded, which would result in peak broadening, loss of resolution, shifting retention times and formation of leading peaks.

5.2 *Column*—Any column capable of resolving methyl isobutyl ketone from the impurities that may be present. Possible impurities are hydrocarbons, acetone, 2-propanol, 2-pentanone, 3-pentanone, mesityl oxide, mesityl oxide isomer, and methyl isobutyl carbinol. Columns that meet this requirement are described in Table 1. Other columns, including capillary columns, may be used, provided the user establishes that a column gives the required separation and the peak shapes are satisfactory for measurement so that the precision requirements of Section 12 are met.

5.3 *Specimen Introduction System*—Any system capable of introducing a representative specimen onto the column. Microlitre syringes have been used successfully.

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

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[2] IUPAC approved name is 4-methyl-2-pentanone.

[3] *Annual Book of ASTM Standards*, Vol 06.04.

[4] *Annual Book of ASTM Standards*, Vol 05.01.

[5] *Annual Book of ASTM Standards*, Vol 15.05.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

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

TABLE 1 Columns and Conditions Used Successfully in Cooperative Work (See Note 2)

| | Case I | Case II | Case III | Case IV | Case V | Case VI |
|---|---|---|---|---|---|---|
| *Column:* | | | | | | |
| Liquid phase | polyethylene glycol, MW 1450 | polyethylene glycol, MW 540 | ethylene oxide/ propylene oxide copolymer | polyethylene glycol, MW 20M | polyethylene glycol, MW 3350 | polyethylene glycol |
| Liquid phase, weight % | 15 | 20 | 20 | 25 | 25 | 1.2 µm film |
| Support | diatomaceous earth, acid washed | diatomaceous earth | diatomaceous earth, acid washed | diatomaceous earth | diatomaceous earth | capillary |
| Support mesh size | 60 to 80 | 60 to 80 | 45 to 60 | 60 to 80 | 60 to 80 | N/A |
| Length, ft (m) | 20 (6.1) | 18 (5.5) | 20 (6.1) | 10 (3.0) | 12 (3.7) | 33 (10) |
| Diameter, in. (mm) | ⅛ (3.2) | ¼ (6.4) | ¼(6.4) | ⅛ (3.2) | ¼ (6.4) | 0.021 (0.53) |
| Temperature, °C | 90 | 100 | 160 | 75 to 200 programmed at 4°/min | 145 | 40 to 180 at 5°/min |
| Carrier gas: | helium | helium | helium | helium | helium | helium |
| Flow rate, mL/min | 30 | 50 | 60 | 20 | 80 | 5 |
| Typical retention time, min: | | | | | | |
| Methyl isobutyl ketone | 9.3 | 27.2 | 8.1 | 11.2 | 7.7 | 1.84 |
| Relative retention time, MIBK = 1.00: | | | | | | |
| Acetone | 0.42 | 0.39 | 0.52 | 0.42 | 0.39 | 0.36 |
| 2-propanol | 0.66 | | 0.57 | 0.65 | 0.56 | 0.59 |
| 2- and 3-pentanone | 0.85 | 0.82 | 0.78 | ... | ... | 0.79 |
| Methyl isobutyl ketone | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| α-Mesityl oxide | 1.45 | 1.41 | 1.27 | ... | ... | ... |
| β-Mesityl oxide | 1.89 | 1.85 | 1.63 | 1.24 | 1.52 | ... |
| Methyl isobutyl carbinol | 2.11 | 2.07 | 1.48 | 1.42 | 1.95 | 2.24 |

5.4 *Recorder*—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 and stability to meet the requirements of 5.1.

## 6. Reagents and Materials

6.1 *Carrier Gas*—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 flame ionization detectors. The minimum purity of the carrier gas used should be 99.95 mol %.

NOTE 1—**Precaution:** If hydrogen is used, take special safety precautions to ensure that the system is free from leaks and that the effluent is vented properly.

6.2 *Column Materials*:

6.2.1 *Liquid Phase*—The materials successfully used in cooperative test work are listed in Table 1. (See Note 2.)

NOTE 2—Suppliers of liquid phases and supports can be found in Research Report RR:D01-1042, available from ASTM Headquarters.

6.2.2 *Solid Support*—The materials and their mesh sizes successfully used in cooperative work are shown in Table 1. (See Note 2.)

6.2.3 *Tubing Material*—Copper, stainless steel, and aluminum have been found satisfactory for column tubing. The tubing must be nonreactive with the substrate, sample, and carrier gas and be of uniform internal diameter.

6.3 *Standards for Calibration and Identification*—Standard samples of all components present are needed for identification by retention time and for calibration for quantitative measurements.

## 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.

NOTE 3—A suitable method for column preparation is described in Test Method D 2593. Additional useful information may be found in Practice E 260.

7.1.1 Prepacked columns conforming to requirements listed in Table 1 and in 5.2 and 6.2 may be obtained from any reputable chromatography supply company.

7.2 *Chromatograph*—Install the column in the chromatograph and establish the operating conditions required to give the desired separation. Allow sufficient time for the instrument to reach equilibrium as indicated by a stable recorder baseline. Control the detector temperature so that it is constant to within 1°C without thermostat cycling that causes an uneven baseline. Adjust the carrier-gas flow rate to a constant value.

## 8. Calibration and Standardization

8.1 *Identification*—Select the conditions of column temperature and carrier gas flow that will give the necessary resolution of the components. Determine the retention time of each component by injecting small amounts either separately or in known mixtures. Relative component retention times along with the typical retention time for methyl isobutyl ketone are given in Table 1.

8.2 *Standardization*—The area under each peak of the chromatogram is considered a quantitative measure of the corresponding compound. The relative area is proportional to concentration if the detector responds equally to all the sample components. When flame ionization detectors are used the response to different components is generally significantly different. 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) components or known blends. When thermal conductivity detectors are used for the analysis of high-purity methyl isobutyl ketone, the difference between area percent and weight percent is within the precision of the test method.

NOTE 4—Much data on thermal conductivity and flame ionization detector responses may be found in the literature. Useful information is given by Messner, et al[7] and by Dietz.[8]

## 9. Procedure

9.1 Introduce a representative specimen into the chromatograph using a microlitre syringe. Use sufficient specimen to ensure a minimum of 10 % recorder deflection for a 0.1 % concentration of impurity at the most sensitive setting of the instrument.

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

## 10. Calculation

10.1 Measure the area of all peaks (Note 5) and multiply each area 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 water and acidity present as determined in accordance with Test Methods D 1364 and D 1613.

NOTE 5—Peak areas may be determined by any method that meets the precision limits given in Section 12. Methods found to be acceptable are planimetering and integration.

10.2 Calculate the weight percent $W$ of each component as follows:

$$W = (A/B) \times (100 - C) \tag{1}$$

where:
$A$ = corrected peak response,
$B$ = sum of corrected peak responses, and
$C$ = sum of water and acidity.

## 11. Report

11.1 Report the following information: weight percent of methyl isobutyl ketone and any impurities of interest to the nearest 0.01 % absolute. Duplicate runs for major components that agree within 0.05 % absolute are acceptable for averaging (95 % confidence level).

## 12. Precision and Bias [9]

12.1 *Precision*—The precision statements are based upon an interlab-oratory study in which one operator in six different laboratories analyzed two samples of methyl isobutyl ketone in duplicate on two days. One sample represented commercial material having a purity of 99.8 % and containing 0.03 % methyl isobutyl carbinol and the other was prepared by adding 0.28 % of methyl isobutyl carbinol to the first sample. The results were analyzed in accordance with Practice E 180. Because one laboratory failed to report trace impurities, their results were omitted from the calculation of the precision statements. The within-laboratory standard deviation and between-laboratory standard deviation were found to be as follows:

| | Within Laboratory | Between Laboratory |
|---|---|---|
| Methyl isobutyl ketone | 0.014 | 0.078 |
| Methyl isobutyl carbinol | 0.011 | 0.044 |
| Degrees of freedom | 10 | 4 |

Based upon these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level for methyl isobutyl ketone having a purity of 99 to 100 % and containing from 0.0 to 0.5 % of the impurity methyl isobutyl carbinol.

12.1.1 *Repeatability*—Two results, each the mean of duplicates, obtained by the same operator on different days should be considered suspect if they differ by more than 0.05 % absolute for methyl isobutyl ketone or 0.03 % absolute for methyl isobutyl carbinol.

12.1.2 *Reproducibility*—Two results, each the mean of duplicates, obtained by operators in different laboratories should be considered suspect if they differ by more than 0.30 % absolute for methyl isobutyl ketone or 0.17 % absolute for methyl isobutyl carbinol.

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

## 13. Keywords

13.1 gas chromatography; ketone; methyl isobutyl ketone; MIBK; purity; solvent

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[7] Messner, A. E., et al, *Analytical Chemistry*, Vol 31, 1959, pp. 230–233.

[8] Dietz, W. A., *Journal of Gas Chromatography*, Vol 5, No. 2, February 1967, pp. 68–71.

[9] Supporting data are available from ASTM Headquarters. Request RR:D01-1042.

## SUMMARY OF CHANGES

Committee D-1 has identified the location of selected changes to this standard since the last date of issue that may impact the use of this standard.

(*1*) References to brand names and to specific suppliers of GC column liquid phases and supports have been removed from this test method and added to Research Report RR:D01-1042.

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