Designation: D 3893 – 99

Standard Test Method for Purity of Methyl Amyl Ketone and Methyl Isoamyl Ketone by Gas Chromatography[1]

This standard is issued under the fixed designation D 3893; 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 determination of the purity of methyl amyl ketone and methyl isoamyl ketone. In addition, the method determines total ketones and various impurities which may include acetone, isopropyl alcohol, methyl propyl ketone, methyl isobutyl ketone, methyl butyl ketone, methyl isobutyl carbinol, mesityl oxide, methyl isoamyl ketone, methyl butyl carbinol, methyl amyl ketone, and diisobutyl ketone.

1.2 Water and acid cannot be determined by this test method. They must be determined by other appropriate ASTM procedures, and the results used to normalize the chromatographic data.

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.*

1.4 For hazard information and guidance, see the supplier's Material Safety Data Sheet.

2. Referenced Documents

2.1 *ASTM Standards:*

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 Products[2]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[3]

3. Summary of Method

3.1 A representative specimen is introduced onto a gas-liquid partition column. 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 relative concentrations are determined by relating the individual peak responses to the total peak response. Water and acidity are measured by Test Methods D 1364 and D 1613, respectively, and the results are used to normalize the values obtained by gas chromatography.

4. Significance and Use

4.1 This procedure is designed to determine the purity of the two ketones, methyl isoamyl ketone and methyl amyl ketone, and to obtain the concentration of their various impurities, several of which are critical in the application of these solvents.

5. Apparatus

5.1 *Chromatograph*—Any gas-liquid chromatographic instrument having either a thermal conductivity or flame ionization detector and sufficient sensitivity and stability to obtain for 0.01 % impurity in the specimen a recorder deflection of at least 20 mm at a signal-to-noise ratio of at least 5 to 1. A recording integrator or computer data processing system may also be used.

5.1.1 The injection port of the chromatograph must have a volume of at least 1.2 mL to provide for proper vaporization of the specimen. The use of a smaller injection port or on-column injection causes peak broadening and tailing.

5.2 *Column*—Four and one half m of 3.2-mm stainless steel tubing packed with 80 to 90-mesh acid-washed, base-washed, and silanized diatomaceous earth support coated with 10.0 % 20 000 molecular weight polyethylene glycol and a 8.33 % phenyl methyl (50:50) silicone. A capillary column, capable of the required separation may also be used.

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

5.4 *Recorder*—A recording potentiometer with a full-scale deflection of 1 mV, full-scale response time of 1 s or less, and sufficient sensitivity and stability 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 flame ionization detectors. The minimum purity of the carrier gas used should be 99.95 mol %. An oxygen removal system is recommended for the carrier gas.

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

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

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

6.1.1 **Warning**—If hydrogen is used, take special safety precautions 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*—20 000 molecular weight polyethylene glycol and phenyl methyl (50:50) silicone.

6.2.2 *Solid Support*—Acid-washed, base-washed, and silanized diatomaceous earth, 80 to 90 mesh.

6.2.3 *Solvents*—Methylene chloride, reagent grade.

6.2.4 *Tubing Material*—The stainless steel tubing must be of uniform internal diameter and must be clean. Wash the inside of the tubing with methylene chloride, then water, and finally methyl alcohol and blow dry with nitrogen.

6.3 *Standards for Calibration and Identification*—Standard samples of all components are needed for establishing identification by retention time and for calibration for quantitative measurements. In most cases, the pure compounds required for calibration cannot be purchased and must be purified by distillation before use.

7. Preparation of Column

7.1 Place 50 g of the solid support, 80 to 90 mesh, in a large evaporating dish. Dissolve 12.5 g of the polyethylene glycol in about 40 mL of methylene chloride and add to the solid support. Add additional methylene chloride to wet and cover the solid support. Evaporate the methylene chloride in a fume hood with gentle stirring and under a gentle stream of nitrogen.

7.2 Place 50 g of the solid support in a large evaporating dish. Dissolve 10 g of the phenyl methyl silicone in about 40 mL of methylene chloride and add to the solid support. Add additional methylene chloride to wet and cover the solid support. Evaporate the methylene chloride in a fume hood with gentle stirring and under a gentle stream of nitrogen.

7.3 Add 12 g of the packing prepared in 7.1 and 12 g of the packing prepared in 7.2 to a small glass bottle or beaker and mix well. The mixture is used as the column packing material.

7.4 *Column Preparation*—The method used to pack the column is not critical provided that the finished column produces the required separation of all of the components to be determined.

8. Calibration and Standardization

8.1 *Chromatograph*—Install the column in the chromatograph and adjust the operating parameters as directed in Table 1. Allow sufficient time for the instrument to reach equilibrium as indicated by a stable recorder baseline.

8.2 Determine the retention time of each component by injecting small amounts either separately or in known mixtures. The components should elute close to the typical retention times given in Table 1 and the chromatograms should closely approximate those shown in Fig. 1 and Fig. 2.

8.3 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. The response to different components is generally significantly different for both flame ionization and thermal conductivity detectors. This difference in detector response may be corrected by use of relative response factors obtained by injecting and measuring the response of pure components or known blends. For accurate determination of the impurities, prepare and analyze a known blend containing the impurities in concentrations that approximate the maximum specification limit. Calculate the response factors relative to unity for the major ketone.

TABLE 1 Instrument Conditions and Retention Times

Temperature,° C:		
Column, isothermal	100	
Injection port	170	
Detector block	210	
Carrier gas	Helium	
Flow rate, mL/min	25	
	Methyl Amyl Ketone	Methyl Isoamyl Ketone
Relative retention times, major component = 1.00		
Air	0.04	0.05
Acetone	0.14	0.18
Isopropyl alcohol	0.18	0.23
Methyl propyl ketone	0.31	0.38
Methyl isobutyl ketone	0.35	0.45
Methyl butyl ketone	0.51	0.64
Methyl isobutyl carbinol	0.61	0.77
Mesityl oxide	0.65	0.83
Methyl isoamyl ketone	0.73	1.00
Methyl butyl carbinol	0.82	1.02
Methyl amyl ketone	1.00	1.16
Diisobutyl ketone	1.04	1.25

9. Procedure

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

NOTE 1—The best separation of the impurities has been obtained with specimen sizes of 1 or 2 µL.

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

10. Calculation

10.1 Measure the area of all peaks (Note 2) and multiply each area by the appropriate attenuation factor to express the peak areas on a common basis. Apply the appropriate detector response to each component to obtain the corrected peak response. 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 by the ASTM methods given in 2.1.

NOTE 2—Peak areas may be determined by any method that meets the precision limits given in Section 12. For best results determine peak areas by electronic integration.

10.2 Calculate the weight percent of each component as follows:

$$Weight\ \% = \frac{A}{B} \times (100 - C) \tag{1}$$