Designation: E1616 – 08

Standard Test Method for
Analysis of Acetic Anhydride Using Gas Chromatography[1]

This standard is issued under the fixed designation E1616; 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 describes the determination of assay and impurities in acetic anhydride by gas chromatography. The acetic anhydride should be at least 95 % pure.

1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

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.* For specific hazards statements see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, see Practice E355.

4. Summary of Test Method

4.1 The sample is injected onto a gas chromatographic column. The components are separated as they pass through the column with helium carrier gas, their presence in the effluent is detected by a flame ionization detector, and recorded as a chromatogram. The concentrations of sample components are calculated as weight percentages using area normalization.

5. Significance and Use

5.1 This test method provides for the determination of assay and impurities in acetic anhydride. Acetic anhydride is used as an intermediate in many chemical processes. Its relative concentration affects the efficiency of these processes. This test method provides a test procedure for assay and impurity specification acceptance as well as manufacturing control.

6. Interferences

6.1 This test method describes the chromatographic separation of possible impurities in acetic anhydride. Other impurities could coelute with the known components and cause an interference. Therefore, an efficient gas chromatographic column in good condition should be used in order to ensure the necessary chromatographic separations and proper peak shapes so that good quantitative data may be obtained.

6.2 This analysis is based upon the assumption that all components are eluted from the gas chromatographic column.

7. Apparatus

7.1 *Gas Chromatograph*—Any gas chromatograph equipped with a flame ionization detector and a split injection system for use with capillary columns that can be operated at the conditions given in Table 1.

7.2 *Column*—The column must give satisfactory resolution and proper peak shapes for the components listed in Fig. 1. Table 1 contains a description of a column that has been found satisfactory.

7.3 *Recorder/Integrator*—Electronic integration is recommended for this analysis.

7.4 *Syringe,* 10-µL capacity.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall 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.[3] Other grades may be used,

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[1] This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicalsand is the direct responsibility of Subcommittee E15.02 on Product Standards.

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[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] *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 *Analar 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.

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

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TABLE 1 Instrument Conditions for Acetic Anhydride Analysis

Column:	
Tubing	fused silica
Stationary phase	cross-linked methyl silicone
Film thickness, µm	0.52
Length, m	50
Inside diameter, mm	0.32
Temperature, °C:	
Inlet	250
Detector	250
Column	80
Carrier Gas:	
Helium	
Injection System:	
Split injection; 100:1 split ratio	
Detector:	
Flame ionization	
Detector Gases, mL/min:	
Hydrogen	30
Air	350
Helium, makeup	30

provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *High-Purity Acetic Anhydride (99.8 % or Greater Purity)*—It is important that the acetic anhydride used to prepare calibration standards be as pure as possible. If the acetic anhydride specified by this test method is not suitable for standard preparation, it should be redistilled prior to use or another source found. Note that American Chemical Society reagent grade acetic anhydride may not be sufficiently pure for this procedure. Its titration assay will include other anhydrides present as well as acetic anhydride.

8.3 *Carrier Gas*—Chromatographic-grade helium.

8.4 *Detector Gas*, air—Breathing quality grade.

8.5 *Detector Gas*, hydrogen—99.95 % grade.

8.6 Pure compounds for calibration could include acetic acid, ethylidene diacetate, mesityl oxide, and acetonitrile. The purity of all reagents should be 99 % or greater. If the purity is less than 99 %, the concentration and identification of impurities must be known so that the composition of the standard can be adjusted for the presence of the impurities.

8.7 Propionic anhydride and propionic acid are not included in the calibration of this test method. The propionic anhydride or propionic acid would react over time to form the mixed anhydride, acetic-propionic anhydride.

9. Hazards

9.1 Consult current Occupational Safety and Health Administration (OSHA) regulations and supplier's Material Safety Data Sheets for all materials used in this test method.

9.2 Acetic anhydride is a corrosive, both as a liquid and a vapor. It is severely damaging to the eyes and skin. It can cause delayed burns if not removed immediately.

9.3 Acetic anhydride is combustible. Its vapor is flammable in the range from 2.7 to 10.3 volume % in air. Possible ignition sources shall be avoided.

9.4 **Warning**—Acetic anhydride reacts violently with water. Handle and dispose of all samples so as to minimize any contact with water.

10. Preparation of Apparatus

10.1 Follow the manufacturer's instructions for mounting and conditioning the column into the chromatograph and adjusting the instrument to the conditions described in Table 1. Allow sufficient time for the equipment to reach equilibrium.

11. Calibration

11.1 Prior to standard preparation, the acetic anhydride used to prepare the calibration standard must be analyzed to determine purity. It is difficult to obtain acetic anhydride that is free of detectable levels of acetic acid; however, with purification, the amount of acetic acid in the anhydride can be minimized. To perform this blank run, inject 1.0 µL of the acetic anhydride onto the chromatographic column. Analyze the blank in accordance with the conditions specified in Table 1. If any impurity is present at a concentration of greater than 0.05 % by area, it is advisable to purify the acetic anhydride prior to use.

11.1.1 The most likely impurity to remain in acetic anhydride, even after purification, is acetic acid. Retain the results of this blank run for later use in the determination of response factors for the calibrated components noted in this test method.

11.1.2 Relative retention times for possible components are given in Table 2 and a chromatogram is shown in Fig. 1.

11.2 A calibration standard should be prepared containing at least acetic acid and acetic anhydride. Other components may be calibrated as needed. Approximate amounts are given in Table 3.

11.2.1 During standard preparation, the exact amounts of all components shall be recorded.

11.3 After analyzing the acetic anhydride blank, analyze the calibration standard described in 11.2. Inject 1.0 µL of the standard onto the chromatographic column. Analyze the standard in accordance with the conditions specified in Table 1.

11.4 Calculate response factors to four decimal places for all components relative to acetic anhydride using the following equation:

$$F_x = \frac{(W_x)(R_s)}{(W_s)(R_x - R_b)} \qquad (1)$$

where:

F_x = response factor for Compound X relative to acetic anhydride,
W_x = weight of Compound X, g,
R_s = peak response of acetic anhydride,
W_s = weight of acetic anhydride, g,
R_x = peak response of Compound X in the standard, and
R_b = peak response of Compound X in the blank.

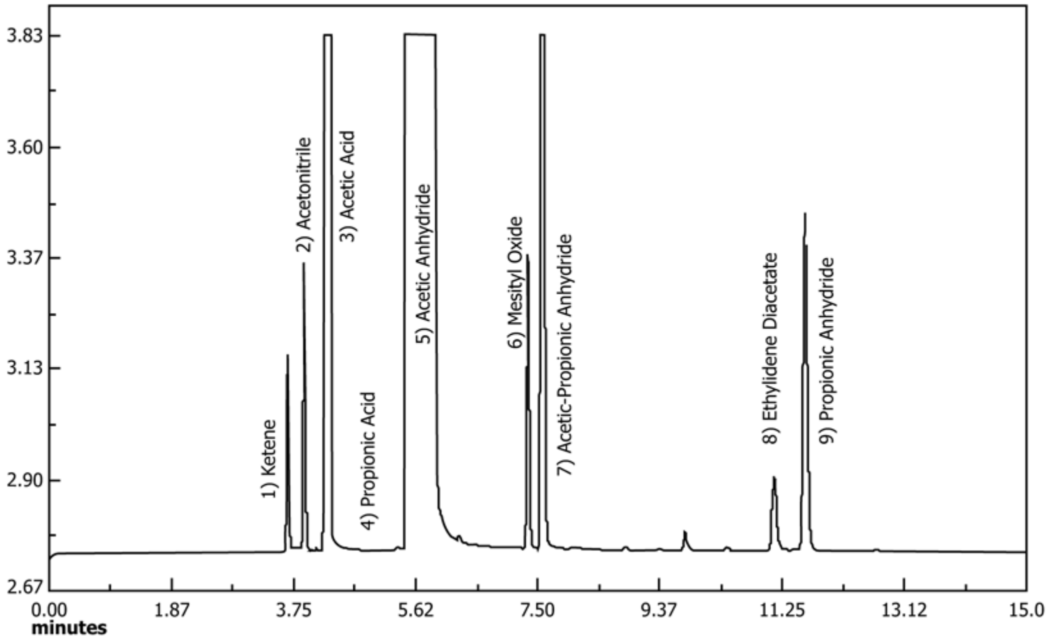

FIG. 1 Chromatogram of Acetic Anhydride Spiked with Possible Impurities

TABLE 2 Relative Retention Times for Possible Impurities in Acetic Anhydride

Component	Relative Retention Time
Ketene	0.62
Acetonitrile	0.67
Acetic acid	0.75
Propionic acid	0.91
Acetic anhydride	1.00
Mesityl oxide	1.25
Acetic propionic anhydride	1.29
Ethylidene diacetate	1.90
Propionic anhydride	1.98

TABLE 3 Calibration Standard Composition for Acetic Anhydride Analysis

Component	Weight%
Acetic acid	0.50 to 1.5
Acetic anhydride	98.0 to 99.5
Acetonitrile	0.01 to 0.05
Ethylidene diacetate	0.01 to 0.05
Mesityl oxide	0.01 to 0.05

The only components for which response factors are determined are acetic acid, ethylidene diacetate, acetonitrile, and mesityl oxide. All other components are assigned relative response factors of 1.0000.

11.5 It is advisable that the determination of response factors be made on the basis of duplicate analyses.

11.6 Response factors should be checked after any perceptible change in column or instrument performance.

12. Procedure

12.1 Inject 1.0 µL of sample onto the chromatographic column.

12.2 Record and integrate the chromatogram using the conditions given in Table 1.

12.3 A typical chromatogram of acetic anhydride spiked with known impurities is shown in Fig. 1.

13. Calculation

13.1 Calculate the concentrations of sample components using the following equation:

$$C_{x,}\ \%\ mass\ (m/m) = \frac{(F_x)(R_x)(100)}{\sum(R_x)(F_x)} \quad (2)$$

where:

C_x = Compound X, % mass (m/m),
R_x = peak response of Compound X,
F_x = relative response factor of Compound X determined in 11.4, and
$\sum R_xF_x$ = sum of the individual component peak responses (R_x) multiplied by their relative response factors (F_x).

14. Report

14.1 Report the following information:

14.1.1 Individual components to the nearest 0.01 % mass (m/m).

14.1.2 For concentrations of impurities less than 0.01 % mass (m/m), report as <0.01 % mass (m/m).

14.1.3 Acetic anhydride content to the nearest 0.01 % mass (m/m).

15. Precision and Bias

15.1 *Precision:*

15.1.1 The precision data given in Table 4 were performed in one laboratory. An interlaboratory study to determine repeatability and reproducibility has not been completed.

15.1.2 The precision of this test method on samples of approximately 95 % mass (m/m) acetic anhydride was determined. Twenty samples of acetic anhydride were split into two aliquots. These 40 samples were randomly analyzed by any of 16 analysts using one gas chromatograph and a chromatographic data system over a two week period in one laboratory. These results are given for Sample 1 in Table 4.

TABLE 4 Precision Data

Component	Average Concentration, %	Standard Deviation	95 % Limits, %
Sample 1			
Acetic acid	4.24	0.039	0.11
Acetic anhydride	95.24	0.043	0.12
Acetic-propionic anhydride	.20	0.004	0.01
Ethylidene diacetate	0.07	0.003	0.01
Sample 2			
Acetic anhydride	99.82	0.032	0.09

15.1.3 The precision of this test method on samples of greater than 99 % mass (m/m) acetic anhydride was determined. Thirty samples of acetic anhydride were split into two aliquots. These 60 samples were randomly analyzed by any of 20 analysts using one gas chromatograph and a chromatographic data system over a 20 day period in one laboratory. The results are given for Sample 2 in Table 4.

15.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for this test method, bias has not been determined.

16. Keywords

16.1 acetic anhydride; anhydride; gas chromatography

SUMMARY OF CHANGES

Committee E15 has identified the location of selected changes to this standard since the last issue (E1616–94(2002)$^{\varepsilon 1}$) that may impact the use of this standard.

(1) Updated units of measure to comply with the International System of Units (SI).
(2) Addition of numbered section in Scope, 1.2, stating the SI units are to be considered standard.
(3) Corrected spelling of "resonse" to "response" in 11.4.
(4) Addition of Summary of Changes section.

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