Designation: E411 − 17a

Standard Test Method for Trace Quantities of Carbonyl Compounds with 2,4-Dinitrophenylhydrazine[1]

This standard is issued under the fixed designation E411; 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 total carbonyl in the range from 0.5 to 50 µg calculated as CO.

1.2 This test method is intended to be general and does not include steps for sample preparation.

1.3 Acetals that hydrolyze under the conditions of the test are also determined.

1.4 Carbonyl derivatives such as acetals and imines that are easily hydrolyzed may be determined by an alternative procedure.

1.5 The developed color is not stable and must be measured within a specified period.

NOTE 1—Other test methods for the determination of traces of carbonyl compounds are given in Test Methods D1089, D1612, D2119, and D2191.

1.6 Review the current appropriate Safety Data Sheets (SDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *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.* Specific hazards statements are given in Section 7 and Section 8.

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1089 Method of Test for Carbonyl Content of Butadiene (Withdrawn 1984)[3]

D1193 Specification for Reagent Water

D1612 Test Method for Acetone in Methanol (Withdrawn 2011)[3]

D2119 Test Method for Aldehydes in Styrene Monomer

D2191 Test Method for Acetaldehyde Content of Vinyl Acetate

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E300 Practice for Sampling Industrial Chemicals

3. Summary of Test Method

3.1 The sample containing traces of carbonyl compounds is reacted with an acidic solution of 2,4-dinitrophenylhydrazine to form the hydrazone which, upon reaction with potassium hydroxide, forms a wine-red color, presumably due to a resonating quinoidal ion. The intensity of the red color, which is a function of the carbonyl concentration, is determined photometrically and the amount of carbonyl is read directly from a previously prepared calibration curve. This test method is based upon the work of Lappin and Clark.[4]

4. Significance and Use

4.1 This test method is applicable to the determination of trace amounts of aldehydes and ketones in aqueous solutions and a wide variety of organic solvents.

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[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.15 on Industrial and Specialty General 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] The last approved version of this historical standard is referenced on www.astm.org.

[4] Lappin, G. R., and Clark, L. C., *Analytical Chemistry,* Vol 23, 1951, p. 541.

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

5. Interferences

5.1 This test method has been found to be relatively free from interferences. It is necessary, however, to test a sample to ensure that it does not interfere.

5.2 Carbonyl compounds containing conjugated unsaturation interfere by absorbing at a different wavelength than other carbonyl compounds.

5.3 Acetals that are only partially hydrolyzed under the conditions of the test will interfere. A higher reaction temperature is required to effect complete hydrolysis.

5.4 Certain carbonyl compounds such as diisobutyl ketone have been found to undergo incomplete reactions and thus give low results. These compounds may be determined if a suitable calibration is made using the compound in question.

5.5 Because of the extreme sensitivity of this test method, it is necessary to perform the test in a room from which acetone or other carbonyl compound vapors are excluded.

6. Apparatus

6.1 *Spectrophotometer or Photometer,* capable of measuring light absorption at 480 nm and holding a 1-cm cell.

NOTE 2—If a filter photometer is used, a narrow band filter having its maximum transmission at approximately 480 nm should be used. A discussion of photometers and photometric practice is given in Practice E60.

6.2 *Absorption Cells,* 1-cm.

6.3 All glassware must be cleaned before use. Rinse thoroughly with water and finally with methanol. *Do not use acetone to dry the glassware*.

NOTE 3—The precision and bias reported in this test method were determined using chromic acid cleaning solution to clean the glassware. The effect on precision and bias of using other cleaning materials has not been determined.

7. Reagents

7.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, 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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Types II or III reagent water as defined in Specification D1193.

7.3 *Methanol, Carbonyl-free*—To 4 L of methanol add 20 g of 2,4-dinitrophenylhydrazine and 2 mL of hydrochloric acid (HCl, sp gr 1.19). Reflux for 2 h and then distill using a 2 to 3-ft fractionating column. Discard the first 200 mL of distillate. Continue the distillation until approximately 75 % of the methanol has distilled over.

7.3.1 **Warning**—Do not allow the pot to begin to go dry because there is danger of a violent decomposition of the residue. (See 8.2.) If stored in a tightly capped bottle, the methanol will remain carbonyl-free indefinitely. Properly prepared methanol will have an absorbance of 0.08 or less when used as a blank (11.2 – 11.4).

7.4 *Potassium Hydroxide Solution* (100 g/L)—Dissolve 100 g of potassium hydroxide (KOH) in 200 mL of water. Cool and dilute to 1 L with methanol.

7.5 *2,4-Dinitrophenylhydrazine* (1 g/L)—Dissolve 0.10 g of 2,4-dinitrophenylhydrazine (**Warning—**See 8.2) in 50 mL of carbonyl-free methanol containing 4 mL of hydrochloric acid (HCl, sp gr 1.19) and dilute to 100 mL with water. This solution is unstable and must be discarded after two weeks.

8. Safety Hazards

8.1 **Warning**—The toxicity of 2,4-dinitrophenylhydrazine has not been established. For this reason, handle with customary care. Avoid ingestion and contact of the compound with the skin and eyes.

8.2 **Warning**—2,4-Dinitrophenylhydrazine is an explosive and may ignite violently in contact with an open flame or electrical spark. Handle with caution. Avoid all sources of heat.

9. Sampling

9.1 Special precautions may be necessary to ensure that the sample taken for analysis is representative of the whole. Refer to Practice E300 for a detailed discussion of sampling procedures.

10. Calibration

10.1 Add 50 mL of carbonyl-free methanol to a 100-mL glass stoppered volumetric flask. To the flask transfer an amount of the carbonyl compound being determined that will contain 25 mg of CO, weighing to the nearest 0.1 mg (see Note 4). Dilute the contents of the flask to the mark with carbonyl-free methanol and mix well (see Note 5). (See 5.5 and 6.3.)

NOTE 4—The correct weight may be calculated as follows:

$$W = 0.893 \times E \quad (1)$$

where:

W = weight, mg,
E = equivalent weight of compound, and
0.893 = derived as a solution to the equation: $W \times 28/E = 25$, where 28 is the molecular weight of CO, and 25 is milligrams of CO to be determined. Solve this equation for W. Thus: $W = 25 \times E/28$, which simplifies to $W = (25/28) \cdot E$. 25/28 = 0.893.

NOTE 5—For most routine work a calibration based on 2-butanone is satisfactory. (See 5.4.)

10.2 Prepare a series of standards by transferring 2, 4, 6, 8, and 10-mL aliquots of this stock solution to respective 100-mL glass-stoppered volumetric flasks. Dilute the contents of each flask to the mark with carbonyl-free methanol and mix well.

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[5] *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.

Two millilitres of each of these standards contain approximately 10, 20, 30, 40, and 50μ g of carbonyl, respectively. Calculate the exact weight as follows:

$$S = 5.60 \times [(W \times V)/E] \quad (2)$$

where:

S = weight of carbonyl in 2 mL of solution, µg,
W = weight of sample added to stock solution, mg,
E = equivalent weight of compound,
V = volume of aliquot, mL, and
5.60 = collection of constants: $S = (W$ mg · 1 g/1000 mg)/100 mL · (V mL/100 mL) · (1 eq 2-butanone/E) · (1 eq C = O/1 eq 2-butanone) · (28 g/eq C = O) · (1000000 ug/g) · 2 = 5.6 · [(W · V)/E].

10.3 Using suitable pipets, transfer 2 mL of each standard to respective 25-mL glass-stoppered volumetric flasks. Develop the color and measure the absorbance of each standard as described in 11.2 – 11.4.

10.4 Plot, on linear graph paper, micrograms of carbonyl as a function of the net absorbance.

NOTE 6—If the photometer reading is transmittance, convert to absorbance as follows:

$$A = \log_{10} 100/T \quad (3)$$

where:

A = absorbance, and
T = transmittance.

11. Procedure

11.1 Using a suitable pipet, transfer 2 mL of a sample containing 0.5 to 50 µg of carbonyl to a 25-mL dry glass-stoppered volumetric flask that has previously been tared to the nearest 0.1 mg. Restopper and again weigh to the nearest 0.1 mg to obtain the exact sample weight. (See 5.5 and 6.3.)

NOTE 7—If 2 mL of the sample contains more than 50 µg of carbonyl, a suitable dilution in water or carbonyl-free methanol should be made.

11.2 Transfer 2 mL of carbonyl-free methanol to a second 25-mL glass-stoppered volumetric flask for use as a reagent blank.

11.3 To each flask, transfer, by means of a pipet, 2 mL of the 2,4-dinitrophenylhydrazine solution. Stopper and allow to set at room temperature for 30 ± 2 min (see Note 8). Dilute to the mark with the potassium hydroxide solution. Stopper and mix well.

NOTE 8—If a determination of easily hydrolyzed imines and acetals is required, use a reaction temperature of 60°C. A hot-water bath is a convenient source of heat. Cool before adding the potassium hydroxide solution.

11.4 At 12 ± 1 min after adding the potassium hydroxide solution, measure the absorbance of each solution at approximately 480 nm (see Note 9) in a 1-cm cell using a suitable photometer. Use a 1-cm cell filled with water to set the instrument at zero absorbance or 100 % transmittances.

NOTE 9—The maximum absorbance of the quinoidal ion occurs at about 430 nm. The absorbance-concentration relationship is more linear, however, at 480 nm. For this reason the latter wavelength is used.

11.5 Calculate the net absorbance due to carbonyl compounds in the sample by subtracting the absorbance of the reagent blank from that of the sample determinations.

11.6 Refer to a previously prepared calibration curve to determine the micrograms of carbonyl found.

12. Calculations

12.1 Calculate the carbonyl content of the sample as follows:

$$\text{CO, µg/g} = \frac{A}{B} \quad (4)$$

where:

A = weight of carbonyl found, µg, and
B = sample weight, g, or sample volume, mL × sp gr.

12.2 If it is desired to express the carbonyl content as a specific compound, multiply the content calculated above by the factor E/28.01, where E is the equivalent weight of the compound.

13. Report

13.1 Report the carbonyl content to the nearest 0.1 µg/g. Duplicate runs that agree within 0.5 µg/g absolute are acceptable for averaging (95 % probability).

14. Precision and Bias

14.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 10).

14.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.16 µg/g at 26 df. The 95 % limit for the difference between two such determinations is 0.4 µg/g absolute.

14.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst in different days, has been estimated to be 0.16 µg/g absolute at 13 df. The 95 % limit for the difference between two such averages is 0.4 µg/g absolute.

14.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories has been estimated to be 6.04 % relative at 5 df. The 95 % limit for the difference between two such averages is 17 % relative.

NOTE 10—The precision estimates are based on an interlaboratory study performed in 1969 on two samples of methanol containing 4 and 24 µg/g total carbonyl added as acetone. Seven laboratories analyzed the samples in duplicate on each of two days.[6] Practice E180 – 90 was used in developing these precision statements.

14.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

15. Quality Guidelines

15.1 Laboratories shall have a quality control system in place.

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1006. Contact ASTM Customer Service at service@astm.org.

15.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

15.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

15.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

15.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

16. Keywords

16.1 aldehydes; carbonyl; 2,4-dinitrophenylhydrazine; ketones

SUMMARY OF CHANGES

Subcommittee D16.15 has identified the location of selected changes to this standard since the last issue (E411–17) that may impact the use of this standard. (Approved July 1, 2017.)

(1) Section 15 Quality Guidelines was added.

Subcommittee D16.15 has identified the location of selected changes to this standard since the last issue (E411–12) that may impact the use of this standard. (Approved April 15, 2017.)

(1) Removed "Material" from MSDS statement in Scope section 1.6.

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