Designation: D 2192 – 96 (Reapproved 2000)

Standard Test Method for Purity of Aldehydes and Ketones[1]

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1. Scope

1.1 This test method covers the determination of the purity of certain commercially available aldehydes and ketones.

1.2 In addition to all aldehydes and ketones, all compounds such as vinyl alkyl ethers, acetals, and ketals, that hydrolyze under the conditions of the reaction to form free carbonyl groups, react with the reagent and consequently interfere. Water, alcohols, saturated esters, and hydrocarbons do not react with the reagent, but large amounts of inert organic solvents are undesirable because of the effect on the indicator.

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 hazard statements, see Section 7.

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

2. Referenced Documents

2.1 *ASTM Standards:*

D 268 Guide for Sampling and Testing Volatile Solvents and Chemical Intermediates for Use in Paint and Related Coatings and Materials[2]

D 1193 Specification for Reagent Water[3]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[4]

E 222 Test Methods for Hydroxyl Groups by Acetic Anhydride Acetylation[4]

3. Summary of Test Method

3.1 Hydroxylamine hydrochloride is converted in part to free hydroxylamine by reaction with a known amount of aqueous triethanolamine.

$$NH_2OH{\cdot}HCl + (HOCH_2CH_2)_3N \rightarrow \quad (1)$$
$$NH_2OH + (HOCH_2CH_2)_3N{\cdot}HCl$$

The free hydroxylamine reacts with the aldehyde or ketone to form the corresponding oxime.

$$RR_1C{=}0 + NH_2OH \rightarrow RR_1C{=}H{=}NOH + H_2O, \quad (2)$$

where:

R = alkyl group and

R_1 = alkyl group or hydrogen.

The amount of hydroxylamine consumed, which is determined by titration of the excess base with standard sulfuric acid, is a measure of the aldehyde or ketone originally present.

3.2 Since the determination is based on an acidimetric titration, a suitable correction must be applied if the sample is not neutral to bromophenol blue indicator.

4. Significance and Use

4.1 This test method provides a measurement of purity (assay) of aldehydes and ketones. The results of these measurements can be used for specification acceptance.

4.2 The precision of this test method is applicable only to material having a purity of 98 to 100 %.

5. Apparatus

5.1 *Pressure Bottle*, 200 to 350-mL capacity, with lever type closure and made of heat-resistant glass.

5.2 *Container for Pressure Bottle*— A suitable safety device to contain the pressure bottle. A metal container with a hinged top and perforated bottom, a strong synthetic fabric or canvas bag, or a safety shield may be used.

5.3 *Ampoule*, 1 or 2-mL capacity.

5.4 *Weighing Pipet*, Lunge or similar type.

5.5 *Burets*, 50-mL capacity.

5.6 *Transfer Pipet*, 50-mL capacity.

5.7 *Glass Rod*, 8-mm, several pieces approximately 1 in. long.

5.8 *Boiling Water Bath*.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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,

[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.

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

[3] *Annual Book of ASTM Standards*, Vol 11.01.

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

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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type IV of Specification D 1193.

6.3 *Bromophenol Blue Indicator* (0.04 % Alcoholic Solution)—Dissolve 0.04 g of bromophenol blue (tetrabromophenolsulfonphthalein) in 100 mL of methyl alcohol. Titrate this solution with 0.1 *N* sodium hydroxide (NaOH) solution to a reddish-bronze color. If an off-color is obtained at this point, it is probably due to the age of the indicator and fresh indicator should be used to prepare a new solution.

6.4 *Cylinder Nitrogen*.

6.5 *Hydroxylamine Hydrochloride, Standard* (0.5 N Alcoholic Solution)—Dissolve 35 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 150 mL of water and dilute to 1 L with 99 % isopropanol.

6.6 *Isopropanol* (99 %).

6.7 *Sulfuric Acid, Standard* (0.5 N)—Prepare and standardize 0.5 *N* sulfuric acid (H_2SO_4) in accordance with Practice E 200, Sections 24 through 27.

6.8 *Triethanolamine, Standard* (0.5 N Aqueous Solution)—Dissolve 65 mL (74 g) of 98 % triethanolamine in water and dilute to 1 L with water. Adjust the normality of this solution so that it is slightly below the normality of the H_2SO_4 being used.

7. Procedure

7.1 Sample the material in accordance with Guide D 268.

7.2 Add 15 mL of a 0.04 % alcoholic solution of bromophenol blue indicator to 500 mL of the hydroxylamine hydrochloride solution. From a buret add 0.5 *N* triethanolamine until the solution appears greenish-blue by transmitted light. Prepare the solution fresh before each series of analyses.

7.3 Prepare a sufficient number of heat-resistant pressure bottles to make all blank and sample determinations in duplicate. Replace the rubber gaskets if necessary and make sure the caps can be fastened securely.

7.4 Using a graduated cylinder, add 65 mL of the neutralized hydroxylamine hydrochloride to each bottle. Using a transfer pipet, add 50.0 mL of the 0.5 *N* triethanolamine solution to each bottle.

7.5 Before capping, purge the bottles for 2 min with a gentle stream of cylinder nitrogen. This is best accomplished by means of a glass tube inserted through the neck of the bottle and clamped so that the opening is just above the surface of the liquid.

7.6 Reserve two of the bottles for the blank determination. Into each of the other bottles introduce an amount of sample containing not more than 0.015 mol of aldehyde or ketone. For substantially pure material, weigh the specimen to the nearest 0.1 mg, using the amount and procedure specified in Table 1.

7.6.1 **Warning:** Acetaldehyde is a highly volatile, flammable material; observe all necessary safety precautions. Handle samples only in a fume hood that is free from open flames, electric heaters, and other sources of ignition. Cool all samples in an ice bath before the containers are opened. Weigh the acetaldehyde in a sealed glass ampoule. The actual procedure for filling and sealing the ampoule will vary somewhat with the type of ampoule being used. One convenient method is to pack commercially available ampoules in powdered, solid carbon dioxide, introduce the specimen by means of a chilled hypodermic syringe, and seal the ampoule with a gas torch.

7.7 If a sealed glass ampoule is used to weigh the specimen, add several pieces of 8-mm glass rod and shake the bottle vigorously to break the ampoule.

7.8 React the solutions at room temperature or at 98°C according to the directions in Table 1.

7.8.1 *Reaction at 98°C* (**Warning**—See 7.8.1.1.)—Place the specimen and blank bottles as close together as possible in a boiling water bath maintained at least at 98°C for the time specified in Table 1. Maintain sufficient water in the bath to just cover the liquid in the bottles. Remove the bottles from the bath after the specified time and allow them to cool in air to room temperature. When the bottles have cooled, remove them from the safety device and continue as described in 7.9.

7.8.1.1 **Warning:** Enclose each bottle securely in a suitable container (metal or strong fabric) to restrain fragments of glass should the pressure bottle rupture.

7.8.2 *Reaction at Room Temperature*—Allow the specimens and the blanks to stand together at room temperature for the length of time specified in Table 1. Swirl the bottles occasionally.

7.9 Cool each of the bottles slightly with tap water and uncap carefully to prevent loss of the contents. Allow the contents to return to room temperature.

NOTE 1—Bromophenol blue indicator is temperature sensitive, and a difference of 10°C at the end point causes a discrepancy of approximately 0.3 mL of 0.5 *N* H_2SO_4. To achieve the best precision, it is imperative that the blank and the specimen be at the same temperature at the end point. A water bath at room temperature is a convenient means of conditioning the specimen and the blanks prior to the titration.

7.10 Titrate each of the blanks with standard 0.5 *N* H_2SO_4 to a greenish-blue end point. Titrate each of the specimens with standard 0.5 *N* H_2SO_4 to the color of the blanks, approaching the end point dropwise until the colors match by transmitted light.

NOTE 2—If the solution becomes cloudy upon titration, add sufficient

TABLE 1 Specimen Size and Reaction Conditions

Compound	Specimen, g[A]	Minimum Reaction Conditions	
		Time, min	Temperature,° C
Acetaldehyde (**Precaution,** Note 1)	0.5 to 0.7[B]	30	25
Methyl isobutyl ketone	1.1 to 1.4[B]	60	25
Methyl isoamyl ketone	1.1 to 1.7	30	25
Isophorone	1.4 to 2.0	60	98

[A] Use a suitable weighing pipet unless otherwise specified.
[B] Use a sealed glass ampoule.

[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.

isopropanol to the specimen solution to effect homogeneity and add an equal amount of isopropanol also to the blank.

TABLE 2 Aldehyde and Ketone Factors

Compound	Factor[A]
Acetaldehyde	0.04405
Methyl isobutyl ketone	0.1002
Methyl isoamyl ketone	0.1142
Isophorone	0.1382

[A] $$\text{Factor} = \frac{\text{Molecular weight of compound}}{\text{Number of reacting groups} \times 1000}$$

7.11 Measure the temperature of the acid titrant. If the temperature of the reagent at the time the analysis is made is not the same as it was when the reagent was standardized, apply a correction to the normality. Use a $\Delta N/T$ of 0.00014 per degree Celsius in making the temperature correction.[6]

8. Calculation

8.1 Calculate the weight percent of aldehyde or ketone, *A*, as follows (Note 3): Table 2

$$A = [((B - V)F \times N)/S] \times 100 \quad (3)$$

where:

- V = H_2SO_4 required for titration of the specimen (see 7.10), mL
- B = H_2SO_4 required for titration of the blanks (see 7.10), average, mL
- N = normality of the H_2SO_4,
- F = factor specified in Table 2 for the compound being determined, and
- S = sample used (see 7.6), g.

NOTE 3—If the sample is acidic to bromophenol blue indicator, it is recommended that a suitable correction be applied to the purity value. Refer to Test Method E 222.

9. Report

9.1 Report all results to the nearest 0.1 %.

10. Precision and Bias

10.1 *Precision*—In interlaboratory studies of this test method, the within-laboratory and between-laboratory standard deviations were found to be as shown in Table 3 and Table 4. Based on these deviations, the following criteria should be used for judging the acceptability at the 95 % confidence level of results obtained on materials having a purity of 98 to 100 %.

10.2 *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 the amount shown in Table 3.

TABLE 3 Within-Laboratory Deviations

	Acetaldehyde	Methyl Isoamyl Ketone	Isophorone
Standard deviation	0.33	0.22	0.18
Degrees of freedom	20	42	42
Repeatability	1.0	2.6	0.6

TABLE 4 Between-Laboratory Deviations

	Acetaldehyde	Methyl Isoamyl Ketone	Isophorone
Standard deviation	0.33	0.41	0.63
Degrees of freedom	20	19	19
Reproducibility	1.0	1.2	1.9

10.3 *Reproducibility*—Two results, each the mean of duplicates, obtained by operators in different laboratories, should be considered suspect if they differ by more than the amount shown in Table 4.

NOTE 4—The preceding precision statements for acetaldehyde are based upon two separate interlaboratory studies using two different samples having purities above 99 %. In the first study duplicate determinations were made on each sample by two analysts on two different days in each of three laboratories. The second study included the same test program in each of four laboratories.

The precision statements for methyl isoamyl ketone and isophorone are based upon two separate interlaboratory studies using two different samples of each chemical. In both studies, one analyst in each of eleven different laboratories made duplicate determinations on each sample on two different days.

10.4 *Bias*—The bias of this test method has not been determined because suitable standards are unavailable.

11. Keywords

11.1 aldehyde; ketones; purity

[6] See Table 1 of Practice E 200.