Designation: D 6133 – 00

Standard Test Method for Acetone, *p*-Chlorobenzotrifluoride, Methyl Acetate or *t*-Butyl Acetate Content of Solvent-Reducible and Water-Reducible Paints, Coatings, Resins, and Raw Materials by Direct Injection Into a Gas Chromatograph[1]

This standard is issued under the fixed designation D 6133; 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 is for the determination of the total-concentration of acetone, *p*-chlorobenzotrifluoride, methyl acetate, or *t*-butyl acetate, or combination of any of the four, in solvent-reducible and water-reducible paints, coatings, resins, and raw materials. Because unknown compounds that coelute with the anallyte being measured or with the internal standard, will lead to erroneous results, this test method should only be used for materials of known composition so that the possibility of interferences can be eliminated. The established working range of this test method is from 1 % to 100 % acetone by weight.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 3271 Practice for Direct Injection of Solvent-Reducible Paints into a Gas Chromatograph for Solvent Analysis[2]

D 3272 Practice for Vacuum Distillation of Solvents from Solvent-Reducible Paints for Analysis[2]

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

3. Summary of Test Method

3.1 A suitable aliquot of whole paint is internally standardized, diluted with an appropriate solvent, and then injected into a gas chromatographic column that separates the chosen analytes from other volatile components. The analyte content is determined from area calculations of the materials producing peaks on the chromatogram.

4. Significance and Use

4.1 With the need to calculate volatile organic content (VOC) of paints, and with acetone, *p*-chlorobenzotrifluoride, methyl acetate and *t*-butyl acetate[4] considered as exempt volatille compounds, it is necessary to know the content of these analytes. This gas chromatographic test method provides a relatively simple and direct way to determine their content. However, because the dectors used in this test method are not selective, and because some coatings are very complex mixtures, compounds may be present in the sample that coelute with the analyte, giving a result that is erroneously high. Or a component may elute with the internal standard, giving a result that is erroneously low. It is therefore important to know the composition of the sample to ensure that there are no interferences, under the analysis conditions used.

5. Apparatus

5.1 *Gas Chromatograph*—Any instrument with temperature programming capability may be used. It should be equipped with either a thermal conductivity, flame ionization or photo-ionization detector (see Table 1).

5.2 *Column*—Any column that provides baseline separation of the analyte of interest (acetone, *p*-chlorobenzotrifluoride, methyl acetate or *t*-butyl acetate), the internal standard, and any volatile present in the samples may be used. It should be understood that column performance may be influenced by manufacturing conditions, such as type of deactivation and chemical bonding/crosslinking used. One or more of the following column types may be used. In terms of durability and over all efficiency, a bonded phase poly (5 % phenyl 95 % dimethylsiloxane) type of column should be considered first. (Any reference to specific product brands does not indicate an endorsement for that particular brand of column).

5.2.1 *Capillary*, 25 to 60 m, 0.25 mm-inside diameter, 0.25 to 1.0-µm film thickness, fused silica bonded phase poly (5 % phenyl 95 % dimethylsiloxane (DB-5, HP-5, Rtx-5, Ultra-2, BP-5, CP-Sil 8 CB, etc.)).

[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 D01.21 on Chemical Analysis of Paints and Paint Materials.

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[2] *Annual Book of ASTM Standards*, Vol 06.01.

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

[4] At the time of the writing of this test method, *t*-butyl acetate was not yet approved as an exempt solvent, but was under review by te USEPA and was expected to be approved. Therefore, it has been included in this test method.

TABLE 1 Suggested Instrument Conditions

Detector	Flame Ionization Detection (FID)
Hydrogen Flow	30 mL/min
Air Flow	400 mL/min
Make-up (Helium)	30 mL/min
Carrier Gas (Hydrogen)	40 cm/s
Detector Temperature	250°C
Injection Port Temperature	200°C[A]
Split Ratio	50:1[B]
Initial Oven Temperature	40°C
Initial Temperature Hold Time	5 min
Program Rate 1	4°C/min
Program Time 1	5 min
Final Temperature 1	60°C
Program Rate 2	20°C/min
Program Time 2	8 min
Final Temperature 2	220°C
Final Temperature Hold Time	2 min
Total Run Time	20 min
Injection Volume	1.0 µL

[A]The injection port temperature can be decreased to permit the analysis of thermally unstable samples; however, each case must be individually investigated.
[B]The split ratio may be adjusted according to the theoretical level of solvent composition.

5.2.2 *Capillary*, 25 to 60 m, 0.25-mm inside diameter, 0.25 to 1.0-µm film thickness, fused silica FFAP (polyethylene glycol nitrophthalic acid ester phase).

5.2.3 *Capillary*, 25 to 60 m, 0.25-mm inside diameter, 0.25 to 1.4-µm film thickness, fused silica bonded phase poly (6 % cyanophenylpropyl 94 % dimethylsiloxane) (DB-624, SPB-624, Rtx-624, etc.).

5.3 *Recorder*—A recording potentiometer with a full-scale deflection of 1 to 10 mV, full-scale response time of 2 s or less and sufficient sensitivity and stability to meet the requirements of 5.1. The use of a reporting electronic integrator or computer based data system is preferred.

6. Column Peak Interferences

6.1 The following compounds are known to co-elute or otherwise interfere with the analysis on a DB-5 type column:
(a) *Acetone*—isopropanol, propylene oxide, acetonitrile, and
(b) *Cyclohexanol*—*sec*-amyl acetate.

6.2 The following compound is known to co-elute or otherwise interfere with the analysis on an FFAP type column:
(a) *Cyclohexanol*—butyl cellosolve.

6.3 The analyst must verify that, under the analysis conditions being used, none of the components of the sample interfere with the analyte being quantitated or with the internal standard being used.

7. Reagents and Materials

7.1 *Purity of Reagents*—Use reagent grade chemicals in all tests, unless otherwise specified. Other grades may be used, provided it is first ascertained that the reagent is sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Tetrahydrofuran (THF)*—high performance liquid chromatography (HPLC) grade, uninhibited.

7.3 *Cyclohexanol*—98+ %.

7.4 *Acetone*—HPLC grade.

7.5 *p-Chlorobenzotrifluoride*—98 + %.

7.6 *Methyl Acetate*—99 + %.

7.7 *t-Butyl Acetate*—99 + %.

7.8 *Water*—nanopure.

7.9 *Chromatography Gases*:
Helium of 99.9995 % purity or higher.
Hydrogen of 99.9995 % minimum purity (see Note 1).
Air, “dry” quality, free of hydrocarbons.

NOTE 1—The preferred choice of carrier gas is hydrogen, but helium or nitrogen may also be used. Chromatographic analysis time will increase and there may be a possible reduction in resolution.

7.10 *Liquid Charging Devices*—micro syringes of 10 or 25 µL capacity.

7.11 *Analytical Balance*—four places (0.0001 g).

7.12 *Sealable Vials*—7-mL screw cap.

7.13 *Medicine Droppers*.

7.14 *Autosampler Vials*.

7.15 *Pipete*—5-mL glass or autopipete.

8. Hazards

8.1 Check the supplier’s Material Safety Data Sheet (MSDS) on all chemicals before use.

9. Preparation of Apparatus

9.1 Install the column in the chromatograph following the manufacturer’s directions and establish the operating conditions required to give the desired separation (see Table 1). Allow sufficient time for the instrument to reach equilibrium as indicated by a stable base line.

10. Calibration

10.1 Using the information in Table 1 (as a guide), select the conditions of temperature and carrier gas flow that give the necessary resolution of the desired analytes from interferences in the samples.

10.2 *Determination of Relative Response Factors*—Cyclohexanol, or another suitable compound, is used as an internal standard. The internal standard used should be a compound that is not in the sample matrix, and does not co-elute with any other component of the sample. Most analyses can be done utilizing cyclohexanol for the internal standard providing it is soluble in the diluent solvent. The response factor for each analyte relative to the standard is determined by means of the following procedure. It is good practice to determine the relative retention time daily or with each series of determinations.

10.2.1 Prepare a standard with the desired analytes and the internal standard. This is done in the following manner: A 7-mL sealable vial is tared on an analytical balance. Each desired analyte and the internal standard are added at the 1 drop (~0.02 g) level and their weights recorded. All weights should be recorded to 0.1 mg. Deliver 5 mL of dilution solvent (THF) to this vial (see Note 2). Lower concentrations may be achieved through further dilution with THF if necessary.

NOTE 2—The solvent should always be injected separately for observation of contaminants and possible interference peaks, especially in trace analysis. The suggested solvents do not preclude the selection of any other solvent for dilution at the analyst’s discretion.

10.2.2 Inject a 1.0 µL aliquot of the standard mixture into the injection port of the gas chromatograph. At the end of the chromatographic run, calibrate the integrator by following the