Designation: D6133 – 02 (Reapproved 2014)

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

This standard is issued under the fixed designation D6133; 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 co-elute with the analyte 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 % for each analyte by weight.

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

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3271 Practice for Direct Injection of Solvent-Reducible Paints Into a Gas Chromatograph for Solvent Analysis
D3272 Practice for Vacuum Distillation of Solvents From Solvent-Reducible Paints For Analysis (Withdrawn 2008)[3]
D6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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 volatile 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 detectors 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. Test Method D6438 employs mass-spectral detection of analytes and may be used as an alternative method.

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

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

5. Apparatus

5.1 *Gas Chromatograph*—Any instrument with temperature programming capability may be used. It should be equipped with a flame 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.)).

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 % cyanopropyl/phenyl, 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.

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.

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 manufacturer's procedure for internal standard weight percent calibration. If this capability is not available, refer to the following calculations. See Figs. 1-3 for typical chromatograms using the three listed columns.

10.2.3 The response factor of each analyte is calculated as follows:

$$R_{analyte} = \frac{W_i \times A_{analyte}}{W_{analyte} \times A_i} \tag{1}$$

where:

$R_{analyte}$ = response factor for the analyte being calibrated,
W_i = weight of internal standard,
$W_{analyte}$ = weight of the analyte being calibrated,
$A_{analyte}$ = peak area for the analyte being calibrated, and
A_i = peak area for the internal standard.

11. Procedure

11.1 Samples are prepared with respect to the amount of the selected analytes in the sample, or the viscosity, or both. A diluting solvent must be chosen that satisfactorily dissolves the sample and at the same time does not interfere with or obscure the analyte peaks in the sample. Most samples are easily dissolved in THF, while a 50/50 blend of nanopure water and THF will disperse most latex samples.

11.2 The prepared sample must be easily dispensed into the syringe. For this reason, some samples may need to be diluted further. Best results are obtained when the analyte concentration is reduced to about 1 % in the prepared sample. This is accomplished by diluting the sample (1 g) with 1 g of diluting solvent for every percent of analyte present in the original sample.

11.3 Inject a 1.0 µL aliquot of the prepared sample into the chromatographic column. The reporting integrator will display the peak retention times and areas of the analytes and internal standard. The integrator will report the results directly in weight percentages based on the total sample. If a reporting integrator is not available, manual calculations can be done.

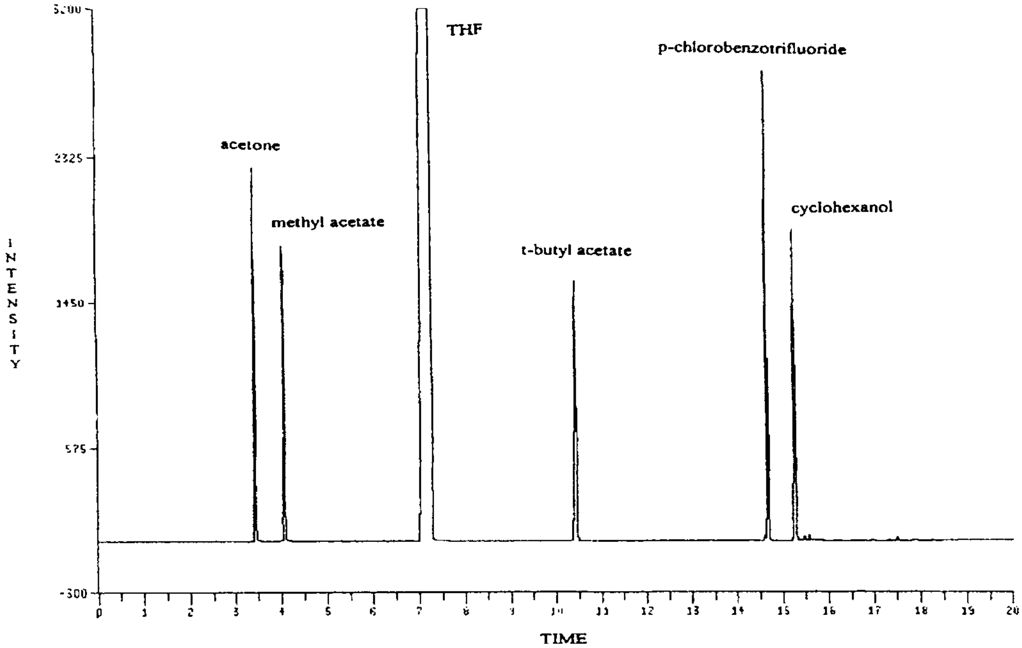

FIG. 1 GC Trace of Solvent Mix in Tetrahydrofuran (THF) on a 30 m, 0.25 mm ID Column With 5 % Phenyl/95 % Dimethylsiloxane Phase

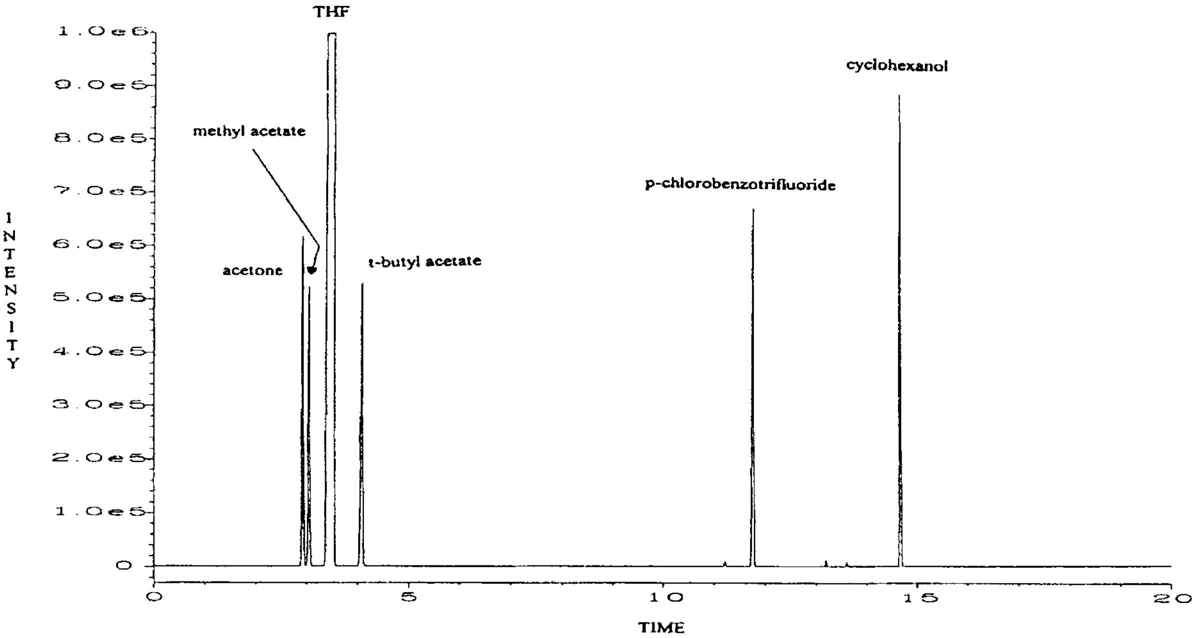

FIG. 2 GC Trace of Solvent Mix in Tetrahydrofuran (THF) on a 30 m, 0.25 mm ID Column With FFAP Phase

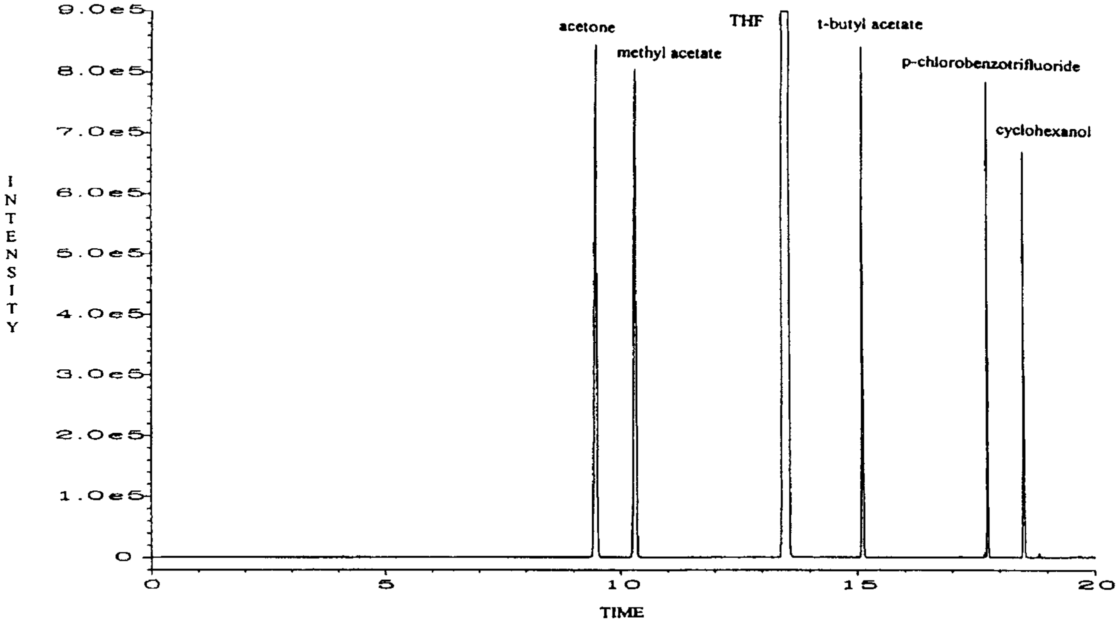

FIG. 3 GC Trace of Solvent Mix in Tetrahydrofuran (THF) on a 60 m, 0.25 mm ID Column With 624 Phase

11.4 If the sample contains solvent or monomer peak interferences (for example on a DB-5 column, isopropanol has the same retention time as acetone), a second capillary column with a different phase (FFAP for example) must be used to achieve adequate separation. If available, mass spectral confirmation may also be used in place of analysis on a second column, if the mass spectra are sufficiently different to allow isolation of the compounds of interest.

11.5 For difficult or pigmented samples, the samples may be cleaned up by vacuum distillation (see Practice D3272), or centrifugation.

11.6 Samples may also be screened for acetone, *p*-chlorobenzotrifluoride, methyl acetate, or *t*-butyl acetate content using Practice D3271.

12. Calculation

12.1 Calculate the weight percent of any of the analytes in the sample from data obtained from the sample run (see 11.3) as follows:

$$Analyte, \% = \frac{A_{analyte} \times W_i \times 100}{A_i \times W_s \times R_{analyte}} \quad (2)$$

TABLE 2 Precision Statistics for *p*-Chlorobenzotrifluoride, *t*-Butyl Acetate, Methyl Acetate, and Acetone

Material	Average, Mass Percent	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
p-Chlorobenzotrifluoride					
Sample 1	56.80	0.476	2.426	1.33	6.79
Sample 2	32.97	0.494	1.550	1.38	4.34
Sample 3	28.47	0.143	1.241	0.40	3.48
Sample 4	22.22	0.221	0.985	0.62	2.76
t-Butyl Acetate					
Sample 3	33.39	0.303	1.590	0.85	4.45
Sample 2	15.58	0.263	0.741	0.74	2.08
Sample 4	7.66	0.114	0.555	0.32	1.55
Methyl Acetate					
Sample 4	35.27	0.587	2.196	1.65	6.15
Sample 3	11.17	0.138	0.830	0.39	2.32
Sample 2	2.66	0.054	0.472	0.15	1.32
Acetone					
Sample 2	21.76	0.376	1.330	1.05	3.73
Sample 4	14.46	0.233	0.892	0.65	2.50
Sample 3	2.87	0.055	0.400	0.16	1.12

TABLE 3 Average 95 % Repeatability and 95 % Reproducibility Limit Coefficients of Variation

Analyte	95 % Repeatability Coefficient of Variation	95 % Reproducibility Coefficient of Variation
p-Chlorobenzotrifluoride	2.7	12.4
t-Butyl Acetate	3.8	15.6
Methyl Acetate	4.6	29.3
Acetone	5.0	24.5

where:

$A_{analyte}$ = area of the analyte peak,
A_i = area of the internal standard peak,
W_i = weight of internal standard added to the sample,
W_s = weight of sample, and
$R_{analyte}$ = response factor for the analyte (determined in 10.2.3).

13. Precision and Bias

13.1 *Precision*—The precision estimates for *p*-chlorobenzotrifluoride, *t*-butyl acetate, methyl acetate, and acetone are based on an interlaboratory study in which 7 different laboratories analyzed three times, 4 samples of various solventborne materials containing from 22 to 57 % *p*-chlorobenzotrifluoride, 8 to 33 % *t*-butyl acetate, 3 to 35 % methyl acetate, and 3 to 22 % acetone. The results obtained were analyzed statistically in accordance with Practice E691. Precision statistics were calculated for the total mass percent of each analyte in the 4 coatings and are presented in Table 2. The terms repeatability limit and reproducibility limit are used as specified in Practice E177.

13.1.1 The average 95 % Repeatability Limit (within laboratory) coefficient or variation (relative) for each analyte, which represents the 95 % confidence limit for the difference between two determinations in the same laboratory, is given in Table 3.

13.1.2 The average 95 % Reproducibility Limit (between laboratories) coefficient of variation (relative) for each analyte, which represents the 95 % confidence limit for the difference between two determinations in different laboratories, is given in Table 3.

13.2 *Bias*—Bias has not been determined.

14. Keywords

14.1 acetone; acetone content by gas chromatography; exempt volatile compounds; gas chromatography; methyl acetate; methyl acetate content by gas chromatography; *p*-chlorobenzotrifluoride; *p*-chlorobenzotrifluoride content by gas chromatography; *t*-butyl acetate; *t*-butyl acetate content by gas chromatography; VOC