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.

Designation: D6438 – 05 (Reapproved 2022)

Standard Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography[1]

This standard is issued under the fixed designation D6438; 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 acetone, methyl acetate, or parachlorobenzotrifluoride (PCBTF), or combination of any of the three, in paints and coatings, by solid phase microextraction (SPME) headspace sampling, and subsequent injection into a gas chromatograph. It has been evaluated for cellulose nitrate, acrylic, and urethane solvent-borne systems. The established working range of this test method is: acetone, 28 to 90 %; methyl acetate, 12 to 22 %; parachlorobenzotrifluoride, 10 to 17 %. There is no reason to believe that it will not work outside these ranges. A minor modification of this test method would make it suitable for the analysis of the same analytes in water-borne coatings (see Note 1).

NOTE 1—Water-borne paints are internally standardized and diluted with water followed by addition of solid sodium chloride.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *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]

D3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings

D6133 Test Method for Acetone, *p*-Chlorobenzotrifluoride, Methyl Acetate or *t*-Butyl Acetate Content of Solvent-borne and Waterborne Paints, Coatings, Resins, and Raw Materials by Direct Injection Into a Gas Chromatograph

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

3. Terminology

3.1 *Abbreviations:*

3.1.1 *PCBTF*—parachlorobenzotrifluoride (4-chlorobenzotrifluoride)

3.1.2 *MCBTF*—metachlorobenzotrifluoride (3-chlorobenzotrifluoride)

3.1.3 *SPME*—solid phase microextraction

3.1.4 *VOC*—volatile organic compound

3.1.5 *PEG/DVB*—polyethylene glycol/divinylbenzene

3.1.6 *FID*—flame ionization detector

3.1.7 *MS*—mass selective or mass spectral

3.1.8 *SIM*—selected ion monitoring

3.1.9 *GC*—gas chromatograph

3.1.10 *Sr*—repeatability standard deviations

3.1.11 *SR*—reproducibility standard deviations

3.1.12 *r*—repeatability, 95 % confidence limit

[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.

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3.1.13 *R*—reproducibility, 95 % confidence limit

4. Summary of Test Method

4.1 A suitable aliquot of whole solvent-borne paint is internally standardized and diluted with dioctyl phthalate. The headspace of this solution is sampled with an SPME fiber, which is then thermally desorbed in the injection port of a gas chromatograph onto a suitable capillary column. Either a flame ionization or mass specific detector may be used to measure peak areas of analytes and internal standards.

5. Significance and Use

5.1 In order to calculate the volatile organic content (VOC) of paints containing EPA exempt solvents, it is necessary to know the acetone, methyl acetate, or parachlorobenzotrifluoride content. This gas chromatographic test method provides a simple and direct way for measuring these solvents. Each analyte is measured with respect to a unique internal standard. For acetone, the internal standard used is acetone-d6, for methyl acetate it is methyl acetate-d3, and for PCBTF it is metachlorobenzotrifluoride (MCBTF). These unique analyte/internal standard pairs behave very nearly as single solvents with respect to evaporation rate and adsorption rate onto a coated silica fiber (SPME) but are separable on a gas chromatograph (GC) capillary column. The only critical analytical technique required for successfully performing this test method is the ability of an analyst to weigh a paint sample and internal standard, corresponding to the analyte of interest, into a septum capped vial. After weighing, solvent evaporation has no effect on the final value of the determination. Since whole paint is not injected into the gas chromatograph, the analytical system is never compromised.

6. Apparatus

6.1 *Manual SPME Holder,* [4] fitted with partially crosslinked polyethylene glycol/divinylbenzene (PEG/DVB) fiber assembly, 65-µm film thickness.

[4] The sole source of supply of the manual holder and fibers known to the committee at this time is Supelco Company, Supelco Park, Bellefonte, PA 16823-0048. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

TABLE 1 FID Instrument Conditions

Detector:	Flame ionization
Column:	60 m × 0.25 mm 100 % polyethylene glycol, 0.5-µm film thickness
Carrier Gas:	Helium
Flow Rage:	1.0 mL per minute (20 cm per second)
Split Ratio:	200 to 1
Fiber desorption time:	5 to 6 s[A]
Temperature, °C	
Inlet	260°
Detector	270°
Initial	35° for 12 min
Rate 1	30° per minute to 100°, hold 10 min
Rate 2	30° per minute to 240°, hold 2 min

[A] If the fiber desorption is carried out longer than 5 or 6 s, the acetone peaks exhibit tailing. A 5 to 6-s desorption time transfers 98 to 99 % of the analytes to the capillary column. The fiber may be cleaned by inserting it into the GC inlet for 15 s after analytes of interest have eluted.

6.2 *Gas Chromatograph, FID Detection*—Any capillary gas chromatograph equipped with a flame ionization detector may be used. Temperature programming capability is desirable, but isothermal operations may be utilized.

6.2.1 For FID instrument conditions, see Table 1.

6.2.2 *Inlet Liner,* 0.75-mm should be placed in the injection port.[4]

6.2.3 *Integrator*—Any electronic integrator that can accurately quantify a gas chromatographic peak area is acceptable.

6.3 *Gas Chromatograph, Mass Selective (MS) Detection*—Any capillary gas chromatograph equipped with a mass selective detector may be used. The detector must be capable of measuring in the selected ion monitoring (SIM) mode at dwell times of 100 milliseconds or less.

6.3.1 For MS instrument conditions, see Table 2.

6.3.2 *Inlet liner,* 0.75-mm, should be placed in the injection port.[4]

6.3.3 The instrument should have a software data system to allow extraction and integration of the SIM ions.

7. Column and Fiber Conditioning

7.1 Either or both capillary columns should be conditioned according to the manufacturer's recommendation. The columns may then be used indefinitely without further conditioning.

7.2 The SPME fiber should be conditioned and used according to the manufacturer's recommendation.

7.3 The SPME fiber should be inserted into a 260 °C injection port for 30 s prior to daily use.

8. Reagents and Materials

8.1 *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,

TABLE 2 MS Instrument Conditions

Detector:	Electron ionization or mass selective
Detection Mode:	Selected ion monitoring (SIM) of ions m/e 58, 64, 74, 77, and 180
Dwell Time:	100 milliseconds or less
Solvent Delay:	0.0 min
Column:	25 m × 0.20 mm 5 % phenyl/95 % methyl polydimethylsiloxane
Carrier Gas:	Helium
Flow Rate:	1.0 mL per minute (20 cm per second)
Split Ratio:	200 to 1
Fiber desorption time:	5 to 6 s[A]
Temperatures, °C	
Inlet	260°
Detector	280°
Initial	40° for 2 min
Rate 1	10° per minute to 90°, hold 1 min
Rate 2	40° per minute to 240°, hold 1 min

[A] If the fiber desorption is carried out longer than 5 or 6 s, the acetone peaks exhibit tailing. A 5 to 6-s desorption time transfers 98 to 99 % of the analytes to the capillary column. The fiber may be cleaned by inserting it into the GC inlet for 15 s after analytes of interest have eluted.