



Designation: D 6438 – 99

Standard Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography¹

This standard is issued under the fixed designation D 6438; 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 *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 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings²

D 6133 Test Method for Acetone Content of Solvent-Reducible and Water-Reducible Paints, Coatings, Resins, and Raw Materials by Direct Injection into A Gas Chromatograph²

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals³

3. Terminology

3.1 Abbreviations:

PCBTF parachlorobenzotrifluoride,
(4-chlorobenzotrifluoride)
MCBTF metachlorobenzotrifluoride
(3-chlorobenzotrifluoride)
SPME solid phase microextraction
VOC volatile organic compound
PEG/DVB polyethylene glycol/divinylbenzene
FID flame ionization detector
MS mass selective or mass spectral
SIM selected ion monitoring
GC gas chromatograph
Sr repeatability standard deviations
SR reproducibility standard deviations
r repeatability, 95 % confidence limit
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

¹ This test method is under the jurisdiction of ASTM Committee D-1 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 *Annual Book of ASTM Standards*, Vol 06.01.

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

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.

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.

TABLE 1 FID Instrument Conditions

Detector:	Flame ionization
Column:	60 m \times 0.25 mm 100 % polyethylene glycol, 0.5- μm film thickness
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 ⁴
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

⁴If 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.

6.2.2 *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.

⁴The 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 Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

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 \times 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 ⁴
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

⁴If 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.

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, 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.

8.2 *Carrier Gas*, Helium of 99.995 % or higher purity.

8.3 *Acetone* -d6, 99.9 % isotopic purity.

8.4 *Methyl Acetate* -d3, 99.9 % isotopic purity (see Note 2).

8.5 *Parachlorobenzotrifluoride*, technical grade, 99+ % (see Note 3).

8.6 *Metachlorobenzotrifluoride*, 97 %, (see Note 4).

8.7 *Dedicated Syringes*, 250- μL syringes, and *Disposal Syringes*, 1.0 mL.

8.8 *Septum Vials*, 22 or 40 mL, with fluorocarbon-faced silicone septa.

NOTE 2—Methyl acetate-d3 was prepared by the acid-catalyzed reaction of methanol with acetic-d3 acid, 99.9 % isotopic purity.

NOTE 3—Parachlorobenzotrifluoride contained 0.5 % of the meta isomer and 0.1 % of the ortho isomer.

NOTE 4—The metachlorobenzotrifluoride standard was chromatographically analyzed on a 60-meter 100 % polyethylene glycol column (see 6.2) and exhibited only a single peak.

9. Preparation of Standards

9.1 Place 6-mL dioctyl phthalate into a 22 or 40-mL vial and seal with a septum cap.

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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.