Designation: D 6438 – 99

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 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 Coatings[2]

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 Chromatograph[2]

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

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 capped vial. After weighing, solvent evaporation has no effect on the final value of the determination. Since whole paint is not

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[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.

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.

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, 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.

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.

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.

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.

9.2 Using dedicated 250-µL syringes, weigh approximately 100 mg each of parachlorobenzotrifluoride and metachlorobenzotrifluoride to 0.1mg into the vial. Excess solvent should be wiped from the syringe needle prior to piercing the septum. Any solvent adhering to the outside of the septum cap after making the transfer should be wiped off with tissue. Weigh the amounts of PCBTF and MCBTF to 0.1 mg. Repeat the

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

[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 Pharmacopia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

procedure by adding approximately 150 mg each of acetone, acetone-d6, methyl acetate, and methyl acetate-d3, and weigh each component to 0.1 mg.

9.3 Manually shake the vial for 15 s to mix the contents and then let the vial stand at room temperature for 30 min.

9.4 Remove the cap and wipe the septum to remove solvent from the inner surface and reseal immediately, or replace the septum with a new one.

9.5 Sample the headspace with the SPME fiber for 60 s.

9.6 Desorb the SPME fiber for 5 to 6 s in the injection port of the gas chromatograph using either the conditions described in 6.2 or 6.3.

9.7 Clean the fiber by placing it in the GC injection port for 15 s after the analytes of interest have passed through the capillary column.

9.8 If using the GC/FID procedure measure the peak areas of the three analytes and three standards by integration (See Note 5). Curve fitting software for measuring peak areas is advantageous in some instances.

NOTE 5—The approximate retention times in minutes are as follows: acetone-d6, 10.35; acetone, 10.56; methyl acetate-d3, 11.06; methyl acetate, 11.22: MCBTF, 22.33; PCBTF, 23.53.

9.9 If using the GC/MS procedure, measure the peak areas for the extracted ions indicated in Table 3.

9.10 Calculate response factors (RF) for acetone, methyl acetate, and PCBTF according to the equation given in 10.4. The numerical values should agree within 1 % of each other.

10. Procedure

10.1 Using a disposable 1-mL syringe, weigh 0.5 to 1.0 g of well mixed paint (see Note 6 and Practice D 3925) into a septum-capped vial containing 6 mL of dioctyl phthalate. The paint should drop directly into the dioctyl phthalate. Carry out the same procedures as described in 9.3-9.7.

NOTE 6—Since acetone and methyl acetate are extremely volatile, it is advisable to split the initial paint sample to be tested into two or more samples in suitable secondary containers.

10.2 Determine which, if any, of the three exempt solvents are present in the paint sample and if interfering peaks are present at the retention times corresponding to the retention times of the internal standards (see Note 7).

NOTE 7—The area of an interfering peak, if any, found in 10.2, may be subtracted from the area of the standard peak when carrying out 10.5.

10.3 Into a septum-capped vial containing 6 mL dioctyl phthalate, weigh 0.5 to 1.0 g of paint sample to 0.1 mg. Add 100 mg of each of the internal standards, corresponding to the analytes found in 10.1. Carry out the same procedure as described in 9.3-9.9.

TABLE 3 Approximate Retention Times and Masses of Analytes and Internal Standards

Analyte/Internal Standard	m/e	Retention Time, min
Acetone	58	1.26
Acetone-d6	64	1.26
Methyl acetate	74	1.34
Methyl acetate-d3	77	1.34
MCBTF	180	4.84
PCBTF	180	4.90

10.4 Calculate analyte concentrations according to the following equations:

$$RF = \frac{AA \times MI}{AI \times MA} \tag{1}$$

and

$$\%\ \text{Analyte} = \frac{AA \times MI \times 100}{AI \times RF \times MC} \tag{2}$$

where:

RF = response factor,
AA = area of analyte,
MI = mass of internal standard,
AI = area of internal standard,
MA = mass of analyte, and
MC = mass of coating.

10.5 Repeat the procedure given in 10.3 using paint and internal standard amounts such that the relative peak areas of the analyte and its internal standard chromatographic peak areas are approximately the same size. A duplicate injection of the same sample should give relative peak areas that agree within 1 % of each other.

10.6 Samples may also be analyzed for acetone content using Test Method D 6133.

11. Precision and Bias

11.1 *Precision*—A round robin was conducted involving five laboratories. All of the laboratories used the SPME sampling technique. Three of the laboratories used flame ionization (FID) detection to measure analyte amounts and two of the laboratories used mass spectral (MS) detection to measure analyte amounts.

11.2 Six commercial solvent-borne coatings were analyzed. Four of the coatings contained acetone and two of the same four coatings contained both acetone and parachlorobenzotrifluoride. Coatings containing methyl acetate were not yet available in the marketplace and were therefore prepared by adding known amounts of methyl acetate to different cellulose nitrate lacquers.

11.3 Precision data was calculated separately for the three laboratories using FID detection and the two laboratories using MS detection and also for the combination of FID and MS detection. Average values, repeatability standard deviations (Sr), and reproducibility standard deviations (SR) are given for each coating and exempt solvent in Table 4 and Table 5.

11.4 The results were analyzed for precision using Practice E 180.

11.5 *Precision (Within-Laboratory, Between-Days Variability, Formerly Called Repeatability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, have been estimated to be 0.42 % absolute at 39 df for acetone, 0.35 % absolute at 19 df for parachlorobenzotrifluoride, and 0.16 % absolute at 19 df for methyl acetate. The 95 % confidence limit for the difference between two such averages is 1.18 % absolute for acetone, 0.97 % absolute for parachlorobenzotrifluoride, and 0.46 % absolute for methyl acetate.

11.6 *Reproducibility (Multilaboratory)*—The standard deviation of results (each of the average of duplicates), has been estimated to be 0.69 % absolute at 39 df for acetone, 0.53 %

TABLE 4 Precision Data for Acetone

Material	Acetone			
Sample	A	B	C	D
Average, % (FID)	28.4	46.9	29.0	89.3
Average, % (MS)	27.1	47.3	28.6	88.7
Average, % (FID + MS)	28.0	47.0	28.8	89.1
Sr (FID)	0.55	0.54	0.21	0.69
Sr (MS)	0.30	0.17	0.35	0.41
Sr (FID + MS)	0.45	0.39	0.27	0.58
SR (FID)	0.99	0.55	0.31	0.65
SR (MS)	0.29	0.57	0.55	0.49
SR (FID + MS)	1.05	0.58	0.49	0.66
r (FID)	1.54	1.52	.059	1.94
r (MS)	0.83	0.46	0.99	1.14
r (MS + FID)	1.26	1.10	0.75	1.62
R (FID)	2.76	1.54	0.87	1.83
R (MS)	0.82	1.61	1.53	1.36
R (FID + MS)	2.93	1.61	1.38	1.83

TABLE 5 Precision Data for Parachlorobenzotrifluoride and Methyl Acetate

Material	Parachlorobenzo trifluoride		Methyl Acetate[A]	
Sample	A	B	E	F
Average, % (FID)	16.8	10.6	21.0	12.0
Average, % (MS)	16.1	11.1	21.0	12.1
Average, % (FID + MS)	16.5	10.9	21.0	12.0
Sr (FID)	0.49	0.46	0.19	0.19
Sr (MS)	0.20	0.11	0.10	0.15
Sr (FID + MS)	0.38	0.32	0.15	0.17
SR (FID)	0.48	0.58	0.22	0.25
SR (MS)	0.28	0.22	0.34	0.19
SR (FID + MS)	0.55	0.51	0.28	0.22
r (FID)	1.38	1.28	0.53	0.54
r (MS)	0.56	0.30	0.29	0.41
r (MS + FID)	1.05	0.88	0.43	0.49
R (FID)	1.34	1.61	0.63	0.69
R (MS)	0.77	0.62	0.95	0.52
R (FID + MS)	1.53	1.42	0.78	0.63

[A] Cellulose nitrate lacquers obtained from different manufacturers were diluted under carefully controlled laboratory condition to give samples E and F. The calculated values for methyl acetate in these two samples were: Sample E, 21.2 %; Sample F, 12.0 %.

absolute at 19 df for parachlorobenzotrifluoride, and 0.25 % absolute at 19 df for methyl acetate. The 95 % confidence limit for the difference between two such averages is 1.94 % absolute for acetone, 1.47 % absolute for parachlorobenzotrifluoride, and 0.70 % absolute for methyl acetate.

11.7 *Bias*—Bias has not been determined for this test method.