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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Purity of Propylene Glycol Monomethyl Ether, Dipropylene Glycol Monomethyl Ether, and Propylene Glycol Monomethyl Ether Acetate[1]

This standard is issued under the fixed designation D4773; 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 covers the determination by gas chromatography of propylene glycol monomethyl ether (PM), dipropylene glycol monomethyl ether (DPM), and propylene glycol monomethyl ether acetate (PMA).

NOTE 1—Propylene glycol monomethyl ether (PM) is a mixture of two isomers: 1-methoxy-2-propanol and 2-methoxy-1-propanol.

Dipropylene glycol monomethyl ether (DPM) is a mixture of four isomers: 1-(2-methoxy-1-methylethoxy)-2-propanol is one of the major isomers.

Propylene glycol monomethyl ether acetate (PMA) is a mixture of two isomers: 1-methoxy-2-acetoxypropane and 2-methoxy-1-acetoxypropane.

1.1.1 This test method covers the determination of PM in the range from 98 to 100 %, and DPM in the range from 0.08 to 0.6 %.

1.1.2 This test method covers the determination of DPM in the range from 98 to 100 %, PM in the range from 0.05 to 0.3 %, and tripropylene glycol monomethyl ether (TPM) in the range from 0.06 to 0.3 %.

1.1.3 This test method covers the determination of PMA in the range from 99 to 100 %, and PM in the range from 0.03 to 1.0 %.

1.2 Water and acid cannot be determined by this test method and must be measured in accordance with Test Methods D 1364 and D 1613, and the results used to normalize the chromatographic data.

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.*

1.4 For hazard information and guidance, see the supplier's Material Safety Data Sheet.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)[2]

D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products[2]

3. Summary of Test Method

3.1 A representative sample of PM, DPM, or PMA containing the appropriate internal standard is injected into a capillary gas chromatograph and the components are detected with a flame ionization detector. Quantification is made by peak area measurement using internal standardization and a computing integrator.

4. Significance and Use

4.1 This test method is used to determine the purity of PM, DPM, and PMA by subtracting calculated total impurities from 100 %.

4.2 This test method is used to determine the quantity of residual glycol ether present in PMA.

4.3 This test method is used for identifying various impurities in PM, DPM, and PMA.

5. Apparatus

5.1 *Chromatograph*—Any programmed temperature gas chromatograph designed or modified for use with capillary columns. The chromatograph must also be equipped with a flame ionization detector.

5.2 *Column*—Capillary, 5 µm thick film, 10 m by 0.32 mm inside diameter, fused silica coated, with 5 % phenyl methyl silicon liquid phase.

5.3 *Syringe*—10 µL or equivalent to introduce a representative sample onto the column.

5.4 *Computing Integator*, capable of peak summation and a baseline construction.

5.5 *Analytical Balance*, capable of measuring 0.1 mg.

6. Reagents and Materials

6.1 *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,

[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 D01.35 on Solvents, Plasticizers, and Chemical Intermediates.

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[2] *Annual Book of ASTM Standards*, Vol 06.04.

where such specifications are available.[3] 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.

6.2 *Gases*:

6.2.1 *Carrier Gas*—Helium, with a minimum purity of 99.95 mol % for use with a flame ionization detector.

6.2.2 *Detector Gas*—Hydrogen with a minimum purity and air for use with the flame ionization detector.

6.3 *Standards for Calibration and Identification*:

6.3.1 *N-Butyl Acetate*—Distilled-in-glass purity for use as an internal standard in determination of PMA.

6.3.2 *Monochlorobenzene*—Distilled-in-glass purity for use as an internal standard in determination of PM and DPM.

6.3.3 *Dipropylene Glycol Monomethyl Ether (DPM)*—Purity should be determined and the standard solution adjusted for this purity.

6.3.4 *Propylene Glycol Monomethyl Ether (PM)*—Purity should be determined and the standard solution adjusted for this purity.

6.3.5 *Propylene Glycol Monomethyl Ether Acetate (PMA)*—Purity should be determined and the standard solution adjusted for this purity.

6.3.6 *Tripropylene Glycol Monomethyl Ether (TPM)*—Purity should be determined and the standard solution adjusted for this purity.

7. Calibration and Standardization

7.1 *Preparation of Calibration Standard Solution*:

7.1.1 *Propylene Glycol Monomethyl Ether (PM)*—Weigh into a vial to within 0.1 mg, 10.00 g of PM calibration standard (see 6.3.4) and 0.02 g of DPM. Check these reagents for purity under the conditions used in the procedures and, if interfering compounds are present, adjustment must be made in preparing the standard.

7.1.2 *Dipropylene Glycol Monomethyl Ether (DPM)*—Weigh into a vial to within 0.1 mg, 10.00 g of DPM calibration standard (see 6.3.3), 0.02 g of PM calibration standard (see 6.3.4), and 0.02 g of TPM (see 6.3.6). Check these reagents for purity under the conditions used in the procedure and, if interfering compounds are present, adjustment must be made in preparing the standard.

7.1.3 *Propylene Glycol Monomethyl Ether Acetate (PMA)*—Weigh into a vial to within 0.1 mg, 10.00 g of PMA calibration standard (see 6.3.5) and 0.04 g of PM. Check these reagents for purity under the conditions used in the procedure and, if interfering compounds are present, adjustment must be made in preparing the standard.

7.2 *Preparation of Standard*:

7.2.1 Weigh into a vial to within 0.1 mg, 1.0 g of the desired calibration standard solution (see 7.1.1 for PM, 7.1.2 for DPM and 7.1.3 for PMA).

7.2.2 Into the respective vials for PM and DPM, weigh to within 0.1 mg, 1.0 g of monochlorobenzene internal standard (see 6.3.2), tightly seal with a polyethylene-lined cap, and mix thoroughly.

7.2.3 Into the vial containing PMA, weigh to within 0.1 mg, 1.0 g of *n*-butyl acetate internal standard (see 6.3.1), tightly seal with a polyethylene lined cap, and mix thoroughly.

7.3 *Chromatographic Conditions*:

Column: capillary fused silica

Length, m	10
Inside diameter, mm	0.32
Film thickness, µm	5
Injection temperature, °C	300
Detector temperature, °C	300
Split:	30:1
Specimen size,µ L	0.5 needle flash
Oven temperature, °C at 8°C/min	80–260
Column flow, mL/min (He)	1.2
Makeup flow, mL/min (He)	24
Internal standard:	

PM	DPM	PMA
Monochlorobenzene	monochlorobenzene	*n*-butyl acetate

7.4 *Calibration for Propylene Glycol Monomethyl Ether (PM)*:

7.4.1 Make a needle-flash injection of the standard into the chromatograph and separate according to the chromatographic conditions in 7.3. At the end of the run, set the peak summing windows to sum the isomer peaks as shown in Areas I and II of Fig. 1.

7.4.2 Program the integrator to set the baseline at the same time peak summation begins for the PM isomers. Force the integrator to extend a baseline horizontally from the set baseline.

7.4.3 Make another needle-flash injection of the standard and calibrate the integrator according to the manufacturer's operating instruction for an internal standard method. Response factors should agree within the precision of this test method. If not, recalibrate and repeat the analysis.

7.4.4 If manual calculations are used, calculate the response factors *RF* for each component as follows:

$$RF = (A \times B)/(C \times D) \quad (1)$$

where:

A = peak area of internal standard,
B = component of interest in standard, g,
C = peak area for component of interest in standard, and
D = internal standard in standard mixture, g.

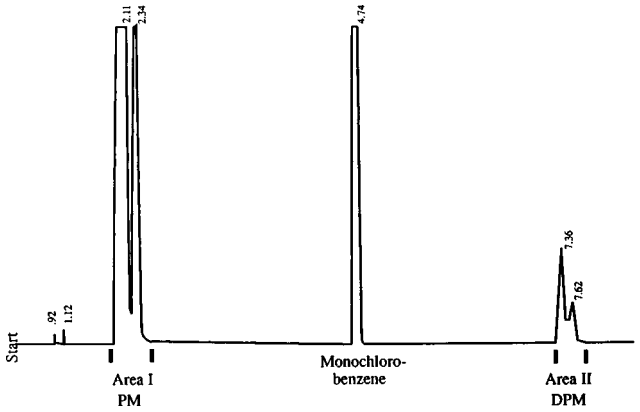

FIG. 1 Chromatographic Data for PM

[3] "Reagent Chemicals, American Chemical Society Specifications,'' Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards,'' by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia.''

7.5 *Calibration for Dipropylene Glycol Monomethyl Ether (DPM)*:

7.5.1 Make a needle-flash injection of the standard into the chromatograph and separate according to the chromatographic conditions in 7.3. At the end of the run, set the peak summing windows to sum the PM, DPM, and TPM isomer peaks as shown in Areas I, II, and III, respectively, of Fig. 2.

7.5.2 Program the integrator to set the baseline at the same time peak summation begins for the DPM isomers. Force the integrator to extend a baseline horizontally from the set baseline for the DPM isomer peaks.

7.5.3 Make another needle-flash injection of the standard and calibrate the integrator according to the manufacturer's operating instruction for an internal standard method. Response factors should agree within the precision of this test method. If not, recalibrate and repeat the analysis.

7.5.4 If manual calculations are used, calculate the response factors *RF* for each component as follows:

$$RF = (A \times B)/(C \times D) \quad (2)$$

where:

A = peak area of internal standard,
B = component of interest in standard, g,
C = peak area for component of interest in standard, and
D = internal standard in standard mixture, g.

7.6 *Calibration for Propylene Glycol Monomethyl Ether Acetate (PMA)*:

7.6.1 Make a needle-flash injection of the standard into the chromatograph and separate according to the chromatographic conditions in 7.3. At the end of the run, set the peak summing windows to sum the PM and PMA isomer peaks as shown in Areas I and II, respectively, of Fig. 3.

7.6.2 Program the integrator to set the baseline at the same time peak summation begins for the PMA isomers. Force the integrator to extend a baseline horizontally from the set baseline.

7.6.3 Program the integrator to set the baseline and force a baseline horizontally prior to the elution of the PM peak.

7.6.4 Make another needle-flash injection of the standard and calibrate the integrator according to the manufacturer's operating instruction for an internal standard method. Response factors should agree within the precision of this test method. If not, recalibrate and repeat the analysis.

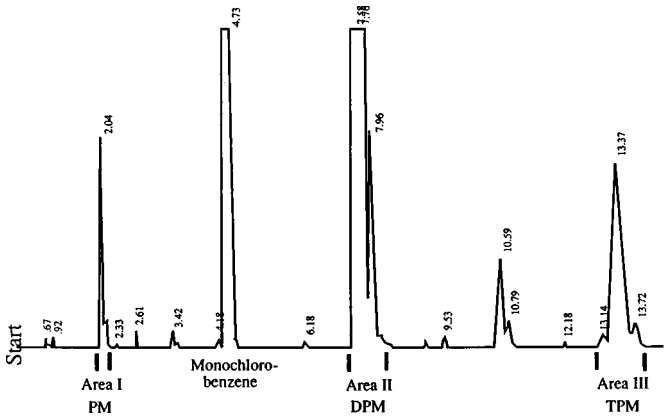

FIG. 2 Chromatographic Data for DPM

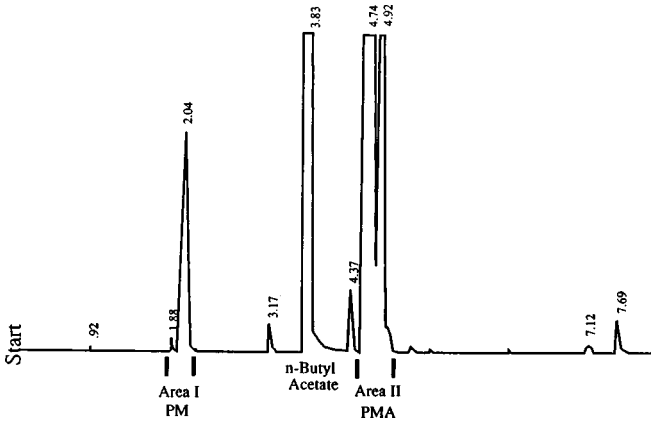

FIG. 3 Chromatographic Data For PMA

7.6.5 If manual calculations are used, calculate the response factors *RF* for each component as follows:

$$RF = (A \times B)/(C \times D) \quad (3)$$

where:

A = peak area of internal standard,
B = component of interest in standard, g,
C = peak area for component of interest in standard, and
D = internal standard in standard mixture, g.

8. Procedure

8.1 Weigh 1.0 g of the specimen to the nearest 0.1 mg into a vial.

8.2 Into the same vial, weigh 1.0 g of the appropriate internal standard (see 6.3.1 for PMA and 6.3.2 for PM and DPM). Tightly close with a polyethylene-lined cap and mix thoroughly.

8.3 Enter internal standard and specimen weight into the integrator.

8.4 Make a needle-flash injection into the chromatograph and separate according to the conditions in 7.3.

9. Calculation

9.1 *Total Weight Percent Impurities*—The response factors of the standardized impurities are used to calculate the total weight percent of all detected organic impurities.

9.1.1 Calculate the total weight percent impurities in PM using the response factor determined for DPM (see 7.4).

9.1.2 Calculate the total weight percent impurities in DPM using the response factor determined for PM for components with a retention time before DPM, and using the response factor determined for TPM for components with a retention time after DPM (see 7.5).

9.1.3 Calculate the total weight percent impurities in PMA using the response factor determined for PM (see 7.6).

NOTE 2—Peak areas may be determined by any method that meets the precision limits given in Section 11. Electronic integration of peak areas was employed to obtain the results used to establish the precision of this test method.

9.2 *Weight Percent Assay*—Calculate the weight percent assay, *W*, as follows:

$$W = 100 - (A + B) \quad (4)$$

where:
A = total weight percent impurities and
B = sum of percent water and acidity.

10. Report

10.1 Report the following information:

10.1.1 The adjusted percent of the component of interest as calculated in Section 9 and

10.1.2 The water and acid present in the specimen as calculated in accordance with Test Methods D 1364 and D 1613.

11. Precision and Bias

11.1 An interlaboratory study of this test method in which seven operators in seven laboratories analyzed four specimens of each product is the basis for the following:

11.1.1 *Propylene Glycol Monomethyl Ether (PM)*—Materials containing 98.3 to 99.4 % PM and 0.09 to 0.42 % DPM had a within-laboratory standard deviation of 0.015 for DPM with 1 df and the between-laboratory standard deviation was found to be 0.06 for DPM with 13 df. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

11.1.1.1 *Repeatability*—Two results, each the mean of duplicates by the same operator, should be considered suspect if they differ by more than 0.016 for DPM.

11.1.1.2 *Reproducibility*—Two results, each the mean of duplicates obtained by operators in different laboratories, should be considered suspect if they differ by more than 0.12 for DPM.

11.1.2 *Dipropylene Glycol Monomethyl Ether (DPM)*—Materials containing 97.1 to 98.2 % DPM, 0.12 to 0.38 % PM, and 0.10 to 0.37 % TPM had a within-laboratory standard deviation of 0.02 for PM and 0.03 for TPM with 1 df and between-laboratory standard deviation was found to be 0.03 for PM and 0.05 for TPM with 13 df. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

11.1.2.1 *Repeatability*—Two results, each the mean of duplicates by the same operator, should be considered suspect if they differ by more than 0.04 for PM and 0.06 for TPM.

11.1.2.2 *Reproducibility*—Two results, each the mean of duplicates obtained by operators in different laboratories, should be considered suspect if they differ by more than 0.06 for PM and 0.12 for TPM.

11.1.3 *Propylene Glycol Monomethyl Ether Acetate (PMA)*—Materials containing 98.8 to 99.8 % PMA and 0.11 to 0.47 % PM had a within-laboratory standard deviation of 0.01 for PM with 1 df and a between-laboratory standard deviation of 0.06 for PM with 13 df. Based on these standard deviations, the following criteria should be used for judging acceptability of results at the 95 % confidence level:

11.1.3.1 *Repeatability*—Two results, each the mean of duplicates obtained by the same operator on different days, should be considered suspect if they differ by more than 0.02 for PM.

11.1.3.2 —*Reproducibility*—Two results, each the mean of duplicates obtained by operators in different laboratories, should be considered suspect if they differ by more than 0.12 for PM.

12. Keywords

12.1 propylene glycol monomethyl ether; dipropylene glycol monomethyl ether; propylene glycol monomethyl ether acetate