Designation: ~~F1884 – 04 (Reapproved 2011)~~ F1884 – 04 (Reapproved 2018)

Standard Test Methods for Determining Residual Solvents in Packaging Materials[1]

This standard is issued under the fixed designation F1884; 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 determination of the amount of residual solvents released from within a packaging material contained in a sealed vial under a given set of time and temperature conditions and is a recommended alternative for Test Method F151.

1.2 This test method covers a procedure for quantitating volatile compounds whose identity has been established and which are retained in packaging materials.

1.3 The analyst should determine the sensitivity and reproducibility of the method by carrying out appropriate studies on the solvents of interest. The analyst is referred to Practice E260 for guidance.

1.4 For purposes of verifying the identity of or identifying unknown volatile compounds the analyst is encouraged to incorporate techniques such as gas chromatography/mass spectroscopy, gas chromatography/infrared spectroscopy or other suitable techniques in conjunction with this test method.

1.5 Sensitivity of this test method in the determination of the concentration of a given retained solvent must be determined on a case by case basis due to the variation in the substrate/solvent interaction between different types of samples.

1.6 This test method does not address the determination of total retained solvents in a packaging material. Techniques such as multiple headspace extraction can be employed to this end. The analyst is referred to the manual supplied with the GC-Autosampling system for guidance.

1.7 The values stated in SI units are to be regarded as the standard.

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

1.9 *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]

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E260 Practice for Packed Column Gas Chromatography
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
F151 Test Method for Residual Solvents in Flexible Barrier Materials (Withdrawn 2004)[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *ream*—3000 ft^2 = 278.7 m^2 = 27.87×10^6 cm^2.

[1] This test method is under the jurisdiction of ASTM Committee F02 on ~~Flexible~~Primary Barrier Packaging and is the direct responsibility of Subcommittee F02.15 on Chemical/Safety Properties.

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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.

3.1.2 *retained solvents*—those chemical species, which are retained by packaging material and can be detected in the headspace of sealed sample vials under conditions of elevated temperature.

4. Summary of Test Method

4.1 Retained volatile organic solvents are determined by subjecting the packaging material to elevated temperatures in a headspace sampling system with subsequent gas chromatography of the headspace and detection using a suitable detection device such as a flame ionization detector (FID).

4.2 Volatile components can then be quantified by comparison with standards of known concentration.

4.3 Qualitative analysis may be carried out on a gas chromatograph (GC) coupled to an appropriate detector capable of compound detection / identification, such as a mass spectrometer or infrared detector.

5. Significance and Use

5.1 This test method is intended to measure volatile organic compounds that are emitted from packaging materials under high-temperature conditions.

5.2 This test method may be useful in assisting in the development and manufacture of packaging materials having minimal retained packaging ink/adhesive solvents.

5.3 Modification of this procedure by utilizing appropriate qualitative GC detection devices such as a mass spectrometer in place of the flame ionization detector may provide identification of volatile organics of unknown identity.

6. Interferences

6.1 *Gas Chromatography*—Because of the potentially large number of chemical species that can be analyzed using this methodology, not all species will be resolved from one another on a particular GC column under a given set of conditions. Techniques available to the analyst to verify the identity of chemical species being quantitated include retention time comparisons using alternate GC conditions or using an alternate GC column. Good judgment in the interpretation of chromatographic results is always important. Refer to Practice E260 for guidance.

6.2 *Apparatus*—Because this method is designed for detecting trace quantities of organic compounds, contaminants can lead to misinterpretation of results. Preparing apparatus properly and carrying out blank determinations is essential to minimize this possibility.

TEST METHOD A

7. Apparatus and Reagents

7.1 Gas chromatograph equipped as follows:

7.1.1 *FID Detector,* compatible with capillary columns.

7.1.2 *Injector,* split/split-less compatible with capillary columns.

7.1.3 *Column,* DB-5, 30m, 0.25 mm ID, 1 µm film thickness, Cat. No. 122–5033, or 0.32 mm, Cat. No. 123–5033.[4] A short piece of deactivated fused silica column may be placed between the injector and the column to serve as a guard column.

7.1.4 *Peak Area Integration System,* compatible with GC system in use. Alternately, a chart recorder and hand integration can be used.

7.1.5 Auto sampler is recommended.

7.2 *Standard Solutions,* consisting of the organic solvent mixture of interest, at concentrations that simulate the expected retention levels. 4-Heptanone may be added to the solutions for use as an internal standard as described in Practice E260.

7.2.1 An example of a working standard is listed below. The standard used will vary based on the solvents present in the sample to be tested. The quantities shown in the table will result in roughly equivalent size peaks due to differences in detector response. If the solvents are mixed neat, adding 1 µL per gram of material in the headspace vial provides a good starting point for calibration.

7.2.2 If desired, water may be used as the diluent for the standard. The solvents are diluted in 1 L of water, typically 2 mL of the resulting solution is added per gram of sample in the headspace vial for calibration. 2 mL of 20 µl/L of 4-heptanone containing solution in water can be used as an internal standard.

NOTE 1—Water will change the partition coefficient between the sample and retained solvents.

Solvent	µL/L	µg/mL
Methanol	120	94.96

[4] The sole source of supply of the apparatus known to the committee at this time is J. and W. Scientific, Cat. No. 122-5033 and Cat. No. 123-5033. 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, which you may attend.

Ethanol	80	63.14
2-Propanol	60	47.13
n-Propanol	60	48.21
Methylethyl ketone	40	32.20
Ethylacetate	40	36.08
2-Propylacetate	20	17.08
Benzene	10	8.76
Methylisobutylketone	20	16.02
Toluene	10	8.70
Heptanone	20	16.42

7.3 *Vials,* 20 mL. To ensure against extraneous peaks in the gas chromatographic traces, wash vials thoroughly and dry in a 125°C air oven for a minimum of 4 h before using.

7.4 *Vial Crimp Caps.*

7.5 *Septa,* Teflon/Silicone. To ensure that the septa are free of volatiles, condition the septa in a vacuum oven at 130°C for 16 h.

7.6 *Crimping Tool for Vials.* [4,5]

7.7 *Syringe*—2 mL gas tight with valve.[4,6] Store syringe in 90°C oven between uses.

7.8 *4-Heptanone.* [4,7]

7.9 *For Manual Injection Only*—Hot air oven and heat resistant gloves.

8. Instrument Setup

8.1 Set up the gas chromatographic system per the manufacturer's recommendations and as follows:

8.1.1 *Injector Temperature*—250°C.

8.1.2 *Detector Temperature*—250°C.

8.1.3 *Column Temperature:*

8.1.3.1 Initial 40°C for 4 min.

8.1.3.2 *Program*—Adjust temperature program to give a retention window of at least 15 min to ensure optimum separation of solvents.

8.1.4 Attenuation or sensitivity, or both, set to give a detector response of 40 % or more of full scale on the recorder or integrator of the expected internal standard and standard sample response. See Practice E260 for guidance.

8.2 Set up autosampler, if used, to heat vials for 20 min at 90°C before autoinjection.

9. Calibration Procedure

9.1 *Standard Curve:*

9.1.1 Prepare blanks by heating a sample of the packaging material of interest (enough sample can be prepared at one time for several analysis runs) in a vacuum oven at 90°C for 24 h. Remove the blanks and store in a closed container. Blanks should be cut to the same relative size as the sample prior to heating in the vacuum oven.

9.1.2 To prepare a calibration standard place a blank (cut to appropriate size) in the 20 mL headspace vial and add the appropriate amount of standard solvent mix to the vial. Immediately cap and crimp the vial with the Teflon side of the septum toward the vial. It is suggested that blanks be fortified at five different concentrations along with an unfortified blank be prepared for calibration. See Practice E260 for guidance.

9.2 *Manual Injection:*

9.2.1 If using a syringe and hot air oven, heat each vial for 20 min at 90°C. Ensure that the syringe is heated to at least 90°C before taking headspace samples from the vials for injection into the chromatograph.

NOTE 2—When handling the hot syringe be sure that hands are adequately protected. Fill the gas tight syringe with 1 mL of air, close valve and insert the needle through the septum into the preheated vial. Open valve, inject the air into vial. Draw ½ mL of gas from vial into syringe, inject back into vial. Repeat 2 times. Draw exactly 1 mL of gas into syringe and close valve. Insert needle into injector of GC and inject.

NOTE 3—Consistent technique from injection to injection of standards and sample is required. This step should take no more than 30 s.

9.3 *Automated Injection*—The recommended method of injecting the headspace gas into the GC is use of an automated headspace sampling system where the vials are heated to 90°C for 20 min and then the headspace of each vial is automatically injected onto the GC column.

9.4 Repeat the procedure for all five calibration standards and the blank.

9.5 Construct a standard calibration curve from the data obtained using standard techniques as defined in Practice E260.

[5] The sole source of supply of the apparatus known to the committee at this time is Cat. No. 33280, Supelco Inc., Bellefonte, PA 16823.

[6] The sole source of supply of the apparatus known to the committee at this time is Cat. No. 050034, Alltech, 2051 Waukegan Rd., Deerfield, IL 60015.

[7] The sole source of supply of the apparatus known to the committee at this time is Cat. No. 10, 174-5, Aldrich, 940 W. St. Paul Ave., Milwaukee, WI 53233.

NOTE 4—Longer heating times may be used if it is deemed necessary to ensure that the solvent in the headspace of the vial has totally equilibrated with the sample.

10. Sampling

10.1 Samples should be taken in such a manner as to represent the entire web. The analyst should cut several layers deep into a roll of packaging material, discarding the outer layers, to ensure the sampling is representative of the entire roll. Samples should be taken from the left, center and right side of the web.

NOTE 5—Consideration should also be given when sampling rolls within a production lot to ensure uniformity within the production run.

10.2 Samples should be taken and handled in such a way as to minimize loss of solvent from the sample between the time the sample is taken, cut and loaded into the sample vial. Taking samples at press side, cutting and loading into vials immediately is the preferred method. Alternately, full web samples can be collected at press side and placed in a sealed container (samples can also be wrapped tightly in foil) for transport to the lab for cutting and loading into vials.

10.3 When taking samples from roll stock, discard the first 8 to 10 layers before taking samples from the next 30 to 40 layers to ensure that the samples are representative of the entire roll.

10.4 When possible, samples should have 100 % ink coverage in the area selected for testing. Selecting an area with 100 % ink coverage will ensure that the testing will elucidate a worst case. Using a sample area with representative ink coverage may also be considered.

10.5 The sample size is dictated by the thickness of the sample and the ease of filling the vial. The sample size will vary from 5 to 50 $in.^2$ Typically, the vial will be less than 20 % full by volume. Alternately the ratio of the weight of the sample in grams to the volume of the vial in millilitres should not exceed 1 to 10. In the case of a 20-mL sample vial, the weight of the sample should not exceed 2 g.

10.6 The preferred method of cutting samples is the use of a punch press or die.

10.7 Add the appropriate amount of internal standard (if used) to the vial.

10.8 Immediately cap and crimp the vial with the Teflon side of the septa toward the vial.

11. Procedure

11.1 *Manual Injection:*

11.1.1 For those using the syringe, place the sample (vial) in a forced air oven at 90°C for 20 min.

NOTE 6—Longer heating times may be used if it is deemed necessary to ensure that the solvent in the headspace of the vial has totally equilibrated with the sample.

NOTE 7—When handling the hot syringe be sure that hands are adequately protected. Fill the preheated gas-tight syringe with 1 mL of air, close valve and insert the needle through the septum into the above conditioned vial. Open valve, inject the air into vial. Draw ½ mL of gas from vial into syringe, inject back into vial. Repeat 2 times. Draw exactly 1 mL of gas into syringe and close valve. Insert needle into injector of GC and inject.

NOTE 8—Consistent technique from injection to injection of standards and sample is required. This step should take no more than 30 s.

11.2 *Automated Injection:*

11.2.1 The recommended method of injecting the headspace gas into the GC is use of an automated headspace sampling system where the vials are heated to 90°C for 20 min and then the headspace of the vial is automatically injected onto the GC column.

NOTE 9—Longer heating times may be used if it is deemed necessary to ensure that the solvent in the headspace of the vial has totally equilibrated with the sample.

11.3 Chromatograph the sample under the same conditions used for establishment of the standard curve.

11.4 Run a blank and one calibration standard along with each sample set to ensure system integrity.

11.5 Sample sets should contain a minimum of three replicates per sample.

12. Calculation

12.1 Calculate the amounts of retained solvents as follows:

12.1.1 Measure the area of the analyte peak and compare to the area with that from the standard curve and determine the concentration of the analyte in mg/ream of retained solvent. Normalize the analyte peak area with that of the internal standard peak area if the internal standard method is used before calculating the retained solvent concentration.

NOTE 10—The above methodologies are described in Practice E260.

12.2 Add each of the analyte concentrations together to yield a total retained solvent in mg/ream.

13. Report

13.1 Report the following information:

13.1.1 The identification of each known analyte peak observed,