Designation: F2466 – 10

Standard Practice for Determining Silicone Volatiles in Silicone Rubber for Transportation Applications[1]

This standard is issued under the fixed designation F2466; 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 practice covers a means to determine the percent silicone-producing volatiles present in heat-cured silicone rubber and room temperature-cured silicones (RTV).

1.2 Silicone-producing volatiles contribute to fouling of oxygen sensor systems used in the control of vehicle emissions.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3182 Practice for Rubber—Materials, Equipment, and Procedures for Mixing Standard Compounds and Preparing Standard Vulcanized Sheets

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Summary of Practice

3.1 This practice consists of four (4) basic steps: (*1*) the silicone is cured to its elastomeric form, (*2*) the volatiles are extracted from the cured material, (*3*) the extract is separated and measured by gas chromatography (GC), and (*4*) the GC results are quantified using a siloxane calibration.

4. Significance and Use

4.1 Use of this practice in conjunction with realistic maximum volatility tolerance level can help minimize the risk of oxygen sensor dysfunction from formed-in-place-sealants in transportation applications. This practice provides a method for determination of percentage volatiles in silicone elastomers. The volatile silicones from a commercial silicone are primarily cyclo dimethyl-siloxane. Other species present having GC retention times similar to those of the cyclics are assumed to be silicone as well.

5. Apparatus

5.1 *Gas Chromatograph,* fused silica capillary column system equipped with a flame ionization detector, split-type capillary column injector, temperature programming capability and an appropriate data recording system. An alternative unit may be an equivalent instrument equipped with a thermal conductivity detector, or as agreed upon between producer and user. Specific column and operating conditions should be selected to optimize instrument response and chromatographic resolution, particularly separation of the internal standard from extracted sample components.

5.2 *Column,* suggested to be used is 30 to 60 m by 0.25 mm with 0.25 to 1.5 µm DB-1 or DB-5 fused silica capillary column or equivalent.

5.3 Operating conditions are:

5.3.1 *Column*—50 to 320°C at 10°C/min (a post-analysis period may be required to elute higher boiling components prior to subsequent analyses).

5.3.2 *Injector*—290°C.

5.3.3 *Detector*—325°C.

5.3.4 *Sample Size*—1 µL.

5.3.5 *Injector Split Ratio*—2:1 to 50:1 (adjusted as needed).

5.3.6 *Helium or Nitrogen,* for the carrier gas.

5.3.7 *Carrier Gas Flow Velocity*—1 to 2 mL/min (adjusted as needed for column dimensions).

5.4 *Humidity Chamber,* or controlled lab environment.

5.5 *Wrist-Action Mechanical Shaker.*

5.6 *Analytical Balance,* with glass draft shield capable of 0.0001 g accuracy.

5.7 *30-mL Vials,* flint glass, with screw cap (polyethylene lined).

[1] This practice is under the jurisdiction of ASTM Committee F03 on Gaskets and is the direct responsibility of Subcommittee F03.50 on Analytical Test Methods.

Current edition approved May 1, 2010. Published June 2010. Originally approved in 2005. Last previous edition approved in 2005 as F2466 – 05. DOI: 10.1520/F2466-10.

[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.

5.8 *Syringe,* capable of accurately delivering 20 ± 0.1 µL (no plastic elements used due to solvents used).

5.9 Solvents and standards used are pentane (99 %) and dodecane (99 %), both spectral grade.

5.10 *Rigid Plates (Glass or Aluminum),* 0.90 mm thick, for cutting the wet formed-in-place sealant.

5.11 Automated devices shall be used for measuring and calculating peaks.

6. Test Specimens

6.1 Heat-cured silicone rubber samples shall be procured from either actual production parts, or shall be compression-molded ASTM tensile plaques (Practice D3182, 2.0 ± 0.2 mm thick). Cure conditions of the tensile plaques shall mirror cure conditions used on the production parts. If actual production parts are used to obtain test samples, best practice would be to cut sample so that it is not thicker than the above stated tensile plaque thickness.

6.2 Room temperature-vulcanized (RTV) samples shall be prepared by spreading the liquid using a suitable device, into consistent 0.90 ± 0.20 mm plaques. Avoid entrapped air and knit lines when preparing the sample.

6.3 Three 1-g samples shall be cut from the plaque. These samples shall be taken from near one corner, at the center of the plaque, and near the corner at a diagonal from the first.

7. Standard Solutions[3]

7.1 Add 0.1 g (weighed to the nearest 0.1 mg) of each pure cyclic (>98 %) to 1.0 g of dodecane (99 %) (weighed to the nearest 0.1 mg). Ten millilitres ± 0.1 mL pentane is added and the container is sealed to prevent leakage/evaporation. New standard mixtures should be prepared if existing one is more than seven (7) days old.

7.2 Calibration of the standard solution is achieved by injecting 1 µL (need verify use with SE 30 column – will need to attenuate response or dilute solution) standard solution sample. Response factors for the individual cyclics are calculated using the following equation:

$$RfDn = \frac{Wt\,Dn}{ADn} * \frac{ADoD}{WtDoD} \quad (1)$$

where:

Rf = response factor
Dn = the cyclic siloxane species from a 4 member to a 10 member ring
RfDn = the response factor for each siloxane species from 4 to 10
WtDn = the weight of each siloxane species from 4 to 10 used in the standard solution
ADn = the area under the curve for each siloxane species from 4 to 10
DoD = the dodecane standard, which is arbitrarily given a response factor of "1" (one), and is used as the basis for calculating the response factors of the various know and unknow siloxane species
ADoD = the area under the curve for the dodecane standard
WtDoD = the weight of the dodecane used in the standard solutions

7.3 Response factors for cyclic species vary in a relatively linear manner from D_5 through D_{10}, so that response factors for cyclics not in the standard solution can be calculated from the known response factors of the cyclics in the standard solution. A sample calculation for response factors of standards available, and a Linear Least Squares Analysis to determine response factors of cyclics that are unavailable can be found in Appendix X1.

7.4 All of the unknowns that appear in the analysis (between D_4 and D_{10}) are assumed to be dimethyl siloxanes. All unknowns are given, as response factors, the average response factor calculated for the difunctional cyclosiloxane monomers D_4 through D_{10}.

8. Conditioning

8.1 Allow RTV samples to cure for 24 h, but not to exceed 72 h at 25°C and 50 ± 10 % relative humidity.

9. Procedure

9.1 *Extraction*—Pre-weigh each cured sample to 1.0 ± 0.2 g (record weight to the nearest 0.0001 g) and set aside.

9.2 Weigh 0.010 ± 0.005 g of dodecane (record weight to the nearest 0.0001 g) and place sample into the 30-mL vial. To this add 10 mL of pentane. Immediately place the pre-weighed sample into the vial, and seal the container to prevent leakage/evaporation. Weight precision of the dodecane and test sample are extremely important for reproducible results. The sample vial is placed on a wrist shaker for 16 h.

NOTE 1—The sequence is important due to the volatility of the solvents. used.

NOTE 2—See 10.1.1 regarding dodecane measurement.

9.3 Inject 1 to 5 µL into the GC injection port. (Injection volume is dependant on the injector split ratio).

9.4 After the elution is complete (about 35 min) identify the peaks and quantify them by integration using the following equations (sample calculations are shown in Appendix X2):

$$\%Dn = \frac{RfDn*ADn}{ADoD} * \frac{WtDoD}{SaWt} * 100 \quad (2)$$

where:

SaWt = the weight of the silicone part

9.4.1 Perform Eq 2 for D_4 through D_{10}.

$$\%\ Un = \frac{AveRfDn*AUn}{ADoD} * \frac{WtDoD}{SaWt} * 100 \quad (3)$$

where:

Un = the unknown cyclic siloxanes in the sample

[3] The sole source of supply of the standards solutions known to the committee at this time is Ohio Valley Specialty Chemicals, 115 Industrial Road, Marietta, OH, 45750, 1-800-729-6972, Catalog number 34569/Cyclic Standard Kit D3 through D10. 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.

AveRfDn = the average of the response factors from D_3 to D_{10}

9.4.2 Perform Eq 3 for all unknowns that elute between D_4 and D_{10}.

9.4.3 % Siloxane Volatiles = Sum of % cyclics D_4 through D_{10} and sum of % unknowns eluting from D_4 through D_{10}.

NOTE 3—Silicone volatiles below D_5 may not be detected at their correct levels due to their loss from the sealant as it cures for 24 h at 25°C and 50 % relative humidity. Dodecane can mask D_5 forms and the beginning of the first unknown. Any D_3 not lost would be masked by impurities in pentane. Weight precision is extremely important if the results are to be reproducible.

10. Potential Failure Modes of Test Procedure

10.1 Methods/techniques of weighing can be a major source of error. It's imperative that the technician be as exacting as possible when weighing the following materials:

(1) Each standard cyclic siloxane species,

(2) Dodecane added to standard solutions, and to extraction sample vials, and

(3) Each cut test sample to be added to extraction vial.

10.1.1 In order to reduce error associated with weighing the small quantity of dodecane directly into the sample vial, it is recommended to first prepare a standard solution using a larger dodecane weight. This is done by weight out approximately 0.1 g dodecane (record weight to the nearest 0.0001g) into a 10-mL class A volumetric flask. Dilute to the line with pentane, and calcualte the actual concentration per mL of dodecane, based on the previously recorded weight. One millilitre (1 mL) of this standard solution is added to each sample vial using a Hamilton pipette.

10.2 *Loss of Small Amounts of DoD From Extraction Vial Due to Incidental Splash*—Incidental fluid loss due to splash when adding dodecane, pentane, and pre-weighed silicone sample to extraction vial will greatly affect results. Care should be taken when adding materials to extraction vial, and until cap is tightly sealed. Any loss of material, no matter how small, must result in discarding that sample and preparing a new one.

11. Reporting

11.1 Three data points shall be reported for each sample as % total volatiles.

11.2 Final results for siloxane should be expressed as 0.00 %. Report D_4 through D_{10} for total volatiles as cyclics plus unknowns (Un_4 through Un_{10}).

11.3 All observed and recorded data on which calculations are based.

11.4 Date of the test, cure conditions, and thickness of the sample.

12. Precision and Bias[4]

12.1 The precision of this test method is based on an interlaboratory study conducted in 2008. Each of four laboratories tested five different materials for silicone volatiles (the results from these five tested in one of the laboratories were unusable due to the utilization of improper response factors). Every "test result" represents an individual determination. All laboratories were asked to report three replicate results for each sample. Except for the limited number of participating laboratories, Practice E691 was followed for the design and analysis of the data.

12.1.1 *Repeatability limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

12.1.1.1 Repeatability limits are listed in Table 1 below.

12.1.2 *Reproducibility limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

12.1.2.1 Reproducibility limits are listed in Table 1 below.

12.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

12.1.4 Any judgment in accordance with statements 12.1.1 and 12.1.2 would normally have an approximate 95 % probability of being correct; however, the precision statistics obtained in this ILS must not be treated as exact mathematical quantities which are applicable to all circumstances and uses. The limited number of laboratories reporting results guarantees that there will be times when differences greater than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95 % probability limit would imply. Consider the repeatability limit and the reproducibility limit as general guides, and the associated probability of 95 % as only a rough indicator of what can be expected.

12.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

12.3 The precision statement was determined through statistical examination of 45 results, from three laboratories, on five materials. These five materials were described as the following:

(1) Material 1: Acetoxy RTV -Q3-7057LV

(2) Material 2: Alkoxy RTV - 3-0115

(3) Material 3: Amine RTV - A2000

(4) Material 4: High viscosity Oxime - 5900

TABLE 1 Silicone Volatiles (%)

Material	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	S_r	S_R	r	R
1	0.286	0.038	0.099	0.107	0.278
2	0.236	0.048	0.092	0.133	0.258
3	0.216	0.035	0.059	0.098	0.166
4	0.137	0.020	0.077	0.057	0.216
5	0.171	0.023	0.077	0.063	0.215

[A] The average of the laboratories' calculated averages.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:F03-1017.

(5) Material 5: Low Viscosity Oxime RTV - 5910

12.4 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

13. Keywords

13.1 percent volatiles; silicone; transportation and oxygen sensor systems

APPENDIXES

(Nonmandatory Information)

X1. CALCULATION OF RESPONSE FACTORS

X1.1 *Sample Calculations for Response Factors (Rf)*:

X1.1.1 Standard solution contains the following:

D_3 = 0.10049
D_4 = 0.10286
D_5 = 0.10346
D_6 = 0.10883
D_9 = 0.10701
C_{12} = 0.99878

X1.1.2 For this standard solution, the area under the curve for each component was averaged over 10 runs:

D_3 = 10 011.5
D_4 = 10 163.6
D_5 = 9905.5
D_6 = 9669.6
D_9 = 8244.7
C_{12} = 283 415.2

X1.1.3 Response Factor (R*f*) calculations for the individual cyclic species per 7.2 can be calculated with the above data. For example, for D_5:

$$RfD_5 = \frac{0.10346}{9905.5} \times \frac{283\,415.2}{0.99878} = 2.9638$$

X1.1.4 A similar calculation for Response Factor was done for all D_n's and summarized as:

RfD_3 = 2.8482
RfD_4 = 2.8718
RfD_5 = 2.9638
$R\,fD_6$ = 3.1937
RfD_9 = 3.6244
$R\,fC_{12}$ = 1.0

X1.1.5 Subsection 7.3 states that R*f* for cyclic species vary in a relatively linear manner from D_5 through D_{10} although our example actually uses D_3 and D_4 species, the linearity still appears to hold true. The user can utilize the linear least squares equations to determine slope and Y-intercept. Based on the above data, and with some round off error, the values are:

where y = mx + b
y- intercept = b = –16.2857
Slope = m = 6.9945

X1.1.6 Solving for D_7, D_8, and D_{10} for which we do not have standards:

$$D_7 = x = \frac{7 - (-16.2857)}{6.9945} = 3.3291$$

$$D_8 = x = \frac{8 - (-16.2857)}{6.9945} = 3.4721$$

$$D_{10} = x = \frac{10 - (-16.2857)}{6.9945} = 3.7581$$

X2. CALCULATION OF % VOLATILES

X2.1 Area of:

D_4 = 9372
D_5 = 19 483
D_6 = 33 219
D_7 = 27 544
D_8 = 13 129
D_9 = 10 949
D_{10} = 6105
Un = 7585
DoD = 1 081 313

X2.2 Using the response factor for D_5 of 2.9638, a dodecane weight of 0.0145g, and an RTV weight of 1.0097 g, Eq 2 becomes:

$$\%\ D_5 = \frac{2.9638 * 19\,483}{1\,081\,313} * \frac{0.0145 * 100}{1.0097} = 0.077\ \%$$

X2.3 Using Eq 2 the remainder of the D_4 through D_{10} series can be solved for:

D_4 = 0.036 %
D_5 = 0.077 %
D_6 = 0.141 %
D_7 = 0.122 %
D_8 = 0.061 %
D_9 = 0.053 %
D_{10} = 0.030 %

X2.4 Using Eq 3 and an average response factor of D_3 through D_{10} of 3.2577, the user can solve for the % of the unknown:

$$\%\ Un = \frac{32\,577 * 7585}{1\,081\,313} * \frac{0.0145 * 100}{1.0097} = 0.033\ \%$$

X2.5 The total % siloxane volatiles from D_3 through D_{10} including the unknown are added and equal 0.553 %.