VOLATILITY RATE BY THERMOGRAVIMETRY
An ASTM interlaboratory study for ASTM international E2008

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ASTM Committee E37 on Thermal Measurements published a new test method 'Standard Test Method for Volatility Rate by Thermogravimetry' in June 1999 with the designation E 2008. This approach to assessing volatility utilizes an extension of the pin-hole technology previously employed by E37 for vapor pressure determinations using differential scanning calorimetry (ASTM E 1782). After publication of the test method E 2008, an Interlaboratory Study was undertaken to develop a 'Precision and Bias' statement to be assigned with the test method. This paper provides some background data that supports the claim that E 2008 is generally insensitive to experimental conditions other than temperature. The Interlaboratory Study showing the statistical review is also discussed.

Keywords: interlaboratory study, pin-hole technology, thermogravimetry, volatility rate

Introduction

ASTM Committee E37 on Thermal Measurements published a new test method 'Standard Test Method for Volatility Rate by Thermogravimetry' in June 1999 with the designation E 2008 [1]. This approach to assessing volatility utilizes an extension of the pinhole technology previously employed by E37 for the ASTM E 1782 standard test method for 'Determining Vapor Pressure by Thermal Analysis' [2]. Since volatility is a characteristic of a material and not an equilibrium thermodynamic property, its magnitude is strongly impacted by a host of external factors including temperature, surface area, purge conditions, etc. Consequently it is highly variable and its determination is quite method dependent. However, using a hermetically sealable crucible with a specific pinhole size it was found that only temperature affects the observed mass loss rate. Purge gas, purge gas flow rate, surface area, and particle size of solids were observed to have no effect on results, with the exception of the manner in which they might influence the measurement of temperature within a given thermogravimetric analyser (TG).

After publication of the test method E 2008, an Interlaboratory Study was undertaken to develop a 'Precision and Bias' statement to be assigned with the test method. Eight laboratories using four models of TG instrumentation from three different vendors participated in this study. Distilled water, squalane and camphor were used in the study. Both an isothermal and a slow dynamic scan protocol were utilized as part of the study.

This paper provides some background data that supports the claim that E 2008 is generally insensitive to experimental conditions other than temperature. It also discuss the Interlaboratory Study showing the statistical review that yielded the precision results.

Experimental

Developmental studies

Volatility rate measurements are accomplished using TG with the specimen of interest encapsulated in a hermetically sealable crucible with a lid having a pinhole of a specific dimension. Early developmental studies leading to the establishment of an ASTM standard test method utilized a number of pinhole sizes ranging from 25 µm to 3 mm. An open crucible of 4.2 mm diameter was also included in a number of measurements. Measurements conducted in conformance with ASTM E 2008 are required to use a pinhole diameter between 330 and 380 µm.

Use of E 2008 allows the operator to conduct either isothermal or constant heating rate measurements. In the isothermal test the specimen is rapidly heated to the intended test temperature and thereafter maintained constant to ±1°C for 30 min. For the alternative constant heating rate test the specimen is heated slowly from a starting temperature (usually ambient) up to some limit temperature at 2.0±0.1°C min^{-1}.

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Table 1 Participating laboratories for ILT

Scientists	Affiliations	Apparatus
Brenda Edwards	Tredegar Film Products	TAI TGA 2950
Charles Tannous	ICI Paints	TAI TGA 2950
John J. Tria	Solutia Inc	Perkin-Elmer TGA7
Marie Vachon	Canadian Explosives Research Laboratory	TAI TGA 2950
Roger Blaine	TA Instruments (TAI)	TAI TGA Q500
Steve Sauerbrunn	Mettler-Toledo (M-T)	M-T TGA/SDTA851
Thao Luong	Atofina Chemicals Ltd.	TAI TGA 2950
Tim McClure	Massachusetts Institute of Technology	Perkin-Elmer TGA7

Coupling an encapsulated specimen to the instrument atmosphere through a specified pinhole minimizes external influence on the volatility rate. A 50–100 mL min^{-1} inert gas purge of the TG is recommended to avoid condensation of volatile materials inside the instrument and to promote better temperature uniformity.

Interlaboratory study

An interlaboratory test (ILT) was conducted to produce a precision and bias statement for the ASTM test method E 2008. As listed in Table 1, eight laboratories using four models of TG instrumentation from three different vendors participated in this study.

The volatility rates for camphor at 60°C and for squalane at 300°C were determined using the ASTM Standard E 2008 Method A – isothermal test [1]. About 4 to 8 mg specimens were placed in containers sealed with pinhole (360 µm diameter) lids, and were held at the selected isothermal temperature for 30 min. Five replicates were obtained from each participating laboratory. The volatility rates for water at 50 and 80°C were determined using Method B – constant heating rate test in five replicates. Specimens of about 4–5 mg placed in pinhole containers were heated from 25 to 85°C at 2°C min^{-1}.

The samples of camphor and squalane were obtained from Sigma-Aldrich as 99% pure materials, and were provided to the participants. For water, the laboratories were asked to use distilled water from their laboratories. All specimen containers and pinhole lids used in this study were Differential Scanning Calorimetry crucibles from the respective instrument vendors. They were also provided to the ILT participants. Each laboratory was asked to perform mass and temperature calibrations in accordance with the instrument manufacturer's recommendation and the ASTM Standard E 1582 [3], respectively.

Results and discussion

Results for developmental studies

Volatility is generally taken to be the tendency of a solid or liquid material to pass into the vapor state at ordinary temperatures. This conversion of a condensed phase to a vapor is a daily concern for all of us whether it involves release of fumes from a chemical process, the drying of our laundry, or the evaporation of our beer. Though an every day occurrence, volatility is difficult to measure in a way that is meaningful to all. This is because volatility is not a thermodynamic property of a material. Rather it is a consequence of a thermodynamic property – vapor pressure – acted upon by extrinsic or environmental factors including temperature, surface area, and purge.

A glance at the ASTM Index for Standard Methods reveals numerous methods for evaporation loss, evaporation rate and volatility [4]. Typically these test methods are directed at particular classes of materials like paints, plastics, water, and assorted petroleum products and involve very specific procedural conditions.

During development of test method E 1782, 'Standard Test Method for Determining Vapor Pressure by Thermal Analysis', ASTM Committee E37 on thermal measurements and rheology noted preboiling vaporization of liquids could be managed by use of a pinhole having specific dimension, with an otherwise hermetically sealed specimen container. It was believed that the pinhole minimized any pressure difference between the inside of the specimen crucible and the instrument atmosphere. The atmosphere inside the specimen container would saturate with specimen vapors. For very small holes the rate of mass transfer by diffusion through the hole was less than that through the self-generated atmosphere within the crucible.

Enlarging the pinhole was observed to enhance the preboiling vaporization [5]. Since volatility is associated with conversion to the vapor phase at temperatures generally much lower than the normal boiling temperature of a material, such enhancement, if controllable, is desirable as a measurement approach.
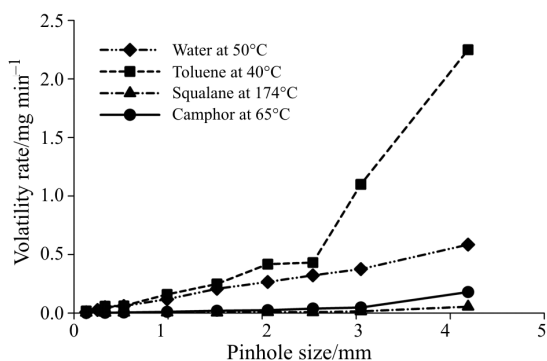
Fig. 1 Effect of pinhole size on observed volatility rate

Fig. 2 Isothermal TG curve for water using a 0.99 mm pinhole

Ideally then, it is desirable to select a pinhole size, which allows the diffusion rate of vapor through the pinhole to equal the self-diffusion rate of the materials. The challenge became that of maximizing the rate of volatilization to maximize signal-to-noise ratio over a range of materials without sacrificing repeatability and reproducibility.

Initial studies therefore focused on the pinhole size effects. Four materials including liquids water, squalane and toluene and solid camphor were examined with a range of pinhole sizes. The isothermal test was used to avoid complications associated with a constant heating rate during this early stage of the method development. The results are summarized in Fig. 1.

It is obvious that volatility rate increases with increasing pinhole diameter and that this rate increase is more pronounced as the normal boiling point is approached. The change in volatility rate observed for pinholes between 0.25 and 0.53 mm appears to be linear suggesting the pinhole is maintaining control of the escape of vapor molecules into the instrument purge even for the most volatile material, toluene. While a larger signal-to-noise ratio was anticipated using pinholes with a diameter of 0.53 mm, it was also recognized that the pinhole might be too large if the material was examined under conditions in which it was more volatile. Consequently, a somewhat smaller pinhole size range was examined for use in a standard test method.

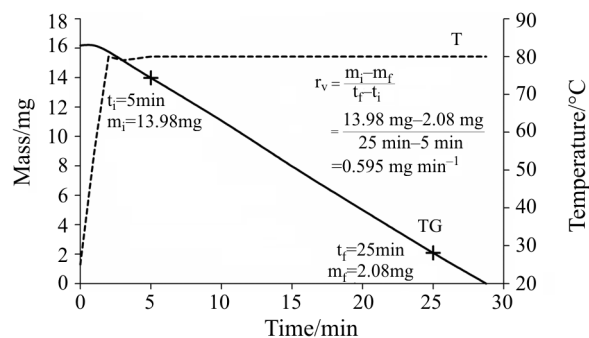Water at 50°C and camphor at 65°C were utilized for this refined pinhole size study. The results in

Table 2 reflect values for 5 measurements over a 6-week period from two different laboratories. Based on these results it was decided to limit the size of the pinhole for method E 2008 to a narrow range of 0.33 to 0.38 mm.

An attempt was made to examine the sensitivity of volatility rate results to controllable extrinsic factors in the measurement such as surface area and purge rate. Using nominally equivalent diameter crucibles it is not practical to examine surface area effects with liquid specimens. The effect of surface area was studied using samples of camphor in three different forms: coarse granule, fine powder and pressed disk. The solid camphor was provided in the form of coarse granules. The fine powders were obtained by grinding the granules. For the pressed disk, the ground powders were pressed in the crucible to form a pellet, whose effective surface area should have been significantly reduced. From the data in Table 3 it is apparent that the pinholes significantly diminish the surface area effect. Values reported were recorded at 65°C.

It is common practice to operate a TG with an inert gas purge. An order of magnitude difference in nitrogen purge gas rate was examined in a single instrument using the open crucibles (diameter=4.2 mm). The open crucible case is anticipated to represent worst case. The data of Table 4 suggests that the purge rate is a minor effect with an open crucible. It was therefore assumed that its impact would be inconsequential for pinhole crucibles provided it did not re-

Table 2 Effect of pinhole size on observed volatility rate

Material	Pinhole size/mm					
	0.33	0.34	0.38	0.40	0.46	0.51
Water at 50°C						
Mean volatility rate/μg min^{-1}	31.8	34.2	38.2	46.4	47.6	63.8
Standard deviation/μg min^{-1}	2.17	2.28	1.09	4.22	0.89	5.09
Camphor at 65°C						
Mean volatility rate/μg min^{-1}	2.48		2.92		3.68	
Standard deviation/μg min^{-1}	0.15		0.16		0.07	

Table 3 Effect of camphor surface area on observed volatility rate

Pinhole size/mm	Powder/μg min^{-1}	Granules/μg min^{-1}	Pressed disk/μg min^{-1}
0.53	5	5	5
0.99	12	11	
4.19	323	286	213

Table 4 Effect of instrument purge rate on observed volatility rate

Sample	T/°C	Volatility rate/μg min^{-1} at			
		10 mL min^{-1}	30 mL min^{-1}	50 mL min^{-1}	100 mL min^{-1}
Camphor	65	140	130	180	160
	80	350	290	380	380
	100	800	730	880	900
	120	1370	1260	1600	1670
Squalane	200	260	–	240	230
	250	1440	–	1540	1470
	300	5880	–	6260	6050
Toluene	40	3280	–	3260	3300
	50	4880	–	4890	4950
	60	6720	–	6800	6840

sult in significant temperature excursions or gradients. One can estimate the impact of temperature changes from Table 4 as well.

A final concern to be addressed before publication of the test method was that of the isothermal test compared to a constant heating rate test. Figures 2 and 3 illustrate typical test outcomes for each approach using water as a specimen.

The isothermal test determines the volatility rate as the average rate of mass loss per unit time. If the mass loss rate is relatively constant, this constitutes a simple slope determination. As shown in Fig. 2, the volatility rate (r_v) was obtained from the difference in mass at an initial time (m_i) and the mass at a final time (m_f) for the isothermal temperature divided by the elapsed time (i.e. $t_f - t_i$).

The disadvantage of the isothermal test is that it is relatively time consuming and allows for only one temperature determination per test. The advantage is that mass transfer as mass loss is at steady state for a stable temperature. If the rate is not relatively constant then a change in composition or a variation in temperature is likely occurring.

The constant heating rate test utilizes a slow linear increase in temperature and takes the instantaneous slope (first derivative) at any temperature as the volatility rate (Fig. 3). Use of a 2°C min^{-1} constant heating rate has been recommended for E 2008. This is supported by the data in Table 5.

The obvious advantage of the constant heating rate approach is the determination of many tempera-

ture values in a single test with one specimen. The disadvantage of this approach is that the temperature accuracy may be in question. Also compositional changes if occurring, may not be readily detected.

The basic understanding developed above is that a pinhole can be used to control the leakage of vapor molecules from a saturated crucible atmosphere into the instrument atmosphere of a TG. Provided the pinhole size is sufficiently small to restrict the mass transfer rate in this leakage to a level less than or equal to that of the self-diffusion rate, the observed rate of mass loss is essentially dependent upon only temperature. Under these conditions use of test method E 2008 is suitable as a generic approach for assessment of the volatility rate of a material. The values generated using E 2008 have no absolute significance but are suitable
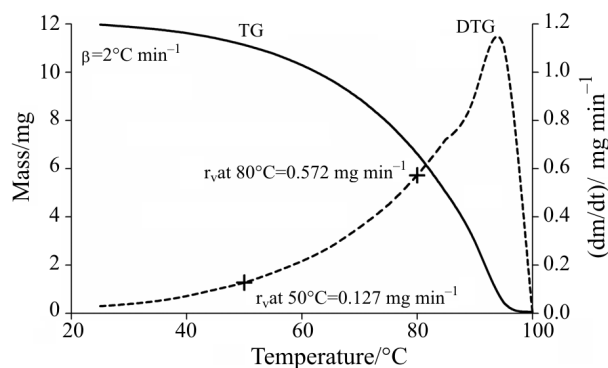
Fig. 3 TG and DTG curve for water at 2°C min^{-1} using a 0.99 mm pinhole

Table 5 Comparison of isothermal and constant heating rate results for water

Pinhole/mm	Test	Volatility rate at 50°C/μg min^{-1}	Volatility rate at 80°C/μg min^{-1}
0.99	isothermal	124	597
	2°C min^{-1}	127	572
0.53	isothermal	64	–
	2°C min^{-1}	65	–

for direct comparison of materials as a relative indication of volatility independent of any specific application.

Statistical data summary for interlaboratory study

A standard test method is only valuable if it can be utilized in any laboratory to produce credible analytical results. Hence, an ILT was conducted to produce a precision and bias statement for the ASTM Standard E 2008 Method. Eight laboratories using four models of TG instrumentation from three different vendors participated in this study. The volatility rates for camphor and squalane were determined using the isothermal test. The constant heating rate test was used to determine the volatility rates for water at two temperatures.

Results received from the participating laboratories were statistically analyzed using the ASTM E 691 Interlaboratory Data Analysis Software [6]. Repeatabil-

ity (k) and reproducibility (h) outliers were identified. Any data set obtained from k outliers, in which two or more single data points exceeded the limit of two times the standard deviation (S), was discarded. Any data set obtained from h outliers, whose results appear to deviate markedly in value from those obtained by the other participants (i.e. the h values exceeded the critical value of the h consistency statistics at the 0.5% significant level), was also discarded.

Statistical data for the isothermal test

The volatility rates for camphor at 60°C and for squalane at 300°C were determined using the ASTM Standard E 2008 Method A – isothermal test. Five replicates were obtained from each participating laboratory, and the average volatility rates for each laboratory are summarized in Table 6. To remove any evaluation bias, the participants were coded by number

Table 6 Results summary for the ILT studies

Lab	Camphor		Squalane		Water at 50°C		Water at 80°C	
	r_v/μg min^{-1}	σ/μg min^{-1}	r_v/μg min^{-1}	σ/μg min^{-1}	r_v/μg min^{-1}	σ/μg min^{-1}	r_v/μg min^{-1}	σ/μg min^{-1}
1	2.371	0.140	99.1	11.2	41.84	1.91	196.9	1.7
2	2.499	0.283	76.2	9.7	46.43	8.52	230.2	38.1
3	5.012h	0.618k	167.0	21.2	45.44	5.00	218.8	21.9
4	2.460	0.166	167.8	53.3	50.29	9.57	237.2	37.7
5	2.221	0.255	272.7	125.6k	38.72	7.36	185.1	13.7
6	3.782	3.638k	410.3	206.5k	143.96h	85.03k	272.4	99.5k
7	1.932	0.064	74.5	2.3	36.70	1.63	151.3	5.7
8	2.382	0.173	90.0	1.2	51.62	7.05	214.0	20.7
$\bar{x}$	2.311		112.9		44.44		204.8	
S	0.209		44.3		5.63		29.7	
S_r	0.194		24.2		6.54		23.9	
S_R	0.271		49.3		8.12		36.6	
r	0.543		67.8		18.3		67.0	
R	0.760		138		22.7		102	
n	6		6		7		7	

r_v = average volatility rate for each laboratory, σ = standard deviation for each laboratory, h = reproducibility outlier; results discarded, k = repeatability outlier; results discarded, $\bar{x}$ = mean of the averages excluded outliers, S = standard deviation of averages, S_r = repeatability standard deviation, S_R = reproducibility standard deviation, r = 95% repeatability limit, R = 95% reproducibility limit, n = number of laboratories included in the statistical analysis

using the sequence in the order in which the results were received (Table 6).

Camphor

The data obtained for the volatility rates for camphor at 60°C were analyzed using ASTM E 691 Interlaboratory Data Analysis Software. The results show that the k value for Lab 6 (2.77) exceeded the critical value (1.79). Upon examination of the raw data, it was observed that two data points exceeded the 2S limit. Therefore, Lab 6 was identified as a k outlier and its whole set of data for camphor was discarded.

The results from seven laboratories (Lab 1–5, 7 and 8) were re-examined with ASTM E 691. The results show that Lab 3 was a k and a h outlier, therefore its data set was discarded. The results from six laboratories (Lab 1, 2, 4, 5, 7 and 8) were re-examined with ASTM E 691. As summarized in Table 6, a mean value of 2.311 μg min^{-1} was obtained with a repeatability standard deviation of 0.194 μg min^{-1} and a reproducibility standard deviation of 0.271 μg min^{-1}.

Squalane

The data reported by eight laboratories (Labs 1–8) for the volatility rates of squalane at 300°C were analyzed. Lab 6 was found to be a k outlier, and there were two data points that exceeded the 2S limit. It was observed that Lab 6 used sample sizes of 14–18 mg, which were about 2 times larger than specified in the protocol (4–8 mg). Therefore, the whole set of data obtained from Lab 6 was discarded.

The results from seven laboratories (Lab 1–5, 7 and 8) were re-examined with ASTM E 691. The results show that Lab 5 was a k outlier. Since there were two data points that exceeded the 2S limit, the whole data set was discarded.

The results from six laboratories (Lab 1–4, 7 and 8) were re-examined with ASTM E 691. A mean value of 112.9 μg min^{-1} was obtained with a repeatability standard deviation of 24.2 μg min^{-1} and a reproducibility standard deviation of 49.3 μg min^{-1} (Table 6).

Statistical data for the constant heating rate test

The volatility rates for water were studied using Method B – constant heating rate test at a heating rate 2°C min^{-1}. The volatility rates at 50 and 80°C were determined from the first derivative of the mass loss curve at these two temperatures. The average volatility rates for each laboratory are also listed in Table 6.

The volatility rates for water were reported from eight laboratories (Labs 1–8). The data obtained were analyzed using ASTM E 691. Lab 6 was found to be a k outlier for the data at both temperatures. In both cases, there were two data points that exceeded the 2S limit. Lab 6 also used larger sample sizes (14–22 mg) than specified in the protocol (4–8 mg). The two sets of data obtained from Lab 6 were discarded.

The results from seven laboratories (Lab 1–5, 7 and 8) were re-examined with ASTM E 691. Mean values of 44.44 and 204.8 μg min^{-1} were obtained for the volatility rates of water at 50 and 80°C, respectively. The repeatability standard deviations (6.54 and 23.9 μg min^{-1}) and the reproducibility standard deviations (8.12 and 36.6 μg min^{-1}) were obtained for these temperatures, as summarized in Table 6.

Conclusions

A test method has been developed for the determination of volatility rate of materials and this method has been found to be nominally independent of extrinsic experimental parameters including surface area and purge rate. This behaviour is accomplished by use of a pinhole to control the mass transfer leakage of vapor from a saturated crucible atmosphere in a thermogravimetric analyzer. The corresponding mass loss is a direct measure of the volatility rate for a specific temperature. The volatility rate is suitable for direct comparison of materials independent of their application. The measurements can be conducted with nominal equivalence of results using either an isothermal test approach or a constant heating rate test approach. This test method has been published as ASTM E 2008, 'Standard Test Method for Volatility Rate by Thermogravimetry'.

Suitability of this test method has been addressed through an interlaboratory study involving eight laboratories. The technical results for this ILT are summarized in the following Precision and Bias statement, which was approved by Committee E 37:

Precision and bias

The precision and bias of this standard method were determined in an interlaboratory test (ILT) in 2003. Eight laboratories using thermogravimetric analyzers from three manufacturers and four instrument models participated in the ILT. The volatility rates for camphor at 60°C and squalane at 300°C were determined using the isothermal test. The constant heating rate test was used to determine the volatility rates for water at 50 and 80°C. Each laboratory reported the volatility rates in quintuplicate. The statistical analysis was conducted in accordance with ASTM E 691.

Table 7 Precision

Material	$T/°C$	Average volatility Rate/μg min^{-1}	S_r/μg min^{-1}	S_R/μg min^{-1}	r/μg min^{-1}	R/μg min^{-1}
Camphor	60	2.311	0.194	0.271	0.543	0.760
Squalane	300	112.9	24.2	49.3	67.8	138
Water	50	44.44	6.54	8.12	18.3	22.7
Water	80	204.8	23.9	36.6	67.0	102

Precision

- Within laboratory variability may be described using the repeatability value (r) obtained by multiplying the repeatability standard deviation (S_r) by 2.8. The repeatability value estimates the 95% confidence limit. That is, two within laboratory results should be considered suspect if they differ by more than the repeatability value (r).
- Between laboratory variability may be estimated using the reproducibility value (R) obtained by multiplying the reproducibility standard deviation (S_R) by 2.8. The reproducibility value estimates the 95% confidence limit. That is, two between laboratory results should be considered suspect if they differ by more than the reproducibility value (R).
- The terms repeatability limit and reproducibility limit in Table 7 are used as specified in ASTM E 177.

Bias

- Bias is the difference between a test result and an accepted reference value. There is no accepted reference value for volatility rates for camphor, squalane and water. Therefore no bias information can be provided.

Acknowledgements

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