Validation of Thermogravimetric Analysis Performance Using Mass Loss Reference Materials

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ABSTRACT

A protocol is proposed to validate the measurement of mass loss and residue content by thermogravimetry. Validation figures-of-merit of linearity, repeatability, detection limit, quantitation limit, and bias are provided. The procedure is implemented using a set of newly available Mass Loss Reference Materials.

INTRODUCTION

Validation is the process of providing documented evidence that something does what it is intended to do (1). When applied to analytical methods, it means that a specific set of analytical figures-of-merit are measured and reported. These figures-of-merit include linearity, repeatability, detection limit, quantitation limit, and bias. To provide validation of a test method, a well-documented protocol is conducted. Typically replicate determinations are performed at the high, medium and low levels of the applicable range as well as on a blank in which no analyte is present. Repeatability and linearity are derived from the replicate determinations at three levels while detection limit, quantitation limits and bias are derived from the replicates of the blank determination.

In a typical validation scheme, only a single parameter is determined. For example, enthalpy is the measured and validated parameter in differential scanning calorimetry (DSC) (2). By contrast, in thermogravimetry (TGA) two experimental parameters are simultaneously determined: mass loss and residue (3). For a binary mixture, these two parameters sum together to equal 100 %. For validation purposes the linearity, repeatability, detection limit and quantitation limit are equivalent for the two measurements. That is, a precision of 0.1 % for mass loss is equivalent to a precision of 0.1 % for residue determination. However, for bias the values are equal, but are opposite in sign. That is a 0.1% bias for mass loss is a -0.1% bias for residue.

The TGA analytical balance may be calibrated using masses of known and traceable certification (4). In contrast, validation requires a series of test specimens that have known levels of the quantity to be determined. In thermogravimetry this means a known level of mass loss or residue at high, medium and low level. This requires the use of Mass

Loss Reference Materials of known and, preferably, certified and traceable values. Until recently there have been no mass loss reference materials suitable for TGA.

In 1993, the Polish Committee for Standardization, Measures and Quality Control investigated copper sulfate pentahydrate for this purpose (5) but this material was never commercialized. In 1994 the California Environmental Protection Agency conducted a series of interlaboratory tests for mass loss using mass loss materials created by Rose (6). The results of this test method were published by Pino and co-workers (7) and resulted in the development of ASTM International E1868 (8).

Increasing demand for TGA mass loss validation is evident by the work of ASTM International Committee E37 on Thermal Measurements and its Work Item WK3391 (9). Reference materials of known, certified and traceable mass loss are needed for this procedure.

The original work by Rose in the development of mass loss reference materials focused on a low boiling liquid that is soluble in a high boiling liquid. The high boiling liquid must have a boiling temperature high enough that there is little volatility at the boiling temperature of the low boiling liquid. In addition both materials must be miscible, available in high purity, low toxicity, and stable for a long time.

REFERENCE MATERIALS

2-Ethoxyethylacetate (EEA) was selected as the low boiling liquid. It is readily available in high purity (99+ % purity, Aldrich Chemical, Milwaukee, WI), is stable, has a boiling temperature of 156 °C and minimum volatility at ambient temperature. The volatility of EEA at ambient temperature is less than that of water and will not quickly evaporate while awaiting analysis. The mass loss profile for the pure EEA in Figure 1 shows that the material cleanly evaporates with no residue.

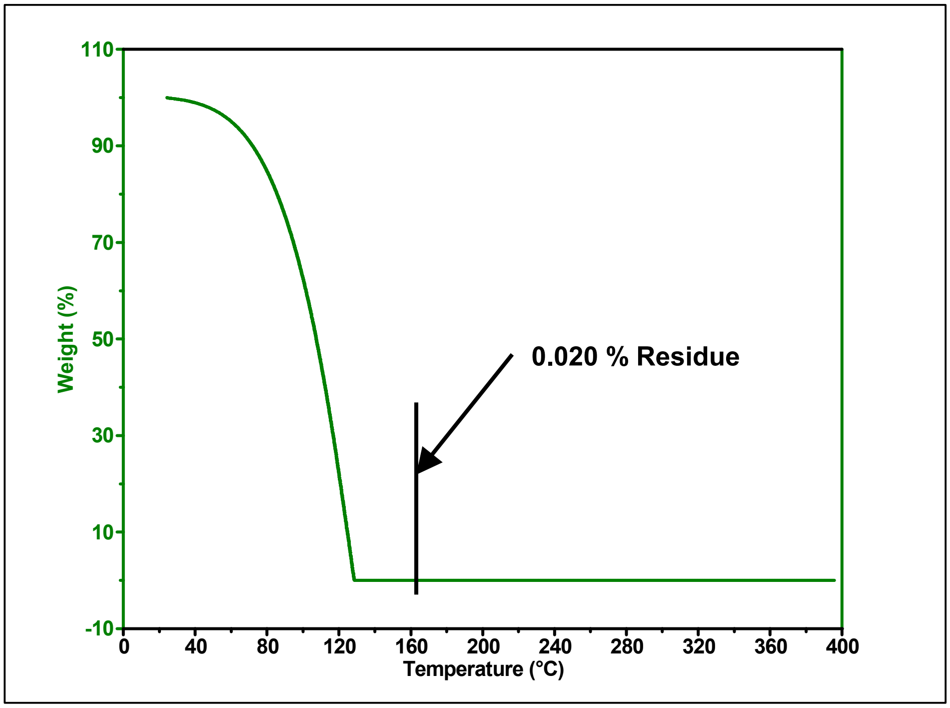

Figure 1 - Mass Loss Profile for 2-Ethoxyethylacetate

A polyol was selected as the high boiling liquid since it is available as high purity materials in liquid form for easy mixing and is non-toxic. Pluricol® TP4400 (BASF, Wyandotte, MI) was selected. As supplied, the material has a very low water content (< 0.05 %). The mass loss profile for the Pluicol polyol in Figure 2 shows that the material has low volatility at 160 °C of 0.6 %. In contrast, EEA has completely volatilized at 160 °C.

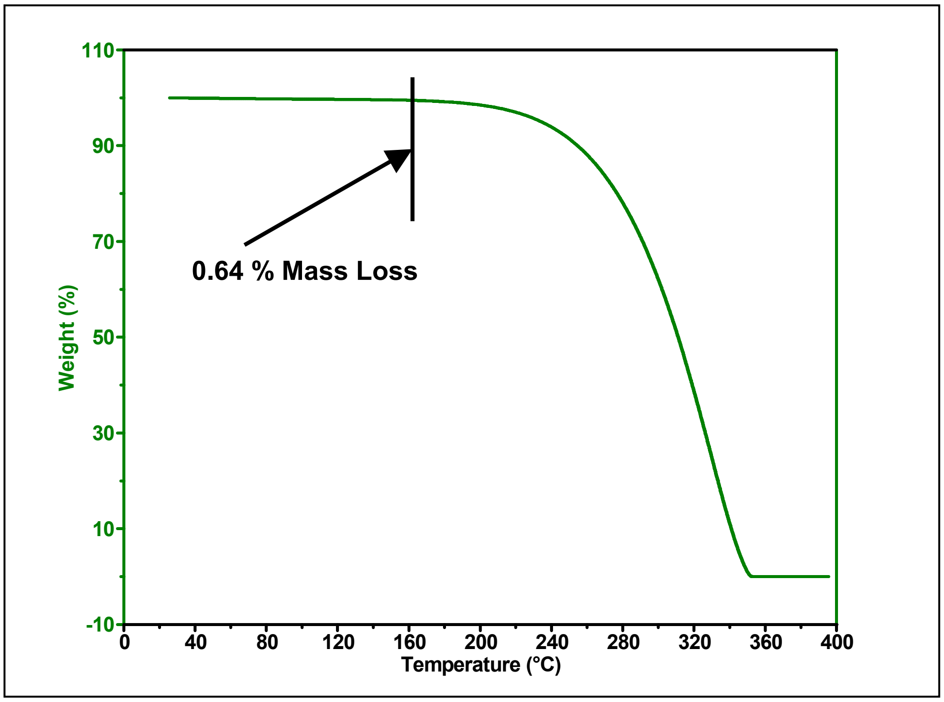

Figure 2 - Mass Loss Profile for Polyol

Mass Loss Reference Materials[1] were created by weighing with a certified and traceable balance and known amounts of EEA and polyol to achieve nominal values of 2, 50 and 98 % mass loss including the small volatility of the polyol. These blends were well mixed for several hours as the polyol is a very viscous fluid. The well-mixed master batch was then bottled and stored in 1 mL quantities in amber, sealed serum bottles. A suitable quantity of the reference material may be withdrawn from the serum bottle using a syringe for each analysis thereby minimizing the potential for changing volatility due to partial evaporation or degradation of the components due to oxidation.

The actual end-use mass loss for each lot of material was determined using 10 replicate determinations on a series of thermogravimetric analyzers as shown in Table 1.

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[1] Available from TA Instruments, 109 Lukens Drive, New Castle, DE 19720

	0 % Mass Loss	2 % Mass Loss	50 % Mass Loss	98 % Mass Loss
	(%)	(%)	(%)	(%)
TGA 1	0.013502 ± 0.003449	1.788 ± 0.0951	49.535 ± 0.0714	97.912 ±0.0432
TGA 2	-0.04263 ± 0.001982	1.780 ± 0.0996	49.524 ± 0.0597	97.880 ± 0.0141
TGA 3	0.01024 ± 0.008348	1.782 ± 0.0484	48.945 ± 0.121	97.787 ± 0.0216
Repeat Std. Dev. (r)	± 0.005339	± 0.08427	± 0.0881	± 0.0290
Repro. Std. Dev. (R)	± 0.009457	± 0.00416	± 0.338	± 0.0649
Mean	0.0064	1.7833	49.33	97.860
Gage R & r	± 0.0084	± 0.0084	± 0.34	± 0.071

Table 1[2] - Certification of Mass Loss Reference Materials

This approach verifies the mass loss content of the materials and provides information to certify the mass loss value. The within laboratory repeatability standard deviation (r) and between laboratory reproducibility standard deviation (R) are combined into the "gage R & r" value as the root of the sum of their squares providing an overall precision value for the reported mean value.

Tests conducted in our laboratory in 2003 on the sealed materials from the California EPA tests of 1994 show that these materials are stable for at least 10 years.

VALIDATION PROCEDURE

In thermogravimetry, mass is the dependent parameter measured as a function of the independent parameter temperature. In a typical TGA experiment temperature is changed at a linear rate. As a practical operational matter, obtaining the same amount of initial mass for each test specimen is difficult. For convenience, the measured mass of the test specimen is normalized to the initial mass of the test specimen throughout the analytical curve. The initial mass percent is labeled as 100 % while that of the tared empty sample container is assigned the value of 0 %. This normalization process provides for direct comparison of thermal curves even if the initial mass of the specimens is different.

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[2] In statistical treatments of this nature, all available significant figures are carried throughout the intermediate calculations. Rounding is performed at the final presentation of data consistent with the measurement precision

Likewise, the mass remaining may be compared to the initial mass and is identified as the “residue”(3). Therefore “mass loss” and “residue” for a binary system are complementary. That is, while mass loss increases, residue decreases. The sum of mass loss and residue is equal to 100 %.

In the proposed TGA validation procedure (9), replicate determinations are made at a high, medium and low mass loss region exemplified in the proposed test method. The 2, 50 and 98 % mass loss reference materials are used. A nominal 40 mg initial mass (obtained by micropipette) is used to cover the nominal range of the TGA during its application. Initially, a minimum of three replicates is performed with the largest mass loss reference material (i.e., 98 % volatile content). The end of the volatility mass loss region is identified from the first derivative of the mass loss curve shown in Figure 3. The mass loss value of 160 °C is selected as the point representing maximum resolution between the weight loss regions of the high volatility and low volatility components. (It should be noted that the point maximum resolution might vary as a function of heating rate. For this study, a heating rate of 10 °C/min was selected providing the balance between resolution and productivity.) The selected value of 160 °C is then used as the measurement point for all of the subsequent determinations.

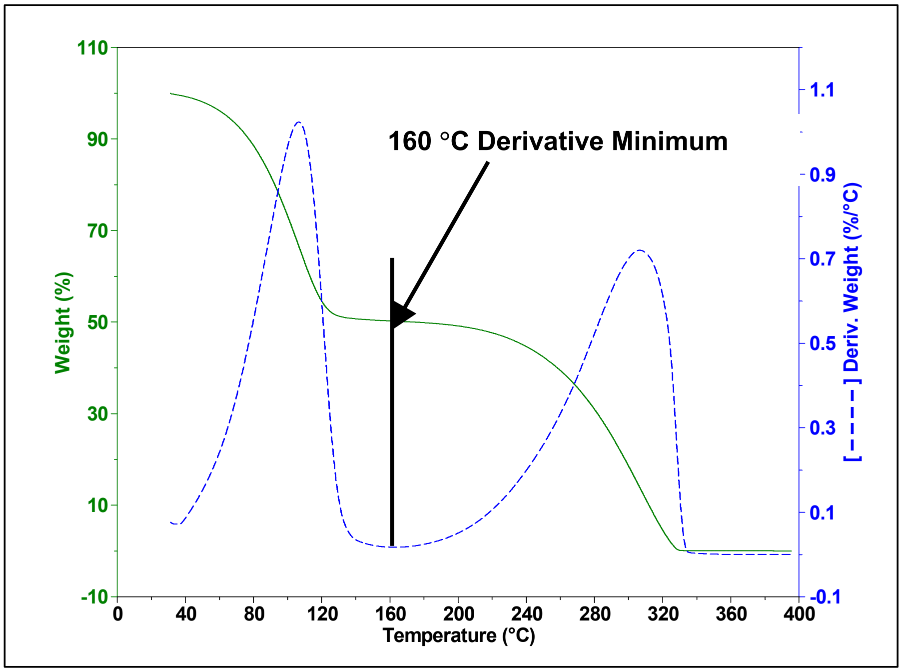
160 °C Derivative Minimum

Figure 3 - Mass Loss Profile for 50 % Mass Loss Reference Material

The term “linearity” describes the conformity of an instrument’s response to a straight line. The most common non-linearity is a “bow” or curvature in a single direction. Traditionally, linearity was measured by drawing a straight line between the maximum and the minimum point then observing the maximum deviation from this line at any intermediate position. This deviation is expressed as a percent of full scale.

In the modern world of computer data treatment, this mechanical determination of linearity is replaced by a more sophisticated approach. The mean values determined for the high, medium and low mass loss are used to create a best-fit straight line shown in Figure 4. Linearity is then determined by measuring the maximum deviation of the measured data from the best-fit line. In thermogravimetry, data points are commonly expressed as a percent of full scale so linearity is just the maximum deviation as illustrated.

For replicate determinations of the mass loss of the three reference materials, the mean value and standard deviation are determined. Using the mean values, a least squares best-fit is determined (10) using the known mass loss reference values as the independent values and the mean of the determined values as the dependent value. The slope and intercept of the best-fit straight line are obtained. For each point, the difference value is determined from the mean value obtained and the corresponding best-fit value at that same point. The point with the maximum deviation is identified and its value reported as the linearity value in mass percent.

As a second validation parameter, method repeatability is obtained from the standard deviations values for these three sets of replicate determinations. The method validation repeatability is determined by statistically "pooling" the standard deviations for the three replicate determinations (10).

In any validation procedure, a blank run with an empty sample container is performed where no analyte is present as shown in Figure 5. This represents a baseline run where there is no sample present but the temperature of the experiment is changed in the same manner as that for the test specimen. Such an instrumental baseline may vary due to buoyancy or other instrumental effects. The blank value must be determined using the mass scale, rather than the mass percent scale, since the initial mass is 0 mg. To compare the results, this mass value is assigned the nominal 40 mg specimen size.

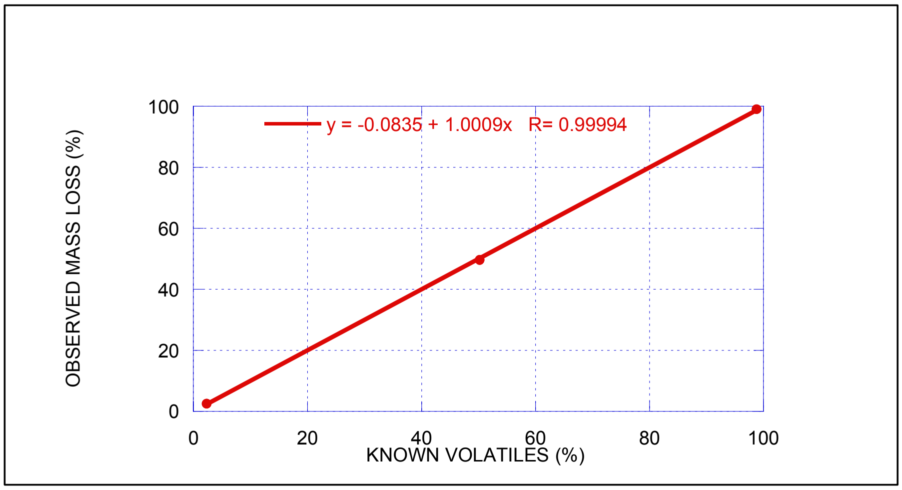

Figure 4 - Determination of Best-Fit Straight Line

It is assumed that the baseline for an empty sample container is the same as that with a test specimen. This is a reasonable approximation verified by experiment since the volume of the sample container is much larger than that of the test specimen so buoyancy effects will be minimal.

A third parameter associated with a validation procedure is method sensitivity. No standard definition currently exists in thermal analysis for this term even though it is broadly used with quite different meanings depending upon context. Sometimes a multiple of the short-term noise is used to express sensitivity. Other times the resolution of the analog to digital converter is used. These terms are useful to characterize the electronic sensitivity of the TGA apparatus but are not very useful to the user who is interested in analytical sensitivity. The Dutch Society for Thermal Analysis (TAWN) has developed a working determination of sensitivity based upon the liquid crystal material azoxyanisole (11).

The proposed ASTM International TGA validation standard avoids the use of "sensitivity" term and instead defines two sensitivity related terms - detection limit and quantitation limit. Detection limit is defined to be 3.3 times the blank standard deviation and is intended to identify the mass loss (or residue) that represents the smallest detectable amount. Quantitation limit is 10 times this blank standard deviation value and is the smallest amount that may be quantified with reasonable accuracy and precision (1).

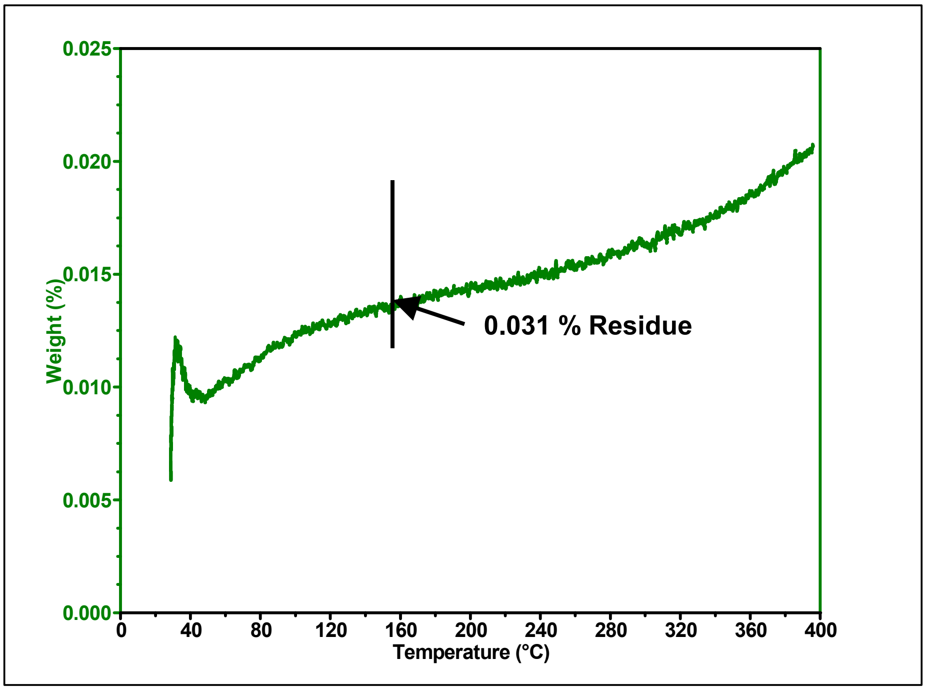

Figure 4 - Baseline/Blank Determination (nom. 40 mg sample)

The final validation parameter is bias; the difference between the known value and the value obtained. The bias is determined from the mean value of the blank compared to the known zero amount of the analyte. The bias for the mass loss determination and that for the residue determination are in opposite directions. So a positive bias from residue corresponds to a negative bias for mass loss. All other values, linearity, repeatability, detection limit and quantitation limit are equivalent for mass loss and residue measurement.

EXAMPLE VALIDATION

The determination of linearity is illustrated in Table 2 for replicate determinations performed on a mass loss reference material set. The mean value for replicates and the standard deviation are determined. The observed mean values are then compared to the known values for the reference material through a least squares best-fit such as that shown in Figure 4. For the set of data in Table 2, the best-fit line has a slope of 1.0009 and an intercept of -0.0835. The "perfect" values would be 1.0000 and 0.0000. Nonetheless, the correlation coefficient for this fit is 0.99994 indicating a good fit.

Determination	Low Loss (%)	Medium Loss (%)	High Loss (%)
1	99.08	49.73	2.384
2	99.05	49.16	2.684
3	99.08	49.84	2.658
4	99.05	49.75	2.338
5	99.05	-----	2.519
Mean	99.062	49.620	2.5167
Std. Dev.	0.0164	0.3104	0.1561
n	5	4	5
Known Loss (%)	98.76 ± 0.30	50.25 ± 0.62	2.30 ± 0.30

Table 2[2] - Replicate Determinations of Mass Loss Reference Materials

The best-fit equation is then used to determine which of the three mean values is the most distant from the best-fit straight line as shown in Table 3. The most distant mean value is then used to determine linearity, found here to be 0.59 mass %.

Expected Mass Loss (%)	Y = Observed Mass Loss (%)	Y' = Best-Fit Mass Loss (%)	$\lvert Y' - Y \rvert$ (%)
2.3	2.219	2.517	0.298
50.25	50.212	49.620	0.592
98.76	98.785	99.062	0.297

Table 3 -Determination of Linearity

Repeatability is the "pooled" standard deviation of the three replicated determinations. The pooled value is the square root of the (n - 1) weighted variance for the three replicated determinations. For the results in Table 2,

$$r = \left[\frac{(4 \times 0.1561^2) + (3 \times 0.3104^2) + (4 \times 0.0164^2)}{(4 + 3 + 4)} \right]^{1/2} = 0.19 \text{ mass \%.}$$

Turning to the blank determination, example experimental data is given in Table 4. Residue is initially determined in terms of milligrams but is then converted to mass %

using a nominal 40 mg specimen size. The normalized mean value and standard deviation are 0.0095 and 0.011 mass %, respectively.

Determination	Residue (mg)	Residue (mass %)
1	0.003457	0.008643
2	0.005871	0.01468
3	-0.000346	-0.000865
4	0.005486	0.01372
5	0.007591	0.01898
Mean	0.0038	0.0095
Std. Dev.	0.0043	0.012
n	5	5

Table 4 - Blank (Baseline) Determination

The detection limit and quantitation limit are simply multiples of the blank standard deviation:

Detection Limit = 3.3 x 0.011 mass % = 0.036 mass %
Quantitation Limit = 10 x 0.011 mass % = 0.11 mass %

The bias for both the residue and mass loss is taken as the difference between the mean blank value and 0 and is equal to 0.0095 %. As residue and mass loss are complementary, the bias value for residue is a positive value and that for mass loss a negative one. The linearity, repeatability, detection limit and quantitation limit are equal for mass loss and residue determinations.

SUMMARY

The validation process provides quantitative values for linearity, repeatability, detection limit, quantitation limit, and bias for both the mass loss and residue determinations. For one example test case, linearity was found to be 0.59 mass %, repeatability was 0.19 mass %, detection and quantitation limits were 0.036 and 0.11 mass %, respectively and bias was 0.0095%. The overall validation procedure takes less that an eight-hour shift to accomplish.

The development and commercialization of a set of mass loss reference materials permits the development of a standard for validation of mass loss and residue determinations by thermogravimetry.

REFERENCES

1. E 2161, *Terminology Relating to Performance Validation in Thermal Analysis*, ASTM International, West Conshohocken, PA.
2. E 2253, *Enthalpy Measurement Validation of Differential Scanning Calorimetry*, ASTM International, West Conshohocken, PA.
3. E 1131, *Compositional Analysis by Thermogravimetry,* ASTM International, West Conshohocken, PA.
4. E 2040, *Mass Scale Calibration of Thermogravimetric Analyzers,* ASTM International, West Conshohocken, PA.

5. W. Trabczynski, Polish Committee for Standardization, Measurers and Quality Control, *Personal Communication*, **1993.**
6. John E. Rose, *Personal Communication*, **2003.**
7. J.A. Pino, T.A. Barry, J.E. Rose, *Proceedings of the 110th Conference of American Official Analytical Chemists*, **1996**
8. E 1868, *Loss-on-Drying by Thermogravimetry*, ASTM International, West Conshohocken, PA.
9. WK3391, *Mass Loss and Residue Measurement Validation by Thermogravimetry,* ASTM International. West Conshohocken, PA.
10. E 1970, *Statistical Treatment of Thermoanalytical Data*, ASTM International, West Conshohocken, PA.
11. P.J. van Ekeren, C.M. Holl, A.J. Witteveen, *A Comparative Test for Differential Scanning Calorimeters,* Journal of Thermal Analysis, **1997**, 49, pp. 1105-1114.

KEYWORDS

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