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Articles

Observations of Anomalous Mass-Loss Behavior in SRM Coals and Cokes on Drying

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The determination of moisture content in coal and coke is required for the accurate reporting of physical and chemical constituents on a *dry mass* basis. Interlaboratory comparisons are reported on a *dry mass* basis and require reproducible assessments of moisture content to minimize differences among laboratories. Comparability between laboratories is necessary to ensure equity in trade and to avoid costly disputes between buyer and seller. Moisture loss was measured as mass (M) loss as a function of time (t) at constant temperature in a dynamic inert nitrogen atmosphere on 10 SRM coals (7 bituminous and 3 subbituminous) and 4 SRM cokes. Three different patterns of mass-loss were observed—ideal ($dM/dt = 0$), and two anomalous behaviors, negative deviation ($dM/dt < 0$) and positive deviation ($dM/dt > 0$). Bituminous coals with lower moisture (1−4%) and volatile content (33−38%) tend to display either ideal or positive behavior while subbituminous coals with higher moisture (12−17%) and volatile content (41−47%) display negative behavior. The identification of these different mass-loss patterns demonstrates the potential for method bias depending on the drying end-point definition (ASTM and LECO) used.

Moisture is an important variable in meeting SO_x and NO_x emissions standards, combustion efficiency specifications, grindability, inventory management, freight costs, and handling characteristics of coals and cokes. Coal is the single largest energy source (38%) for the production of electricity worldwide. In the United States, 92% of the fossil fuel reserves (based on heat content) come from coal, with more than 1 billion short tons mined annually.[1] In 2000, 92% of the coal mined was used to produce 52% of the U.S. electricity. Cokes, which are derived from coal (foundry and furnace), and petroleum refining byproducts ("green"—raw and calcined) are also of great commercial importance being essential to the making of iron and aluminum. Approximately 70% of the global steel production depends on coal feedstocks.

The accurate and, more importantly, reproducible determination of moisture content in coal and coke is fundamental to the characterization of these important materials for three reasons. First, any bias in the moisture determination of the analytical sample is directly transmitted to each analyte reported on a dry mass basis. Second, comparable reporting of physical and chemical constituents in coal and coke on a dry mass basis can be no better than the reproducibility of the moisture used to determine the dry mass value. Interlaboratory comparisons, which are used to evaluate laboratory performance, are reported on a dry mass basis. Coal and coke calibration and quality control samples, which are critical to production and utilization efficiency, are also characterized on a dry mass basis. Third, the moisture in the analysis sample is used as part of the measurement of total moisture. Typically, total moisture of a gross sample, which may represent a production lot or consignment, is determined in steps with the last component of the total moisture being determined in the analysis sample. Any errors in moisture of the analysis sample will directly affect the total moisture value.

Measurement traceability to the SI (Le Système International d'Unites) in the United States is provided by the National Institute of Standards and Technology (NIST) with Standard Reference

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(1) *BP Amoco Statistical Review of World Energy*; Pillans & Wilson Greenaway: London, 1999 (http://www.bpamoco.com/worldenergy).

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Materials (SRMs) being the primary link for coal and coke.[2] Consequently, the determination of certified mass fractions reported on a dry mass basis at NIST, for example, sulfur, requires the water content in the sample to be determined as accurately as possible to minimize the bias and uncertainty in the dry mass correction of the measured value. The gravimetric determination of moisture in the analysis sample by ASTM D5142 refers to the residual moisture as defined by ASTM D121.[3,4] While this is a good approximation of the water content of the analysis sample, it includes any material lost or gained under the prescribed conditions of ASTM D5341.[5] These may include among other things, volatile matter, oxygen, and carbon dioxide. At this time, the measurement of moisture used for correction to a dry basis is not traceable to the SI; however, the measurement of sulfur is. Ultimately, the estimated uncertainty of the moisture correction is included in the expanded uncertainty of the certified dry sulfur value.

EXPERIMENTAL SECTION

Background. The certified values for all NIST coal and coke SRMs are reported on a dry mass basis based on moisture values gravimetrically determined by drying in a nitrogen atmosphere to a constant mass. The gravimetric technique has been used at NIST in part because these techniques are the most widely used in the coal and coke industries. During the certification of sulfur mass fractions in coal Standard Reference Materials (2682b, 2684b, 2685b), Winchester et al.[6] reported that although the coal SRMs had reached a constant mass as defined by ASTM D5142-90, one of the coal SRMs continued to lose mass over the 2-h study period. ASTM D5142-90 (reapproved 1998) Standard Test Method for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures defines the moisture analysis to be complete when two successive weighings agree within the plateau deviation specified by the automated internal balance (commonly ±0.05%). It is possible that this criterion may never be met if a sample continues to lose moisture. This observation prompted us to study systematically the mass-loss behaviors of SRM coals and cokes.

In this paper, we describe the mass-loss behaviors exhibited by 10 SRM coals and 4 SRM cokes using a thermogravimetric analyzer that meets the criteria for ASTM D5142. This paper will show the assumption that a true constant mass (ideal behavior) can be obtained by drying is often false. In addition, the relative relationships of constant mass (end points) based on the definitions of ASTM D5142, LECO guidelines, and NIST coal certificates will be shown using the exact same data for various coals and cokes. These relative relationships of the end points are shown without uncertainties, because within the context of the data presented the relationships are fixed. Furthermore, we assess the implications of these behaviors upon mass-loss determination, the calculation of the final mass fraction determinations, and the effect on coal and coke quality assessments. While the specific causes of the different behaviors are not known, oxidation is considered a possible cause for both the positive and negative cases. Finally, the techniques NIST has been using for the determination of moisture and the mass-loss behaviors observed are discussed in detail.

Sampling Identification and Details. The SRMs studied include all the coal and coke SRMs that are currently available and some earlier coal SRMs: coals—subbituminous SRMs 1635, 2682a and b; bituminous 1632b, 2683a, 1632c, 2684a, 2685a and b, and 2692b; cokes—SRMs 2718 (green petroleum coke), 2719 (calcined petroleum coke), 2775 (foundry coke), and 2776 (furnace coke). Bituminous and subbituminous coals were the focus of this investigation as they are the most (91%) widely used by U.S. industry. Each SRM has been ground to pass through a 250-μm (No. 60) sieve and homogenized.

Analytical Method. Each SRM analyzed was dried in a LECO TGA 501 thermogravimetric analyzer[7] with dry nitrogen flow at 7 L/min and a temperature of ~107 °C (range 104−107 °C) for 5 h. The ASTM D5142-90 (reapproved 1998) allows for drying in a nitrogen atmosphere to a constant mass or for 1 h (section 9.3.2) at a temperature within the range of 104−110 °C. Dry nitrogen is brought into the 7.7-L analyzer chamber through inlets in the front and rear of the instrument via two small ceramic tubes ~20 cm long attached to a "T" fitting. The analyzer consists of an electronics unit for furnace control and data management and a multiple sample furnace that allows up to 19 samples to be analyzed sequentially. After an analysis profile has been created and selected, empty crucibles are loaded into the furnace carousel and tare weights are obtained. Then ~1-g test samples are manually loaded into the crucibles using a glass scoop, and the initial (wet) mass is recorded. The mass loss of each sample is monitored and recorded every 3 min, and the furnace temperature is controlled according to the selected profile. The nitrogen gas used to purge the sample chamber has the following manufacturer's specifications: N_2 >99.998%, O_2 <5 mg/L (ppm), CO <2 mg/L (ppm), CO_2 <2 mg/L (ppm), and a dew point of −84 °C (−119 °F). All of these metrics surpass the ASTM D5142-96 specifications. The oxygen concentration of the nitrogen is monitored continuously and is typically 0.7−0.9 μmol/mol of gas (0.7−0.9 ppm). The determinations of moisture content are calculated as relative mass loss, where the fractional loss is the difference between the wet mass and the mass loss upon heating divided by the wet mass. The output from the balance is a sequence of voltages over time corresponding to the mass of each sample. The data are downloaded from the instrument and analyzed off-line.

The accuracy and precision of the LECO TGA501 instrument was monitored in real time for each experiment using surrogate samples of high-purity gold wire. For each set of SRM moisture determinations, at least three sets of gold wires (set being one large and one small gold piece) weighing ~1 g were added to

(2) NIST Policy on Traceability. National Institute of Standards and Technology, 2001 (http://www.nist.gov/traceability).

(3) American Society for Testing and Materials (D5142-90). *Annu. Book ASTM Stand.* **2000**, 05.05, 459−463.

(4) American Society for Testing and Materials (D121-99). *Annu. Book ASTM Stand.* **2000**, 05.06, 1−12.

(5) American Society for Testing and Materials (D5341-99). *Annu. Book ASTM Stand.* **2000**, 05.06, 449−452.

(6) Winchester, M. R.; Kelly, W. R.; Mann, J. L.; Guthrie, W. F.; MacDonald, B. S.; Turk, G. C. *Fresenius' J. Anal. Chem.* **2001**, *370*, 234−240.

(7) Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

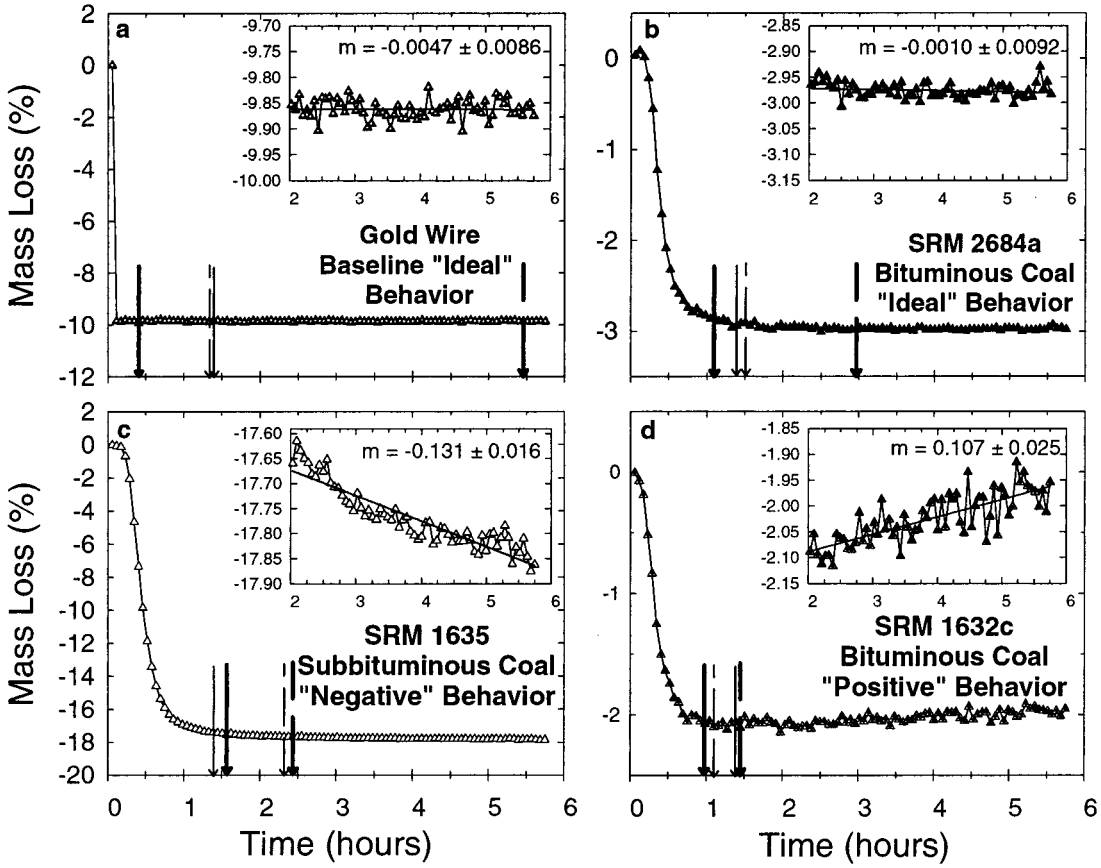

Figure 1. 1. The three behaviors observed for the 6-h study period: ideal (a, b), negative (c), and positive (d). For each behavior, the corresponding SRM and type is given. The inset graphs show the slope of the curve from the point where it begins to plateau to the end of the experiment and the associated 95% confidence interval. All the inset graphs are on the same scale. The solid arrow (ASTM D5142-90 1 h), the bold solid arrow (ASTM D5142-90 to constant mass), the long dashed arrow (Manufacturer's (LECO) definition), and the thick dashed arrow (NIST definition) marked on the curves represent the four definitions used to assess when the moisture determination is complete.

three different sample crucibles. After the initial mass of the set was recorded, the small piece of wire was removed, creating a known mass loss for that sample, which could be compared to that determined by the instrument. The known mass loss for the gold wires ranged from 1.8 to 9.8%, relative. Recognizing that any gains and losses in mass of the gold wires beyond measurement noise are negligible under these test conditions, the pooled standard deviation of the weighings of the wires serves as a measure of the accuracy and stability of the instrument. In addition, the gold wire "drying" data provide a baseline "ideal" behavior.

RESULTS AND DISCUSSION

The coal SRMs chosen for analysis exhibited three different types of mass-loss behaviors: (1) ideal, defined as reaching a constant mass ($dM/dt = 0$); (2) negative deviation, defined as continuing to lose mass ($dM/dt < 0$); and (3) positive deviation, defined as gaining mass after an initially losing mass ($dM/dt > 0$). Panels b−d of Figure 1 illustrate these behaviors as plots of relative mass loss as a function of time. Each symbol represents a single reading of the balance, and the time interval between symbols is ~3 min. Approximately 20 min is required for the oven to reach the temperature range defined by ASTM (104−110 °C). Figure 1a shows the ideal behavior of a gold wire sample, which reaches constant mass after the initial reading and demonstrates the ability of the instrument to make accurate mass measurements with changing temperature. Panels b−d of Figure 1 show examples of the three different mass-loss behaviors for three different coal SRMs. The insets in each graph show the expanded views of the behavior between 2 and 5 h, using identical scales for the abscissa and ordinate and the slope and associated 95% confidence derived from a least-squares regression of the data. The four vertical arrows on each graph denote the time where the moisture analysis is complete according to the two definitions given in ASTM D5142-90 (reapproved 1998) sections 9.3.2 and 9.3.3, the manufacturer's (LECO) definition, and the definition used at NIST.

Ideal Behavior. The gold wire in Figure 1a exhibits what we define as "ideal" behavior. Because gains and losses in mass are negligible for the gold wires, their mass should remain constant (excluding the first measurement that includes both gold wire pieces) through the entire experiment, and a regression of the data should yield a slope that is statistically identical to zero. The mass losses for the gold wire using the ASTM and LECO definitions were, 9.85 (1 h), 9.84 (constant mass), and 9.87% (LECO). All mass losses were within one standard deviation of the gold wire measurements ($1\sigma = 0.035\%$). The mass readings exhibited random behavior and approximately normal distribution. The readings plotted in Figure 1a, excluding the first measure-

ment, pass the Box−Jenkins autocorrelation test and the "mean square successive difference" test at >99.9% level of confidence for randomness and have a slope (2 h ≤ t ≤ 5 h) that is statistically indistinguishable from zero ($m = +0.0047 \pm 0.0086$) at a 95% level of confidence.[8−10] In addition, a normal probability plot (not shown) of the data defines a linear array.

Implicit in both ASTM and LECO drying procedures is that the procedure achieves constant mass at the drying temperature and in the time specified and that the mass loss results essentially from water only. The two procedures in ASTM D5142-90 are believed to produce reproducible mass losses for all coals and cokes. As a consequence, they were expected to behave ideally reaching a constant mass and a slope of zero. The mass loss of a bituminous coal, SRM 2684a, shown in Figure 1b appears to reach constant mass at ∼75 min, defined as the time where the curve begins to plateau, and continues to maintain this mass to the end of the experiment. The behavior of this coal between 2 and 5.75 h is statistically indistinguishable from that of the gold wires (see insets in Figure 1a and b), and the data pass the three tests for randomness mentioned above and, therefore, exhibit ideal behavior. But each ASTM D5142-90 criterion for when the analysis is complete results in different moisture values because the sample is still losing mass at these times, as shown by the two solid arrows. According to the two ASTM D5142-90 definitions the analysis is complete either after 1 h or when two successive weighings agree within the plateau deviation specified by the instrument (constant mass), which is 0.05%. For SRM 2684a the mass loss after 1 h was ∼2.90%, and the mass loss after two consecutive weighings within 0.05% was 2.87%. The LECO instrument company suggests that mass loss is complete when three successive mass changes differ by less than 0.05%, which yields a value of 2.91%. All three criteria result in mass losses that are less than the plateau value of 2.976 ± 0.015 (95% CI, $n = 59$) obtained from the regression intercept and are therefore biased relative to each other and to the plateau value. These different results are based on the exact same raw data. Therefore, their relative differences actually reflect the effect of their respective end points or constant mass. The assumption that a given drying procedure will achieve a constant mass at the temperature specified and within the time specified was clearly not universally observed, making comparable moisture values within and between methods for different coals and cokes difficult. For this coal, the LECO criterion appears to be closer to the point on the curve where the slope approaches zero—the point where constant mass is reached.

Negative Behavior. SRM 1635 (Figure 1c), a high-moisture subbituminous coal, demonstrates what we define as negative, anomalous deviation from the "ideal" behavior, as shown by the negative slope between 2 and 5 h. Nevertheless, by the criteria of ASTM D5142-90 and LECO, it reaches constant mass as indicated in the figure; however, there is a continued mass loss with time as shown by the statistically significant negative slope (−0.131 ± 0.016; 95% CI). In this case, if the analysis were taken to be complete as defined by ASTM D5142, the mass loss would be 17.38% after 1 h and 17.44% at constant mass. Using the LECO definition, the value would be 17.47%. There is a significant difference between the 1 h mass loss and the two other determinations (ASTM (constant mass) and LECO) (standard deviation, 0.035%). If the behavior is ideal, then one would expect these differences to be minimal. SRMs 1635 and 1632c (see Figure 1c and d) appear to have a noiser mass-loss behavior compared to the two ideal samples (the gold wire and SRM 2684a). Taking into consideration the increased noise, doubling the standard deviation (0.071%) for the window of acceptability could be used to determine the end point. In this case, the mass loss at 1 h is no longer significantly different from the second ASTM definition; however, it does remain significantly different from that determined by the LECO definition. If we were to define the variability due to noise as three times the standard deviation for the population of the gold wires, there would be no statistical difference between the three mass losses.

The three different moistures observed for SRM 1635 raise questions as to what is the best criterion for "dry" or at what point has this material reached a slope of zero or constant mass. At the end of 5 h, the mass loss reaches 17.86%, which is significantly greater than the earlier values (17.38, 17.44, and 17.47%). With this type of behavior, there is the potential to underestimate the moisture content by assuming the continued loss in mass is moisture. If the continued loss of mass results from volatile matter or moisture that is actually chemically part of the coal, or products of oxidation, for example, CO_2, then there is the potential to overestimate the moisture content.

Positive Behavior. Positive behavior (anomalous as it deviates from the "ideal" behavior) was observed in bituminous coal SRM 1632c (Figure 1d). The initial behavior is identical to other coals. At first there is a sharp decline in mass followed by an inflection point at ∼1 h and then a small mass gain thereafter with a constant slope (slope, +0.107 ± 0.025). The drying procedures yielded the following mass losses: ASTM D5142-90 (1 h) 2.07%, ASTM D5142-90 (to constant mass) 2.06%, and LECO 2.08%. The standard deviation of the gold wire population for this study was ±0.056%; hence, there is no statistically significant difference among the mass losses determined. Nevertheless, this behavior suggests the minima of the curve could be found and thus serve as a method to ensure comparability.

Summary. The behaviors observed in the graphs were not unique but are representative of behaviors observed for other SRMs. Table 1 lists all the coal SRMs studied (column 1), the type of coal (column 2), the average slope and 95% confidence interval (column 3) between 2 and 5 h, the behavior displayed by each (column 4), and the nominal moisture (column 5) and volatile content (column 6). The data suggest there is a qualitative relationship between moisture loss behaviors, the type of coal, and their associated moisture and volatile contents.

The bituminous coals (SRMs 1632b, 1632c, 2684a, 2685a, 2685b, 2692b) with lower moisture (1−4%) and volatile (33−38%) content tend to display either ideal or positive behavior while the subbituminous coals (SRMs 1635, 2682a, 2682b) with higher moisture (12−17%) and volatile (42−47%) content display negative behavior as demonstrated by the slopes of the curves. This suggests that the various behaviors observed may be a consequence of moisture effects, volatilization, and oxidation either by the addition of O_2 or removal of CO_2. It is noteworthy that the

(8) von Neumann, J.; Kent, R. H.; Bellinson, H. R.; Hart, B. I. *Ann. Math. Stat.* **1941**, *12*, 153−162.
(9) Bennett, Carl A. *Ind. Eng. Chem.* **1951**, *43*, 2063−2067.
(10) Hart, B. I. *Ann. Math. Stat.* **1942**, *13*, 445−447.

Table 1. Mass-Loss Behaviors of Coals

SRM	type	slope and CI[a] (%)	behavior	nominal moisture content (%)	total volatile content (%)
1632b	bituminous	0.017 ± 0.022	ideal	1.6	35
2683a	bituminous	0.018 ± 0.035	ideal	1.6	35
1632c	bituminous	0.070 ± 0.026	positive	2.0	36
1635	subbituminous	−0.11 ± 0.024	negative	17	41.84
2682a	subbituminous	−0.082 ± 0.020	negative	16.7	46.54[b]
2682b	subbituminous	−0.12 ± 0.034	negative	12.8	46.54[b]
2684a	bituminous	−0.0029 ± 0.010	ideal	3.8	36.43[b]
2685a	bituminous	−0.016 ± 0.023	ideal	2.0	37.61[b]
2685b	bituminous	−0.015 ± 0.020	ideal	2.3	37.61[b]
2692b	bituminous	0.056 ± 0.021	positive	1.2	33.06[b]

[a] The 95% confidence interval. [b] Volatile content is from round robin data reported by CANSPECs.

two bituminous coals that exhibited positive behavior (1632c, 2692b) are the coals that were the most recently prepared to 250-μm (No. 60) particle size, suggesting that their particle surfaces may be more available for further oxidation and subsequent mass gain**.** *All behaviors observed were repeatable on different days and occurred simultaneously in the same experiment. Therefore, the observed behaviors are NOT spurious artifacts of the experimental system but are intrinsic to the coals and cokes under the stated test conditions.*

Effect of the Uncertainty on a Measurand. A bias in the determination of the dry mass of the sample will bias the final calculated value of a measurand reported on a per mass basis and is the most important reason for having accurate, precise, and reproducible assessments of moisture content. The dry mass correction and its uncertainty can be significant contributors to the uncertainty budget of a particular measurand such as sulfur concentration and caloric value. The concentration of an element or the physical property on a dry mass basis is equal to the mass of the element determined on a dry sample or the quantity determined divided by the wet mass of sample times the fractional mass loss:

$$[\mathrm{X}] = \frac{X_\mathrm{w}}{M_\mathrm{w}(1 - L/100)} \tag{1}$$

where X_w is the mass of the analyte or the physical measurand, M_w is the mass of undried sample, and L is the absolute value of the mass loss in relative percent on drying by a prescribed technique.

The uncertainty expressed as a variance is equal to the following expression:

$$\mathrm{Var}\ (\mathrm{X}) = s_x^2 + \frac{s_{\mathrm{M_w}}^2}{M_\mathrm{w}^2} + \frac{s_\mathrm{L}^2}{(100 + L)^2} \tag{2}$$

where the right-hand side are the variances for the n independent measurements, the determination of the sample mass, and determination of the mass loss. The final term in the above equation gives the contribution of moisture determinations to the uncertainty in the final result. If we accept that the measurements of the gold wires represent the best capability of the instrument, then the standard deviation of their population represents the *smallest* possible uncertainty to be expected in the mass-loss measurements. The relative standard deviation was typically below 0.04% but occasionally reached 0.05%. For those SRMs with lower moisture content (1−4%), an uncertainty of 0.04% in moisture content contributes 0.039−0.040% relative, to the final sulfur calculation. For those with higher moisture content (12−17%), uncertainty in the moisture determination contributes 0.034−0.036% relative, to the final sulfur calculation.

Bias between moisture determination methods is the most important issue, and the likelihood of such an occurrence is high given the different end points that are used for moisture coupled with the different drying behaviors that have been documented in this study. The difference between two methods, method i relative to j, is given by the following:

$$\Delta[\mathbf{X}]\% = \frac{\Delta L_\mathrm{ij}}{(100 + L_\mathrm{ij})} \times 100 \tag{3}$$

where $\Delta L_\mathrm{ij} = M_\mathrm{i} - M_\mathrm{j}$ and M_i and M_j are in units of relative percent mass loss for this formulation. The moisture difference for a given sample between methods translates to approximately the same difference in the measurand. It has been demonstrated that this observed difference between LECO and the two ASTM end-point definitions is negligible for the gold wires, 0.02 and 0.03%, the ideal behavior (SRM 2684a) 0.01 and 0.04%, and for SRM 1632c exhibiting positive behavior (0.01−0.02%). However, SRM 1635, exhibiting negative behavior, showed a 0.08% difference between LECO and ASTM (1 h) and only a 0.03% difference between LECO and ASTM (constant mass), suggesting that the mass loss by ASTM (constant mass) may be the best approximation of the true mass loss of the two ASTM definitions.

Other Considerations. Several other studies were performed to address whether other factors such as physical loss, sample size, and surface-to-volume ratio may be cause for the patterns observed. Physical loss of sample was one of the major concerns with the higher moisture (subbituminous) coal samples that displayed "negative" behavior. To check this, a study was performed with samples covered and uncovered. The negative behavior typical of this SRM was shown to occur in both the uncovered and covered sample sets. This observation supports the belief that the continued loss of mass with time may result from moisture loss and perhaps volatilization of the sample.

Table 2. Mass-Loss Behaviors for Varying Sample Masses

SRM	sample mass (g)	slope and CI[a] (%)	behavior
2684a	0.5	0.012 ± 0.024	ideal
	1.0	0.021 ± 0.022	
	3.0	0.015 ± 0.023	
1635	0.5	−0.078 ± 0.020	negative
	1.0	−0.13 ± 0.022	
	3.0	−0.66 ± 0.054	
1632c	0.5	0.042 ± 0.019	positive
	1.0	0.086 ± 0.019	
	3.0	0.21 ± 0.019	

[a] The confidence interval is expressed as a 95% confidence.

Sample size and the related surface-to-volume ratio was checked. To address these issues, an experiment was performed where sets of three samples of varying mass (0.5, 1.0, and 3.0 g) were taken from SRMs representative of the three behaviors (2684a, ideal; 1635, negative; 1632c, positive). In addition, these samples were placed into aluminum cups placed upon fabricated glass pedestals of varying sizes within the crucibles to keep the exposure of each coal's surface to nitrogen flow constant. Table 2 shows the SRMs used in this experiment (column 1), the sample mass (column 2), the slope and 95% confidence interval (column 3), and the mass-loss behavior pattern (column 4), respectively. The slopes determined for the various sample masses suggest that the variations in sample mass (surface/volume ratio) have no effect on previously observed mass-loss patterns. Although the degree of continued mass loss varied with the different sample sizes (increasing with sample mass), the mass-loss behaviors previously identified by standard drying procedures were observed.

The behaviors exhibited by the cokes were also investigated. As a result of the coking process cokes have lower volatile content; hence, one may expect the cokes to reach a constant mass sooner and demonstrate either the ideal or positive behavior *if* coke behaviors are similar to low volatile content coals. Table 3 shows the four coke SRMs tested (column 1), the type of coke (column 2), the slope and 95% confidence interval (column 3), the behavior displayed by each (column 4), and the nominal moisture (column 5) content. It was observed that the cokes showed either the ideal or negative behavior with no particular correlation to the moisture content although the moisture contents are all similar. SRM 2718 showed ideal behavior while SRMs 2719, 2775, and 2776 showed negative behavior. The negative behavior is not exclusive to the cokes with higher moisture content but span the range. These observations suggest that there may be other explanations for the trend observed in the cokes and requires further investigation.

Coal and cokes readily react with O_2. It is possible that, in addition to the mass loss associated with the loss of moisture, coals and cokes could lose or gain mass during drying by reacting with O_2. The O_2 content of the N_2 gas used at NIST is ~800 nmol/mol. If the O_2 present in the nitrogen were to react with these materials to form CO_2, the maximum relative mass *loss* would be 0.082%. If the reaction were an addition reaction, then the maximum relative mass *gain* would be 0.22%. This assumes a reaction probability of unity.

The final mass determinations used are based on only one mass reading. This does not account for the possible noise in the data and may not be representative of the mass loss in cases where there exists a spike in the data at that point in time. In cases where ideal or positive behavior is exhibited, obtaining the mass loss from the regression or a derivative of a polynomial of the raw data would have the advantage of higher accuracy and an uncertainty that is more statistically valid being based on more degrees of freedom.

NIST Protocol for Moisture Determination. NIST presently uses two different methods for an end-point moisture determination to address the two nonideal behaviors observed in coals. These are summarized in the NIST operational definition of constant mass: "the average mass of the first occurrence of five consecutive masses (or at least a minimum of three), for which the absolute change in mass from one weighing to the next is less than the observed pooled standard deviation of the weighing of at least three gold wires or when the sample mass-loss reaches a slope of zero." The thick dashed arrows in Figure 1a−c mark the mass loss associated with the NIST definition. The mass losses identified were 9.86 (gold wire), 2.99 (SRM 2684a (ideal)), and 17.66% (SRM 1635 (negative)). The mass loss identified for the gold wire (9.86%) is indistinguishable from those (9.85, 9.84, and 9.87%) determined by the other definitions (standard deviation, 0.035%). The mass loss determined for SRM 2684a, 2.99%, falls within the plateau value uncertainty (2.976 ± 0.015%), suggesting that the NIST operational definition better approximates the true mass loss. The mass loss for SRM 1635, 17.66%, is significantly different then all three mass losses (17.38, 17.44, and 17.47%), determined by the other definitions. We have found that using this criterion for the determination of constant mass for the negative mass-loss pattern decreases the time (3 h versus 5) required for analysis while it simultaneously appears to minimize the uncertainty in the final dry sulfur values.

Positive behavior, unlike the negative behavior, permits a unique end point to be defined as the minimum of the curve. One can model the line using a polynomial and then determine the minimum as the point where the first derivative vanishes. Although the minimum does not correspond to the true water content and is likely an overlap of several processes (moisture

Table 3. Mass-Loss Behaviors of Cokes

SRM	type	slope and CI[a] (%)	behavior	nominal moisture content (%)
2718	green (raw) petroleum	0.016 ± 0.020	ideal	~0.4
2719	calcined petroleum	−0.033 ± 0.022	negative	~0.07
2775	foundry (metallurgical)	−0.11 ± 0.021	negative	~0.66
2776	furnace (metallurgical)	−0.059 ± 0.022	negative	~0.33

[a] The confidence interval is expressed as a 95% confidence.

Table 4. Summary of Mass-Loss Determinations for End-Point Definitions

material	type	behavior	A1[a] (%)	A2[a] (%)	L[a] (%)	N[a] (%)
wire	gold	ideal	9.85	9.84	9.87	9.86[b]
SRM 2684a	bituminous	ideal	2.90	2.87	2.91	2.99[b]
SRM 1635	subbituminous	negative	17.38	17.44	17.47	17.66[b]
SRM 1632c	bituminous	positive	2.07	2.06	2.08	2.10[c]

[a] A1, ASTM (1 h); A2, ASTM (constant mass); L, LECO; N, NIST [b] These values were determined using the average mass of the first occurrence of three to five consecutive masses (five being preferred), for which the absolute change in mass from one weighing to the next is less than the observed pooled standard deviation of the weighing of at least three gold wires or when the sample mass loss reaches a slope of zero. [c] This value was determined by modeling the line using a polynomial and then determining the minimum as the point where the first derivative vanishes.

loss, volatilization, oxidation), the minimum may be the closest/best estimate of the true moisture value that can be determined using the thermogravimetric technique. In the case of SRM 1632c, a third-order polynomial was used to model the data in Figure 1d and gave a minimum of 2.10%. Table 4 summarizes the mass-loss determinations for the various operating end-point definitions. The mass loss observed for the ASTM (1 h) (column 4), ASTM (constant mass) (column 5), LECO (column 6), and NIST (column 7) definitions are shown, respectively. The observed differences for the gold wire range from 0.01 to 0.03%, for the ideal behavior (SRM 2684a) from 0.01 to 0.12%, for the negative behavior (SRM 1635) 0.03 to 0.28%, and for the positive behavior (SRM 1632c) 0.01 to 0.04%.

CONCLUSIONS

The coal and coke industries require reproducible measurements of moisture content both for the purposes of equity in trade and for accurate and precise determination of characteristics, such as sulfur content and caloric content, to meet current and future emission standards and improve efficiencies. The identification of the various mass-loss behaviors exhibited by coals and cokes requires careful evaluation of moisture content as any bias has direct impact upon the dry mass values and total moisture content. There are three repeatable patterns of mass loss observed—ideal behavior, negative deviation from ideality, and positive deviation from ideality. These are identified and characterized by their distinctive slopes of the lines defined by mass loss versus time. The ideal behavior seen in the lower moisture and volatile content coals and green (raw) petroleum coke appears to permit moisture content to be determined easily and with limited uncertainty for any end-point definition that has been discussed. As a consequence, potential variation in dry mass correction is small, yielding greater uniformity in dry mass values, for example, sulfur and caloric content, allowing the coal industry to better meet emissions standards. Similarly, for those coals that exhibit positive behavior, constant mass can be determined with relative ease using conventional end-point definitions and the NIST definition.

For cokes and the higher moisture and volatile content coals exhibiting negative behavior, however, it is much more difficult to assess moisture content. These coal and coke samples, by technical definition, reach a constant mass using the ASTM D5142-90 or LECO operating definitions; however, there is a potential for under- or overestimation of the water content as a result of the continued mass loss. The ASTM D5142-90 (1 h) definition results in a lower moisture content than the second ASTM D5142-90 (constant mass) definition and the LECO definition. Using the NIST criteria for constant mass appears to narrow the final uncertainty on a dry mass basis for sulfur content at NIST. It is clear that further testing is required to determine specifically what species and effects are responsible for the mass-loss patterns observed in order to improve upon the present definitions used for moisture content determination.

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