

Organic Matter by Loss on Ignition

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Soil organic matter analysis is run by a variety of standardized procedures in routine soil analysis. Most procedures actually measure some fraction of total organic matter, which is then multiplied by one or more conversion factors to estimate total organic matter content (ex. Walkley-Black, humic matter, or combustion). All fraction measurement procedures suffer from the empirical nature of the conversion factors, which do not provide consistent organic matter estimates for all soils. Because these biases are well known, it is often recommended that only the measured fraction (oxidizable C, humic C, or total C) be reported and that conversion factors specific to soil mineralogy and horizon be employed by the end user to estimate organic matter content (Nelson & Sommers, 1982). Ultimately, since organic matter is measured indirectly, organic matter content of soil can only be defined in terms of a given analytical method (Nelson & Sommers, 1982).

Loss on Ignition (LOI) procedure also has many known biases. Ignition potentially volatilizes soil components other than organic matter, such as water in crystalline clay lattices and allophanes, hydroxyl groups in sesquioxides, and (depending on ignition temperature) thermal breakdown of carbonates (Goldin, 1987). LOI also suffers from a high degree of variability, both with respect to method precision and especially in its correlation with other procedures (Schulte, Kaufmann, & Peters, 1991). Because of the biases and variability of LOI, it is often dismissed as too crude for routine soil analysis (Goldin, 1987) (Jackson, 1958). However, because of equipment expense (combustion), toxicity concerns and hazardous waste expense (Walkley-Black), and sample throughput concerns LOI is still widely used in routine soil analysis as a cost-effective and safe procedure for organic matter analysis. A study of known sources of bias and random error is useful in determining the relative contribution of each to LOI variability and the possibility of minimizing or eliminating each of them.

Since weight loss from a soil sample is the actual measured value, the method is prone to at least two sources of simple error. One of the simplest errors is sample spillage. In 2mm-minus soil, some of the larger aggregates and coarse sand grains can approach 10 mg in mass. For a sample size of 5 g, the inadvertent loss of a single 2mm crumb could be as much as 0.2 % weight loss. Minor spills are easily missed when running large volumes of samples. Careful handling and filling crucibles no more than 2/3 full can greatly minimize this source of random error.

Another simple source of error is incomplete drying. Air-dried soil always contains some residual hygroscopic moisture. Figure 1 compares LOI on several air-dried soils vs the same soils oven-dried at 110 °C. It is apparent that residual moisture can be a very significant error, even in coarse-textured soils. Oven drying at 110 °C for at least 2 hours is usually sufficient to remove residual moisture from 4 - 5 cc volume of soil (Schulte, Kaufman, and Peters).

Figure 1. Drying Effect on LOI

Sample	texture	air dry % LOI	oven dry % LOI	absolute error (moisture)
1	loam	5.69	4.12	1.57
2	loam	7.64	6.21	1.43
3	silt loam	6.85	5.14	1.71
4	sandy loam	8.57	6.81	1.76
5	silt loam	7.74	6.06	1.68
6	loamy sand	4.27	3.40	0.87

Oven drying will remove hygroscopic moisture, but will not drive off water bound in clay crystalline structures. Ignition temperatures are known to volatilize this structural water, as well as hydroxyl groups and other constituents. To document the effect of ignition temperatures on clay mineral components, several American Petroleum Institute (API) reference minerals were run through our routine LOI procedure. The reference samples were powdered by mortar and pestle and by running them through a plate grinder. To maximize particle surface area, only the fraction of each sample passing a 300 um (no. 50) sieve was used. Five 4-cc replicates of each reference mineral were oven-dried overnight at 110 °C and muffled at 375 °C for 2 hours. The same 50-mesh material was run in duplicate for TOC by combustion at 1050 °C and again for TC at 1350 °C, to determine organic-C or carbonate-C content. Results appear in figure 2. Percent organic-C is also presented as potential % OM, using the 1.72 conversion factor. Carbonate-C (TC - TOC) is also presented as potential CO₂ weight loss from heat degradation. These two represent the theoretical maximum bias in % LOI from carbon content, assuming there was complete degradation of both forms at 375 °C after 2 hr.

Figure 2. Reference Clay Minerals

	% LOI	% TOC	% TC	potential % OM	potential % CO ₂
Allophane	5.1	0.25	0.25	0.4	0.0
Attapulgite	5.0	0.20	0.20	0.3	0.0
Bentonite	1.0	0.20	0.25	0.3	0.2
Chlorite	0.3	0.05	0.05	0.1	0.0
Bauxite (Gibbsite+Boehmite)	25.7	0.40	0.60	0.7	0.7
Hematite	< 0.2	0.10	0.45	0.2	1.3
Illite # 35	1.1	0.50	1.05	0.9	3.7
Illite # 36	2.1	0.10	0.10	0.2	0.0
Kaolinite	< 0.2	0.10	0.10	0.2	0.0
Montmorillonite # 48	0.5	0.10	0.15	0.2	0.2
Muscovite	< 0.2	0.05	0.05	0.1	0.0
Pyrophyllite	0.4	0.05	0.05	0.1	0.0
Stilbite	10.9	0.10	0.10	0.2	0.0
Vermiculite	2.7	0.25	0.45	0.4	0.7

Except for Illite # 35, the amount of weight loss for most of the minerals with significant LOI cannot be attributed solely to carbon content. This would indicate a measurable volatilization loss of structural constituents at 375 °C . These API reference minerals undoubtedly differ in degree of weathering, structural water content, and specific molecular structure from the same minerals found in soil clays. But they do illustrate the "built-in" bias in the LOI procedure with respect to soil mineral content. Soil clays are usually a mixture of several different minerals. However, if they are well characterized for a given soil, the likelihood and magnitude of significant error in LOI analysis due to the mineral fraction can be determined and perhaps compensated for by soil series or parent material. A systematic comparison between LOI and other OM methods for all soils within a state or region may be well worth the effort if soil series information is commonly provided with customer samples. LOI conversion or correction factors specific to soil mineralogy could be employed in this way in high volume operations.

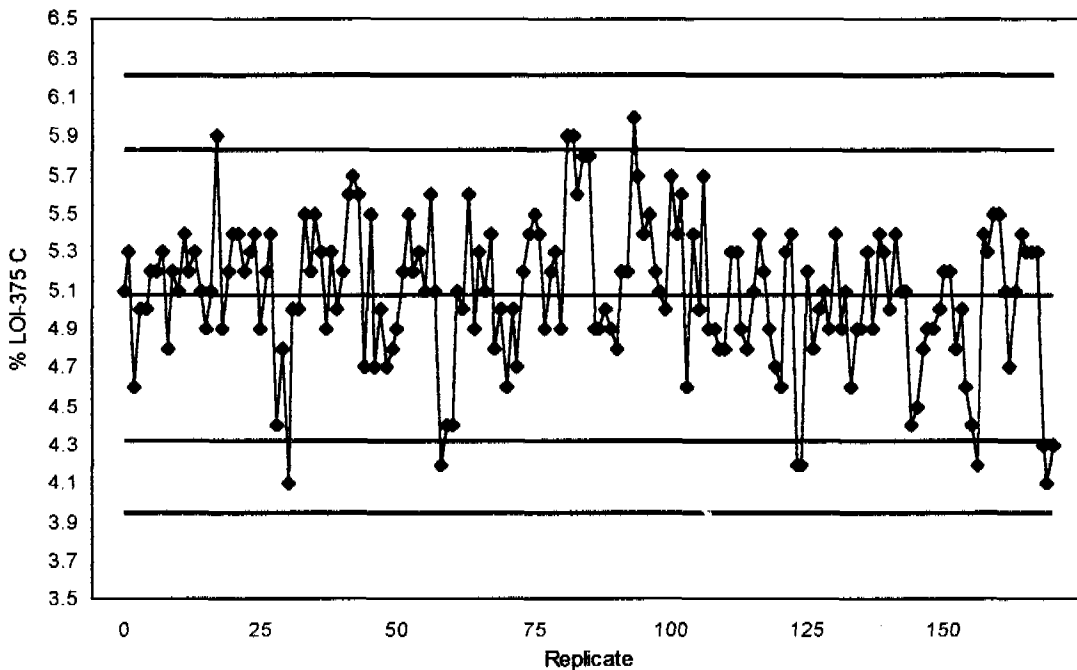
Much of the seemingly random variability in LOI analysis can be attributed to the dynamic environment within an operating muffle furnace. Schulte, Kaufmann, and Peters (1991) studied the effects of sample size, container size, organic matter level, number of samples, and heating time on LOI results. They found no significant effects from number of samples or container size, indicating no overall oxygen depletion in the furnace. They did find a significant effect of ignition time and (in high OM soils) sample size on LOI. Both factors could have affected oxygen diffusion into the sample. Their work demonstrated a good relationship between LOI and Walkley-Black organic matter when sample size and ignition times were kept constant. Both Davis (1974) and Ben-Dor and Banin (1989) showed that ignition temperatures in the range of 400 - 430 °C resulted in no

significant bias from thermal breakdown of carbonates. Jackson (1958) and Ball (1964) both recommended ignition temperatures of $< 400\text{ }^{\circ}\text{C}$ to minimize weight loss from carbonates, structural water in clays, and hydrated salts.

At the University of Maine soil testing lab, organic matter analysis has been part of the routine soil testing package since 1994. Organic matter is measured by LOI at $375\text{ }^{\circ}\text{C}$ for 2 hours, after drying at $110\text{ }^{\circ}\text{C}$ for at least 2 hours to eliminate residual moisture. LOI is then converted to Walkley-Black equivalent organic matter using a regression equation developed from 60 samples chosen to include all productive soils and cropping systems in Maine.

Samples are run in numbered pre-weighed ceramic crucibles in stainless steel rod racks, 2 x 60-sample racks at a time, in a Thermolyne FA1740 muffle furnace. Each rack or tier is 5 samples wide by 12 deep, looking the length of the furnace. For all routine analyses an internal reference soil is run in the sample stream as every 25th sample, both as a daily check on performance and to document long-term method precision and analytical uncertainty. Initial variability statistics from 170 repeat measurements on one of these reference samples appear in an X-chart format in figure 3. It is quite apparent that LOI results are highly variable, with 3 SD control limits at $\pm 1.1\%$ around a mean of 5.1% LOI. This is a relative uncertainty of $\pm 21\%$ for this particular reference sample.

Figure 3. Reference Soil LOI



To determine if temperature could be a source of this variability, a thermocouple probe was used to directly measure furnace temperature during operation. Measured furnace temperature was $28\text{ }^{\circ}\text{C}$ cooler at the front (behind the doors) than in the rear, where the nominal temperature of $375\text{ }^{\circ}\text{C}$ was properly maintained by the thermostat. To minimize temperature variability, an additional ceramic insert was custom made to fit in the recess behind the doors. This decreased the temperature differential to $16\text{ }^{\circ}\text{C}$ front to back, still a substantial temperature gradient.

A study was conducted to further characterize variability within the furnace. Six current and archived internal reference samples were chosen. Basic soil properties appear in figure 4. As an additional point of reference, total organic C by combustion (1050 °C) is shown for each sample. All in-house reference samples are non-calcareous and pass a 2-mm sieve. A full double rack set of 120 subsamples was run for each soil. In addition, two NAPT soils were run for comparison of uniformity of preparation. Characteristics were taken from reported median values for these two soils. Depending on texture, NAPT soils pass either a 1.0 or a 0.65 mm sieve, are more thoroughly homogenized, and are expected to be more uniform than in-house reference soils. There was sufficient NAPT sample for only one 60-sample run each. All sub-samples were scooped at 4 cc to eliminate sample size as a source of variability. The furnace was run with the insert to minimize temperature variability. Full set means and standard deviation statistics appear for all 8 soils in figure 5.

Figure 4. Study Soil Characteristics

Sample	pH	% TOC	texture
S1	5.2	1.77	loam
S2	5.1	2.94	loam
S3	5.9	2.55	silt loam
S4	6.2	3.36	sandy loam
S5	6.1	2.32	silt loam
S6	5.8	1.50	loamy sand
NAPT2001-107(S7)	6.4	1.46	silt loam
NAPT2001-112(S8)	7.9	1.28	sandy loam

Figure 5. LOI Variability Statistics

Sample (n)	mean % LOI	1 SD	CV
S1 (120)	4.12	0.31	7.52
S2 (120)	6.21	0.31	4.99
S3 (120)	5.14	0.33	6.42
S4 (120)	6.81	0.47	6.90
S5 (120)	6.06	0.37	6.11
S6 (120)	3.40	0.22	6.47
S7 (60)	3.57	0.30	8.40
S8 (60)	2.47	0.18	7.29

Variability exhibited by the two well-homogenized NAPT soils was generally comparable to the in-house soil samples. This indicates that non-uniform sub-sampling was probably not a factor in LOI variability. Overall variability of each reference soil was generally comparable to the initial statistics for this method, even with a reduced furnace temperature gradient.

Since all variability within the furnace due to temperature, insulation, air currents, or other factors cannot be completely eliminated, an attempt was made to estimate bias specific to each crucible position. This technique has been used with great success at the Pettiet Agricultural Services lab in Leland MS for the past several years. In our study, set mean LOI was used as the reference point to determine the positional bias within each of the 120 subsample sets. Bias was expressed as a simple proportion of the overall set mean. A correction factor was calculated for each of the 120 positions as the mean of the 6 bias estimates (figure 6).

Figure 6. Average Correction Factor Matrix

(front)					
Bottom Rack					
	0.88	0.86	0.87	0.86	0.86
	0.95	0.95	0.92	0.95	0.89
	0.99	0.99	0.93	0.97	0.96
	1.02	1.00	1.01	1.00	0.97
	1.06	1.02	1.01	1.01	0.99
	1.06	1.08	1.03	1.04	1.01
	1.07	1.00	1.03	1.03	1.02
	1.10	1.09	1.04	1.04	1.03
	1.07	1.05	1.06	1.02	1.02
	1.10	1.05	1.05	1.02	1.02
	1.07	1.00	1.02	1.03	1.00
	1.09	1.04	1.01	1.04	1.00
(front)					
Top Rack					
	0.91	0.93	0.92	0.91	0.90
	0.93	0.92	0.94	0.95	0.96
	0.96	0.97	0.96	0.98	0.99
	0.98	0.99	1.01	0.98	1.00
	1.00	1.03	0.99	1.01	1.01
	1.01	1.03	1.00	1.01	1.05
	1.02	1.01	1.02	1.01	1.01
	1.03	1.01	1.03	1.01	1.03
	1.02	1.03	1.03	1.06	1.02
	1.03	1.02	1.03	1.03	1.01
	1.00	1.01	1.03	1.01	1.00
	1.00	1.01	1.01	1.01	0.95

To correct for bias, apparent LOI at each position is divided by the correction factor calculated for that position. The LOI data for each of the original reference soils was recalculated using this procedure. Set mean and SD were recalculated after correction. The overall variability was reduced for all soils by as much as 49 % (figure 7). The remaining variability should be due to factors other than positional bias in the muffle furnace.

Figure 7. Corrected % LOI Statistics

	Mean % LOI	1 SD	CV	Decrease	1 SD (relative)
S1 (120)	4.11	0.19	4.62	0.12	38.7%
S2 (120)	6.21	0.16	2.58	0.15	48.4%
S3 (120)	5.14	0.22	4.28	0.11	33.3%
S4 (120)	6.80	0.24	3.53	0.23	48.9%
S5 (120)	6.06	0.23	3.80	0.14	37.8%
S6 (120)	3.40	0.16	4.71	0.06	27.3%

Corrected LOI values can be converted to an equivalent Walkley-Black or other OM estimate using regression equations developed using corrected LOI data. Alternative correction techniques are equally valid. Pettiet Lab runs LOI analysis on 264 x 2.0g sample batches at 450 °C for 2 hrs, after drying at 105 °C for 2 hrs. To correct for overall procedural bias, as well as positional bias in the furnace, four reference samples were run at all 264 positions to develop 264 individual regression equations converting LOI at each position directly to Walkley-Black organic matter (Joe Pettiet, personal communication).

Since all factors producing positional bias are not easily measured or even fully understood, correction factors should be assumed to be valid only for a specific lab operation and a specific furnace under a specific set of operating conditions. Changes in sample size and sample loading may affect furnace dynamics in such a way as to render correction factors invalid. For instance, correction factors are not expected to be accurate for LOI runs with less than a full sample load. For smaller sample groups, unused positions should be occupied using new or reused samples in order to maintain the furnace environment as uniform as possible. Absolute consistency in sample size, drying time, cooling time, weighing time, and ignition time are necessary to accurately integrate all factors into bias correction (Joe Pettiet, personal communication).

All bias and variability in LOI analysis cannot be completely eliminated. If the method is run consistently, with constant sample size, complete oven drying, and consistent furnace loading and operation, much of the variability can be eliminated. Knowledge of clay mineralogy and content of each soil can potentially remove even more bias in the relationship between LOI and other procedures used to estimate soil organic matter in routine soil testing.

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