

# Free Moisture and LOI Determination of Hydrated Lime, Limestone, and Cement Utilizing Macro TGA

Jeffery Gast, Adam Darling, Mason Marsh, Dennis Lawrenz | LECO Corporation, St. Joseph, MI USA

## Introduction

Free moisture and Loss On Ignition (LOI) measurement of hydrated lime, limestone, and cement is utilized for determining the mass of material that will be lost when fired in a kiln. The analysis of the material is also a metric for the purity of the raw and processed material. The determination of LOI using a LECO TGA701 macro thermogravimetric analyzer may be separated into distinct temperature steps to distinguish between mass loss from hydroxyl groups and the release of CO<sub>2</sub>.

Current methods for free moisture determination of hydrated lime and limestone are performed separately in a muffle furnace according to ASTM C25. Moisture analysis for cements is typically combined with the LOI determination. The determination of free moisture in hydrated lime and limestone involves weighing the sample and placing the sample in the muffle furnace at 115-120 °C where CO<sub>2</sub> free air is passed over the sample for approximately two hours. After the designated time, the sample is removed and left to cool in a desiccator where it is later weighed. The mass lost is calculated and represents free moisture.

For the determination of LOI, ASTM C25 and ASTM C114 differ on maximum temperature of 1000 °C and 950 °C respectively, however, both methods operate under the same principle. Alternative to the standard method, some have found that a stepped LOI determination at lower temperatures, in addition to the maximum temperature, is useful to determine approximate composition of hydroxyl groups or crystalline water. The value of all the steps combined is typically referred to as the Total LOI.

In contrast to the methods referenced above, an automatic macro thermogravimetric analyzer (TGA) may be used to measure free moisture and LOI at various temperatures without removing the sample from the furnace, therefore, reducing error of the sample reabsorbing lost analyte as it cools, as well as increasing sample throughput. This poster will cover the methodology and results from the determination of free moisture and LOI in hydrated lime, limestone, and cement utilizing the LECO TGA701 analyzer.

## Published Methods

- ASTM C25: Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime
- ASTM C114: Standard Test Methods for Chemical Analysis of Hydraulic Cement

## Methodology Theory of Operation



Figure 1: LECO TGA701

Macro TGA instruments typically utilize a gram-sized sample with a high temperature furnace using an air/nitrogen or oxygen atmosphere for moisture and LOI determination respectively. In the LECO TGA701, samples are weighed into ceramic crucibles located on a rotating carousel, utilizing a high precision internal balance (0.0001 g). Each batch is able to analyze 19 samples with one reference crucible, as shown in Figure 2. The reference crucible is weighed once every revolution on the balance pedestal, shown in Figure 3, to adjust for buoyancy and drift changes and apply the same change to all crucibles.

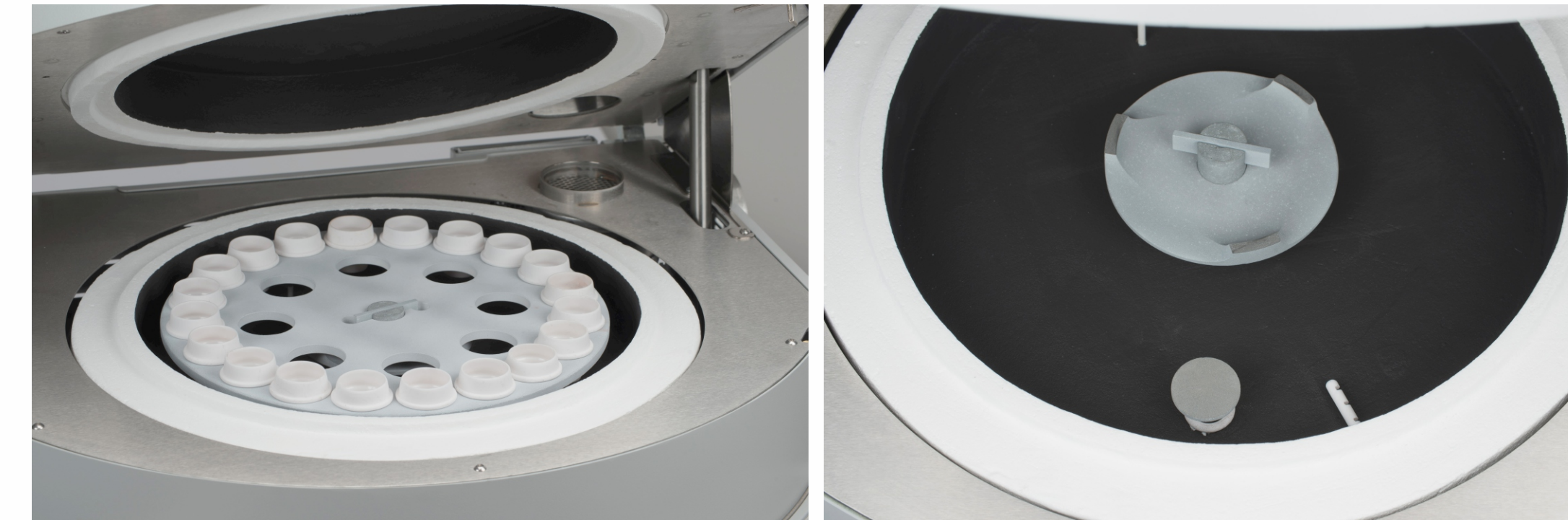


Figure 2: 19 samples plus reference crucible

Figure 3: Balance Pedestal

The sample batch undergoes a pre-programmed analysis method with several steps to determine mass loss due to free moisture and LOI. During the analysis, the samples are weighed every revolution of the carousel in sequence, approximately every three minutes, to monitor the mass loss at each step without the removal of the sample from the furnace. By keeping the sample at temperature for weighing, this reduces the potential for reabsorption of analyte that was lost during the furnace step. The mass loss at any given step can be expressed as a percent loss of the original sample mass.

## Background

The processing and manufacturing of many materials, such as cement, hydrated lime, or limestone typically involve a step where the material undergoes firing in a furnace or kiln. Raw limestone is mined and can be fired to make the base for several materials through the production of calcium oxide or used to make other products such as cement. LOI determination in limestone is important for determining the purity of the material, as well as determining the amount of emissions that will be evolved when fired in the kiln.

Hydrated lime is made by adding water to calcium oxide that is left over from the firing of limestone. The water converts the oxide to hydroxides and also absorbs crystalline water. Hydrated lime has many uses in the food industry, as well as the use as an acid reducer. LOI determination of hydrated lime can indicate purity by the loss of crystalline water below 600 °C and subsequently the loss between 600 °C and 1000 °C is equated to the amount of absorbed CO<sub>2</sub>.

Cement is a combination of several different materials including limestone. The determination of LOI in cement is typically done as total LOI or split loss. Split loss determination takes place at approximately 550 °C and 950 °C. For this poster, cement was analyzed the same as the limestone and hydrated lime at 600 °C and 1000 °C, and results for total LOI are the combination of both steps.

## Calibration and Verification

The TGA701 does not require calibration for free moisture and LOI determination as the measurement result is expressed as a percent of mass loss rather than absolute mass. The LOI method results were verified by analyzing NIST SRM<sup>®</sup> 1d Argillaceous Limestone (Table 6), NIST SRM<sup>®</sup> 633a Portland Cement (Table 7), and LECO LCRM<sup>®</sup> 502-902 Lot: 1000 Calcium Carbonate (Table 3) for LOI and comparing the result against the certificate LOI.

## Sample Data

A sample suite was chosen for this study to demonstrate the analytical performance and application capability of the method configurations to determine free moisture and LOI results in hydrated lime, limestone, and cement utilizing the LECO TGA701. Where possible, materials with certified LOI values were utilized to assess accuracy as well as precision. Sample data represents three separate analysis batches with seven replicates, each providing intra and inter batch precision performance data

Table 1: Commercially Purchased Hydrated Lime

Sample	Mass	Batch	n	% Free Moisture	Std Dev	% LOI @ 600 °C	Std Dev	% LOI @ 1000 °C	Std Dev	% Total Dry LOI
Commercially Purchased Hydrated Lime	~1.0 g	1	7	0.76	0.01	23.1	0.02	1.25	0.02	24.3
		2	7	0.75	0.01	23.1	0.02	1.24	0.02	24.3
		3	7	0.77	0.01	23.1	0.02	1.24	0.02	24.3
<b>Avg</b>				0.76		23.1		1.25		24.3
<b>Std Dev.</b>				0.01		0.02		0.02		0.02

The mass loss at 600 °C is the release of water from Ca(OH)<sub>2</sub> to form CaO and H<sub>2</sub>O. The mass loss at 1000 °C is CO<sub>2</sub> contaminant. The 1.25% mass loss at 1000 °C was confirmed as CO<sub>2</sub> by analyzing the commercially purchased hydrated lime for total carbon utilizing a LECO SC832 high temperature combustion with infrared detection carbon determinator.

Table 2: High Calcium Limestone

Sample	Mass	Batch	n	% Free Moisture	Std Dev	% LOI @ 600 °C	Std Dev	% LOI @ 1000 °C	Std Dev	% Total Dry LOI
High Calcium Limestone	~1.0 g	1	7	0.06	0.03	0.1	0.04	43.61	0.01	43.7
		2	7	0.05	0.01	0.1	0.02	43.62	0.02	43.7
		3	7	0.02	0.02	0.1	0.03	43.65	0.01	43.7
<b>Avg</b>				0.04		0.1		43.63		43.7
<b>Std Dev.</b>				0.03		0.03		0.02		0.03

Limestone comes in various mixtures of calcium carbonate (CaCO<sub>3</sub>), magnesium carbonate (MgCO<sub>3</sub>), and other rock materials. High calcium limestone (High Cal), as shown above in Table 2, typically contains greater than 95% calcium with less than 5% other rock materials. Dolomitic limestone, or limestone containing higher amounts of magnesium carbonate, have higher total LOI than pure calcium carbonate (~44.0%). Pure calcium carbonate, as shown below, does not demonstrate significant mass loss below 600 °C, confirming full recovery of the mass loss at 1000 °C as compared to the High Cal limestone above containing non-carbonate impurities.

Table 3: LECO LCRM<sup>®</sup> Calcium Carbonate

Sample	Mass	Batch	n	% Free Moisture	Std Dev	% LOI @ 600 °C	Std Dev	% LOI @ 1000 °C	Std Dev	% Total Dry LOI
LECO LCRM 502-902 Lot: 1000 Calcium Carbonate (12.01% C (44.0% CO <sub>2</sub> ))	~1.0 g	1	7	<0.01	-	0.02	0.01	43.96	0.01	43.98
		2	7	0.02	0.01	0.03	0.01	43.95	0.01	43.98
		3	7	0.02	0.01	0.02	0.00	43.96	0.01	43.98
<b>Avg</b>				0.02		0.02		43.96		43.98
<b>Std Dev.</b>				0.01		0.01		0.01		0.01

LECO LCRM 502-902 Lot: 1000 Calcium Carbonate was certified at 12.01% C, with the carbon present bound as CO<sub>2</sub>. The carbon value of the calcium carbonate was converted to a mass loss % representing CO<sub>2</sub> (equation below) in order to compare the value to the measured Total LOI mass loss result.

$$\text{Equation: } \% \text{ CO}_2 = \% \text{ C} * 3.664$$

Table 4: Commercially Purchased Portland Cement

Sample	Mass	Batch	n	% Free Moisture	Std Dev	% LOI @ 600 °C	Std Dev	% LOI @ 1000 °C	Std Dev	% Total Dry LOI
Commercially Purchased Portland Cement	~1.0 g	1	7	0.44	0.04	0.45	0.03	1.56	0.02	2.01
		2	7	0.40	0.03	0.46	0.02	1.57	0.01	2.03
		3	7	0.42	0.02	0.45	0.05	1.57	0.01	2.02
<b>Avg</b>				0.42		0.5		1.57		2.02
<b>Std Dev.</b>				0.03		0.04		0.01		0.04

Table 5: Commercially Purchased Hydraulic Cement

Sample	Mass	Batch	n	% Free Moisture	Std Dev	% LOI @ 600 °C	Std Dev	% LOI @ 1000 °C	Std Dev	% Total Dry LOI
Commercially Purchased Hydraulic Cement	~1.0 g	1	7	0.37	0.02	0.70	0.01	1.16	0.02	1.86
		2	7	0.39	0.01	0.66	0.02	1.19	0.03	1.85
		3	7	0.44	0.01	0.70	0.05	1.17	0.05	1.87
<b>Avg</b>				0.40		0.69		1.17		1.86
<b>Std Dev.</b>				0.03		0.04		0.03		0.02

Portland cement and hydraulic cement are typically analyzed at 950 ± 50 °C according to ASTM C114. The mass lost is determined to be moisture and CO<sub>2</sub> loss. The ASTM C114 method utilizes a muffle furnace and manually placing in and removing the sample from the furnace, then placing the sample into a desiccator to be weighed after cooling until constant mass is achieved. This process can involve several cycles of heating, cooling, and weighing before constant mass is achieved. The LECO TGA701 will analyze the sample at each method step to constancy without the need to remove the sample from the furnace, therefore, reducing analysis time and potential for error.

Table 6: NIST SRM<sup>®</sup> 1d Argillaceous Limestone

Sample	Mass	Batch	n	% Free Moisture	Std Dev	% LOI @ 600 °C	Std Dev	% LOI @ 1000 °C	Std Dev	% Total Dry LOI
NIST SRM <sup>®</sup> 1d Argillaceous Limestone 41.57% LOI Dry	~1.0 g	1	1	0.14	-	0.38	-	41.18	-	41.56
		2	1	0.17	-	0.35	-	41.21	-	41.56
		3	1	0.15	-	0.34	-	41.24	-	41.58
<b>Avg</b>				0.15		0.36		41.21		41.57
<b>Std Dev.</b>				0.02		0.02		0.03		0.01

NIST SRM<sup>®</sup> 1d Argillaceous Limestone lists a reference value of 41.57% for LOI at 1000 °C. According to the certificate, the sample was dried before the LOI was determined, therefore, the combination of LOI at 600 °C and 1000 °C represents the reference value. The values obtained from analyzing one sample, with three separate batches analyzed simultaneously with the data collected above, confirms the LOI method for Total Dry LOI.

Table 7: NIST SRM<sup>®</sup> 633a Portland Cement

Sample	Mass	Batch	n	% Free Moisture	Std Dev	% LOI @ 600 °C	Std Dev	% LOI @ 1000 °C	Std Dev	% Total LOI
NIST SRM <sup>®</sup> 633a Portland Cement 2.46% Total LOI	~1.0 g	1	1	0.20	-	0.54	-	1.73	-	2.47
		2	1	0.12	-	0.69	-	1.71	-	2.52
		3	1	0.23	-	0.55	-	1.74	-	2.52
<b>Avg</b>				0.18		0.59		1.73		2.50
<b>Std Dev.</b>				0.06		0.08		0.02		0.03

NIST SRM<sup>®</sup> 633a Portland Cement lists a reference value of 2.46% Total LOI at 950 °C. The values obtained on the TGA701 are within the uncertainty stated on the certificate.

## Conclusion

The LECO TGA701 Thermogravimetric Analyzer was used to perform several methods, historically performed manually, that utilize muffle furnaces, desiccators, and may require other specialized equipment. The automated method of the TGA701 provided repeatable and precise free moisture and LOI results for the matrices tested with values that were successfully confirmed utilizing several reference materials with certified values or reference values for the analysis.

Free moisture and LOI for hydrated lime are typically determined separately, taking at least three hours to complete per ASTM C25. The LECO TGA701 is able to perform both of these analyses using one sample with the measurement of the constituents in a single analysis sequence taking approximately 2.5 hours without significant operator involvement.

The LECO TGA701 offers reduced analysis time, reduced points of error, and full automation of the analysis cycle enabling an automated end point determination while obtaining accurate results for free moisture and LOI in hydrated lime, limestone, and cement products.