



# CHEMICAL ANALYSIS OF LIMESTONE/ CALCIUM OXIDE MATERIALS

## Part 1 The Analytical Choices and Requirements

### Introduction and Background

As calcium-bearing minerals have become more widely used in agriculture, energy, and road-building and more important in the marketplace as a result, their analysis has been subject to a great deal of debate and controversy. Qualitative analysis is critical to justify pricing to suppliers and to give end-users confidence that the materials and the products they ultimately are used in will perform as required.

Three primary methodologies have been established as the commonly accepted criteria for qualitative analysis to provide a comprehensive chemical evaluation of these materials:

- ASTM C25, “Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime.”
- ASTM C1271, Standard Test Method for X-Ray Spectrometric Analysis of Lime and Limestone.”
- ASTM C1301, “Standard Test Method for Major and Trace Elements in Limestone and Lime by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) and Atomic Absorption (AA).”

For the suppliers and the end-users of these materials, the three main questions they want answered are:

- 1) Which method allows the shortest laboratory turnaround time?
- 2) Which method is most cost-effective?
- 3) Which method gives the most accurate results?

The first two questions are addressed in Part I of this paper. The third question is discussed in the second part of this paper.

### Comparison of the Accepted Methods

As the title of this paper, “Chemical Analysis of Limestone,” suggests, the various methods discussed here determine the presence of elements and/or compounds using “classic” wet methods and may use a minimum of sophisticated instruments for the final parameter analysis. Most wet methods involve gravimetric measurements that assess changes in weight and titrimetric measurements, which assess changes in volume. Some

of the methods were quantitatively proven to be exact or empirical more than 100 years ago; these methods are most often used in referee analyses when required to resolve disputed results.

**ASTM C25** is the oldest of the chemical reference methods normally available to the testing laboratory. Although ASTM C25 does often allow a degree of substitution in the



means of final detection through instrumental analysis, the required separations are often quite lengthy and may involve overnight digestions. In addition, turnaround times with this method are consistently and negatively affected by other chemical separations, filtrations, titrations, and gravimetric procedures. Further impacts on turnaround time with this method occur when tests involving lengthy titrations for equivalency or reactivity are required

since primary method requires many hours of manual attention by a skilled technician.

The **ASTM C1271** and **ASTM C1301** methods were developed over time in concert with the development of technology in modern analytical instrumentation. For chemical evaluations using ASTM C1271, X-ray Fluorescence (XRF) is the mandated means of final detection; this method requires that a homogenized and powdered sample be either physically blended with an inert (non-interfering) binder, or that the powdered sample be fused with an alkali salt before analysis. Similar to ICP in the paragraph above, the more modern XRF equipment can perform the final analyses in a sequential or simultaneous mode depending on manufacturer and model.



For most analytical parameters, ASTM C1301 requires the total dissolution of a homogenized part of the sample. This dissolution may or may not be completed with common laboratory acids; alkali fusions are often required as well to dissolve complex carbides and silicates that may be in the materials. The final material analyses are completed using either Atomic Absorption Spectroscopy (AAS), which is completed one element at a time, or by Inductively Coupled Plasma (ICP), which can evaluate samples sequentially or simultaneously depending on the specific instrument design. Not surprisingly, AAS has become a more antiquated method of chemical analysis with most modern laboratories relying on ICP or X-ray spectrometry.



Given the differences in these three methods, strict adherence to the requirements of ASTM C25 will, unfortunately, require more time in the laboratory than the other methods. On the other hand, the initial and annualized costs of using ICP and XRF to obtain the better production and turnaround times of these methods could exceed \$100k.

Although the ASTM C25, ASTM C1271, and ASTM C1301 methods appear to be drastically different in their analytical approaches, they do have several key elements in common. First and perhaps most importantly, to adequately perform any of these analyses, a laboratory must be fully accredited by a nationally recognized program. Expenditures for capital equipment, consumable materials, and the presence of a trained analytical staff are required for all three methods, with costs still borne even during non-production times. With the annualized costs often exceeding several hundred thousand dollars, this level of comprehensive support normally can only be met by a handful of major producers. As a result, both producers and vendors generally depend on the commercial testing laboratories for use on a turn-key basis.

*Conclusions:* Three main test methods, ASTM C25, C1271, and C1301, are used for the chemical and physical analysis of limestone and other calcium-oxide materials. ASTM C25 involves primarily classical wet methods that involve more time and labor but use less analytical instrumentation. ASTM C1271 and C1301 can produce test data more quickly but require the expense and maintenance of sophisticated analytical instrumentation.

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### **Part 2      An Analytical Comparison of Methods**

#### **Review of Methods**

To recap, the ASTM analytical test methods discussed in Part I of this paper were ASTM C25 (Wet Methods), ASTM C1271 (X-ray Spectrometric), and ASTM C1301 (ICP and AA Spectrophotometry). The selection of a particular method is often made on the basis of availability of specific equipment in the laboratory, as well as the need for accuracy and quick turnaround times after sample submission.

All three methods possess inherent weaknesses. Classical wet methods are susceptible to physical interferences such as weight loss (sample splattering) and weight gain (foreign contaminants and moisture) and tend to depend more on technique. X-ray spectrometric methods require that the chemical and physical compositions of the sample closely match the reference materials used to calibrate the instrument, but the availability of certified reference materials is limited. ICP and AA spectrophotometric methods suffer from chemical, physical, and spectral interferences including wavelength absorbance,



inconsistencies in the introduction of the dissolved sample into the instrument, and overlapping and unresolved wavelength peaks.

The Analytical Services Division at Bowser-Morner, Inc. has employed all three methods in the past. The data produced strongly indicate that analyses using X-ray spectrometric

methods produce better-quality data than other two methods. As discussed above, this method requires that the sample composition must be similar to the standards used to calibrate the instrument, which can be a limiting factor.

**Terminology**

In the comparison of analytical methods, three specific terms are routinely utilized to describe the comparative accuracy of methods:

- *Repeatability, r*, normally indicates multiple analyses of the same sample, in the same laboratory, performed by the same analyst, at the same relative time.
- *Reproducibility, R*, is considered on the basis of the analysis of the same (split) sample, different laboratories, different analysts, different equipment, all within a short time period.
- *Uncertainty, UnC*, (or estimated uncertainty) considers the same sample with accepted values, analyzed multiple times by the same laboratory over a relatively longer period of time.

**Comparison of Data**

The two tables below are presented to show the repeatability, reproducibility, and uncertainty from the analysis of two NIST reference materials (1d and 88b).

NIST 1d (Wt %)		XRF (ASTM C1271)			AA/ICP (ASTM C1301)			Wet (ASTM C25)		
Compound	Value	ASTM <i>r</i>	ASTM <i>R</i>	BMI <i>UnC</i>	ASTM <i>r</i>	ASTM <i>R</i>	BMI <i>UnC</i>	ASTM <i>r</i>	ASTM <i>R</i>	BMI <i>UnC</i>
Al <sub>2</sub> O <sub>3</sub>	0.53	0.055	0.137	0.012	Note	Note		0.165	0.223	0.160
CaCO <sub>3</sub>	94.33	0.689	1.737	0.762	Note	Note		0.996	1.820	1.100
MgCO <sub>3</sub>	0.63	0.099	0.395	0.098	Note	Note	0.090	0.330	0.439	
Fe <sub>2</sub> O <sub>3</sub>	0.32	0.015	0.053	0.016	Note	Note	0.050	0.064	0.183	
SiO <sub>2</sub>	4.08	0.339	0.488	0.152	Note	Note		0.128	0.146	0.160

NIST 88b (Wt %)		XRF (ASTM C 1271)			AA/ICP (ASTM C 1301)			Wet (ASTM C 25)		
Compound	Value	ASTM <i>r</i>	ASTM <i>R</i>	BMI <i>UnC</i>	ASTM <i>r</i>	ASTM <i>R</i>	BMI <i>UnC</i>	ASTM <i>r</i>	ASTM <i>R</i>	BMI <i>UnC</i>
Al <sub>2</sub> O <sub>3</sub>	0.34	0.035	0.115	0.012	Note	Note		0.165	0.223	0.090
CaCO <sub>3</sub>	53.46	0.689	1.737	0.206	Note	Note		0.662	1.209	0.900
MgCO <sub>3</sub>	43.98	NA	1.973	0.224	Note	Note	1.630	0.652	1.716	
Fe <sub>2</sub> O <sub>3</sub>	0.28	0.013	0.049	0.026	Note	Note	0.060	0.064	0.183	
SiO <sub>2</sub>	1.13	0.101	0.214	0.084	Note	Note		0.128	0.146	0.100

Note: ASTM C1301 does not include a Precision and Bias Statement



All three terms ( $r$ ,  $R$ , and  $UnC$ ) are accepted in the review of laboratory results, but only uncertainty addresses long term consistency of the method, and may also be useful in the indication of any “bias” that may be found in the laboratory procedures.

A review of the data above shows that the analyses for the five primary constituents of limestone (oxides or carbonates of aluminum, calcium, magnesium, iron, and silicon) by X-ray, ICP, and wet methods all provide reproducible results. However, the X-ray data under most considerations provide less variance than the other methods while providing faster production turnaround times.

A few examples where X-ray produces better quality results include:

- $\text{CaCO}_3$  at  $94.3 \pm 0.76\%$  by X-ray ( $94.3 \pm 1.1\%$  by wet)
- $\text{MgCO}_3$  at  $43.9 \pm 0.22\%$  by X-ray ( $43.9 \pm 1.6\%$  by ICP)
- $\text{Fe}_2\text{O}_3$  at  $0.32 \pm 0.02\%$  by X-ray ( $0.32 \pm 0.05\%$  by ICP)

The results above were correlated and based on more than 50 separate determinations in the analytical laboratories of Bowser-Morner, and the results specific to ICP (ASTM C1301) and wet methods (ASTM C25) were correlated over several years. Very few laboratories, commercial or in-house, have the necessary analytical depth to provide such comparable data. In our organization, however, that level of analytical depth is regarded as essential in our organization due to the extreme variety of sample composition received and evaluated by our technical staff.

*Conclusions:* The quantitative evaluation of the five primary constituents in limestone is best reported by X-ray spectrometric methods. Due to the extended analytical range of the X-ray equipment, a variety of other minor and trace constituents can also be addressed, and similar results comparable to the wet and ICP are obtained. However, to best cover the natural possibilities of other mineral carbonates and calcareous materials, a full-service laboratory should have experience with all three analytical methods, X-ray, wet methods, and ICP.