

A new methodical approach based on Compton scattering and XRF: quantitative analysis of CO₂ and loss on ignition in quicklime

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The authors present and discuss a method for simultaneous quantitative analysis of total loss on ignition (LOI) (CO₂ + H₂O) and CO₂ content separate from the LOI, in an industrial environment of quicklime production. Total LOI is determined by the Compton scattered RhK α tube radiation which is used directly in the calibration equation. The resulting calibration curve for LOI, including matrix correction shows an accuracy of 0.15 mass%. The carbon content (CO₂) is distinguished from total LOI by measuring CK α radiation, which is possible with the required accuracy by employing a new multilayer analyzer with greatly improved background characteristics. The method aims at high reliability and sample throughput and at becoming a less time-consuming alternative to the conventional method of LOI determination by weighing sequences before and after “ignition” at 1050 °C. © 2015 International Centre for Diffraction Data. [doi:10.1017/S0885715615000275]

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I. THE ANALYTICAL PROBLEM

Quicklime (“burnt lime”, CaO) is formed from lime-stone (CaCO₃) by calcination above 900 °C. At an industrial level there are various types of furnaces for producing different grades of quicklime, such as a lime kiln (Figure 1). They heat up the material to temperatures above 900 °C causing the decomposition of lime stone, CaCO₃ → CaO + CO₂.

After the process some CO₂ and combined water remain in the product and degrade the desired (standardized) quality. For example, the Japanese Industrial Standard JIS R 9001:2006 defines material only as “special grade” if the remaining CO₂ is kept below 2 mass%.

Volatile light components are usually referred to as “loss on ignition” (LOI); in quicklime these are mainly CO₂ and combined water (labile hydroxy-compound). LOI is conventionally quantified by standardized weighing sequences before and after “ignition” at 1050 ± 50 °C, which is, however, laborious and time consuming.

The analytical challenge is to keep continuous control of total LOI as well as CO₂ during the calcination process by a quick (high throughput) and accurate method. Furthermore, impurities such as SiO₂, Al₂O₃, P₂O₅, MgO, and Fe₂O₃ influence the analytical data and require proper correction. The investigations and methodical development shown in this paper aim at demonstrating the superior ability of X-ray fluorescence analysis (XRF) for the determination of CO₂ and LOI in view of JIS R 9011:2006, which at the present time does not yet designate XRF a conforming method.



Figure 1. (Color online) Lime kiln for quicklime production.

II. THE PROPOSED SOLUTION

Highlights are:

- Compton intensity is used as prime analytical information for quantifying LOI. While the new developed method includes inter-element corrections for the influence of varying

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contents of CO₂ and trace elements, it is not solely a compensation tool for matrix effects.

- For separating the CO₂ content from the total LOI, CK α radiation is measured with high accuracy by taking advantage of a synthetic multilayer crystal with optimized background shape and height characteristics (see Section V).

It is assumed (and confirmed by the employed reference materials) that in the present application no carbon is present (or negligible) except as CO₂, and the analyte material after the calcination process is basically a binary system, [CaO] + [LOI] + (impurities).

III. THE COMPTON SCATTERING APPROACH

Using Compton scattered radiation from oxides became popular by Reynold's (1963) observation that the total mass attenuation coefficient of a sample for the Compton energy is in good approximation proportional to the reciprocal Compton scattered intensity of that material:

$$\mu_{S, E_{\text{Compton}}} = \sum_j W_j \cdot \mu_{j, E_{\text{Compton}}} = A \cdot \frac{1}{n_{E_{\text{Compton}}}}$$

This purely empirical model is the base of several methods for analyses of minerals (oxides) and does not require any theoretical modeling of Compton scattering. Applied to the present system of CaO + LOI this means that the *inverse* Compton intensity increases *roughly* in proportion to the concentration of CaO because of its dominating attenuation coefficient, or that the (*direct*) Compton intensity increases in reasonably good approximation linearly with LOI.

A more elaborate and accurate (however laborious) model was presented by Kataoka *et al.* (2006): Compton scattered intensities for arbitrary samples are computed by Monte Carlo methods, based entirely on a fundamental parameter approach; this requires

- an accurate ray-tracing model for incident and scattered radiation paths (Figure 2) within the instrument,
- and accurate numerical values of differential scattering cross-sections.

Figure 3 shows Monte Carlo computed RhK α Compton scattering intensities from pure elements ($Z < 10$) based on a fundamental parameters approach. When the mass thickness is small, Compton scattering intensities are approximately constant among the elements except hydrogen and

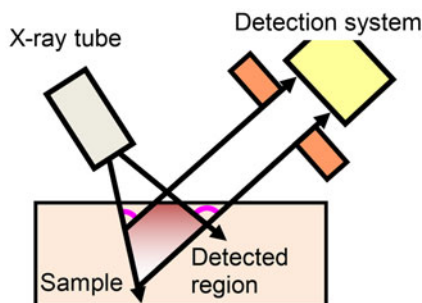


Figure 2. (Color online) Basic geometry and radiation paths.

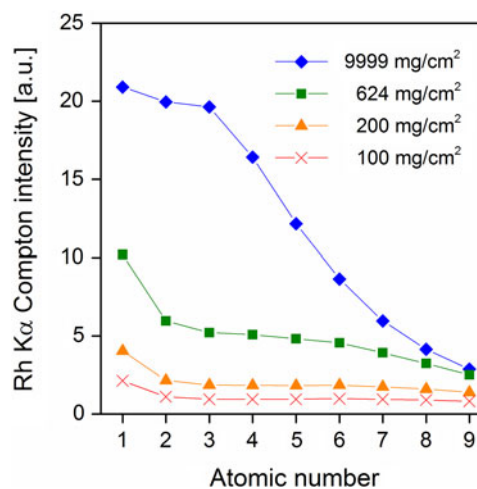


Figure 3. (Color online) Computed Compton intensities from pure elements ($Z < 10$) for several mass thicknesses and bulk (9999 mg cm^{-2}).

proportional to their scattering coefficients. For the bulk material they are increasingly sensitive to lighter elements and approximately proportional to the reciprocal mass attenuation coefficients. This correlation is of advantage in the present application.

A. Matrix corrections for Compton intensities

The analyte materials contain up to 2 mass% impurities, such as MgO, SiO₂, Al₂O₃, Fe₂O₃, and others. While their absolute concentrations are low (<0.5%), their relative amounts vary greatly and require accounting for their individual influence on the measured Compton counts rates. A simple equation similar to popular forerunners was found suitable:

$$W_{\text{LOI}} = (A \cdot I_C + B) \cdot \left(1 + \sum_j \alpha_j \cdot W_j \right)$$

where W_{LOI} and W_j are weight fractions of LOI and matrix components; I_C the Compton photon count rate; α_j the matrix influence coefficients; A and B are calibration constants. The matrix influence coefficient for Fe₂O₃ was the highest among the investigated impurities (Table I). The overall influence of the matrix is shown in Figure 4. Here the accuracy is defined as root-mean-square error of the data points from the calibration line. It includes CO₂ as a correcting component in addition to impurities and thereby allows accounting for changes of the CO₂/H₂O ratio due to loss on ignition conditions during calibration. Its contribution is, however, comparably very small.

TABLE I. Values of matrix influence coefficients.

Correcting component	Matrix coefficient
CO ₂	0.0206
MgO	-0.1077
SiO ₂	-0.1010
Al ₂ O ₃	-0.1029
Fe ₂ O ₃	0.1772
P ₂ O ₅	-0.0958
S	-0.0403

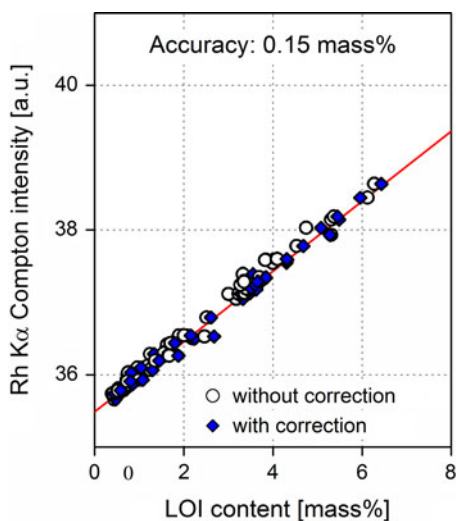


Figure 4. (Color online) Calibration curve for LOI with matrix correction.

IV. SAMPLES AND SAMPLE PREPARATION

The raw sample material was taken from the production site, broken to small pieces by a jaw crusher, and ground by a cross-beater mill until more than 90% of the material reached a target grain size of less than 100 μm . Immediately thereafter the material was temporarily filled into air-tight containers in order to avoid reaction with moisture in the ambient air. Just before the measurement (recommended: within 1 min) the samples were taken from the container and pressed at 250 kN in aluminum rings of 43 mm diameter. No binder was used in order to avoid possible interferences by carbon.

A. Standard samples

For CO_2 : 50 samples were made from quicklime products with CO_2 reference concentrations up to 7.3 mass%; for LOI: 60 samples were made from quicklime products with LOI reference concentrations up to 6.3 mass%; they were measured by the capacitance method and weight loss by ignition at 1050 $^\circ\text{C}$, respectively, as defined by JIS R9011:2006 (Table II).

The reference samples were collected from materials with a wide range of concentrations, including non-conforming products, for the purpose of studying calibration curves for LOI and CO_2 .

V. MEASUREMENTS AND INSTRUMENTATION

All measurements have been carried out with a wavelength dispersive spectrometer Rigaku ZSX Primus II with

TABLE II. Concentration ranges of the reference materials for LOI analysis.

Analytical component	Concentration range (mass%)
LOI	0.44–6.31
CaO	91.4–98.4
MgO	0.49–1.49
SiO_2	0.02–0.30
Al_2O_3	0.01–0.21
Fe_2O_3	0.019–0.32
P_2O_5	0.014–0.16
S	0.006–0.16
CO_2	0.13–5.30

TABLE III. Instrumentation.

	For carbon ($CK\alpha$)	For LOI ($RhK\alpha$ Compton)
Slit	For ultra-light elements	Standard
Crystal	RX61F special crystal	LiF(200)
Detector	F-PC	SC
Counting times	40 s 2×20 s	20 s 2×10 s
Peak BG		

“tube above” geometry. This design is an advantage for pressed powder materials as in the present application because loose particles cannot drop to the window of the tube or contaminate the X-ray path. The settings are shown in Table III.

The measurements of $CK\alpha$ aimed at achieving highest reasonably possible intensities and sensitivity: advantage was taken of the reduced background height (particularly at the high-energy side of the peak) as well as shape, of the new RX61F multilayer analyzer in comparison with the standard version, RX61 (Figure 5). An important improvement is that the background shape is not a function of the CO_2 concentration.

VI. SYSTEM CALIBRATION AND PERFORMANCE

The system was calibrated using the reference materials mentioned above for LOI (by Compton scattering) as well as for CO_2 (by $CK\alpha$).

The calibrations were made using both, computed intensities with a fundamental parameter method and measured intensities of $RhK\alpha$ Compton scattering (Figure 6). The calibration curve of measured intensities shows good accuracy and is almost identical to that of computed intensities, demonstrating that this approach is effective for the determination of LOI. With respect to sample treatment this includes the successful protection of the ground samples from contact with air and moisture.

Calibration curves for CO_2 have been obtained experimentally for three different kinds of furnaces (A, B, and C) and evaluated individually as well as jointly by combining all data to one set. The accuracy for furnace B was worse than the others possibly because of the raw limestone, which was a mixture of several sources. The results show that the individual evaluations deliver clearly better accuracies than the total average (Figure 7); this confirms that the methodical accuracy was satisfactory for the intended application since it was comparable with that of the capacitance method, typically 0.1 mass%. With respect to sample composition it verifies the assumption that practically all of the carbon in quicklime is bound to CO_2 .

VII. CONCLUSIONS

Total LOI (i.e., $\text{H}_2\text{O} + \text{CO}_2$), and therein separately CO_2 , in quicklime produced from CaCO_3 in an industrial calcination process can be quickly and reliably determined by XRF. The required experimental data are obtained by measuring the total LOI by the scattered Compton peak from a characteristic X-ray tube line and $CK\alpha$ by a state-of-the-art X-ray spectrometer with an optimized multilayer crystal analyzer. A correction algorithm similar to classical influence coefficient

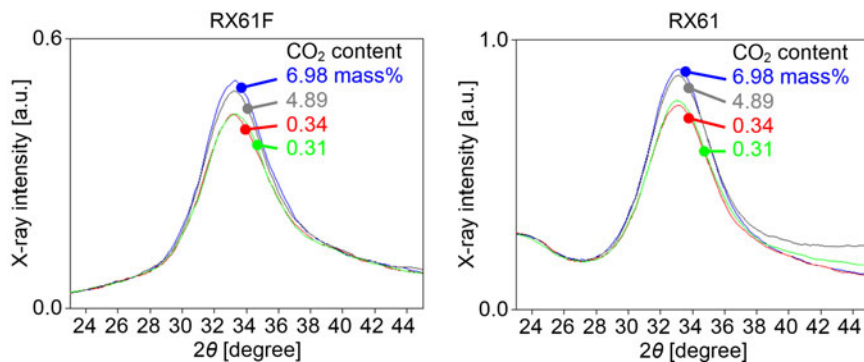


Figure 5. (Color online) $CK\alpha$ peak and BG shapes with RX61F and RX61 multilayer analyzers.

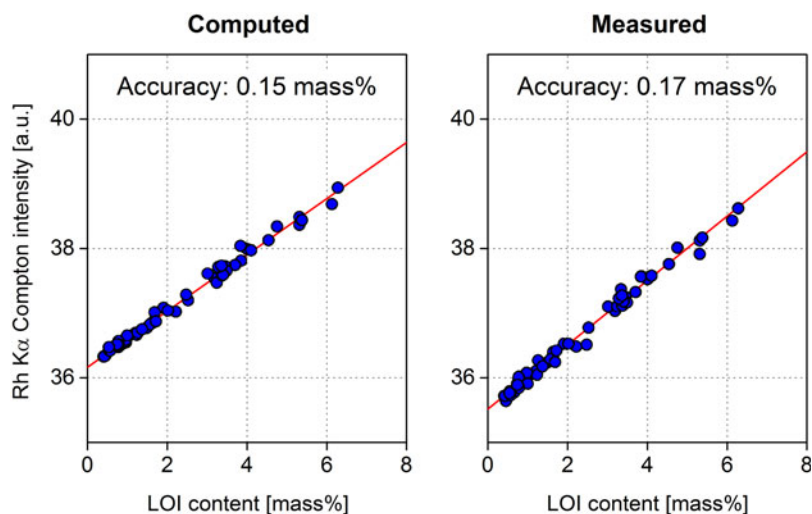


Figure 6. (Color online) Computed and measured calibration curves for LOI.

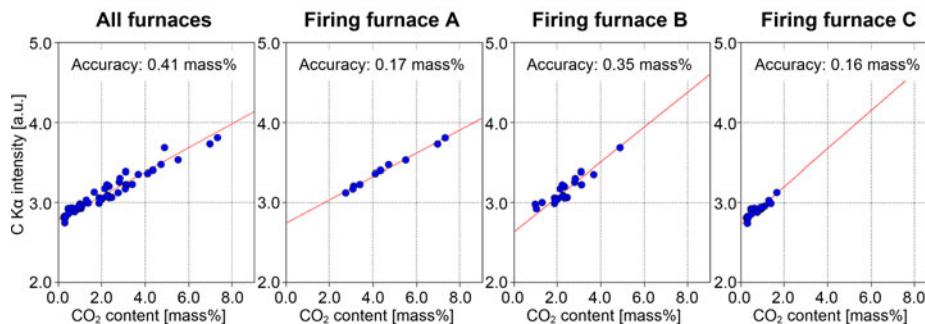


Figure 7. (Color online) Calibration curves for CO_2 for three different furnaces and for all measurements.

approaches accounts for inter-element effects that enhance or reduce the Compton intensities by CO_2 and impurities. The system calibration was carried out by reference samples for LOI and CO_2 measured in compliance with Japanese Industrial Standard JIS R 9011:2006.

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