

MINERALOGICAL ANALYSIS OF WEIPA BAUXITE USING NIR SPECTROSCOPY

Luke McArthur, Colin Greensill

PELM, Central Queensland University, Faculty of Science, Health and Engineering, Rockhampton, Australia, 4701.

Abstract

The mineralogical analysis of bauxite is complicated by the presence of numerous chemically similar minerals. Techniques such as x ray fluorescence and atomic spectroscopy cannot discriminate minerals of similar composition. Analysis by x-ray diffraction is difficult because of the poor crystallinity of mineral structures after grinding. Wet chemical methods can provide accurate determinations but are prohibitively slow and expensive for a large number of samples. Since near infra-red spectroscopy is sensitive to the lattice structure and chemical composition of minerals containing hydrogen groups, it offers an alternative method of analysis with the added benefits of being both rapid and inexpensive. In this work, a laboratory-based near infrared system was developed for the quantification of kaolinite in Weipa bauxite. Kaolinite was quantified to an accuracy of 0.89% m/m (root mean squared error of prediction) for a 9 second measurement. Gibbsite, boehmite, hydrohematite and goethite were also studied and acceptable prediction errors were observed demonstrating the suitability of near infrared spectroscopy for mineralogical analysis of Weipa bauxite.

KEYWORDS: NIRS, Near Infrared, Kaolinite, Mineral, Gibbsite

Introduction

Bauxite is the ore from which alumina is extracted using the Bayer process. Alumina, in turn, is smelted to produce aluminium. Bauxite quality is primarily determined by the concentration of three minerals; kaolinite, gibbsite, and boehmite. The alumina yield is determined by gibbsite and to a lesser extent, boehmite content. Kaolinite is a soluble impurity and must be removed through formation of sodalite which consumes valuable caustic soda. Obviously quantification of bauxite mineralogy is of great value to bauxite mining and alumina refining industries. However, mineralogical determinations are complicated by the numerous minerals of very similar chemical composition which cannot be directly discriminated using techniques such as X-ray fluorescence (XRF) and atomic spectroscopy. X-ray diffraction and wet chemical methods offer accurate measurement for various minerals, but are time consuming, prohibiting large scale routine analysis.

Near infrared spectroscopy (NIRS) offers a rapid and economical alternative for quantitative mineralogical determinations. NIRS utilises the 12 500 – 4 000 cm^{-1} region of the electromagnetic spectrum, residence to the numerous bands arising from vibrational overtones and combinational transitions of OH, CH, NH functional groups (Bakeev, K.A. 2004). The strong dependence of band position to molecular structure and atomic composition suggests that bauxite minerals containing hydroxyl (OH) groups such as kaolinite, gibbsite, boehmite, hydrohematite and goethite should possess a characteristic presence in the near infrared red (NIR) spectrum. The main advantage of NIRS is low absorptivity of NIR radiation. This characteristic permits analysis of solid samples with large path length without the requirement for a costly and sometimes hazardous preparation. NIRS is however a secondary method and due to the inherently poor resolution of NIR spectra, requires careful calibration for quantitative analysis.

Surprisingly, quantitative mineralogical analysis of bauxite using NIRS remains relatively unexplored, or at least undocumented in the public domain. A number of studies have been conducted analysing the spectra of bauxite minerals including kaolinite (Ruan, H.D. et al. 2001; Frost, R.L. et al. 2002; Petit, S. et al. 2004; Carmody, O. et al. 2005), gibbsite and boehmite demonstrating that the NIR spectra of these bauxite minerals were characteristic of the location of hydroxyl groups within the lattice structure. Walker appears to be the first and only researcher to analyse bauxite (Walker, G.S. 1993; Walker, G.S. 1994) and published preliminary work developing quantitative calibration models using the PIMA II portable instrument (Walker, G.S. 1996). Walker developed partial least squares-based (PLS) calibration models for kaolinite, gibbsite, boehmite, hematite, and with corresponding R^2 values of 0.73, 0.87, 0.89 and 0.85, respectively. It is expected that these results could be improved by utilising modern laboratory grade instruments as well as application of new chemometric data treatment prior to PLS calibration.

The aim of this study was to develop a NIR spectroscopic system for quantitative measurement of kaolinite within Weipa bauxites. This study also examined the feasibility of extending analysis to other minerals such as gibbsite, boehmite, hydrohematite and goethite.

Experimental

Sample Sets

Comalco's Centre for Research and Technical Services (CRTS) provided 263 bauxite samples from two different mine sites in the Weipa region. To develop calibrations for kaolinite, gibbsite, boehmite and hydrohematite, samples were divided into a calibration set consisting of 204 samples and a validation set consisting of 59 samples. For goethite calibration, the samples from a single mine site were used since bauxites from the other site did not contain any goethite. The goethite calibration and validation sets contained 98 and 25 samples respectively. The calibration and validation sets had similar and heavily skewed distributions of the mineral contents. A summary of the sample sets is given in Table 1.

Table 1 Summary of the mineral contents for samples within the calibration and validation sets. All contents in %m/m.

MINERAL	CALIBRATION SET N=204				VALIDATION SET N=59			
	MIN	MAX	MEAN	STDEV	MIN	MAX	MEAN	STDEV
Kaolinite	5.9	73.5	16.0	8.3	5.2	53.4	16.1	10.1
Gibbsite	5.3	81.7	46.2	18.4	15.3	73.9	44.7	16.0
Boehmite	-0.1	53.4	19.0	13.9	0.4	51.1	20.1	14.2
Hydrohematite	2.9	25.3	10.7	5.3	3.2	23.9	10.7	4.5
	CALIBRATION SET N=98				VALIDATION SET N=25			
Goethite	0.78	5.05	1.8	0.73	0.8	2.8	1.8	0.52

Weipa bauxites have only two silica bearing minerals; kaolinite and quartz. Kaolinite content was therefore determined through the difference between total silica obtained from XRF and quartz content measured using a gravimetric digestion in hydrofluoric acid. Gibbsite, boehmite, hydrohematite and goethite contents were derived using a propriety Comalco algorithm which receives the XRF, loss on ignition and kaolinite measurements as inputs. Although a more direct reference would be preferable, this method would suffice for a feasibility study.

Bauxite samples were sieved, ground (95% < 75µm), and dried (2hrs at 105°C) in preparation for NIR analysis.

Spectral Acquisition

The NIR Multi-Purpose Analyzer (MPA) (Bruker Optik GmbH, Ettlingen Germany), a Fourier Transform (FT) NIR spectrophotometer, was used in this study. Samples were presented to the MPA using disposable vials in conjunction with sample carousel. The vials, approximately 20 mm outer diameter, were filled with 5 g of sample yielding a sample thickness of 15-20 mm. Spectral measurement was performed over the instruments full range, 12 000 - 3 600 cm⁻¹, (830 – 2780 nm) at 16 cm⁻¹ resolution. Each sample had ten spectra measured, each spectra took approximately 9 s to acquire, being the average of 32 forward and backward scans.

Model Development

Quantitative calibration models were developed using partial least squares (PLS) regression. Model accuracy was assessed using the root mean squared error of prediction (RMSEP) when applied to the independent validation set.

To optimise the calibration models, the best single spectral window was found by iteratively searching all possible windows and developing PLS models based on the autoscaled data. Once the spectral window had been determined, another iterative search was performed to find the best permutation of data treatments. The data treatments trialled included autoscaling (AS), mean centring (MC), first and second order Savitzky Golay derivatives (SG_x where x is the order of differentiation), multiplicative scatter correction (MSC), standard normal variate (SNV) and orthogonal signal correction (OSC_x where x is the number of components to use in the correction).

Software

The manufacturers recommended software, OPUS 5.5 (Bruker Optik GmbH, 2005.), was used to control and interface to the MPA. Data treatment and PLS modelling was performed using Matlab® 7.1 (Mathworks, Inc. 2005) with PLS Toolbox 3.5 (Eigenvector Research, Inc. 2004).

Results

Kaolinite and gibbsite are major constituents in Weipa bauxite and consequently dominate the NIR spectra. Figure 1 illustrates the spectral variation with differing levels of kaolinite and differing levels of gibbsite. Increasing kaolinite content is characterised by increasing absorbance at four dominant peaks located at 7167, 7067, 4527 and 4193cm⁻¹ and a shoulder at 4622cm⁻¹. Increasing levels of gibbsite was characterised primarily by an increase of the large peak at 4404cm⁻¹ accompanied by a finer structure with peaks at 7150, 7058, 6958, 6896, 6842, 6580, and 6456cm⁻¹.

The impact of the remaining minerals of interest; boehmite, goethite and hydrohematite, was difficult to observe visually since they could not be isolated from significant amounts of kaolinite or gibbsite. This observation highlights the requirement for application of chemometric techniques such as PLS for quantitative calibration.

The development of quantitative calibration for kaolinite was successful (RMSEP = 0.89 %). Amongst the data treatments trialled, very few combinations offered improvement over a rudimentary autoscaling treatment. Scatter correction treatments; MSC and SNV, yielded no improvement when applied independently or in conjunction with autoscaling. This indicated that multiplicative type scattering was not a major source of spectral variation. Derivatisation also offered limited improvement, however, when preceded by MSC, or SNV results improved. In general, the best data treatment was orthogonal signal correction which in most cases could be utilised in combination with autoscaled data to both improve calibration performance. Table 2 shows the calibration results for three models. The first model for each data set is the model developed using only autoscaled data, the remaining two provided the best predictive ability.

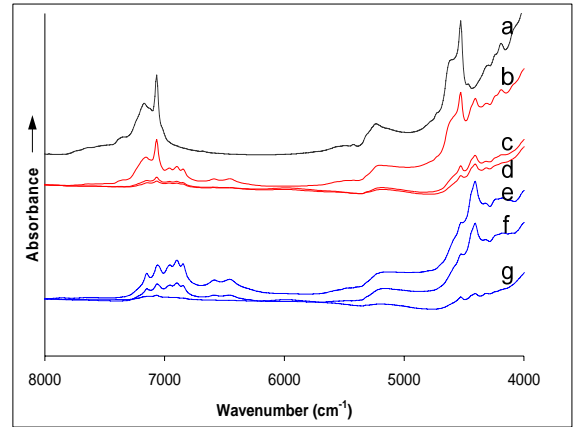


Figure 1 MPA NIR Spectra of
(a) pure kaolinite
(e-g) bauxites with low kaolinite content with high, medium and low gibbsite contents
(b-d) bauxites with high, medium and low kaolinite contents and low gibbsite content.

Spectra are offset for clarity.

Table 2 Calibration results for kaolinite (RMSEP and bias are in %m/m)

System	Treatment	RMSEP	R ²	BIAS
MPA	AS	1.3	0.99	0.48
MPA	SNV, SG2, AS	0.94	0.99	0.14
MPA	AS, OSC2	0.89	0.99	0.22

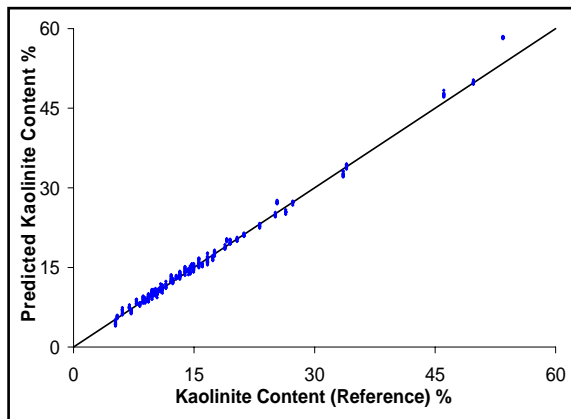


Figure 2 Predicted vs Reference values for the AS, OSC2 Kaolinite model.

Treating the spectral data with the combination of autoscaling followed by two component OSC produced the best PLS calibration model. Under this calibration, the kaolinite content in the validation set was quantified with an accuracy of 0.89 %, significantly better than the other calibrations at a 5 % level of significance (Fearn, T. 1996). Figure 2 shows the system predictions plotted against the reference values for the validation set. For the lower concentrations, predictions were tightly clustered around the ideal predicted = reference line, but residuals increased at larger concentrations. This is not surprising given the skewed nature of the kaolinite distribution within the calibration set. The residual of the high concentration samples could be reduced by addition of more calibration samples in this high concentration range.

Models developed for the other minerals also proved successful, achieving RMSEPs of 1.9, 1.7, 0.9 and 0.11% for gibbsite, boehmite,

hydrohematite, and goethite respectively with corresponding R^2 values greater 0.95 (refer Table 3). The small RMSEP for the goethite calibration (0.11 %) demonstrates the good sensitivity of the NIRS technique even with, in this case, approximately half the prediction error attributed to repeatability of the spectral measurement.

The ratio of the number of samples to the standard deviation of mineral content was much greater for goethite than the other minerals. These statistics of the data sets in this study raised a question about the effect of the relationship between the number of samples and the standard deviation of the set. An analysis of the ratio of number of samples (N), to the standard deviation for the minerals (refer Table 3) revealed a strong correlation to RMSEP ($R^2 = 0.9$). This result suggests that a significant improvement in the accuracy of the calibrations for kaolinite, gibbsite, boehmite and hydrohematite could be achieved by increasing the size of the calibration sets.

Table 3 PLS calibration models developed for remaining minerals. RMSEP in %m/m. The final column contains the ratio of the number of samples relative to the standard deviation of the reference for the calibration set

	Treatment	RMSEP	R^2	N:STDEV
Gibbsite	AS, OSC2	1.9	0.99	11
Boehmite	SNV, MC	1.7	0.98	15
Hydrohematite	AS, OSC2	0.94	0.95	38
Goethite	AS, OSC1	0.11	0.96	134

Conclusions

NIRS has demonstrated good capability for rapid quantification of a variety of minerals in Weipa bauxites. The system, based on a MPA FTNIR instrument, quantified kaolinite in the Weipa bauxites to an accuracy of approximately 0.89 %m/m in a 9 s measurement.

Gibbsite, boehmite and hydrohematite and goethite contents were successfully calibrated against the reference with accuracies of 1.8, 1.7, 0.9 and 0.11 %m/m respectively using the same system. Although reference values were obtained using a secondary reference method, the calibrations models developed for these minerals gave low RMSEPs and near unity R. These results clearly demonstrate that NIRS is capable of accurately quantifying of these minerals in addition to kaolinite.

Acknowledgements

Acknowledgement and thanks are extended to Comalco CRTS for financial support of the project in addition to providing bauxite samples and reference analyses. Many thanks are also given to Analytical Technologies division of Biolab for organising access to the MPA instrument.

References

- Bakeev, K. A. (2004). Near Infrared Spectroscopy as a Process Analytical Tool Part I: Laboratory Applications. *Spectroscopy* **18**(11): 32 - 35.
- Carmody, O., J. Kristof, et al. (2005). A spectroscopic study of mechanochemically activated kaolinite with the aid of chemometrics. *Journal of Colloid and Interface Science* **287**(1): 43-56.
- Fearn, T. (1996). Comparing standard deviations. *NIR news* **7**(5): 5-6.
- Frost, R. L., E. Mako, et al. (2002). Modification of kaolinite surfaces through mechanochemical treatment - a mid-IR and near-IR spectroscopic study. *Spectrochimica Acta Part A* **58**(13): 2849-2859.
- Petit, S., A. Decarreau, et al. (2004). Refined relationship between the position of the fundamental OH stretching and the first overtones for clays. *Physics and Chemistry of Minerals*, **31**(9): 585 - 592.
- Ruan, H. D., R. L. Frost, et al. (2001). Application of Near-Infrared spectroscopy to the study of Alumina phases. *Applied Spectroscopy* **55**(2): 190 - 196.
- Walker, G. S. (1993). VIS-NIR and MIR Analysis of Selected Minerals and Bauxite Pisoliths. In "ICAM '93 Proceedings", *Proc. International Congress on Applied Mineralogy*. p238-241. CSIRO W.A. Laboratories, Fremantle, Australia.
- Walker, G. S. (1994). Near Infrared Analysis as a means of Characterising Selected Minerals and Bauxite Pisoliths. In "Leaping Ahead With Near Infrared Spectroscopy", *Proc. 6th International Conference on NIR Spectroscopy*. p12-18. Near Infrared Spectroscopy Group, Lorne, Australia.
- Walker, G. S. (1996). Use of Near Infrared For the Quantitative Analysis of Minerals. *Applied Mineralogy*.