

# DETERMINATION OF QUARTZ CONCENTRATIONS IN BAUXITE VIA HF-FREE ACID DIGEST AND DIFFERENTIAL SCANNING CALORIMETRY

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## ABSTRACT

Quartz concentrations in bauxite contribute to process soda and alumina losses via binding with the mineral residue in red mud. Queensland Alumina Limited plant samples were historically analysed for quartz using a multi-stage wet chemistry digestion method that included several additions of hydrofluoric acid to clarify the final quartz product. Continual safety concerns with the handling and management of hydrofluoric acid led to the development of an alternative method to determine quartz concentrations in bauxite and red mud via differential scanning calorimetry (DSC).

Natural quartz in bauxite and mud undergoes an alpha/beta phase transformation in the region of 560 – 575°C, however the DSC thermogram is generally difficult to see in a raw bauxite sample due to the much larger boehmite peak at 510 – 540°C. A digestion method was developed to concentrate the quartz content so it was suitable for DSC scanning.

Samples were digested in a heated mixed acid solution, filtered, charred and then ignited. DSC analysis of the digest residue could then successfully resolve the quartz peak, where it was compared to known standard calibration curve, and back calculated to give percentage of quartz in bauxite and mud.

## 1. INTRODUCTION

The quartz content of bauxite and red mud is a key contributor to sodium hydroxide losses in the Bayer process. Approximately 25% of the quartz content in typical Weipa monohydrate bauxites dissolves under high temperature digestion conditions, known as quartz attack. Trihydrate bauxite is subject to less stringent plant digestion conditions and hence lessened quartz attack. At Queensland Alumina Limited (QAL), determination of the quartz concentration of the bauxite and last washer underflow is undertaken on a monthly basis by wet chemistry. Results are used to determine the amount of sodium hydroxide and alumina lost from the process through binding with “quartz phase” silica in red mud.

Wet chemistry methods for the determination of quartz in bauxite are well documented. These use either the difference of total silicon dioxide and Si left after a 150°C bauxite digestion, or alternatively the method QAL uses, acid digestion and a series of weighing steps to determine the percentage quartz from a mix of impure silica components, and then back calculated to determine percentage quartz in bauxite (Feret, Roy, 2001).

An integral part of QAL’s quartz determination is the use of concentrated hydrofluoric acid

(HF) to clarify the final quartz product and dissolve the amorphous silica component. Hydrofluoric acid is a corrosive and acutely toxic chemical. 70% hydrofluoric acid can penetrate tissue within two to three minutes and as little as 2% body burns can be fatal. The burn site must be flushed with water, then hexafluorine or calcium gluconate gel to neutralise the effects of the fluoride (Lawson, 2001).

An onsite hazardous substances risk assessment identified the difficulties in using hydrofluoric acid, and suggested that QAL investigate a HF-free method for quartz determination. Rio Tinto Gove, Weipa and Yarwun use empirical calculation techniques for quartz determination, and Arvida use Rietveld XRD determination (Feret, Roy, 2001). Due to difficulties accessing these methods a literature search was conducted and it was found that quartz in bauxite is detectable by Differential Scanning Calorimetry (DSC) (Wehrli, Kane, 1993), and quartz determination in coal is periodically conducted using DSC (Mayoral, et. al. 2001).

This paper reports a method of determining quartz concentration via differential scanning calorimetry, without the use of hydrofluoric acid in the digestion process.

## 2. METHOD

Power compensated DSC is a routinely used method for the determination of uncalcined gibbsite in product alumina. It has many benefits for Bayer mineral analysis as its milliwatts measurement analysis technique is equivalent to the varying thermal behaviour of process samples and can provide true energy measurements of peak areas for gibbsite, boehmite, goethite, diaspore, kaolin and quartz (Buckman, 1990).

### 2.1 Quartz Peak Detection

As previously reported (Wehrli, Kane, 1993), quartz in bauxite and mud is detectable via DSC as an alpha/beta phase transformation in the temperature range of 560 - 575°C, however this coincides with the boehmite in bauxite dehydroxylation peak at 510 – 540°C. In Weipa bauxites the quartz concentration is typically 0.8 – 1.4 % against typical boehmite concentrations of 10%, causing the boehmite peak to hide the quartz peak on a DSC scan. The acid digest method, used in typical wet chemistry quartz analysis to remove the alumina and iron containing minerals and concentrate up the silica components, has been adapted here to improve the quartz peak resolution by removing the boehmite component.

### 2.2 Sample Preparation

Subsamples of the daily ground bauxite and last washer underflow muds were collected for monthly composites. These were well mixed, and 20g subsamples were taken and dried at 105°C.  $1.2\text{g} \pm 0.1\text{g}$  of each composite was weighed into a beaker and digested on a hotplate with 50mL of a mixed acid solution and 10mL of concentrated nitric acid. The mixed acid solution consisted of concentrated sulphuric acid diluted by 50% with deionised water, and concentrated hydrochloric acid. These were mixed in a 70:30 ratio.

The slurry mix was then reduced on the hot plate until 2 to 3mL of slurry remained, known as the post acid digest. After reduction, each sample was rehydrated with 145mL of hot deionised water and 5mL of concentrated hydrochloric acid to dissolve the soluble salts.

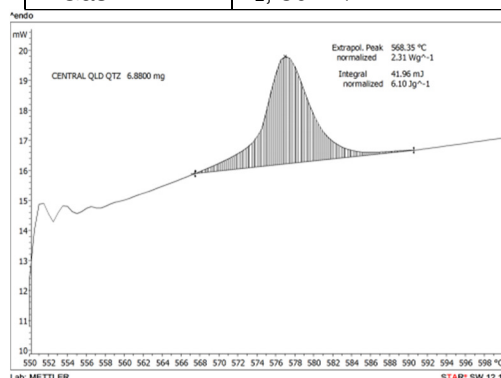
Samples were filtered and the solids and paper were added to pre-weighed platinum crucibles, then heated in a 300°C oven for several hours. The samples were finally combusted at 1050°C for 60 minutes to recover the solid residue, and the cooled crucibles with residue were reweighed.

## 2.3 Differential Scanning Calorimetry Analysis Method

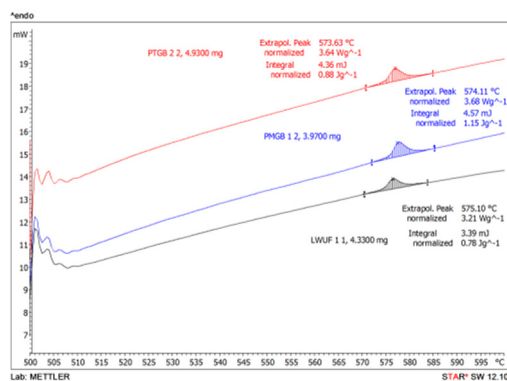
The DSC analysis method was established with the parameters shown in Table 1. The parameters were fine-tuned by repeated scans of a quartz sample obtained from a Central Queensland quarry, x-ray fluorescence (XRF) analysis showed it had a  $\text{SiO}_2$  content of 98.36%, with  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  contributing as minor components (0.82% and 0.64% respectively). This fine-tuning ensured the peak width of the samples would fit within the analysis window, as seen in Figure 1. Example scans of digested red mud (LWUF), digested monohydrate (MGB) and digested trihydrate (TGB) bauxites are shown in Figure 2.

**Table 1. DSC analysis method parameters**

Crucible	Aluminium Standard 40 $\mu\text{L}$
Sample range	2 – 7 mg
Segment 1	
- Temperature	Isothermic – 25 – 500°C
- Duration	2 min
- Gas	N <sub>2</sub> , 30mL/min
Segment 2	
- Start temp	500°C
- End temp	600°C
- Heating rate	30°C/min
- Gas	N <sub>2</sub> , 30mL/min



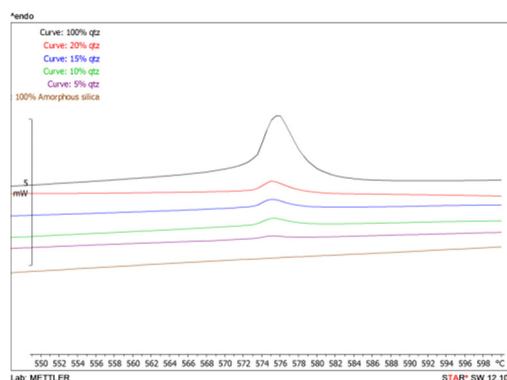
**Figure 1. DSC peak of Central Queensland quartz sample.**



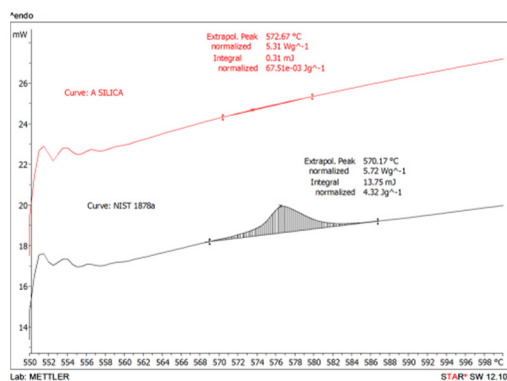
**Figure 2. DSC peaks of digested MGB, TGB and LWUF samples**

## 2.4 Preparation of Calibration Standards

Initially, the DSC calibration standards were prepared by mixing via a mortar and pestle the ground and dried Central Queensland quartz with a synthetic amorphous silicon dioxide form called precipitated silica (CAS 7631-86-9) in ratios of 5, 10, 15 and 20% by weight, shown in Figure 3. This was very time consuming, so after the purchase of a new Mettler Toledo DSC1 in 2015 an alternate method was developed that used a two point calibration with precipitated silica as a 0% standard and a 93.7% standard using National Institute of Standards and Technology (NIST) *Standard Reference Material 1878a Respirable Alpha Quartz*, certified as 93.7% ± 0.21% (crystalline α-quartz) as a substitute (Kaiser, Watters, 2005), shown in Figure 4. This is similar to the two point calibration method used for gibbsite in alumina determination via DSC.



**Figure 3. Original Calibration Standards**



**Figure 4. Two Point Calibration Standards**

## 2.5 Formulae

A flow chart of the full method is shown in Figure 5. The sample preparation method and DSC calibration yield two equations, seen below:

$$\% \text{ Quartz in acid digest residue} = \frac{(J / g \text{ quartz} [DSC] - C)}{m} \quad (1)$$

(Calibration curve required)

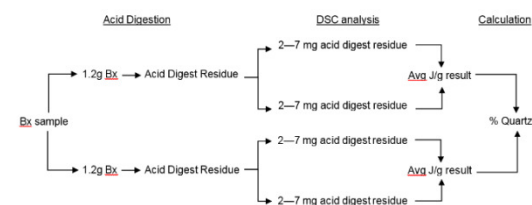
$$\% \text{ Quartz in bauxite} = \bar{x} (\% \text{ quartz in acid digest residue}) \times \frac{(M3 - M2)}{(M1)} \quad (2)$$

Substituting into equation 2 yields:

$$\% \text{ Quartz in bauxite} = \bar{x} \left( \frac{(J / g \text{ quartz} [DSC] - C)}{m} \right) \times \frac{(M3 - M2)}{(M1)} \quad (3)$$

Where

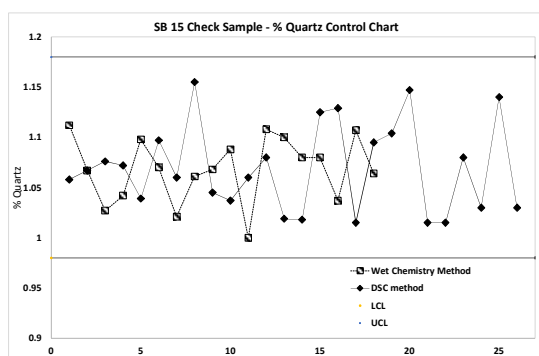
- $M1$  = Mass of bauxite sample
- $M2$  = Mass of platinum crucible
- $M3$  = Mass of acid residue and platinum crucible
- $m, C$  = gradient and Y intercept of DSC calibration line



**Figure 5. Method Flow Chart**

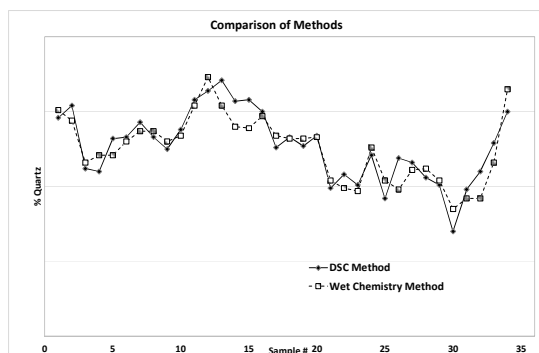
### 3. RESULTS AND DISCUSSION

Rio Tinto bauxite check sample SB15 was used to verify the precision of the method. 40 samples of SB15 were analysed and  $3\sigma$  method precision determined as  $1.10\% \pm 0.23\%$ , against historical wet chemistry values of  $1.07\% \pm 0.10\%$ . In 2014 the method was introduced into routine laboratory analysis. Review of the check sample data collected since method introduction has shown that it is averaging  $1.07\% \pm 0.13\%$ , closer to the historical wet chemistry method (Figure 6).

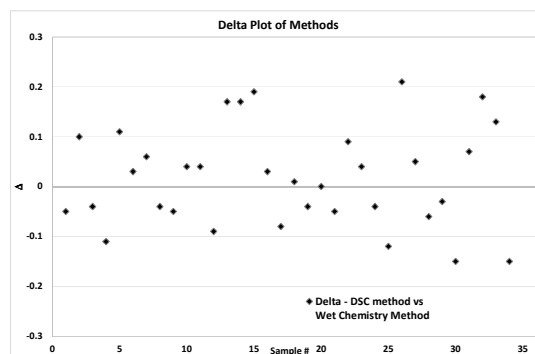


**Figure 6. SB15 % Quartz in Bauxite Control Chart**

Midway through 2015, erroneous check sample data appeared and the method briefly reverted back to the wet chemistry method due to customer concerns. An incident investigation revealed that the ceramic DSC sensor had rotated, a common analytical problem that can cause lower than expected results. The sensor was realigned and an indium and zinc temperature calibration completed. Check sample results returned to normal and the method was reinstated. To ensure future reliability of results indium and zinc calibrations are now completed prior to each monthly quartz analysis.

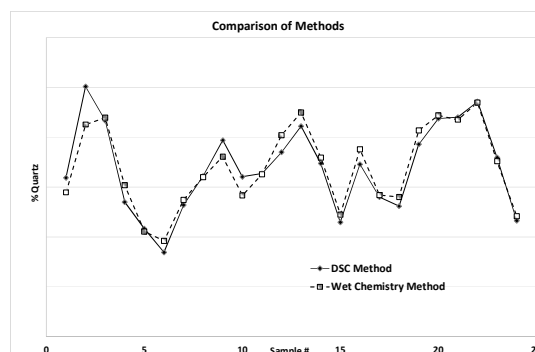


**Figure 7. Bauxite - Comparison of DSC and Wet Chemistry Methods**

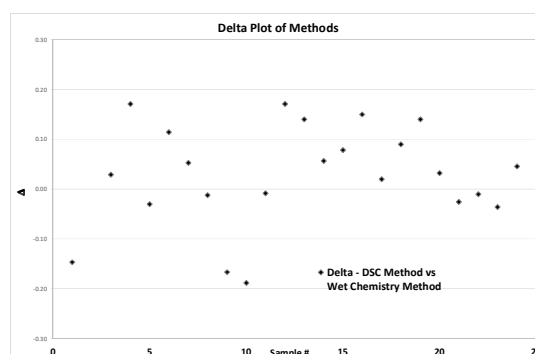


**Figure 8. Bauxite - Delta Plot of DSC and Wet Chemistry Methods**

Historical bauxite samples were analysed during method commissioning, shown in Figures 7 and 8. The DSC method correlates well with the Wet Chemistry method, showing an average quartz concentration delta of 0.02% with a standard deviation of 0.23%, and 0.22% for the DSC and wet chemistry method respectively.



**Figure 9. Red Mud - Comparison of DSC and Wet Chemistry Methods**



**Figure 10. Red Mud - Delta Plot of DSC and Wet Chemistry Methods**

Historical red mud samples were also analysed, shown in Figures 9 and 10. The DSC method again showed good correlation with the Wet Chemistry method, with an average quartz concentration delta of 0.01% and a standard deviation of 0.44% and 0.41% for the DSC and wet chemistry method respectively.

Further analysis of SB15 and historical quartz composites over time have shown that the DSC method is generally 0.01 to 0.03% higher than the wet chemistry method, reflecting the values seen in Figures 6 to 10. It has been theorised that the addition of hydrofluoric acid for the final wet chemistry clarification dissolves some quartz with the amorphous silica component, however this has proven difficult to validate.

Mayoral M.C., Izquierdo M.T., Andres J.M., Rubio B., 2000, Aluminosilicates transformations in combustion followed by DSC, *Thermochimica Acta* Vol 373 Issue 2, 173-180. [https://doi.org/10.1016/S0040-6031\(01\)00459-2](https://doi.org/10.1016/S0040-6031(01)00459-2)

Wehrli, J.T. and Kane, A.R., 1993, Application of Differential Scanning Calorimetry for Characterisation of Bayer Process Solids, *Light Metals* 1993, 175-184.

#### 4. CONCLUSIONS AND FURTHER WORK

A method for determining quartz concentrations in bauxite and red mud by DSC has been successfully developed and achieves the core aim of removing hydrofluoric acid from the determination process while keeping the integrity of the original wet chemistry method intact. The method has been implemented by QAL for routine analysis of monthly bauxite and red mud composites.

There is room for further method improvements via microwave sample digestion and filtration to quicken or remove the time-consuming evaporation step, and also through the commercial production of DSC standards utilising quartz and a thermally inert mineral such as precipitated silica or alpha alumina that would allow the method to be utilised in a variety of industries.

The standard development has shown that the method is flexible and can potentially be adapted to other industries interested in measuring quartz concentrations in minerals without using HF.

#### 5. REFERENCES

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