Measurement of Fluorine Content in Alumina Application Note 21

Summary

- Fast, accurate and repeatable
- No sample preparation
- Simple linear calibration
- Easiest, most reliable technique available; suitable for unskilled personnel

Application

Aluminium is produced by electrolytic reduction of alumina (Al_2O_3) in molten cryolite (Na_3AlF_6) to which aluminium fluoride (AlF_3) has been added to further reduce the melting point. This process results in the emission of fluorine compounds, either as gases (mainly hydrogen fluoride) or dust, which is absorbed by alumina filters in a dry-scrubbing system. Once the alumina filters are saturated they are returned to the electrolytic process, together with aluminium fluoride, to replace lost fluorine.

Thus samples of secondary (fluorinated) alumina are regularly analysed for fluorine content, to monitor the emissions from the manufacturing process. It is also important to measure the fluorine content, or purity, of the aluminium fluoride which is added to the smelter bath to control the efficiency of the process.

Advantages of NMR

Current wet chemical methods for fluorine determination are time-consuming operations, require skilled chemists and involve the use of potentially hazardous chemicals which require disposal, all of which contribute to the cost of the analysis.

The **MQC** benchtop Nuclear Magnetic Resonance (NMR) analyser offers a simple, non-destructive and rapid method for the measurement of fluorine in alumina (and aluminium fluoride). This method may be used for routine analysis in a production environment without any requirement for additional chemicals or specialist operator training.

Method

The analytical technique is based on direct measurement of the Nuclear Magnetic Resonance (NMR) signal of fluorine-19 which has 100% natural abundance. The acquired NMR signal is normalised by the sample mass and then the fluorine content (weight-%) is calculated using an appropriate calibration curve.

Calibration

It is possible to calibrate the **MQC** using only two samples if the reference values are known to be accurate. However, initially it is recommended that the instrument is calibrated by 3-6, preferably more, standards with known fluorine contents evenly spread over the range of interest. NMR is a comparative technique therefore cannot be more accurate than the reference technique against which it is being compared; error is reduced by analysing more reference samples.

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Figures 1 and 2 show calibrations for secondary alumina and aluminium fluoride; the latter can be used to check its purity (theoretically fluorine content should be 67.87%).

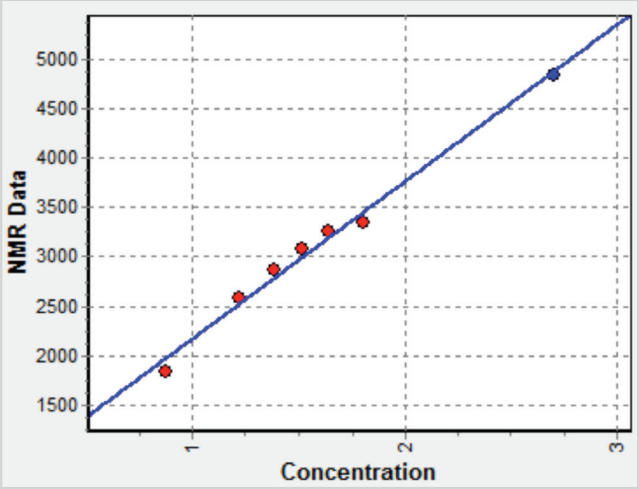

Figure 1: *NMR calibration for fluorine in secondary alumina*

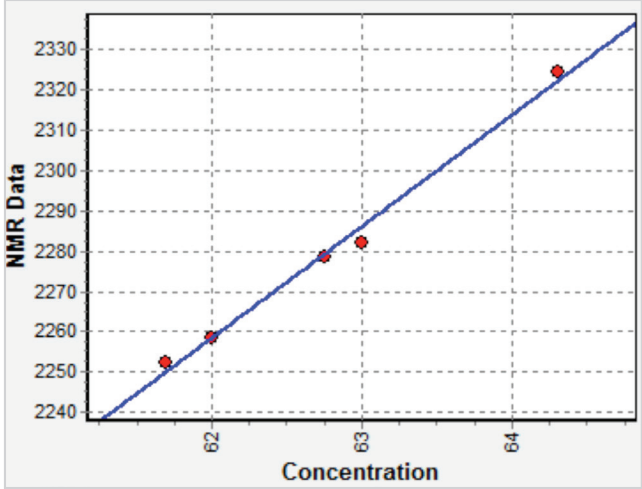

Figure 2: *NMR calibration for fluorine in aluminium fluoride*

Measurement

A tared sample tube is filled to a given height with the powder sample, then weighed prior to NMR analysis. The samples may be conditioned at 40°C for better repeatability. Measurement time is 80 seconds per sample.

Results

Tables 1 and 2 show a good correspondence between the predicted NMR, and given reference values.

Sample ID	Given %F (wt.-%)	Predicted %F (wt.-%)	Difference (wt.-%)
SECAL-1	0.88	0.79	-0.09
SECAL-2	1.39	1.44	+0.05
SECAL-4	1.81	1.74	-0.07
SECAL-5	1.64	1.68	+0.04
SECAL-10	1.52	1.57	+0.05
SECAL-11	1.22	1.26	+0.04
SECAL-15	2.70	2.68	-0.02

Table 1: *NMR results predicted for secondary alumina calibration samples*

Sample ID	Given %F (wt.-%)	Predicted %F (wt.-%)	Difference (wt.-%)
ALF-01	62.00	62.01	+0.01
ALF-02	63.00	62.85	-0.15
ALF-03	64.30	64.38	+0.08
ALF-E2	62.75	62.73	-0.02
ALF-E3	61.70	61.78	+0.08

Table 2: *NMR results predicted for aluminium fluoride calibration samples*

Conclusion

- A primary calibration can cover a concentration range from 0 to 100%
- NMR is very stable over the long term and rarely needs calibration adjustment
- NMR is insensitive to the air voids between grains of powder
- Measurement precision is good compared to wet chemical methods
- Sample measurement time is rapid
- The NMR technique is non-destructive so the same sample may be measured several times before being analysed by other techniques

Complete Package

Oxford Instruments offers a package especially tailored to the measurement of fluorine in alumina.

- Oxford Instruments **MQC**F NMR Analyser
  - 0.55 Tesla (22 MHz) high homogeneity magnet
  - Probe for 26 mm diameter sample tubes (14 ml sample volume)
  - Integrated system controller (no external PC required)
  - Integrated flat-screen display
- **MultiQuant** software including **RI Calibration**, **RI Analysis**, and the **EasyCal** 'Fluorine in Alumina' application which guides the user through the calibration and analysis procedures
- Test/tuning samples
- Glass tubes
- User manual
- Method sheet

Optional items are:

- A precision balance
- A dry heater and aluminium block with holes for sample conditioning at 40°C (optional)

visit **www.oxford-instruments.com/mqc** for more information or email: **industrial@oxinst.com**

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