Measurement of Calcium Fluoride Content in Fluorspar

Application Note 20

Summary

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

Application

The mineral fluorspar (or fluorite) is the most important source of fluorine. The purity (calcium fluoride content) of the mineral will determine its eventual use in the steel, aluminium or chemical industries. The highest grade is used to produce hydrogen fluoride which is a precursor to many important compounds including pharmaceuticals and polymers, e.g. polytetrafluoroethylene (PTFE), known by the commercial name of Teflon. It is therefore important to determine the fluorine content of fluorspar for commercial and quality control purposes.

Advantages of NMR

Conventional wet chemical methods of calcium fluoride (CaF_2) determination include measurement of fluoride by ion selective electrode or ion chromatography, and calcium by complexometric titrimetry (ASTM E815). All of these methods 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 measurement of fluorine in fluorspar which may be used for routine analysis in a production environment without any requirement for additional chemicals and 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. It is assumed that the measured NMR response is linearly proportional to the CaF_2-content of a material. The acquired NMR signal is normalised by the sample mass and then the CaF_2 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 CaF_2 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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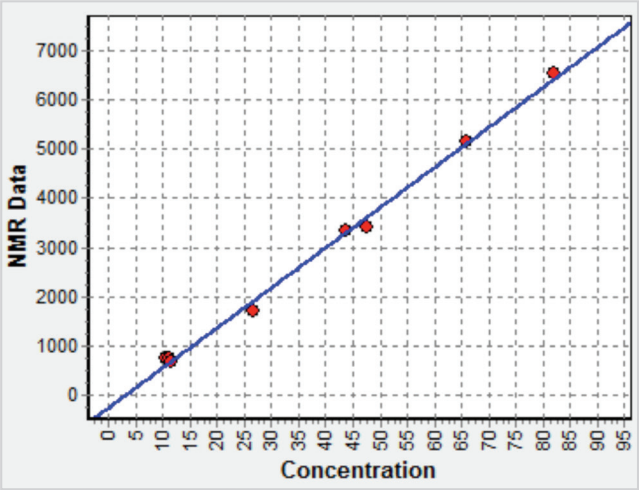
Figure 1: NMR calibration for calcium fluoride in fluorspar



Measurement

A tared sample tube is filled to a given height with the powder sample, then weighed prior to NMR analysis. Measurement time is 80 seconds per sample.

Results

Table 1 shows a comparison of the predicted NMR values against the given reference values. Deviations can be accounted for by error in the reference values as well as fluorine from sources other than calcium fluoride contributing to the NMR signal.

Table 2 shows that the repeatability (or precision) of the NMR measurement of the same sample is excellent.

Table 1: NMR results predicted for calibration samples

Sample ID	Given %CaF_2 (wt.-%)	Predicted %CaF_2 (wt.-%)	Difference %CaF_2 (wt.-%)
FG1	81.9	83.5	+1.6
FG2	66.0	66.3	+0.3
FG3	11.3	12.6	+1.3
FG4	26.8	24.2	-2.6
FG5	47.7	45.1	-2.6
FG6	11.6	11.6	+0.0
FG7	10.7	12.5	+1.8
FG8	43.8	44.1	+0.3

Table 2: Measurement repeatability of the same fluorspar sample

Repeat	Measured CaF_2 content, %
1	37.1
2	37.0
3	37.3
4	37.1
5	37.2
6	37.0
7	37.0
8	37.1
9	37.2
10	37.0
Mean %	37.1
Std. Dev. %	0.1

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 fluorspar.

- 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 Fluorspar' 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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