Quantitative chemical and phase analysis of fluorspar using wavelength dispersive X-Ray fluorescence (WDXRF) and X-Ray diffraction (XRD)

Authors: Ratnesh Panday, Laboratory Manager
Abhijit Sen, Application Manager

Introduction

Fluorspar, the industrial term for the mineral calcium fluorite (CaF_2), is a critical raw material and the primary source of fluorine for various chemical and metallurgical industries. Fluorspar is extensively consumed in the production of hydrofluoric acid, aluminium fluoride, cryolite, and as a flux in iron and steelmaking, cement, glass, and ceramic industries. Commercial fluorspar is classified into acid grade (>97% CaF_2) and sub-acid grades (70-80% CaF_2), including metallurgical (80-90% CaF_2), and ceramic grades (85-95% CaF_2), based on CaF_2 content and impurity levels.

However, the utilization efficiency of fluorspar can rapidly change due to significant variations in mineralogy, gangue phases, and trace-element chemistry. In today's fast paced industry, a quick and accurate chemical and mineralogical characterization of fluorspar is essential for grade evaluation, process control, and end-use performance assessment.

Instrument and method

WDXRF

The Thermo Scientific™ ARL PERFORM'X™ Series Spectrometer used in this analysis is configured with four collimators, a nine-position crystal changer, two detectors, helium purge and the 5GN+ Rh X-ray tube for the best performance from ultra-light to heaviest elements. The ARL PERFORM'X spectrometer offers advanced LoVap technology in its X-ray tube. The gearless goniometer with dual sample loading operates at fast slew speed caters excitation of different elements as per user curated methodologies with speed, flexibility and reliability. Ease of operation is obtained through the innovative Thermo Scientific™ OXSAS™ XRF Analysis Software.

XRD

The Thermo Scientific™ ARL™ X'TRA Companion XRD is a simple, easy-to-use benchtop instrument for routine phase analysis as well as more advanced applications. The ARL X'TRA Companion XRD uses a θ/θ goniometer (160 mm radius) in Bragg-Brentano geometry coupled with a 600 W X-ray source (Cu or Co). The radial and axial collimation of the beam is controlled by divergence and Soller slits, while air scattering is reduced by a variable beam knife. An integrated water chiller is available as an option. Thanks to the innovative solid-state pixel detector (55 x 55 µm pitch), the ARL X'TRA Companion XRD provides very fast data collection and comes with one-click Rietveld quantification capabilities and automated result transmission to a LIMS (Laboratory Information Management System).

XRF analysis software

The Thermo Scientific™ UniQuant™ Software represents a ground-breaking solution for standardless semi-quantitative to quantitative XRF analysis. It can analyse elements from fluorine (F) to americium (Am), including their oxide compounds, in a wide array of diverse samples. UniQuant software allows users to input a basic form of priori knowledge about the sample, e.g. sample weight, binder percentage etc. This flexibility ensures accurate calculations and reporting tailored to the specific characteristics of each sample.

Sample and experiment

Two fluorspar process samples were prepared in pressed pellet form using cellulose as binder. Loss on ignition measurement was carried out by heating the sample in electric muffle furnace at 950 °C for 2 hours. The XRF analysis was carried out using an ARL PERFORM'X 4200 W spectrometer equipped with the UniQuant standardless analysis method. Powder XRD data were collected of pristine samples using an ARL X'TRA Companion X-ray diffractometer in reflection geometry, employing a continuous 1D scan with a total acquisition time of 5 minutes. Phase identification and quantitative phase analysis were performed using Profex software, based on the BGMN Rietveld refinement algorithm and applying a fundamental parameters approach.

Table 1. WDXRF analysis result of fluorspar samples

Element	Sample 1		Sample 2	
	Element wt%	Std err %	Element wt%	Std err %
Ca	48.81	0.25	47.98	0.25
F	43.87	0.25	44.06	0.25
Si	1.61	0.06	0.71	0.03
Al	0.32	0.02	0.18	0.007
Na	0.11	0.01	0.07	0.02
Fe	0.16	0.007	4.00	0.10
Mg	0.08	0.005	0.031	0.006
S	0.05	0.002	0.008	0.0006
P	0.04	0.002	0.016	0.0008
LOI	4.69		2.49	
SUM	99.74		99.55	
Calculated fluorite (CaF2)	90.14		90.54	

Table 2. Fluorspar samples powder XRD phase analysis result

Element	Sample 1		Sample 2	
	Wt%	Std err %	Wt%	Std err %
Fluorite	90.00	0.20	90.40	0.20
Calcite	7.10	0.20	2.00	0.10
Hematite	0.02	0.02	4.65	0.05
Quartz	2.94	0.07	2.90	0.20

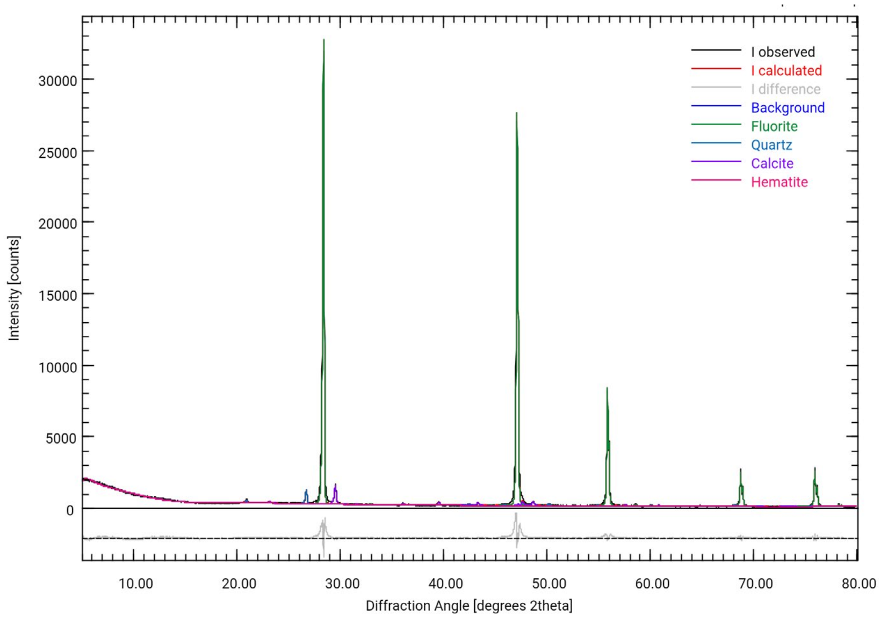

Figure 1: Sample 1 - Rietveld refinement diffractogram

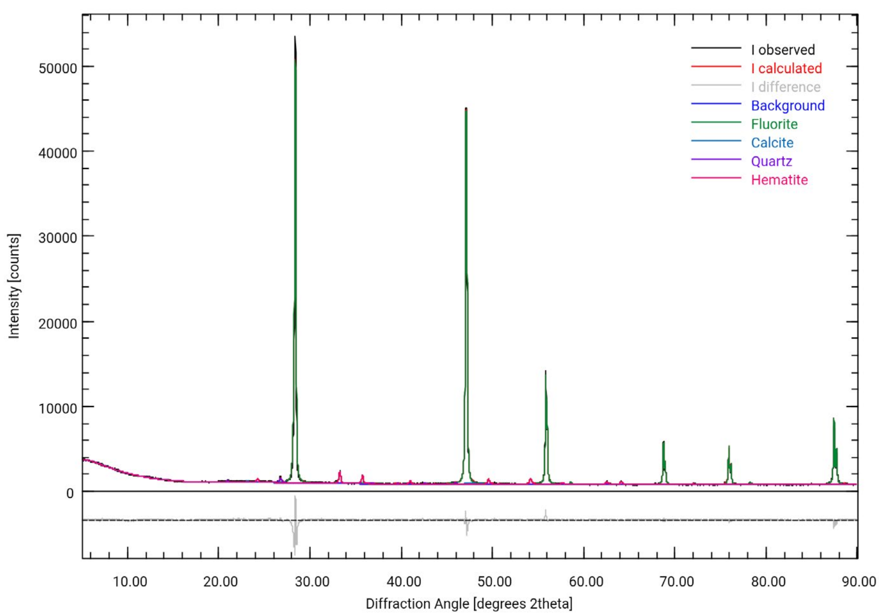

Figure 2: Sample 2 - Rietveld refinement diffractogram

Result discussion

The chemical analysis results demonstrate excellent agreement with the phase quantification obtained by powder X-ray diffraction. XRF analysis indicates that the fluorite content, calculated from the measured fluorine (F) concentration, is 90.14% for Sample-1 and 90.54% for Sample-2. These values are in close alignment with the fluorite phase fractions determined by XRD, which are approximately 90% for Sample-1 and 90.54% for Sample-2. In addition, the minor elemental constituents identified by XRF, namely Fe, Si, and Ca correlate directly with the crystalline phases detected by XRD, specifically hematite (Fe_2O_3), quartz (SiO_2), and calcite ($CaCO_3$), respectively.

This strong concordance between elemental composition and phase composition demonstrates excellent resonance between the performances of the ARL PERFORM'X WDXRF spectrometer and the ARL XTR'A Companion advanced powder X-ray diffractometer. The work also demonstrates that the combinatorial XRF-XRD analytical approach can portray complete evaluation of fluorspar.

Conclusion

The ARL PERFORM'X WDXRF spectrometer and the ARL XTR'A Companion X-ray diffractometer can perform fluorspar analysis at high speed and excellent accuracy. The close agreement between chemically calculated fluorite from XRF and Rietveld-refined fluorite from XRD highlights the robustness of both techniques. Depending on analytical objectives, either technique can be applied independently—XRF for fast chemical grading and XRD for mineralogical validation—or they can be used together for comprehensive characterization.