

Quantitative analysis of the mineral phases carnallite and kieserite in potassium salts by NIR

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Introduction

Near Infrared (NIR) spectroscopy is a powerful analytical technique with a wide array of applications in many industrial fields. It is being used more and more in process analysis, because of its speed and because it requires no or only little sample treatment.

K+S is one of the world-wide leading suppliers of potash and magnesium products, which find a wide range of applications as fertilizers, as well as industrial products. The K+S group runs six mines from which the raw materials potash and magnesium are extracted. Since only 20 to 45% of the salt taken from the mine can actually be used, the crude ore material must undergo a series of separation and enrichment processes before the product is available. The three methods at our disposal are the hot dissolution, the flotation and the electrostatic (ESTA[®]) processes.¹⁻³ For these separation and enrichment processes a rapid and reliable determination of the raw salt composition is indispensable. Carnallite and kieserite are important mineral components in the potash deposits.

Experimental

Instrumentation

All NIR spectra were recorded by a FT-NIR spectrometer⁴ (Bruker Model Matrix E, Figure 1). This spectrometer consists of three major components: the data system, the optics module and the remission module. The remission module is equipped with four light sources, which focus the light through a protective window onto the sample outside the spectrometer. This enables a contactless, continuous measurement of raw material over a conveyor belt in the production line. After interacting with the sample, the diffusely scattered light returns to the remission module and is

Table 1 Measurement parameter

Spectrometer <i>Matrix E</i>	
Resolution	8 cm ⁻¹
Sample scan time	32 scans
Background scan time	32 scans
Detector	InGaAs
Result spectrum	Absorbance

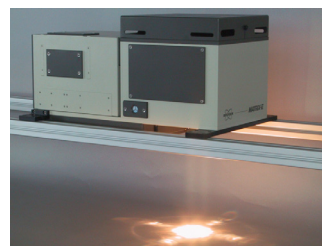


Figure 1 Process FT-NIR Spectrometer Matrix E

directed for modulation into the interferometer and then to the detector of the optics compartment. The spectra consisted of 32 scans in the range of 12000 to 4000 cm^{-1} at a resolution of 8 cm^{-1} . The spectrometer is equipped with a InGaAs detector.

Software

OPUS version 3 (Bruker Optik GmbH, 76275 Ettlingen, Germany) is used for the instrument control, the spectral measurements and also for the chemometrics analysis.

Calibration Samples

175 samples from the industrial production of fertilizers were collected. The elemental analysis of these samples was performed using ICP. The mineral phases were calculated from the sodium, potassium, magnesium, calcium, sulfate and chloride values. In addition the mineralogical structure of the phases were examined by methods based on density differences.

Results and discussion

Spectra and calibration models

Calibration in Laboratory

Some measured spectra of raw salts with different contents of carnallite and kieserite are shown in Figure 2, along with those of pure carnallite and kieserite. The calibration models (Figure 3 and 4) were performed by using the Partial Least Squares (PLS) method built into the OPUS-software. A summary of the statistical accuracy of the calibration models for both components (Table 2) show that the next step of going to an online analysis is feasible.

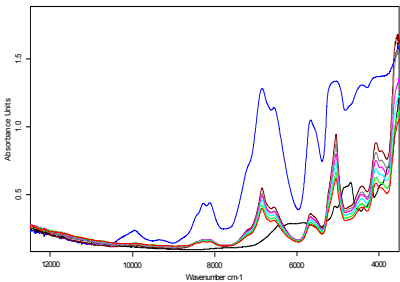
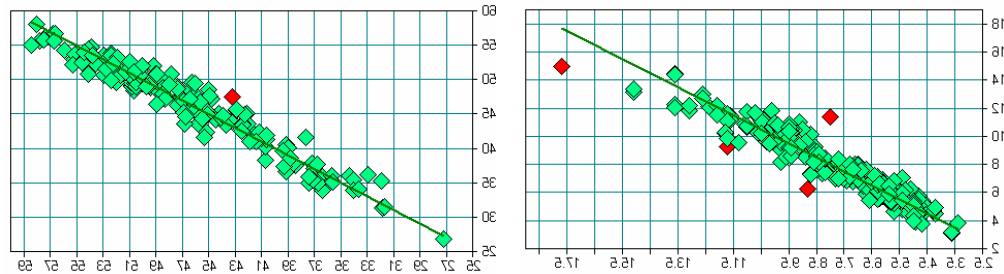


Figure 2 NIR spectra of raw salts: Pure carnallite (blue), pure kieserite (black)



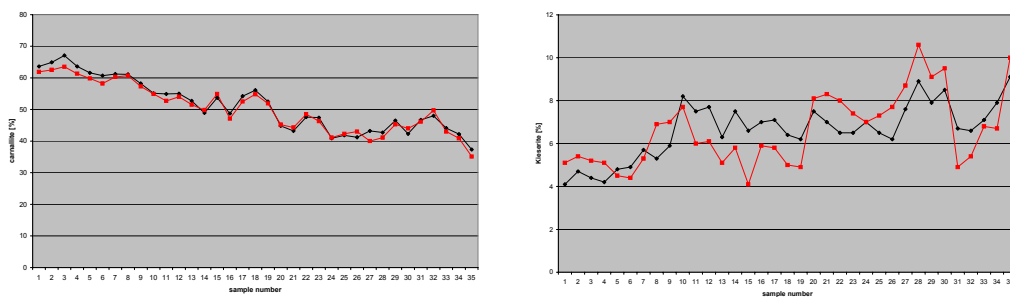
Figures 3 and 4 Predicted versus measured values: carnallite (left) and kieserite (right) in a multi-component system of raw salts

Table 2 Calibration results for carnallite and kieserite in a multi-component system of raw salts

Calibration parameter	Carnallite	Kieserite
Concentration range [%]	25-60	3-18
Factors	7	5
RMSECV	0.8	0.7
Correlation coefficient r^2	0.99	0.95

Online Analysis

For the online measurements the FT-NIR process spectrometer was installed over a conveyor belt carrying approximately 800 t/h raw salt and moving at 3 m/s. This presented us with the problem of dealing with large amounts of dust in such an environment. To keep the dust away from the spectrometer we enclosed it in a pressurised environment under a perspex cover. On the same conveyor belt was an automatic sampling device. The samples collected here were used to validate the calibration models and later to also extend the set of calibration samples. Many collected raw salt samples were analysed in the laboratory using reference methods. Comparisons of the mineral compositions of carnallite and kieserite as measured by laboratory analysis and using online NIR are shown in Figures 5 and 6, respectively. The online NIR follows the trend of the lab analysis, for both components, very well.



Figures 5 and 6 Comparison of online NIR values (red) versus laboratory analysis (black) for carnallite (left) and kieserite (right)

Summary and conclusions

This study demonstrates the potential of near infrared spectrometry for the quantitative analysis of hydrated inorganic salt minerals. The online measurement of carnallite and kieserite over a conveyor belt above ground in the plant was successful. The ultimate aim of this project is to be able to perform a reliable online analysis in a working underground potash mine. Figure 7 shows that the process spectrometer Matrix E, used to measure the raw salt compositions, hanging over a conveyor belt at a depth of 800 m in a working underground mine.

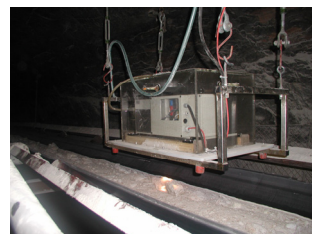


Figure 7 Spectrometer Matrix E over a conveyor belt in 800 m depth

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