X-RAY FLUORESCENCE

Fast Quality Control of Fertilizer with EDXRF

Lab Report 189

Introduction

As the world's population is growing, so is the demand for agricultural products. To provide enough and affordable food for everyone, farmers need to be able to grow and harvest reliably and sustainably. Modern agriculture relies on advanced fertilizers, that are taken up by the plant at a high rate and do not leach into the soil and ground water.

The most common fertilizers used in agriculture are those that provide the essential nutrients nitrogen (N), phosphorus (P), and potassium (K). These are often referred to as NPK fertilizers. Besides these three elements, producers may add metals like Fe, Mn, Zn, and Cu as important micronutrients.

Fertilizer product quality control usually involves the Kjeldahl method for the nitrogen content and ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) for other elements of interest. Both technologies are quite time and resource consuming as they involve, e.g., acid sample digestion. Non-destructive analysis by modern X-ray Fluorescence (XRF) is a great alternative: saving time, reducing costs and making 24/7 QC an easy task.

In the following report we demonstrate the performance of the S2 PUMA Series 2 for quality control of NPK fertilizers.

Optimal spectrometer configuration

The S2 PUMA Series 2, a versatile, high-performance benchtop EDXRF spectrometer, is an excellent solution for demanding industrial applications. The optimized beam path, the 50-Watt power X-ray tube, and the **HighSense™ Silicon Drift Detector** (SDD) ensure short time-to-results in combination with outstanding analytical performance.

The **XY-Autochanger** enables high sample throughput, while remaining completely flexible: You can load mixed batches (liquids, powders, solids …) and load, unload, or prioritize new samples at any time. The **vacuum mode** results in best sensitivity for lighter elements and lowest cost of operation (i.e., no Helium required). And Bruker's unique **SampleCare™** technology protects vital system components, guaranteeing high instrument uptime and ensuring low cost of ownership even in dusty environments (Figure 1).

Sample Preparation

Unknown fertilizer samples and secondary reference material were ground for a couple seconds to reduce the grain size and improve homogeneity. Subsequently, the powdered samples were pressed for 15 seconds at 20 tons into pellets (Figure 2). Alternatively, ground fertilizer samples can also be measured as powders in disposable plastic cups with a thin polymer foil at the bottom. Powder analysis is a bit faster since it does not involve the pressing step. Whereas pressed pellet preparation improves the data quality, especially for lighter elements.

Reference Materials

For this lab report a set of ten secondary reference materials was used to calibrate the S2 PUMA. Reference concentrations were available for S, P, K, and Fe. The concentration ranges are listed in Table 1.

Measurement Method & Calibration

The measurement parameters are listed in Table 2. Vacuum mode was chosen for best light element sensitivity and lowest cost of operation. The calibration statistics are summarized in Table 3. Exemplary calibration curves and peaks are shown in Figure 3. Noteworthy, even air mode produces good data quality for the elements covered by this report, however, vacuum improves the performance for S and P. The sensitivity benefits of vacuum mode are even more significant if lighter elements like Na and Mg need to be analyzed.

Results

A repeatability test was performed to determine the analytical precision (standard deviation). The results are listed in Table 4. The required precision for $N_2H_8SO_4$ and P_2O_5 in NPK fertilizers is usually 0.5 %, and 0.2 % for Fe and K. The S2 PUMA meets these requirements easily with absolute standard deviations ranging from 0.002 % to 0.1 %.

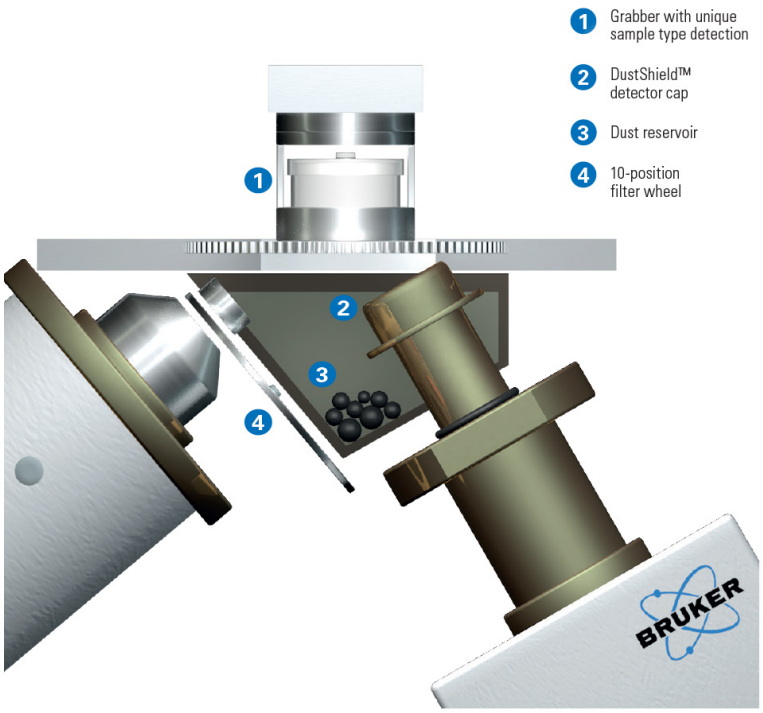

Figure 1
HighSense™ beam path with SampleCare™ for optimal performance and highest uptime.

Figure 2
Ground fertilizer samples can be measured as powder in a plastic cup with a polymer foil at the bottom (left) or as pressed powder pellets (right).

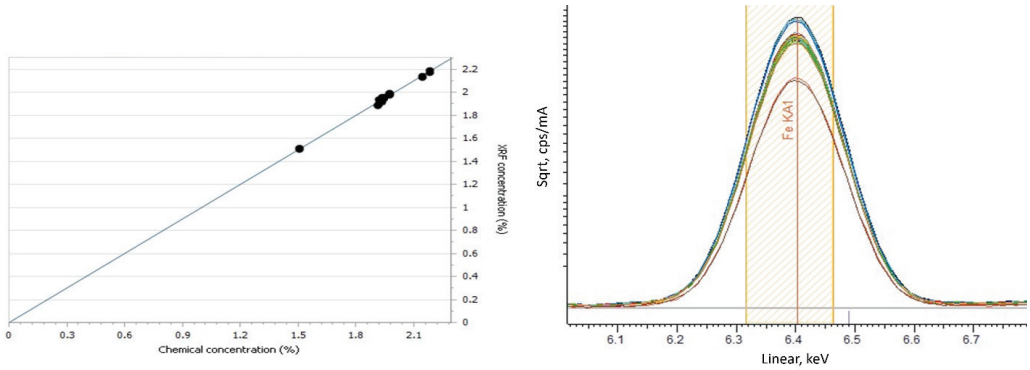

Figure 3
Calibration curve (left) and peaks with integration range (right) for Fe KA.

Table 1
Concentration ranges covered by 10 secondary reference materials. The ammonium sulfate ($N_2H_8SO_4$) concentrations are calculated using the S content.

Compound	Min content, wt%	Max content, wt%
P_2O_5 (%)	2.64	8.91
S (%)	18.75	22.08
→$N_2H_8SO_4$ (%)	77.26	90.98
K_2O (%)	0.150	0.342
Fe (%)	1.51	2.18

Table 2
Measurement parameters.

Elemental Line	Voltage	Current	Filter	Counting time	Sample Rotation	Mode
P, S, K	20 kV	Automatic	none	60 s	Vacuum	On
Fe	40 kV	Automatic	Al (500 µm)	30 s	Vacuum	On

Table 3
Calibration statistics.

Elemental lines	Squared correlation coefficient (R^2)	Standard deviation
P KA	0.99857	0.0349%
S KA	0.98754	0.0863%
K KA	0.96628	0.0060%
Fe KA	0.99149	0.0147%

Table 4
Repeatability test for one sample measured as pressed pellet.

wt%	P_2O_5 [%]	S [%]	→ $N_2H_8SO_4$*	K_2O	Fe
Rep-1	2.873	20.64	85.06	0.184	1.947
Rep-2	2.858	20.64	85.07	0.192	1.950
Rep-3	2.869	20.68	85.24	0.183	1.947
...	...	...	...	...	...
Rep-10	2.841	20.66	85.13	0.174	1.952
Average	**2.859**	**20.66**	**85.16**	**0.183**	**1.949**
Std.Dev.	**0.015**	**0.03**	**0.11**	**0.007**	**0.002**
Rel.Std.Dev.	**0.51%**	**0.13%**	**0.13%**	**3.63%**	**0.10%**

Conclusion

The data shown in this lab report highlights the excellent analytical performance of the S2 PUMA for the analysis of P_2O_5, $N_2H_8SO_4$ (based on total S), K_2O, and Fe in NPK fertilizers. Apart from these compounds, other elements, like Al, Mg, Ca, Mn, Cu, and Zn can easily be added to the analytical scope by using suitable reference materials. Even toxic contaminations such as Cd, Pb, and As can be analyzed accurately with the S2 PUMA.

The 22-position XY-Autochanger and the HighSense technology of the S2 PUMA enable high sample throughput: Time-to-result, including pressed pellet sample preparation, is only 5 minutes!

Benefits of using XRF versus ICP-OES include long-term stability and low cost of operation. The S2 PUMA enables 24/7 operation – no re-calibration necessary! Fertilizer sample preparation is fast and easy. There is no need for expensive or even hazardous consumables. And, thanks to our intuitive software, SPECTRA.ELEMENTS, minimal training is required to get started and run routine QC analysis.

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