APPLICATION NOTE
# XE-2011-3156

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# Quantitative analysis of Fe, Cu, Zn, and Mn in fertilizer granules samples

## With X-Calibur SDD Analyzer


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**Abstract**
Quantitative analysis of five microelements (Mg, Mn, Fe, Cu and Zn) was performed for six fertilizer samples with X-Calibur EDXRF analyzer equipped with a Silicone Drift Detector. Good correlations were obtained for Mg, Mn and Fe. Study of the microelement distribution in each fertilizer pack revealed an uneven elements distribution among the granules. This was supported by the external validation: analysis of sample portions from the fertiliser pack, which not included in the calibration method (external validation).
Qualitative elemental analysis of the fertiliser also performed for all the fertiliser samples.

## SAMPLES

Table 1 summarizes the information of 6 fertiliser standards. The main elements, for which quantitative analysis was performed are marked in red square.

**Table 1:** summary table of fertilizer samples

| Fertilizer ID | B % | S % | Mg % | Mn % | Fe % | Cu % | Zn % | Ca % | Pb ppm | Cd ppm | As ppm | Hg ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **S1** | | | | **6.1** | **12.05** | **2.98** | **3.15** | | 18 | 8 | 13 | 0.2 |
| **S2** | | | **2.19** | **5.99** | **11.78** | **2.83** | **3.39** | | | | | |
| **718** | 1.08 | 7.4 | **6.1** | **2.3** | **3.3** | **0.5** | **3.5** | 11.8 | < 15 | < 4 | <1 | |
| **562** | | | **3.62** | **6.06** | **12.47** | **2.78** | **2.84** | | | | | |
| **566** | | | **3.56** | **6.2** | **13.25** | **3.45** | **2.97** | | | | | |
| **673** | | | **3.62** | **6.3** | **12.13** | **3.39** | **3.08** | | | | | |

## OBJECTIVE

1. **Develop a quantitative method** for Mg, Mn, Fe, Cu and Zn microelement content in each of the six fertiliser samples and evaluate the calibration performance (software option).
2. **Instrument precision:** evaluate of the precision of the X-Calibur SDD EDXRF analyzer
3. **Variability of element distribution in the fertilizer standards:**
4. **External validation:** assessment of the method with additional portions taken from the same batch but not included in the calibration curve
5. Qualitative analysis of the fertiliser samples for the main and trace element content

## BACKGROUND

EDXRF is a quick non-destructive technique for qualitative elemental analysis of major and trace elements, and quantitative for all element content in solids, powders or liquids.
Having the advantage of being extremely quick, easy to operate and requiring hardly no sample preparation has increased the popularity of EDXRF among diverse industries such as Chemicals, Mines & Geology, Petrochemical, polymer and food & beverage.

## ANALYTICAL CONFIGURATION

**Table 2:** Analytical Configuration of X-Calibur SDD analyzer

| | |
|---|---|
| **Instrument** | X-Calibur SDD EDXRF Bench top Spectrometer System with Silicon Drift Detector (SDD) |
| **Excitation** | Rh-Anode X-ray Tube, 50W/50kV. |
| **Detector** | High Performance Silicon Drift Detector (SDD).<br>Resolution: 135eV at 5.9keV |
| **Analysis Time and conditions** | 180 seconds for all elements and 600 seconds for Mg in vacuum |
| **Type of analysis** | Quantitative and Qualitative |
| **Excitation** | Direct excitation with different x-ray tube filters |
| **Environment** | Air atmosphere |
| **Sample Preparation** | Samples were analyzed as received. |

## EXPERIMENTALS

Six samples were provided by the customer for quantitative analysis of Mg, Mn, Fe, Zn and Cu, and qualitative analysis of the main and trace elements. The samples are listed in table 1 above.
The fertilizer samples were analyzed as received from the customer without any sample preparation; the granules were transferred into X ray cups with thin XRF film support and plastic cover (figure 1)

**Figure 1: Instrument stage and measuring EDXRF cups**


Mn, Fe, Zn and Cu were analyzed with Rhodium filter, which was paced between the x-ray tube and the sample in order to selectively reduce the background noise and enhance the signal to noise ratio. Mg was analyzed with low excitation energies in vacuum without the use of filters. During the analysis of low molecular weight elements, as Mg, it is necessary to eliminate the oxygen in the X-ray beam path since otherwise oxygen absorbs the low energy signal emitted by these light elements.
Evaluation of the precision of the instrument was conducted with 10 consecutive measurements of the same sample without moving the sample cup from the sample holder of the instrument.
Assessment of the microelement distribution among the granulates of each fertilizer, was performed

by precision study of 5 different portion of the same fertilizer batch; 5 samples were taken from the same pack.

## RESULTS AND DISCUSSION

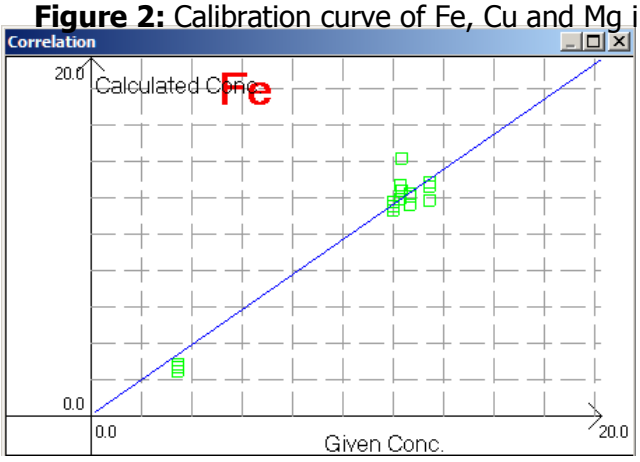
### 1. Quantitative method for Mg, Fe, Cu, Zn and Mn in fertilizers

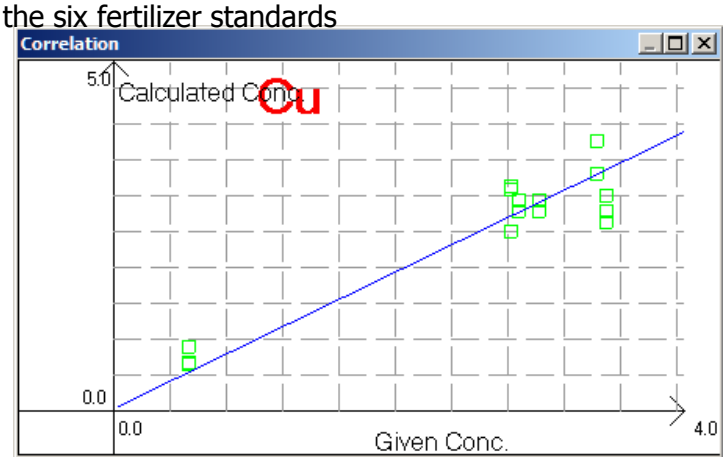
In order to develop a quantitative method for five elements (Mg, Mn, Fe, Zn and Cu) in fertilizer standards by EDXRF technology, two calibration methods were performed: (1) For Mn, Fe, Zn and Cu with Rhodium filter (2) For Mg with low excitation energies in vacuum.
Summary of the calibration results are shown in table 3 and correlation curves for Mg, Fe and Cu in figure 2.

**Table 3: summary of standard composition and calibration results**

| STD ID | Mg % | | Mn % | | Fe % | | Zn % | | Cu % | |
|---|---|---|---|---|---|---|---|---|---|---|
| Statistical data → | Corr =0.9811 Std.Dev=0.36 | | Corr =0.9925 Std.Dev=0.52 | | Corr = 0.9816 Std.Dev= 0.80 | | Corr = 0.9235 Std.Dev=0.09 | | Corr = 0.9423 Std.Dev=0.34 | |
| ↓ Standards | Given conc. | Calc. conc. | Given conc. | Calc. conc. | Given conc. | Calc. conc. | Given conc. | Calc. conc. | Given conc. | Calc. conc. |
| **S1** | ------- | | 6.1 | 6.2 | 12.05 | 12.45 | 3.15 | 2.97 | 2.98 | 2.92 |
| **S2** | 2.19 | 1.73 | 5.99 | 5.93 | 11.78 | 11.66 | 3.39 | 3.39 | 2.83 | 2.95 |
| **718** | 6.1 | 5.9 | 2.3 | 1.3 | 3.3 | 2.6 | 3.5 | 3.5 | 0.5 | 0.7 |
| **562** | 3.62 | 3.86 | 6.06 | 5.98 | 12.47 | 12.11 | 2.84 | 2.95 | 2.78 | 2.97 |
| **566** | 3.56 | 4.15 | 6.2 | 6.2 | 13.25 | 12.58 | 2.97 | 3.02 | 3.45 | 2.87 |
| **673** | 3.62 | 3.19 | 6.3 | 6.7 | 12.13 | 13.45 | 3.08 | 3.03 | 3.39 | 3.62 |

**Figure 2:** Calibration curve of Fe, Cu and Mg in the six fertilizer standards



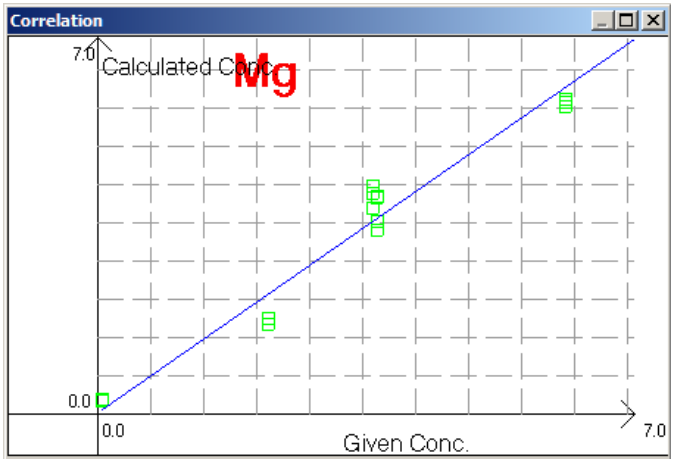



Figure 3 and 4 show 2 typical spectra of 562 fertiliser acquired for the 2 calibrations methods (mentioned before). All five elements were identified in all standards. Additional peaks, which were present in all spectra, are Sulphur and Rhodium, originating from the analyzer X ray tube.

**Figure 3:** Spectrum of 562 fertiliser with Rhodium filter at 40KeV energy range

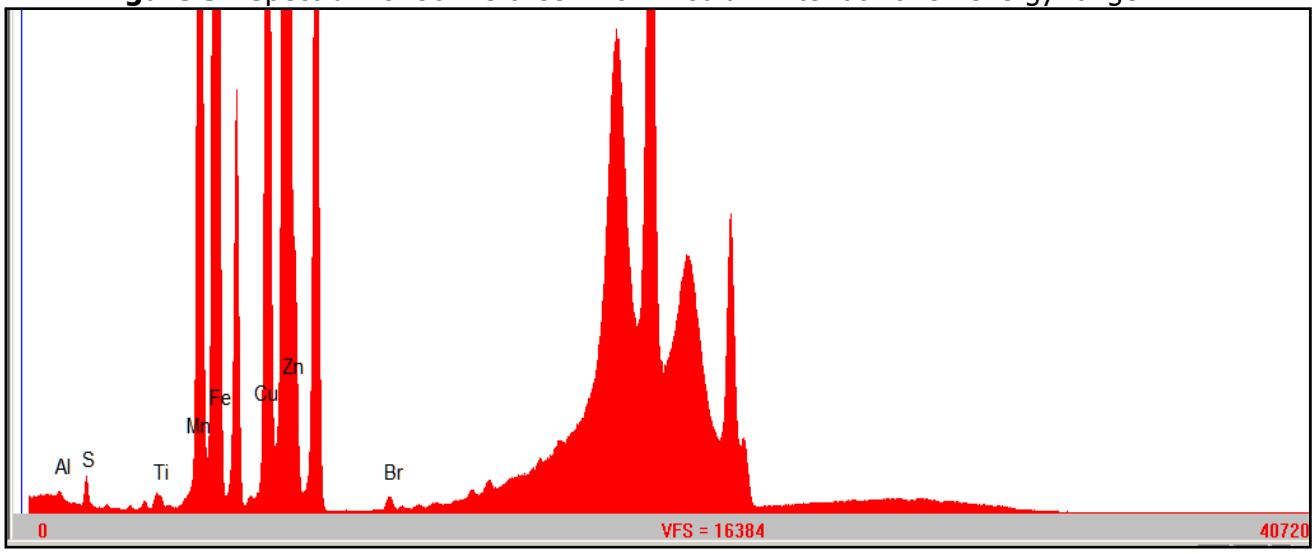
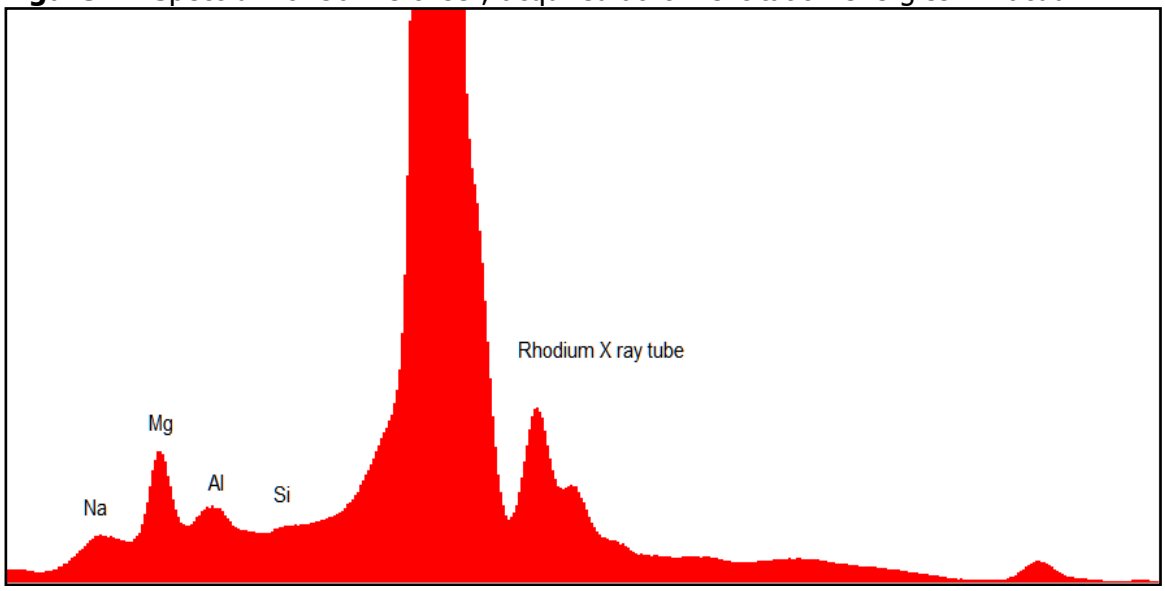



**Figure 4:** Spectrum of 562 fertiliser; acquired at low excitation energies in vacuum




Quantitative analysis in EDXRF is best performed with regression analysis with certified calibration standards. The variability of the standards is crucial for the performance of the method. It is recommended to include, in the calibration curve, standard which are representative of different concentrations, particularly the upper and lower concentration limits. In this work very similar calibration standards were provided. While 562, 566 and 673 are almost identical for all elements,

718 is the only standard that supports the lower edge for Fe and upper limit for Mg. For Zn, all standards showed a very narrow range (2.97-3.5%), which highly effected the correlation of the regression curve. Furthermore, it was not clear whether Zn or any of its oxide forms are present in the fertilizers, and whether there are any differences in the Zn form among the standards. These standards and the nature of microelement distribution in the fertilisers affected the calibration curves particularly for Zn and Mg. In order to improve the correlation for these elements and the accuracy of the quantitative calibration, additional standards should be included, particularly at the upper and lower limits of the concentration curve.

## 2. Instrument precision: the precision of the calibrated X-Calibur SDD EDXRF analyzer

Repeated spectra acquisitions were performed on 562 fertilizer standard without moving the sample cup from the instrument stage between the consecutive acquisitions. The intensity of each element was extracted from spectral data and the precision was calculated as the % relative standard deviation (at one sigma) of the repeated measurements. The precision data was calculated based on total counts in the peaks of the individual elements (Ka peaks were used).

**Table 4: Instrument precision (relative standard deviation at one sigma) for the different elements in 562 fertilizers.** Performed with 10 consecutive spectra acquisition of the same standard without moving the sample from the instrument stage

| Elements | certificate values | Mean | Std.Dev | % RSD | comments |
|---|---|---|---|---|---|
| **Cu** | 2.78 | 2.89 | 0.012 | **0.4** | Acquisition method with Rhodium filter at 40KeV energy spectral range |
| **Zn** | 2.84 | 3 | 0.003 | **0.095** | |
| **Mn** | 6.06 | 5.91 | 0.021 | **0.356** | |
| **Fe** | 12.47 | 12 | 0.043 | **0.358** | |
| **Mg** | 3.62 | 4.26 | 0.04 | **0.932** | Acquisition method with vacuum 10KeV without filters |

## 3. Variability of element distribution in the fertilizer standards:

Evaluation of the distribution of Fe, Cu, Zn, Mn, and Mg among the granules in the fertilizer standard was conducted for 562 and 718 standards. Five different portions form the same package were analyzed for 562 and three for 718 (small amount was provided). The spectra were analyzed quantitatively and the precision for the elements in each pack was calculated (table 5A and 5B).

**Table 5A: Element distribution in 562 fertilizer:**

| elements | certificate values | Mean | Std.Dev | % RSD | comments |
|---|---|---|---|---|---|
| Cu | 2.78 | 2.87 | 0.32 | 11.1 | Acquisition method with Rhodium filter at 40KeV energy spectral range |
| Zn | 2.84 | 2.98 | 0.058 | 1.93 | |
| Mn | 6.06 | 5.95 | 0.136 | 2.28 | |
| Fe | 12.47 | 12 | 0.283 | 2.35 | |
| Mg | 3.62 | 3.98 | 0.345 | 8.66 | Acquisition method with vacuum 10KeV without filters |

**Table 5B: Element distribution in 718**

| elements | certificate values | Mean | Std.Dev | % RSD | comments |
|---|---|---|---|---|---|
| Cu | 0.5 | 0.703 | 0.112 | **15.9** | Acquisition method with Rhodium filter at 40KeV energy spectral range |
| Zn | 3.5 | 3.51 | 0.042 | **1.19** | |
| Mn | 2.3 | 1.22 | 0.094 | **7.74** | |
| Fe | 3.3 | 2.55 | 0.18 | **7.08** | |
| Mg | 6.1 | 5.79 | 0.073 | **1.26** | Acquisition method with vacuum 10KeV without filters |

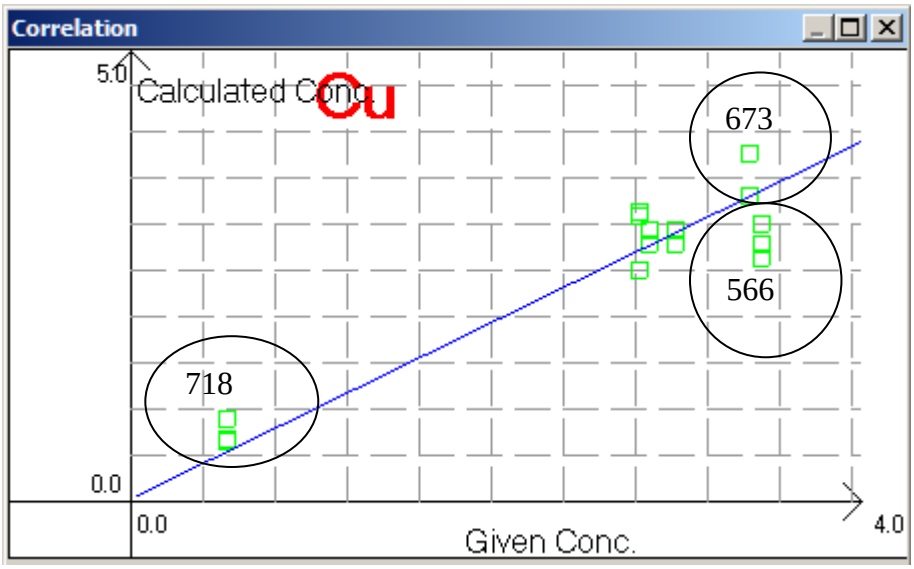
## 4. Comparison of instrument precision and sample precision:

Comparison of the precision study of the instrument and fertilizer 562 (Table 4 and table 5) is shown in table 5 below. The sample precision far exceeds that of the instrument. The variations of the microelement concentration among the granules in a given fertilizer overshadowed the variations generated by the analytical instrument: X-Calibur-SDD analyzer. Therefore the sample itself is a greater contribution to the overall error of the methods than the EDXRF analyzer.

**Table 6: Instrument and sample precision**

| Elements | Instrument precision %RSD | Sample precision % RSD | ratio |
|---|---|---|---|
| **Cu** | **0.4** | **11.1** | **27.8** |
| **Zn** | **0.095** | **1.93** | **20.3** |
| **Mn** | **0.356** | **2.28** | **6.4** |
| **Fe** | **0.358** | **2.35** | **6.7** |
| **Mg** | **0.932** | **8.66** | **9.2** |

Figure 4: **Distribution of Cu in the fertilizer standards**




Further illustration of variability among samples is shown in figure 4 for calculated Cu concentration in the fertilizer standards. Although one figure of certified standards

concentration was reported for all portions of 566 fertilizer, the quantitative method found variations in Cu content (calculated concentration) among these portions taken from the same package (marked in black circle in figure 4) . Same case was shown with 673 and 718.

## 5. External validation

Validation of the calibrated instrument was performed with external samples which were taken from the same fertiliser pack but not included in the calibration curve. The results of the 2 calibration methods are listed in table 7A and B.

Comparing the certificate values and the measured values shown the following:

- Good results were obtained for all elements, more standards should be added for the calibration curves of Zn and Mg in order to improve the accuracy and overcome the uneven distribution of these elements among the granules of a given standard.
- For 562 fertilizer, all the elements were shown to be unevenly distributed among the granules. This is shown by different concentration results obtained for portions taken from the same fertiliser pack.

**Table 7A:** External validation:
Mg% in different samples

| Sample | certificate Mg % | Calculated Mg % |
|---|---|---|
| S2_Vac_4 | 2.19 | 1.63% |
| 718 vac | 6.1 | 5.86% |
| 562 Vac sample4 | 3.62 | 3.60% |
| 562 Vac sample2 | 3.62 | 4.36% |
| 562 Vac sample5 | 3.62 | 4.19% |

**Table 7B:** External validation, % of Fe Mn Zn and Cu for different fertiliser packs.

| Sample ID | Fe % | | Mn % | | Zn % | | Cu % | |
|---|---|---|---|---|---|---|---|---|
| | Certificate | Measured | Certificate | Measured | Certificate | Measured | Certificate | Measured |
| S2_RhF_sample 4 | 11.78 | 11.66% | 5.99 | 5.93% | 3.39 | 3.38% | 2.83 | 3.00% |
| 718 RhF | 3.3 | 2.29% | 2.3 | 1.13% | 3.5 | 3.56% | 0.5 | 0.66% |
| 562-RhF-sample5 | 12.47 | 12.07% | 6.06 | 5.95% | 2.84 | 2.99% | 2.72 | 2.92% |
| 562-RhF-sample4 | 12.47 | 11.81% | 6.06 | 5.83% | 2.84 | 3.07% | 2.72 | 2.53% |
| 566_RhF sample3 | 12.47 | 11.98% | 6.06 | 5.93% | 2.84 | 3.08% | 2.72 | 2.69% |
| 566_RhF sample2 | 12.47 | 12.98% | 6.06 | 6.41% | 2.84 | 2.97% | 2.72 | 3.07% |

## 6. Elemental analysis of the fertiliser samples

Summary of the elements present in each fertilizer sample is shown in table 8.
A representative spectrum for 673 fertilizer in shown in figure 5 bellow, the results are summarized in table 8.

**Table 8: Elements present in the fertilizer samples**

| Fertilizer samples | Elements present |
|---|---|
| **S1** | Na, Mg, Al, Si, S, K, Ca, Ti, Mn, Fe, Cu, Zn, As, Pb, Zr, |
| **S2** | Na, Mg, Al, Si, S, K, Ti, Mn, Fe, Cu, Zn, As, Pb, Y, Zr, |
| **718** | Na, Mg, Al, Si, S, Ca, Mn, Fe, Cu, Zn, Zr |
| **562** | Na, Mg, Al, Si, S, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Y, Zr |
| **566** | Na, Mg, Al, Si, S, Ca, Ti, Mn, Fe, Cu, Zn, As, Y, Zr (trace), Nb (trace) |
| **673** | Na, Mg, Al, S, Ti, Mn, Fe, Cu, Zn, Ni (trace) Y |

**Figure 5:** Spectrum of S2 fertilizer acquired with Rhodium filter

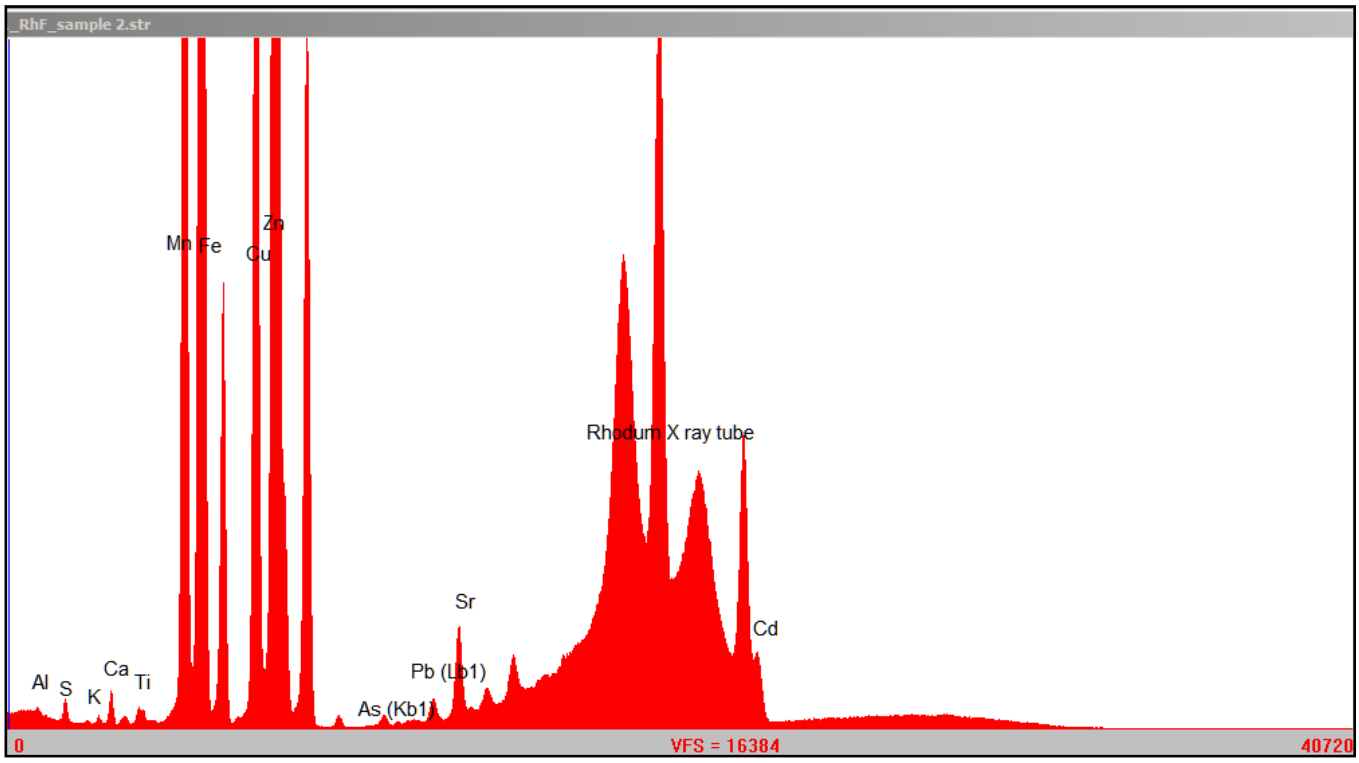
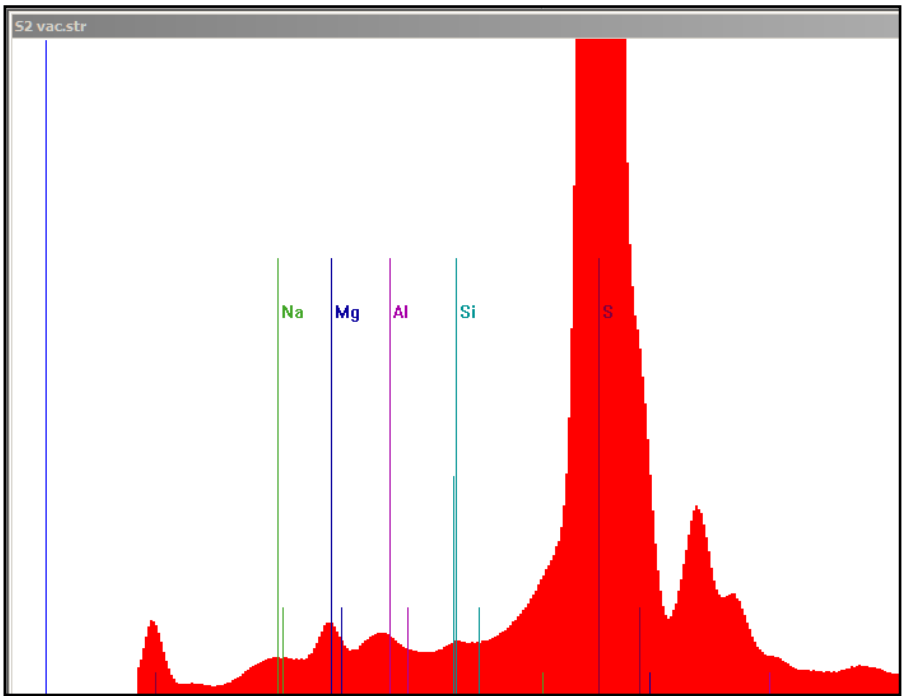


**Figure 5:** Spectrum of S2 fertiliser; acquired at low excitation energies in vacuum




Differently from the expectations, no Cd or Hg was found in the fertilisers. If any of these elements are present, single or sub ppm levels are expected.

## CONCLUSION

Quantitative analysis of five microelements (Mg, Mn, Fe, Cu and Zn) was conducted for six fertilizer standards. Two quantitative calibrations were performed, one for Mg in vacuum and one for the rest of the elements. The distribution of the microelements among the granules was statistically evaluated and its precision values exceeded the instrument precision test. This indicates an uneven distribution of the microelements among the granules in each fertiliser bag. This is regarded as the major contributor to overall inaccuracies in the calibration method.

Further statistical study and evaluation of external samples (not included in the method) showed fairly accurate results for most elements. It provides further evidence for the uneven distribution of the elements within the fertiliser granules. More samples should be added particularly for Mg and Zn in order to improve the method accuracy and overcome the sample microelements distribution among these samples.
Qualitative analysis of the fertilizer standards was performed for all fertilizers and showed minor differences in element composition.

X-Calibur SDD EDXRF Bench top analyser is useful for diverse applications for fertilizer analysis such as elemental analysis, quantiation of microelements and study of microelement distribution within granules and powders. These analytical methods are applicable for oncoming materials, assay of end product, and blending of powders.