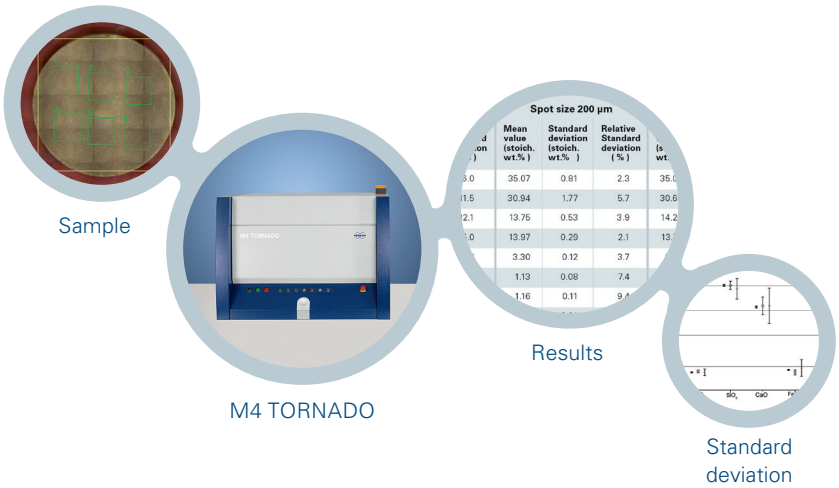

Lab Report XRF 461

Improving the precision of the quantification of non-homogeneous samples using FlexiSpot

Quantitative Micro-XRF analysis integrates information over the complete irradiated and detected sample area. The quantification routine requires a homogeneous sample to correctly calculate its composition. However, most non-manufactured samples, such as geological specimens, are heterogeneous and elements are not as evenly distributed as in manufactured samples such as steel or glass.

Conventional XRF analysis requires significant preparatory effort to make the samples more homogeneous. Using spatially resolved Micro-XRF instead, has the advantage that very little or even no sample preparation is required.

However, when performing analysis with spatial resolution at the micrometer scale, it may be difficult to find positions where the quantitative results are representative for the whole sample or a given partial sample area.

Powders and milled specimens are typical examples that are homogeneous at the millimeter scale, but can show large point-to-point deviations when measured with a resolution of tens of micrometers.

M4 TORNADO's feature FlexiSpot enables large area investigation in micrometer resolution: Samples can not only be measured with a spot size of <20 µm, but with an additional spot size of a few 100 µm. This larger irradiated spot allows more precise quantification of non-homogeneous and irregular shaped samples or samples with uneven surfaces, such as powders, since information is integrated in the analysis over the enlarged detected area.

Functional principle

The polycapillary lens in the M4 TORNADO creates a convergent X-ray beam and thus focuses the X-ray tubes

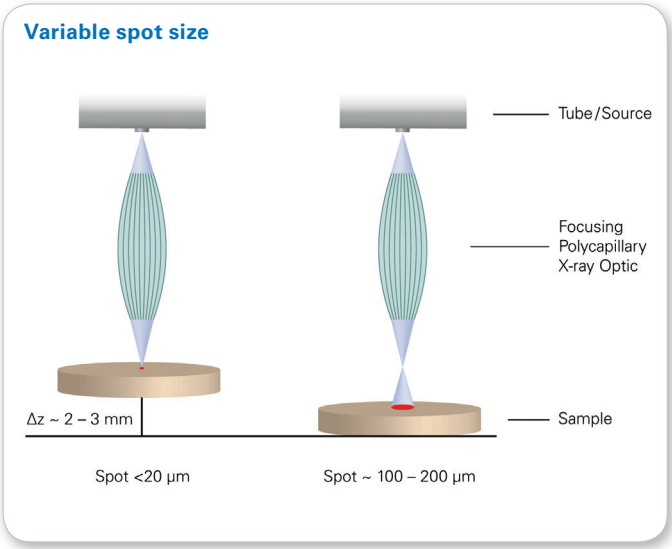

Fig. 1 Functional principle of generating a variable spot size

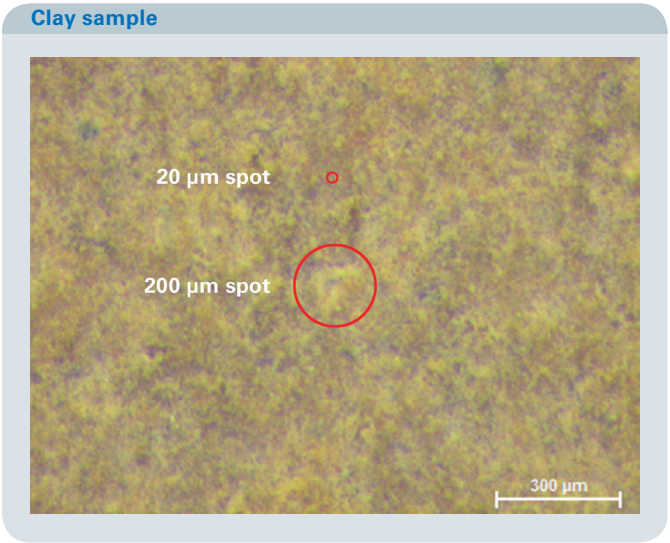

Fig. 2 Clay sample in 100x magnification showing obvious inhomogeneity. The red circles indicate the set excitation spot diameters of 20 µm and 200 µm.

radiation. The plane in which the beam waist lies is called focal plane. The beam width here is <20 µm for Mo Kα radiation.

The FlexiSpot feature bases on the fact that an X-ray beam is wider above and below its focal plane. By moving the sample to an "out-of-focus" position, the irradiated area becomes larger. Taking into account the common beam divergence of polycapillary lenses, spot sizes of 100–200 µm can be achieved by moving the sample approximately 2–3 mm out of the focal plane (see Fig. 1).

Sample preparation

The sample to be analyzed was a clay collected from the Cretaceous-Paleogene-boundary in Petriccio, Italy. The clay was milled and subsequently pressed to a pellet using 20 % binder. This common type of preparation yields reasonably homogeneous material for conventional XRF analysis. However, already in an optical microscope with 100x magnification, the image shows that at a 10 micrometer scale the sample is not homogeneous. Fig. 2 shows the clay pellet sample with the two different spot sizes.

Measurement conditions

The measurements were performed with a Bruker M4 TORNADO equipped with a Rh X-ray tube and a polycapillary lens. It combines high spatial resolution with fast data processing and a motorized high-speed X-Y-Z stage for sample positioning. The following standard measurement conditions were used:

- tube voltage of 50 kV
- current of 200 µA
- no primary beam filter
- chamber pressure of 20 mbar.

Spatially resolved quantitative analysis of an inhomogeneous sample has to be performed on multiple points to reach a representative value for the whole area. The averaged quantitative values can then be considered to be the "correct" result. The credibility of the result is given by the standard deviation of individual results. For very small investigated spots this standard deviation may be very high and thus the results may not be relevant or not meet requirements.

In the Multi-Point workspace of the M4 TORNADO software, six arbitrary positions were defined and measured with spot sizes of 20 µm and 200 µm, respectively (see Fig. 3a–b). In order to obtain good statistics for light and minor elements, the single point measurement time was set to 120 s.

Under the same excitation conditions, a 40 mm x 40 mm section of the sample was then mapped with 50 µm pixel size and a measurement time of 4 ms per pixel. To have an equivalent overall measurement time of 120 s as with point measurements, six areas of 75 mm² each were extracted from the acquired HyperMap data cube (see Fig. 3c).

Results

Table 1 shows the summary of the quantitative results for six measurement positions, each measured with a spot

Measurement points and areas

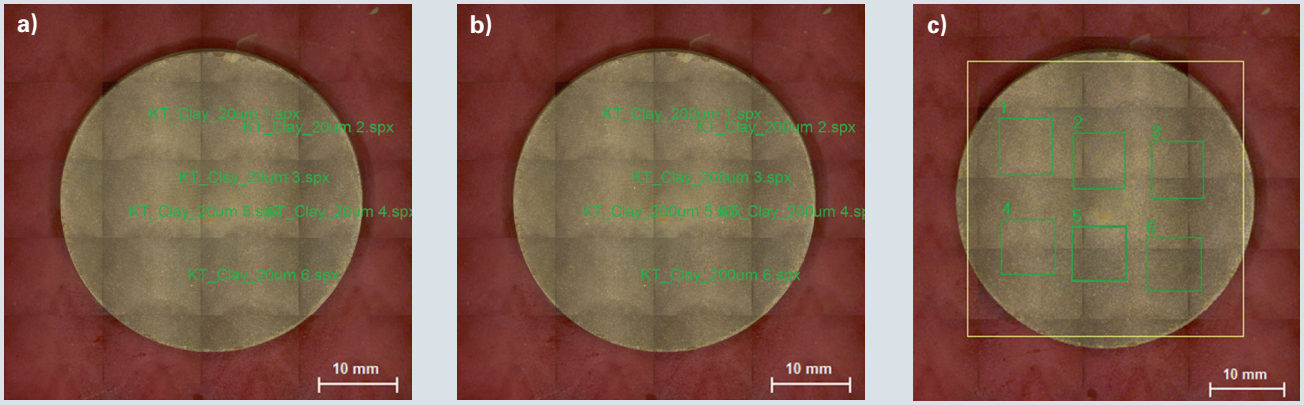

Fig. 3 Mosaic image of the sample with defined measurement positions and areas.

size of 20 µm and 200 µm, as well as six mapping areas, respectively. As it can be seen, the standard deviation for the quantified compositions decreases with increased analyzed sample surface area, while the quantified concentrations remain stable.

Fig. 4 visualizes this trend for the oxides of the main elements SiO_2, CaO, Fe_2O_3, and Al_2O_3. The mean and sigma values for the 75 mm² areas can be considered to be representative for the sample und preset measurement conditions. With smaller investigated areas, the deviations

Table 1 Measured values for different spot and area sizes

Oxide	Spot size 20 µm			Spot size 200 µm			75 mm² area map		
	Mean value (stoich. wt.%)	Standard deviation (stoich. wt.%)	Relative Standard deviation (%)	Mean value (stoich. wt.%)	Standard deviation (stoich. wt.%)	Relative Standard deviation (%)	Mean value (stoich. wt.%)	Standard deviation (stoich. wt.%)	Relative Standard deviation (%)
SiO_2	34.36	2.07	6.0	35.07	0.81	2.3	35.05	0.18	0.5
CaO	30.94	3.55	11.5	30.94	1.77	5.7	30.69	0.20	0.7
Fe_2O_3	14.67	1.77	12.1	13.75	0.53	3.9	14.26	0.09	0.6
Al_2O_3	13.76	0.69	5.0	13.97	0.29	2.1	13.76	0.12	0.9
K_2O	3.37	0.29	8.6	3.30	0.12	3.7	3.42	0.02	0.6
MgO	1.17	0.16	13.6	1.13	0.08	7.4	1.15	0.12	10.8
TiO_2	1.11	0.10	9.4	1.16	0.11	9.4	1.14	0.01	0.9
SrO	0.16	0.02	12.0	0.15	0.01	3.4	0.16	0.00	1.7
MnO	0.14	0.01	9.4	0.13	0.01	5.0	0.13	0.00	2.4
P_2O_5	0.15	0.08	55.5	0.24	0.19	76.3	0.09	0.04	46.1
ZnO	0.047	0.016	34.9	0.041	0.004	10.5	0.041	0.001	2.7
Cr_2O_3	0.048	0.015	32.0	0.038	0.004	11.4	0.038	0.003	8.5
NiO	0.045	0.028	62.5	0.038	0.005	14.4	0.028	0.002	7.2
ZrO_2	0.019	0.004	22.8	0.021	0.003	16.4	0.022	0.002	9.2
Rb_2O_3	0.020	0.003	15.6	0.017	0.002	11.1	0.019	0.001	6.8

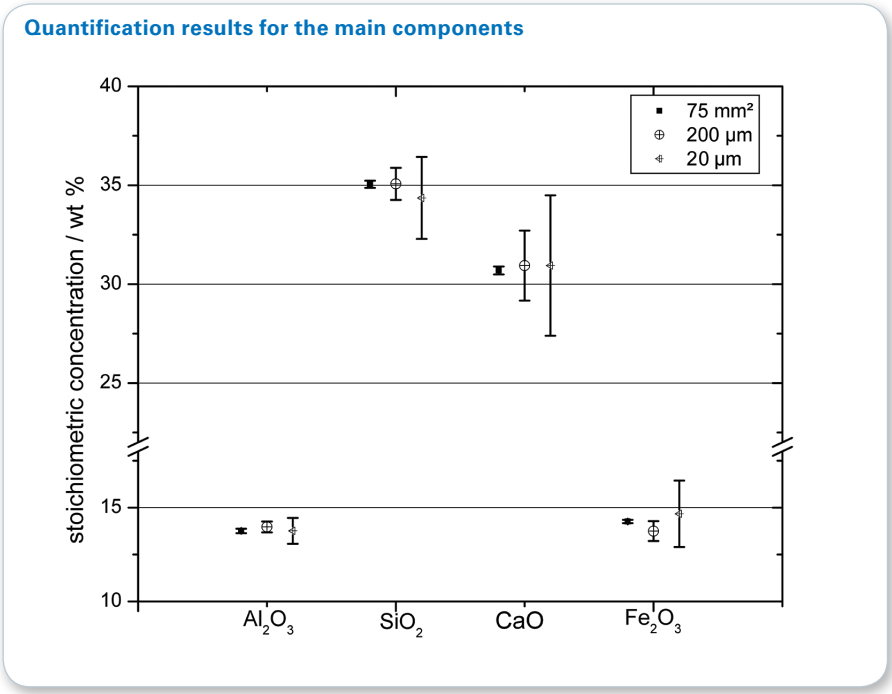

Fig. 4 Quantified values for the main matrix components with two sigma standard deviation (as obtained from six measurements)

of the quantified values become larger while the "correct" value is well within the obtained uncertainties.

Table 1 and Fig. 4 clearly show that the increased spot size of 200 µm yields an improvement of the variations by a factor of 2 or better compared to the standard spot size of 20 µm. Note that this relates to an identical measurement time.

While the graph in Fig. 4 implies that only a full area map gives credible results, it has to be pointed out that the time it takes to gather the information in this area is 5 times the recording time for the multipoint measurements (1:04 h compared to 12 min). For most applications, the variations derived from the point spectra measurements are entirely sufficient.

Only the results of Mg and P, both low concentration light elements, do not follow the strict trend. These deviations are counting statistics of the fluorescence lines and the inhomogeneity of the element distribution.

Conclusion

The comparison of sample measurements with different spot sizes and areas clearly shows significant improvement of relative standard deviations when larger areas are analyzed using M4 TORNADO's FlexiSpot. Point measurements with a spot size of 200 µm provide adequate results in significantly shorter measurement time compared to full area maps.

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