Quantitative µ-XRF of Silicate Materials with Mono- and Polycapillaries

Katharina Dietrich[a, b], Zacharenia Loukou[c], Despoina Papadopoulou[c], Manfred Schreiner[a, b], Nestor C. Tsirliganis[c]

a Institute of Humanities, Sciences and Technologies in Art, Academy of Fine Arts, Schillerplatz 3, A-1010 Vienna, Austria k.dietrich@akbild.ac.at m.schreiner@akbild.ac.at

b Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/151, A-1010 Vienna, Austria

c Cultural and Educational Technology Institute, Archaeometry Laboratory, 58 Tsimisky Str., GR-67100 Xanthi rloukou@ceti.gr dpapa@ceti.gr tnestor@ceti.gr

Within the research project COPRA (Compact Portable Roentgen Analyzer, Project SMT4 CT 98 2237 of the European Union) a µ-XRF (micro x-ray fluorescence) was designed with specific attention to the analysis of objects of art and archaeology. The prototype built during this project is employed at the Institute of Humanities, Sciences and Technologies in Art, Vienna/Austria, while a follow up model is used at the Cultural and Educational Technology Institute, Xanthi/Greece. Both instruments are similar in their general construction and features. They consist of a X-flash LT drift chamber detector of Röntec/Germany and a Mo tube XTF 5011 of Oxford Instruments/USA arranged in a nominal angle of 90°. In the Viennese instrument a polycapillary with 39 mm outgoing focus distance is used for focussing the primary x-ray beam, whereas the device in Xanthi has a monocapillary. The corresponding size of the x-ray spot at the measuring position is approximately 100 µm FWHM (measured Rh K_α) for the polycapillary and <150 µm for the monocapillary (nominal specification).
In a cooperation both instruments have been compared concerning their instrumental characteristics influenced by the different optical systems.

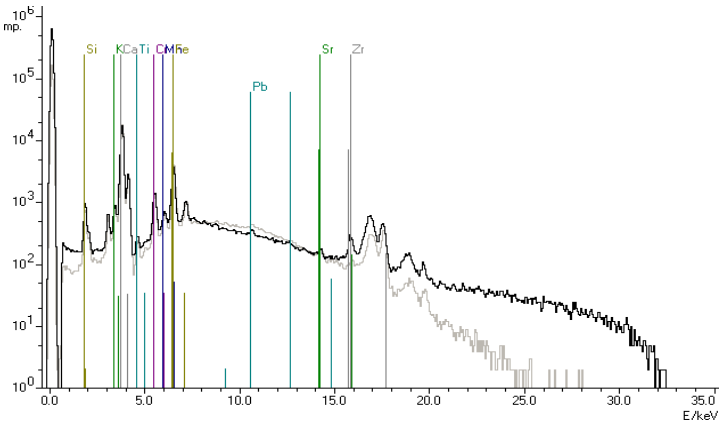

Fig. 1: Spectra of Danone standards N3 obtained with the monocapillary (black line) and the polycapillary (gray line)

In fig. 1 the spectra of the Danone standard N3, a soda-lime-silica glass, obtained with the polycapillary (gray line) as well as the monocapillary (black line) system are shown. Both spectra were received using the same measurement parameters:
35 kV, 0.5 mA and acquisition times of 200 and 800 s for the poly- and the monocapillary instrument, respectively.

The four times longer measurement time with the monocapillary system is necessary due to the lower x-ray intensity of the focussing device and to obtain line intensities sufficient for quantitative analysis. There is apparently a significant time saving when a polycapillary focussing system is used.
On the other hand a cut off for energies above approximately 20 keV must be observed clearly for the polycapillary system, a characteristic of this kind of x-ray optics, due to the dependence of the critical angle of total reflection from the energy of the radiation. Therefore,

for the described excitation conditions the domain for elemental analysis can be extended up to x-ray lines of approximately 30 keV using a monocapillary.
Comparing the different elemental lines in fig. 1, the intensities of the lines between 1 and 15 keV are comparable. Even the L-lines of Pb present as trace element do not show large differences. Considering the impurities of Strontium and Zirconium the cut off of the polycapillary can be observed clearly. Whereas for Sr the intensities are almost alike, the intensity of the Zr line is a multiple higher in the monocapillary-spectrum.

The analysis of glass and ceramics with mono- and polycapillaries

The analysis of glass and ceramics using XRF systems is always complicated, especially when the measurements are carried out in open air, where the absorption of low energetic x-ray radiation is not negligible. For these materials all components with characteristic lines below the energy of the silicon (1.74 keV) as well as P and S (impurities in glass) cannot be detected. This leads only to a partial knowledge of the chemical composition of the matrix, which is an important factor for the quantitative analysis of silicate materials.

Glass analysis

For the analysis of glass the software WinAxil 4.0, Version 4.1.2. from Canberra Eurisys Benelux was used. The calibration was done using the compare mode and the glass standards SRM 620, SRM 1830 and SRM 1831 (and SRM 610 for the monocapillary measurements) from NIST/USA and the standards N1, N2, N3 and N4 from Danone/France (tab. 1). The measurements were carried out using the measuring parameters described above. For both, the measurements with the mono- and polycapillary focussing system, a proper calibration was performed. In order to verify the quality of the calibration in both cases, the µ-XRF spectra of the used standards were consequently reevaluated using the obtained calibration parameters. As can be seen in tab. 1 the calibrations for both instruments are in general comparable. Only the calculated values for silicon seem to be more reliable for the polycapillary measurements. The problem with the evaluation of silicon appears because of the strong absorbance that occurs for the energy of its K-line. Silicon is the major element in glass and ceramics, but it only shows a low intensity of the corresponding x-ray line so that small deviations of the intensities have strong effects in the quantitative results.
Nevertheless, quantitative analysis was performed on forensic glass samples RC, RD, RE (tab. 2) originating from different car front-glasses, using the instrument with the monocapillary offering the advantage of the analysis of strontium.
The samples were used within the COPRA project at the Laboratoire de Police Scientifique de Lyon/France, where they are employed in cases of hit-and-run drivings.
The three car window glasses (see tab. 2) do not show large differences in their composition. The largest difference occurs in the silicon content, where for glass RE a much higher value was obtained than in the other specimen. Glass RC shows a higher amount of calcium, whereas glass RD seems to contain more iron than the other glasses. Iron in silica glass causes the light water blue color of the car front-glasses.

Standard		Sr	K_2O	CaO	TiO_2	Fe_2O_3	MnO	Cr_2O_3	SiO_2
610	**Given**	**0.052%**	**0.06%**	**12.00%**	**0.073%**	**0.065%**	**0.063%**		**72.0%**
	Mono	0.053%	0.18%	11.65%	0.081%	0.078%	0.057%		71.0%
620	**Given**		**0.41%**	**7.11%**	**0.018%**	**0.043%**			**72.1%**
	Mono		0.39%	7.73%	0.018%	0.100%			77.0%
	Poly		0.36%	7.32%	0.017%	0.058%			71.5%
1830	**Given**		**0.04%**	**8.56%**	**0.011%**	**0.121%**			**73.1%**
	Mono		0.13%	8.68%	0.010%	0.167%			73.0%
	Poly		0.11%	8.47%	0.012%	0.137%			71.5%
1831	**Given**		**0.33%**	**8.20%**	**0.019%**	**0.087%**			**73.1%**
	Mono		0.33%	8.24%	0.018%	0.143%			73.5%
	Poly		0.24%	8.38%	0.023%	0.093%			75.2%
N1	**Given**		**0.34%**	**10.76%**	**0.013%**	**0.057%**	**0.003%**		**72.4%**
	Mono		0.32%	10.08%	0.013%	0.100%	0.017%		65.9%
	Poly		0.34%	10.76%	0.013%	0.057%	0.009%	0.000%	74.3%
N2	**Given**		**1.14%**	**11.12%**	**0.068%**	**0.179%**	**0.025%**	**0.016%**	**71.1%**
	Mono		0.94%	10.72%	0.063%	0.180%	0.028%	0.037%	66.7%
	Poly		0.96%	10.83%	0.061%	0.176%	0.024%	0.018%	70.8%
N3	**Given**		**0.54%**	**10.99%**	**0.047%**	**0.462%**	**0.024%**	**0.212%**	**72.1%**
	Mono		0.47%	9.88%	0.047%	0.383%	0.027%	0.191%	63.6%
	Poly		0.50%	10.99%	0.049%	0.450%	0.020%	0.192%	73.9%
N4	**Given**		**0.42%**	**11.77%**	**0.038%**	**0.167%**	**0.020%**	**0.068%**	**71.8%**
	Mono		0.45%	11.65%	0.045%	0.200%	0.026%	0.092%	69.9%
	Poly		0.44%	11.83%	0.045%	0.173%	0.021%	0.066%	74.5%

Tab. 1: Comparison of the results (wt%) achieved with the mono- and polycapillary calibration using WinAxil Software package/Compare mode. Standard 610 was only used for the monocapillary measurements. The table shows the means of at least 5 measurements.

	SiO_2	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	Sr	Sum
RC	71.20%	0.37%	9.78%	0.03%	0.02%	0.02%	0.52%	0.02%	81.93%
RD	71.50%	0.36%	8.38%	0.02%	0.04%	0.02%	0.74%	0.02%	81.10%
RE	78.20%	0.36%	8.81%	0.04%	0.03%	0.02%	0.56%	0.01%	88.05%

Tab. 2: Quantitative evaluation of the forensic glasses. Three samples per front window were analyzed doing at least 5 measurements per sample. The table shows the mean values per front glass in wt%.

Ceramics

The six most important elements in ceramics, Si, Fe, Ca, K, Ti and Mn, were used in the measurements and their spectra were analysed using the WinAxil 4.0, Version 4.0.1. software. The calibration was made using the compare mode and the standards SARM from MINTEK South Africa, AWI and PRI from FNRS-NFWO France. As all the SRMs were in powder form, pressed pellets had to be made (grain size <38 µm). Spectroblend was used as a binder material in ratios ranging from 1:3.5 to 1:4.4 w/w. The measurements were carried out using a voltage of 35 kV and a current of 0.5 mA, and different acquisition times, 500 s for the polycapillary and 1000 s for the monocapillary. The 1000 s were chosen as a compromise in order to achieve larger peak areas without putting too much strain on the tube. For both measurements, with the mono- and polycapillary, a proper calibration was performed. In order to verify the quality of the calibration in both cases, the µ-XRF spectra of the used standards were consequently re-evaluated using the obtained calibration parameters.

Standard		K_2O	CaO	TiO_2	Fe_2O_3	MnO	SiO_2	SUM
SARM	**Given**	**1.96%**	**2.37%**	**0.78%**	**7.18%**	**0.13%**	**66.60%**	**79.02%**
	Mono	1.97%	2.19%	0.79%	6.60%	0.11%	68.83%	80.49%
	Poly	1.96%	2.20%	0.76%	6.62%	0.11%	68.17%	79.82%
AWI	**Given**	**3.06%**	**0.69%**	**0.92%**	**7.21%**	**0.14%**	**60.46%**	**72.48%**
	Mono	3.15%	0.74%	0.95%	7.88%	0.13%	58.22%	71.07%
	Poly	3.57%	0.79%	1.03%	9.07%	0.16%	58.50%	73.12%
PRI	**Given**	**3.79%**	**2.49%**	**0.71%**	**3.32%**	**0.04%**	**68.60%**	**78.95%**
	Mono	3.60%	2.59%	0.66%	3.31%	0.05%	69.26%	79.48%
	Poly	3.57%	2.56%	0.70%	3.21%	0.05%	68.60%	78.69%
Sample 2	**Mono**	1.30%	4.58%	0.65%	4.58%	0.10%	61.57%	72.76%
Sample 6	**Mono**	1.40%	2.13%	0.47%	3.55%	0.08%	52.55%	60.18%

Tab. 3: Comparison of the results (wt%) achieved with the mono- and polycapillary calibration using WinAxil software package/compare mode. Quantitation of ancient ceramic samples. The table shows the means of at least 4 measurements.

As can be seen in tab. 3 the calibration for both instruments yields similar results and the calculated concentrations are in good agreement with the given values. A good agreement was also obtained for silicon, which showed in the case of glass analysis more reliable results using the polycapillary than the monocapillary. The only discrepancy in the results of the ceramic samples is the overestimation of iron with the polycapillary for the AWI standard.
Quantitative analysis was performed with the monocapillary also on two ancient ceramic samples, one prehistoric (sample 6) and one from the middle of the 4^{th} century B.C. (sample 2) that were found in Northern Greece. Pressed pellets were also made (two pellets per sample), at binder ratios ranging from 1:3.4 to 1:4.4 w/w. The results are also shown in tab. 3. The concentration values appear to be absolutely reasonable considering also the fact that their matrices are “unknown”.

Conclusions

For the analysis of glass and ceramics both, mono- and polycapillary focussing optics lead to comparable results, when performing quantitative analysis. In general, the application field has to be taken into account carefully, on the one hand for the domain of elements analyzed and on the other hand for the cost-factor of the different optical systems. Also the acquisition time has to be considered as a criterion, which is approximately 4 times longer with the monocapillary than with the polycapillary system. The size of the output focal spot should not affect the choice of the focussing optic because both, mono- and polycapillaries are available in the µm range.