Comparison of two confocal micro-XRF spectrometers with different design aspects

S. Smolek,¹,* T. Nakazawa,²,³ A. Tabe,² K. Nakano,² K. Tsuji,² C. Streli¹ and P. Wobrauschek¹

Introduction

In the last 20 years, micro X-ray fluorescence spectrometry (micro-XRF) became a powerful tool to determine the spatial distribution of major, minor, and trace elements within a sample, besides others, due to the rapid development of X-ray optics.¹⁻¹⁸

Confocal micro-XRF is an extension of micro-XRF, which allows the determination of the spatial distribution of elements within a sample in three dimensions.⁹⁻¹⁴ Two X-ray optics, usually polycapillaries, are used in this setup. The first polycapillary focuses the primary beam on the sample; the second restricts the field of view of the detector. By overlapping the focal spots of both X-ray optics, a well-defined measurement volume is created. This allows a wide range of applications in various fields (biology, geology, life science, cultural heritage, etc.).¹⁵⁻²³ This allows for different types of measurements to be performed:

1. measurements in the first layer (usually area scans) to obtain an image of the spatial distribution of elements;
2. measurements into the sample (depth profiling) either as line scans or virtual cross section cuts in the sample;
3. full 3D analysis without the need of a reconstruction algorithm (tomography).

The spatial resolution of such a setup is usually in the micrometer regime and the lower limits of detection (LLDs; per spot) in the picogram or microgram per gram range for laboratory X-ray sources.

In this work, two spectrometers with different design targets are compared:

- At Osaka City University (OCU), a spectrometer has been developed and installed that is optimized for high spatial resolution (10 μm for Mo Kα, 17.48 keV).²⁴⁻²⁶
- At the Atominstitut of the Vienna University of Technology (ATI), a spectrometer has been designed and built that is optimized for the analysis of light elements (e.g. F and Na).²⁷,²⁸

Experimental setup

OCU spectrometer

The spectrometer at OCU used a metal ceramic type X-ray tube (MCBM 65B-50) by rtw Röntgen-Technik Dr. Warrikhoff, Neuenhagen bei Berlin, Germany, with a Mo anode as X-ray source. It is an air cooled microfocus X-ray tube with a spot size of 50 x 50 μm². The tube was operated at 50 kV and 0.6 mA (30 W). Two polycapillaries from XOS (East Greenbush, NY, USA) are used in the spectrometer to focus the primary X-rays and restrict the detectors' field of view. The primary polycapillary focused the X-ray to a spot size of about 10 μm for Mo Kα radiation. The second polycapillary was mounted directly on the detector. It also had a spot size of 10 μm for Mo Kα. Both X-ray optics gave a small spot size; however, their working distances (distance between the optic and the sample) were only 2–3 mm.²⁴,²⁵

A silicon drift detector Vortex Ex-50 by Hitachi High-Technologies Science America, Inc. (Northridge, CA, USA) was used to analyze the radiation from the sample (FWHM < 130 eV at 5.9 keV). The signal from the SDD was amplified and shaped by an ORTEC 572A amplifier (ORTEC, Oak Ridge, TN, USA) and was then analyzed by a multichannel analyzer (NT2400/MCA, Laboratory Equipment Co., Tokyo, Japan). The detector was mounted on...
an xyz stage (YA05A-R1 from Kohzu Precision Co., Kawasaki Kanagawa, Japan) driven by computer controlled stepper motors to give submicrometer resolution. This is necessary in order to align both focal spots to a common point. The sample was set on an xyz stage (YA05A-Ri, Kohzu Precision Co.). The xyz stage for the sample was controlled by stepping motors (NT-2400, Laboratory Equipment Co.) with a precision of 0.5 μm.

The whole setup was enclosed by a radiation proof cabinet. A photo of the setup can be seen in Fig. 1. The measurement process is controlled via a computer program called ‘SCAN-2’. This software was developed in cooperation with Laboratory Equipment Co. and is written in LabVIEW. SCAN-2 controlled both the sample stage and the spectrum acquisition enabling an automatic scanning procedure with selected parameters. Different types of measurement modes such as line scans and 2D area scans were possible. All spectra at OCU were taken in ambient air, so absorption of light element fluorescence radiation is expected.

### ATI spectrometer

The ATI confocal micro-XRF spectrometer used an Oxford Instruments ‘Apogee’ (Abingdon, Oxon, UK) low power microfocus X-ray tube (35 μm nominal focus size) as excitation source. Two different anode materials were used: Rh and Mo. Both X-ray tubes could be operated up to 50 kV and 1 mA with a maximum power load of 50 W for the Mo tube and 20 W for the Rh tube. Both X-ray tubes had a thin exit window (125 μm Be) to use the anode materials L-lines for the efficient excitation of light elements. Two polycapillaries from XOS are used in the spectrometer to focus the primary X-rays and restrict the detectors’ field of view. The primary polycapillary has a nominal spot size of 32 μm for Mo Kα radiation. Both optics can be adjusted automatically by means of two xyz stacks of attocube (München, Germany) ANPx101 and ANPz101 positioners.

Fluorescence radiation was detected by means of a 30 mm² Si(Li) detector with an ultra-thin polymer window (UTW, Gresham, now e2v, Milpitas, CA, USA) to minimize absorption of low energy X-ray photons with an FWHM of 175 eV at 5.9 keV. The sample was mounted on a motorized xyz stage with 25 mm of maximum travel and submicrometer resolution (M-112.12S, Physik Instrumente, Karlsruhe/Palmbach, Germany). The sample could easily be exchanged by means of a magnetic kinematic base (Newport, Irvine, CA, USA). An optical video microscope with tenfold magnification (Mitutoyo M Plan Apo, Mitutoyo, Kawasaki-shi, Kanagawa, Japan) was used to position the desired measurement area precisely into the beam.

The whole setup was enclosed in a vacuum chamber (also used for radiation protection) as can be seen in Fig. 2. Measuring under vacuum conditions and using a UTW detector and excitation with lower energies are very important for light element analysis in order to minimize absorption of the low energy fluorescence photons coming from light elements and optimize excitation conditions.

The spectrometer was computer controlled by means of specialized software developed at the Atom Institut. It allowed for automatic long time measurements with automatic spectrum region of interest evaluation for live measurement result preview. Additionally, all spectra were saved for further analysis, e.g. deconvolution with AXIL (QXAS, IAEA version 3.6). Table 1 gives a comparison of components used in both spectrometers. The parameters of the polycapillary X-ray optics can be found in Table 2.

### Discussion and results

#### Spatial resolution

Polycapillary X-ray optics focus the X-rays by means of total reflection inside the capillaries. The critical angle of total reflection is a function of the energy:

\[
\theta = \arcsin \left( \frac{n \lambda}{2R} \right)
\]

where \(n\) is the refractive index of the capillary, \(\lambda\) is the wavelength of the X-rays, and \(R\) is the radius of the capillary. The critical angle decreases with increasing energy, allowing for higher resolution at higher energies.

**Figure 1.** Setup of the Osaka City University spectrometer showing the major components. SD, silicon drift.

**Figure 2.** Setup of the Vienna University of Technology Atom Institut spectrometer. (a) Components in the vacuum chamber and (b) general setup with the vacuum chamber and outside components (reprinted with permission from Ref. 27).
Comparison of two confocal micro-XRF spectrometers

Table 1. Overview of the main components of both spectrometers

| Component          | OCU spectrometer                                                                 | ATI spectrometer                                                                  |
|--------------------|----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| X-ray tube         | rtw MCBM 65B-50 microfocus Mo anode                                               | Oxford ‘Apogee’ microfocus, Mo or Rh anode                                        |
| Detector           | SiL Vortex SDD                                                                    | Gresham 30 mm³ UTW Si(Li) detector                                                |
| X-ray optics       | XOS full and half lens, matching pair                                              | XOS full and half lens, matching pair                                              |
| Sample stage       | 3 × YA05A-Ri, Kohzu Precision Co.                                                 | 3 × Physik Instrumente M-112.125                                                  |

ATI, Vienna University of Technology Atominstutit; OCU, Osaka City University; SDD, silicon drift detector.

Table 2. Parameters of the polycapillary X-ray optics

| Parameter                       | OCU full lens | OCU half lens | ATI full lens | ATI half lens                        |
|---------------------------------|---------------|---------------|---------------|--------------------------------------|
| Nominal spot size               | 10 μm at Mo Kα| 32 μm at Mo Kα| 40 μm at 8 keV| 40 μm at 8 keV                       |
| Intensity boost                 | 7700 at Mo Kα | —             | —             | 39-fold versus 50 μm pinhole         |
| Transmission                    | —             | —             | —             | 11.1% at 8 keV                       |
| Input focal distance (mm)       | 2.5           | 52.70         | 5              | 5                                    |
| Output focal distance (mm)      | 2.8           | —             | 13.50         | —                                    |
| Output beam dimension (mm)      | 5.8           | 7.4           | —             |                                      |

ATI, Vienna University of Technology Atominstutit; OCU, Osaka City University.

\[
\phi_c \approx \frac{2.88}{E} \sqrt{\frac{Z \rho}{A}}
\]

Here, \(\phi_c\) is the critical angle in milliradian, \(E\) is the energy in kiloelectron volt, \(Z\) is the atomic number, \(\rho\) is the density in gram per cubic centimeter, and \(A\) is the atomic weight. This leads to an energy dependent spot size. As two polycapillaries form the confocal measurement volume, its size is dependent on the analyzed element and the fluorescent line used. It is smaller for higher \(Z\) elements (higher energies) and larger for low \(Z\) elements (lower energies) and elements measured using lower energy L-lines.

In order to measure the spatial depth resolution of the spectrometers over a wide range of elements, a set of thin layer standards have been prepared by NTT-AT in Japan. The elements are Al, Ti, Cr, Fe, Ni, Cu, Zr, Mo, and Au; the substrate is Si. The layers have a nominal thickness of 500 nm.

At ATI, the measurements have been performed using the Rh X-ray tube. Scans have been performed perpendicular to the surface. The acquired spectra have been deconvoluted using AXIL (QXAS, IAEA version 3.6). The reconstructed scan curves for each fluorescence line are Gaussian-shaped and were fitted using Origin™ (version 8.6, OriginLab). The obtained measured FWHM data were corrected by the layer thickness to obtain the depth resolution.[8]

\[
\text{FWHM}_{\text{beam}} = \sqrt{\text{FWHM}_{\text{profile}}^2 - \sigma_{\text{layer}}^2}
\]

At OCU, the measurements were performed with the Mo X-ray tube. A thin metal layer sample was mounted on the sample stage and scanned perpendicularly to the sample surface in confocal configuration. Intensities were recorded as a function of scanned distance. The minimum step size was 2 μm over a distance of about 100 μm. The measurement time was 300 s/point. Table 3 summarizes the acquisition parameters.

Table 3. Acquisition parameters for the thin layer SRMs

| Parameter                      | OCU | ATI |
|--------------------------------|-----|-----|
| X-ray tube                     | 50 kV/0.6 mA | 50 kV/0.4 mA |
| Acquisition time/point         | 300 s real time | 50 to 200 s real time |
| Scan length (μm)               | 100 | —   |
| Step size (μm)                 | 2   | 2   |

ATI, Vienna University of Technology Atominstutit; OCU, Osaka City University; SRMs, standard reference materials.

Finally, both datasets have been fitted using a hyperbolic fit function. Figure 3 shows the result for both spectrometers. The higher spatial resolution for the OCU spectrometer can clearly be seen. The explanation is of course the different spot sizes produced by the more advanced polycapillary optics in the OCU instrument compared with the ATI instrument. While only the depth resolution was probed with the thin layer standard, it was found that the spatial resolution in all three dimensions is comparable using a small (10 μm diameter) Cu wire. This test was only performed for the ATI spectrometer but is expected to be similar for the OCU spectrometer.

Lower limits of detection

To obtain information about the LLDs, a National Institute of Standards and Technology standard reference material 1412 Multicomponent Glass has been measured with both spectrometers. The measurement parameters can be found in Table 4. The confocal volume has been positioned to be in the surface layer. The following formula was used to estimate LLDs:

\[
\text{LLD}_{\text{element}} = \frac{3\sqrt{N_B}}{N_N} c_{\text{element}}
\]

\(N_B\) is the background counts, \(N_N\) the net peak area, and \(c_{\text{element}}\) the concentration of the element in the sample. Figure 4 shows...
The results were normalized to 1 mA for better comparison. It can be seen that the LLDs of both spectrometers are comparable for many elements and that they are in the microgram per gram region. However, because the ATI spectrometer has been designed having light element analysis in mind, elements down to C can be detected. This design also yields better LLDs for light elements.

### Depth profiling of paint layer samples

An application of confocal micro-XRF is the nondestructive probing of layered structures in the micrometer range. A scan was performed where the measurement volume was moved perpendicular to the sample surface into the sample. Peaks of characteristic lines appeared at different scan positions depending on the depth of the layer. If the same element was present in different layers, several peaks of this element's characteristic line will appear in the spectrum.

Test samples provided by the Vienna Museum of Fine Arts were measured with both spectrometers. The samples were small test paintings with various different layers of paints and primers on different base materials. The composition and layer structure was known. This test demonstrates the use of the spectrometers having light element analysis in mind, elements down to C can be detected. This design also yields better LLDs for light elements.

**Figure 3.** Comparison of the depth resolution of both spectrometers: Vienna University of Technology Atominstitut (ATI; dashed) and Osaka City University (OCU; solid).

| Parameter                  | OCU | ATI |
|----------------------------|-----|-----|
| Anode material             | Mo  | Mo  |
| Voltage (kV)               | 50  | 50  |
| Current (mA)               | 0.5 | 1   |
| Acquisition time           | 1000 s live time | 1000 s live time |

ATI, Vienna University of Technology Atominstitut; NIST, National Institute of Standards and Technology; OCU, Osaka City University; SRM, standard reference material.

**Table 4.** Measurement parameters for the NIST 1412 SRM

**Figure 4.** Comparison of spectra of National Institute of Standards and Technology (NIST) 1412 standard reference material: Vienna University of Technology Atominstitut (ATI; dashed) and Osaka City University (OCU; solid).
in the field of cultural heritage where nondestructive measuring techniques are important.\cite{31–33}

One sample is presented here exemplarily. Figure 5 shows a photo of the sample with the measurement area indicated by a white circle. The layer structure at this point can be seen in Table 6. As the paint was applied using a brush, no exact layer thickness is specified. Also, layer thickness will vary depending on the exact measurement point in the indicated area, as the brush does not produce a layer with constant thickness.

At ATI, all measurements were performed under vacuum conditions. Table 7 summarizes the measurement parameters. The acquired spectra were deconvoluted using AXIL (QXAS, IAEA version 3.6). The reconstructed scan curves for each element were fitted using Origin™ (version 8.6, OriginLab). One or several Gaussians were fitted to each element to obtain a good agreement with the measurement data. Figure 6 shows the experimental plots and the fitted curves through the data points. The layer sequence was identified correctly. Only Pb and Sn do not match perfectly, which is probably due to the different energies of absorption edges (Sn $L_3 = 3.929$ keV and Pb $L_3 = 13.035$ keV) and fluorescence lines (Sn $L_α = 3.444$ keV and Pb $L_α = 10.551$ keV). This changes the size of the measurement volume (as shown in Fig. 3) and the amount of self-absorption within the layer itself. Self-absorption for Sn $L_α$ radiation is stronger than it is for Pb-$L_α$ radiation. Also, no information could be obtained from layers below the Au, as this layer of pure Au is a strong absorber.

The measurement parameters for OCU can also be seen in Table 7. Region of interest data were used. The scans were also fitted using Origin™ (version 8.6, OriginLab) in the same way that the ATI data were treated. Figure 7 shows the result. Once again, the layer sequence is identified correctly with two exceptions. There is a second Fe peak before the Pb and Sn peaks. This is likely an effect of creating the samples by brushing on paint. As the sample was not perfectly homogeneous and the depth

| Table 5. LLDs for both spectrometers |  |
|--------------------------------------|--|
| Element    | LLDs OCU Mo ($\mu$g/g) | LLDs ATI Mo ($\mu$g/g) |
| Na         | —                      | 2351                 |
| Mg         | —                      | 2734                 |
| Al         | —                      | 702                  |
| Si         | 27,225                  | 338                  |
| K          | 199                     | 201                  |
| Ca         | 151                     | 170                  |
| Fe         | 21                      | 29                   |
| Zn         | 52                      | 42                   |
| Sr         | 337                     | 170                  |
| Cd (L)     | 1202                    | 813                  |
| Ba (L)     | 189                     | 271                  |
| Pb (L)     | 374                     | 195                  |

ATI, Vienna University of Technology Atominstitut; LLDs, lower limits of detection; OCU, Osaka City University.

| Table 6. Layer structure of the measured area of the paint layer sample |  |
|-------------------------------------------------|--|
| Type                        | Material                                      |
| Paint (top layer)            | 2 CuCO$_3$·Cu(OH)$_2$                        |
| Paint                        | Pb$_2$SnO$_4$                                 |
| Paint                        | Fe$_2$O$_3$                                   |
| Paint                        | HgS                                           |
| Metal overlay                | Au                                            |
| Base coat                    | PbCO$_3$·2Pb(OH)$_2$                          |
| Base (bottom layer)          | Cu                                            |

| Table 7. Measurement parameters for the paint layer sample |  |
|-------------------------------------------------|--|
| Parameter            | OCU                  | ATI                   |
| X-ray tube           | Mo anode, 50 kV/0.6 mA | Mo anode, 50 kV/1 mA |
| Acquisitions time    | 500 s real time       | 50 s real time        |
| Step size ($\mu$m)   | 2                    | 5                     |

ATI, Vienna University of Technology Atominstitut; OCU, Osaka City University.

![Figure 5. Photo of the paint layer sample. The white circle indicates the measurement area (reprinted with permission from Ref. 27).](image1)

![Figure 6. Result of the measurement with the Vienna University of Technology Atominstitut spectrometer (adapted from Ref. 27).](image2)
profiling was performed only at one position, the obtained depth profiles are dependent on the exact position because of the heterogeneous structure of the sample. Also, the Hg profile shows two maxima. Again, this is probably due to different measurement volumes and the heterogeneous structure of the sample.

A comparison of both measurements is presented in Fig. 8. The Au layer was used as the reference position and has been set to the same value in both profiles. Even though the curves do not align perfectly, the result is nevertheless comparable. Slight positional differences are due to the fact that the measurement position was not exactly the same for both measurements in Vienna and in Osaka.

The conclusions that can be drawn from this comparison are that a high resolution spectrometer is important for the successful measurement of layered structures and possible substructures. While the resolution of the ATI spectrometer is sufficient to resolve the layers, any substructure is mostly lost and can only be guessed from the unsymmetrical shape of the scan curves. The result is much clearer from the OCU spectrometer.

Also, further work needs to be performed in understanding and interpreting the measurement results from layer structures especially in the case of multi-element layers in order to obtain reliable results from the analysis of unknown samples.

Depth profiling of coated steel samples

As was just demonstrated, this can be important in the field of cultural heritage. However, also different applications require the sample to remain intact. In case of forensic samples, the destruction of the sample during the measurement process is also not desirable as evidence would be lost. Also, if it is needed to do repeated measurements of the same sample in the same measurement position in order to monitor, e.g. a chemical process, the method must be nondestructive. As an example for such an industrial application, confocal micro-XRF measurements have been performed on pieces of multilayered automotive paint on steel.

At OCU, samples were measured according to Table 8. Figure 9 shows the sum spectra of the measurement for both spectrometers. The elemental depth profile was fitted with Gaussians using Origin™ (version 8.6, OriginLab). Figure 10 shows the result of the analysis. Three groups of layers can clearly be seen: Ti and Sn on the top; Mn, Ni, and Zn in the middle; and Fe from the steel on the bottom.

At ATI, the samples were analyzed according to Table 8. The acquired data were deconvoluted using AXIL (QXAS, IAEA version 3.6), and the resulting scan curves were again fitted with Gaussians using Origin™ (version 8.6, OriginLab). Figure 11 shows the result. One can see that the OCU spectrometer completely misses the Al and Si found on the top with the ATI spectrometer. However, the resolution is not sufficient enough to clearly distinguish the different layers.

From the comparison in Fig. 12, it is clear that for optimal analytical performance, a high resolution and the capabilities to analyze a wide range of elements down to the light elements (Al, Si and P) are needed.

![Figure 7](image-url)  
**Figure 7.** Result of the measurement with the Osaka City University spectrometer.

![Figure 8](image-url)  
**Figure 8.** Comparison of the paint layer measurements with the Au layer set to the same relative position.

| Table 8. Measurement parameters for the coated steel samples |
|-----------------|-----------------|
| Parameter       | OCU             | ATI             |
| X-ray tube      | Mo anode, 50 kV/0.6 mA | Rh anode, 50 kV/0.4 mA |
| Acquisitions time | 500 s real time | 200 s real time |
| Step size (μm)  | 2               | 4               |

ATI, Vienna University of Technology Atominstitut; OCU, Osaka City University.
Figure 9. Comparison of sum spectra with counts scaled by number of measured points: Vienna University of Technology Atominstitut (ATI; dashed) and Osaka City University (OCU; solid).

Figure 10. Measurement of the coated steel sample with the Osaka City University spectrometer.

Figure 11. Measurement of the coated steel sample with the Vienna University of Technology Atominstitut spectrometer.
Conclusions and outlook

The comparison of the two different confocal spectrometers showed clearly that a high resolution and the capabilities to analyze a wide range of elements down to the light elements are needed for optimal analytical performance. This can be achieved by carefully choosing the components to enable light element analysis and modern X-ray optics for small beam sizes and by operating the setup under vacuum condition to prevent absorption of the low energy fluorescence radiation in air. The experimental conditions should consider the following: choosing the anode material carefully to optimize low Z element excitation, choosing a thin Be tube exit window, and using a detector with high resolution and an ultra-thin window to detect the low Z fluorescence radiation. A new spectrometer fulfilling the mentioned requirements was built by OCU and will be characterized soon.[34]

If considering the before mentioned aspects, new fields of application open up. Nondestructive investigations in 3D mode can be performed, e.g. analysis of cultural heritage objects, forensic investigations (evidence is saved) such as car paint chips from car accidents, industrial investigation of corrosion processes, and in life science spatially resolved trace element distribution in tissue. An unsolved problem remaining is the quantification of the found elements, as it is necessary to obtain a deep insight into the fundamental processes involved when using X-ray optics.

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