FEASIBILITY OF SUB-MICRON XRF COMBINED TO SCANNING PROBE MICROSCOPY

M. Dehlinger\textsuperscript{1}, C. Fauquet\textsuperscript{1}, F. Jandard\textsuperscript{1}, A. Bjeoumikhov\textsuperscript{2}, S. Bjeoumikhova\textsuperscript{2}, A. Erko\textsuperscript{3}, I. Zizak\textsuperscript{3}, S. Ferrero\textsuperscript{4}, D. Pailharey\textsuperscript{5}, B. Dahmani\textsuperscript{5}, D. Tonneau\textsuperscript{1}

\textsuperscript{1}CNRS, UMR7325, 13288, Marseille, France
Aix-Marseille Univ., CINaM, 13288, Marseille, France
\textsuperscript{2} IFG-GmBH, Rudower Chaussee 29/31, 12489 Berlin, Germany
\textsuperscript{3} HZB-BESSY, Albert Einstein Strasse 15, 12489 Berlin, Germany
\textsuperscript{4} Cie Axess Tech, 750 Chemin de Beaupré, 13760 Saint Cannat, France
\textsuperscript{5} Cie Lovalite, 18 rue Alain Savary, 25000 Besançon, France.

Corresponding author: Prof D. Tonneau
tonneau@cinam.univ-mrs.fr

ABSTRACT

In-lab high lateral resolution XRF tools are needed, mainly in the field of microelectronics and solar cell industries, as non destructive in-depth chemical analysis equipments. In the present work we have used capillary optics for both illumination and fluorescence signal collection. The primary beam provided by a rotating anode (CuK\textsubscript{\textalpha} line) is focused on the sample using a capillary lens (Xray spot diameter 20 \textmu m), while the EDX detector is equipped with a cylindrical capillary. System modelling and simulation are carried out to estimate the ultimate lateral resolution we could reach in chemical analysis using such equipment. The dependence of the fluorescence signal as a function of detection capillary diameter is simulated. The good agreement with the experimental data validates the model. It is demonstrated here that using an elliptical capillary approached in near field mechanical interaction with the surface would obtain a sub micron lateral resolution in XRF analysis, combined with simultaneous sample topography data acquisition.

INTRODUCTION

Among all the X-Ray techniques, XRF is widely used since it provides easy elemental chemical information about samples in ambient conditions. Many XRF-based techniques actually exist, such as EDX, WDS, imaging, total-reflection XRF…. (West et al., 2007; Tsuji et al., 2010; Sakdinawat and D. Attwood, 2010; Adams et al., 1998) and commercial
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instruments are becoming more widespread. Many synchrotrons (e.g. APS, ESRF, Spring8) offer the possibility to tune the incident energy and to provide a high monochromatic X-ray flux at the nm scale. Sample analysis becomes more sophisticated, since samples are complex including a great number of elements, sometimes present as traces (Khuder et al., 2007; Guerra et al., 2008; Horntrich et al., 2011). The large inhomogeneity variations in such samples is often a question to be answered. However, precisely defined calibration procedures and the use of standards allow now more and more accurate quantification (Mantler, 2006; Wolff et al., 2011; Horntrich et al., 2011). Moreover, a great variety of research fields use XRF such as archeology, materials science, pharmaceuticals, biology, art, environment….(West et al., 2007; Tsuji et al., 2010; Sakdinawat and Attwood, 2010; Adams et al., 1998). A great improvement was afforded these last ten years by the development of new X-Ray capillary optics (Arkadiev and Bjeoumikhov, 2006; Snigirev and Snigireva, 2008; Bjeoumikhov et al., 2003; Bjeoumikhov and Bjeoumikhova, 2008; Bjeoumikhov et al., 2009; MacDonald and Gibson, 2003) that allowed the irradiation of small areas with higher flux offering a good signal to noise ratio. Among the possibilities given by this technical breakthrough, is the emergence of µX-ray imaging now frequently used. Tremendous efforts are being developed to shrink the source as much as possible to increase the lateral resolution of the technique. A new generation of X-Ray sources have also emerged with liquid metal-jet anode sources (Hemberg et al., 2003; Otendal et al., 2007) that look very promising for in-lab analysis.

However, a different approach was also proposed in the literature to enhance the lateral resolution of the technique, that has not been extensively exploited. It consists in mounting a polycapillary lens for collecting the fluorescence signal, between the sample and the detector (Yonehara et al., 2009). Taking the advantage of both approaches, using a focused X-ray source, 3D µXRF analysis can be performed in the confocal volume defined by both lenses (Janssens et al., 2004; Woll et al., 2006; Nakano and Tsuji, 2009; Kanngießer et al. 2003; Patterson et al., 2010; Mazel et al., 2011).

In this work, following the same direction, we have built an XRF test-bed using a polycapillary lens to focus the primary Xray beam and a cylindrical capillary to shrink down the aperture of an EDX detector. We have first studied the dependence of the signal magnitude as a function of cylindrical capillary position and capillary diameter. We have modelled and simulated our experiments. The good agreement between experiment and
simulation validated the model and shows the fluorescence signal magnitude is expected to increase as the working distance decreases. From these results we show how a sufficient signal to noise ratio can be achieved to reach a lab-based sub-micron resolution of the technique, and sub 100 nm resolution in XRF analysis with a synchrotron source. This can be realized by coupling XRF analysis and Scanning Probe Microscopy, placing the capillary in near field mechanical interaction with the sample surface (working distance in the range of 10 nm).

EXPERIMENTAL

The experimental set-up is described in a previous paper (Dehlinger et al., 2011a). Briefly an X-ray beam, provided by a rotating anode (CuKα line, 40 kV, 40 mA), is focused on a cobalt sample, using a polycapillary lens. The Gaussian X-ray spot has a FWHM of 20 µm in the focal plane (Dehlinger et al., 2011b). Note that this design data is measured by the constructor using a low power source. The incidence angle is 45°. The X-ray fluorescence is collected by a SDD (Silicon Drift Detector) EDX (Energy Dispersive X-ray) detector equipped with a fused silica cylindrical X-ray capillary of L = 50 mm length and d_cap = 50, 20 or 10 µm diameter. The collection angle is also fixed at 45°. The detector is placed on X, Y, Z stages allowing its displacement parallel to the primary beam (X-axis) across the X-ray spot diameter. The working distance of the capillary is fixed to 5 mm.

Figure 1: Experimental set-up

We have studied the dependence of the X-ray fluorescence signal magnitude as a function of cylindrical capillary position, and of capillary diameter. The system is simulated with
MATLAB™, using a semi-finite element method. These calculations estimate the ultimate resolution we can reach in XRF analysis, using such an experimental configuration involving X-ray capillaries at both illumination and collection.

RESULTS

A spectrum, as shown in Figure 2, is recorded at each position of the detector along X axis, equipped with a 50 µm diameter cylindrical capillary. The ratio Kα / Kβ rays is in good agreement with literature data (Thompson and Vaughan, 2001). On each spectrum, we have calculated the Kα + Kβ peak areas sum. Figure 3 (squares) shows the dependence of the total fluorescence signal as a function of the capillary position along X-axis. In this figure we can note that the FWHM is about 90 µm, much wider than the incident beam focus diameter of 20 µm. In fact, the capillary has an acceptance angle equal to the fused silica critical angle θc which leads to a total field collected by the detection capillary of:

\[
d_{\text{cap}} + 2 D \tan (\theta_c)
\]

In our case, θc = 4.3 mrad (theoretical value of at 6.9 keV, energy of Co Kα line (Bjeoumikhov and Bjeoumikhova 2008) and D = 5 mm. Consequently the total field collected by the cylindrical capillary has a diameter of 93 µm.

![Figure 2: Typical spectrum of cobalt acquired through a 50µm diameter capillary.](image)

As the capillary is displaced along X-axis, the Co signal is expected to be detected over a maximum distance of 113 µm, for an incident spot diameter of 20 µm. The slight difference with the experimental result probably comes from the actual acceptance angle which must be lower than the theoretical value of the glass critical angle.
In order to define the limitation of our XRF set-up in terms of lateral resolution, we have modeled our system and simulated the experiments within MATLAB™. A Gaussian X-ray beam irradiates the sample with an incidence \( \theta \) (figure 4a). The sample is divided in cubic element cells whose top and east faces are illuminated by the primary beam (figure 4b). The fluorescence of each cell is assumed to be emitted by its centre in \( 4\pi \) direction. The capillary collects the part of the fluorescence emitted in the solid angle in which its extremity is seen from the cell center. For some cells, this solid angle can be limited by the critical angle of the capillary. The software takes into account the re-absorption phenomenon, but we have neglected the re-emission process in a first approximation. The simulation parameters are: the primary beam diameter, \( \Phi \); the working distance \( D \); the capillary diameter \( d_{\text{cap}} \); the size of the element cell.

Figure 3: sample fluorescence magnitude as a function of detection capillary position. The capillary diameter is 50µm. (dots) Experimental data. (solid line) Simulation.

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Figure 4: Simulated system. The X-ray incident beam is considered as Gaussian. The parameters are: cell size, capillary diameter, working distance, X-ray spot diameter.

Figure 3 (solid line) shows the simulation results using the following experimental parameters: \( D = 5 \text{ mm}, d_{\text{cap}} = 50 \text{ µm} \). To perfectly fit our experimental data we had to fix the
X-ray spot diameter $\Phi_{\text{spot}}$ at a value of 30 µm, slightly wider than the design data (20 µm). This difference is due to the fact that the spot diameter is wider with the rotating anode than with the microfocused source used by the manufacturer to provide the design data.

Figure 5 shows the dependence of the fluorescence signal magnitude as a function of capillary diameter (experimental data: dots; simulation: solid line). The signal magnitude obtained with a capillary of 10 µm diameter is 100 cps. The results obtained by simulation are still in good agreement with the experimental data, which validate the simulation software.

![Figure 5: Variation of the XRF signal collected as a function of capillary diameter. The working distance is 5 mm. (Dots) Experimental data. (solid line) Simulation.](image)

According to the acceptance angle of the capillary and the large working distance used in our experiments, the resolution of the set-up is presently poor (93 µm at a working distance $D = 5$ mm and for a capillary diameter of 50 µm). To increase the resolution of our XRF set-up, it is of course necessary to decrease the diameter of the detection capillary and to move its extremity as close as possible to the sample surface. This last constraint requires collection of the fluorescence with a cylindrical capillary perpendicular to the sample surface. It is expected that shrinking the area detected by the capillary would decrease the signal magnitude as well. Furthermore, in the case of the collection of fluorescence from a point source with a cylindrical capillary, the signal magnitude collected does not depend on the working distance (Arkadiev and Bjoёмikhov, 2005). Figure 6 shows the dependence of the fluorescence signal magnitude as a function of working distance (results of simulation with a capillary diameter of 50 µm, capillary axis perpendicular to the sample surface). One can note that the signal increases while the capillary extremity is moved towards the sample surface. In fact our
emission zone cannot be considered as a point source since its size is of the same order of magnitude as the capillary diameter. This curve exhibits three different regimes. In zone I, beyond 8 mm, the capillary is far from the sample surface and the fluorescence zone can be considered nearly as a point. A slight signal increase when the working distance decreases is nevertheless observed. When the capillary extremity is at distances smaller than 6 mm from the surface (zone II), the approximation of a point emission zone is no longer pertinent. On one hand, the signal must decrease when the capillary is moved towards the surface due to the reduction of the fluorescence area collected by the capillary. However, this decrease is balanced by a signal increase induced by fluorescence collection in a much wider solid angle. The final behaviour is a signal increase when the working distance is shortened. Finally, at very short working distances (zone III), below 1 mm, the collected fluorescence magnitude remains constant as the capillary is moved. In fact, at very short distances, the fluorescence area detected by the capillary extremity does not vary anymore.

Figure 6: Simulation of the XRF signal dependence on the working distance of the detection capillary. The capillary diameter is 50 µm.

All these experimental and simulation results estimate the ultimate resolution which can be reached in XRF using capillary optics for signal collection using a laboratory source. The collected area on the surface decreases with the capillary diameter. For example, with a 10 µm diameter capillary and a working distance of 5 mm, the area on the sample surface seen by the capillary is a 53 µm diameter disc. If we shrink the capillary diameter down to 1 µm without changing the working distance, the disc diameter will be 44 µm. So, in a rough approximation, the collected flux using a 1 µm instead of 10 µm diameter capillary is the ratio between the two collected areas i.e. $(44/53)^2$. To improve the lateral resolution of the technique, we have to move the detection capillary towards the sample surface as much as
possible, until the acceptance angle contribution to the collection area becomes negligible. This corresponds to the most important signal loss in this extrapolation, since, working at the surface vicinity, the surface collected decreases down to 1µm. The collected signal will be \((1/44)^2\) lower than the signal measured in this study. To get more signal, we thus must use a shorter detection capillary. For example, decreasing its length to 10 mm instead of 50 mm, it would be possible to obtain an extra gain of \((55/10)^2\). Finally, using a 1µm diameter capillary, fixed at “zero” working distance, the signal magnitude expected would be about 0.8 % of the fluorescence signal measured in this study. Replacing the cylindrical capillary by an elliptical one would increase the signal by a factor 20 (Bjoumikhov et al., 2006; Bjeoumikhov et al., 2005), i.e. nearly 20% of the fluorescence signal attained in our study. Finally, using a source with higher brightness, for example working with a liquid metal jet anode electron impact source (Hemberg, 2003; Otendal, 2007) one would obtain a sufficient signal level to achieve sub-micron resolution. Of course, operating with a synchrotron source could probably achieve a sub 100 nm resolution in XRF analysis.

The most important impact of this study is the possibility of coupling XRF analysis and Scanning Probe Microscopy. Indeed, operating at zero working distance suggests that the capillary extremity is positioned in near field mechanical interaction with the sample surface (with a working distance in the range of 10 nm). In this case the elliptical capillary could be used as a probe of a Shear Force Microscope (Tonneau et al., 2011), so that the sample topography and the fluorescence mapping would be simultaneously recorded. Such an instrument would probably allow imaging of a sample with a lateral resolution of 50 nm, and to obtain its chemical mapping by XRF analysis with a lateral resolution of 100 nm.

The coupling between X-rays and Scanning Probe Microscopy is already demonstrated (Larcheri et al., 2008, Fauquet et al, 2011). In this work, the sharp optical fibre (radius of curvature 50 nm), probe of the microscope, collects the visible luminescence emitted by a sample irradiated with a synchrotron source. To avoid beam shadowing effect by the tip, the primary beam is tilted at 20° regarding the sample surface. The apparatus was used to simultaneously acquire the sample topography and the local luminescence mapping. We propose to replace the sharp optical fibre by an elliptical X-ray capillary. In this case, the general idea is to image a surface with an elliptical X-ray capillary approached at the vicinity of the surface in near-field mechanical interaction, then to localize a peculiar object of interest, to position the probe with high precision on the object and to perform its chemical
analysis by XRF. The optimum working distance of such a capillary is far too high (tens of µm) to position its extremity in near-field conditions with the sample. However, it is possible to graft a sharp polymeric conic apex on the capillary extremity. This apex, transparent to X-rays, will position the tip in near-field interaction conditions, maintaining the X-ray capillary at the correct working distance regarding the sample surface.

CONCLUSION

An XRF test-bed, using a primary beam provided by a rotating anode (CuKα), was developed. A capillary lens is used to focus the excitation beam on a 20 µm diameter spot on a cobalt sample. Fluorescence is detected by an EDX detector equipped with a cylindrical capillary with a diameter between 10 to 50 µm. This set-up is tested and simulations are performed to estimate the signal level which could be reached when decreasing the capillary diameter to increase the lateral resolution. The signal level decreases with the capillary diameter, but increases when the detection capillary is closer to the sample surface. Clearly, the feasibility of lab-based sub-micron XRF is demonstrated, using very bright X-ray source such as focused liquid metal jet anode and moving the capillary close to the surface. Elliptical capillaries could also be used, to enhance the detected fluorescence signal level. Finally, moving the capillary extremity to a sub-10 nm distance from the sample surface would position the X-ray capillary in near field mechanical interaction. Then the capillary could be used as a Scanning Probe Microscope probe, giving simultaneously surface topography and chemical mapping at high resolution. Finally, working with a synchrotron source with a such approach would probably achieve a sub-100 nm resolution in chemical mapping by XRF, combined with sample topography.

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