3D MICRO X-RAY FLUORESCENCE ANALYSIS

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The paper introduces the principle and the basic properties of a rapidly emerging X-ray fluorescence (XRF) field in three-dimensional resolved micro XRF by means of a confocal setup. A fundamental parameter expression for the primary intensity was developed successfully in our institute. Its solutions for homogeneous materials permit an understanding of the confocal setup. The solutions also facilitate calibration with thick multi-element reference materials. The application of the 3D micro XRF for the investigation of the succession and composition of paint layers will also be given.

1. Introduction

One of the latest developments in X-Ray Fluorescence Analysis (XRF) is 3D micro-XRF by means of two confocally aligned X-ray optics. Fig. 1 sketches the principle of this type of experimental setup. The foci of two X-ray optics, one in the excitation channel and the other in the detection channel, overlap and define a probing volume. This is typically demonstrated by scanning through the probing volume with thin foils. The count rate is recorded, while the foil is moved stepwise through the probing volume. Fig. 2 depicts a count rate profile obtained with such a depth-scan. The resolution achieved up to now is around 20 μ m.

Over the past three years, a number of appli-



Fig. 1. Sketch of the confocal micro-XRF setup. The primary beam is focused by an X-ray optic. The view of the detector is restricted by a second optic, which is confocally aligned with the focus of the first lens. Thus, fluorescence radiation is only detected from the small probing volume which is defined by the overlapping foci.

cations carried out at various synchrotron radiation facilities demonstrated the usefulness of the new 3D micro-XRF method [2, 3, 4, 8]. In particular, the method is a unique tool if cross sections of the sample cannot be prepared. The investigation of art objects (paintings) has been its first and most frequent application [2, 3, 7, 9]. Three-dimensional imaging has been carried out for samples from geology by Vincze *et al.* They investigated a liquid inclusion in a diamond [8, 1]. Biological specimens were investigated by Janssens *et al.* In a demonstration experiment, the trace element distribution in a small marine lobster was recorded [4].

In contrast to the experimental part, which can be considered as developed to a large extent (at least with respect to synchrotron radia-



Fig. 2. Intensity profile of a Cu-foil. The graph depicts the intensity profile obtained by scanning a thin foil through the probing volume. The experiment was carried out with an excitation energy of 18 keV. The optic in the excitation channel was a polycapillary half lens. For the detection channel a polycapillary conical collimator was applied.

tion sources) the quantification of 3D micro-XRF measurements is in the early stage. Three different approaches have been proposed in the past year. They have in common, that they rely on and try to adapt fundamental parameter methods to the changed experimental setup.

2. Survey on Confocal Setups and Their Basic Properties

A variety of X-ray optics have already been employed for the confocal setup. Glass capillaries of both types have been used; poly-capillaries by Janssens et al. at HASYLAB [4] and by our research group at BESSY [2], a monocapillary by Woll et al. at CHESS [9]. At the ESRF, Vincze et al. employed a compound refractive lens [8]. In contrast to the excitation channel, where any type of optic can be used, for the detection channel, the choice is more limited because the optic has to offer a sufficient solid angle of acceptance and a broad energy bandpass. Therefore, polycapillary halflenses are used for this purpose. In our group, we also tested the application of a polycapillary conical collimator (polyCCC), which is just the tip of a poly-capillary lens [2, 3]. The polyCCC offers a large solid angle of acceptance and a good spatial resolution. However, its use is limited to energies below ca. 10 keV, because this type of glass capillary lens is rather short up to now.

As a consequence of the second optic, the solid angle of detection as well as the amount of sample seen by the detector is reduced. Therefore, in comparison to a conventional micro-XRF setup, the count rates detected are reduced and the lower limits of detection (LLD) are increased. Depending on the source and the optics, LLDs in the range of around 1 to a few 10 ppm are reported for lifetimes of 100 s. The second characteristic parameter, which is of major interest for a depth sensitive method, is the information depth achievable. Obviously, it depends on the absorption by the specimen's matrix elements. An estimate can be given with:

$$x_{\rm LLD} = \frac{2.3}{\overline{\mu}_{\rm lin}} \log_{10} \left(\frac{w}{\rm LLD}\right)$$
(1)

where $\bar{\mu}_{\text{lin}}$ is the effective linear mass attenuation coefficient, *w* is the weight fraction and x_{LLD} is the depth where the number of counts detected just exceeds the statistical limit of significance. The LLD is determined by a measurement with the confocal volume beeing just below the surface, when the intensity detected is at maximum [3]. As an example, Fe with a weight fraction of the 10-fold of its LLD can be detected up to $100 \,\mu\text{m}$ inside a SiO₂ matrix and up to 1 mm inside an organic (H₂O) material.

The extension of the probing volume, and, hence, the resolution of the confocal setup depends on the focal beam width of both optics. It varies with the excitation energy and with the atomic number of the element detected. For example, with an excitation energy of 18 keV and by using halflenses in the excitation as well as in the detection channel, the FWHM of Sr is typically around 20 μ m and the FWHM of Ca is around 50 μ m.

Most activities in 3D micro-XRF spectroscopy have been related to setups at synchrotron sources. Nevertheless, confocal micro-XRF spectrometers using X-ray tubes as source have been built up as well. The first setup of this type was used by Havrilla for the reduction of background radiation from radioactive samples. Another setup was built up by our research group. The lower limits of detection are 10 to 100 times higher than those achieved at a synchrotron source. With 100s live time we obtained 380 ppm, for Y and 2000 ppm for Cu. The FWHM of the profiles obtained with the tabletop setup were around 60 to 80 μ m. However, these characteristics are not yet optimal, the resolutions as well as the LLDs can still be improved with better optics. Havrilla reported the capabilities of the confocal table-top setup for three dimensional imaging with cobalt diffused into marble [10]; we showed its application to the analysis of paint layers (see Fig. 5) [3].

3. Quantitative Analysis

With regard to the development of quantification procedures, the experiments can be distinguished in two main categories: investigations of stratified material (we refer to that type as depth sensitive measurements) and the measurement of three dimensional structured samples. The author expects that the quantification algorithms for both categories will be different. The following approach treats the problem of depth sensitive measurements.

The derivation of the primary intensity equation starts with a thin sample. The count rate curve (intensity profile) obtained for a thin sample is already depicted in Fig. 2. As there is no self-absorption inside the sample, the intensity curve $\Phi(x)$ is proportional to the mass per area. It reflects the sensitivity profile $\eta(x)$ of the spectrometer. This relation can be written as:

$$\Phi(\mathbf{x}) = \Phi_0 \eta(\mathbf{x}) \sigma_{\mathsf{F}} Q \tag{2}$$

 Φ_0 is the incoming flux in counts per second, σ_F is the production cross section (cm²/g) which includes all factors for the atomic processes leading to the emission of a specific fluorescence line, Q is the element's mass per area, $\eta(x)$ is the dimensionless sensitivity profile and $\Phi(x)$ is the count rate detected.

In order to derive the intensity equation for thick samples, an approach similar to the one in conventional XRF is made. Consider a thin layer in a certain depth, ζ , as it is depicted in Fig. 3. As the specimen's composition may vary with depth, the attenuation must be written as an integral. In Eq. (3) the effective linear mass attenuation coefficient $\bar{\mu}_{\rm lin}$ is used, which already includes the attenuation of the incoming and the detected beams. The intensity contribution from this layer in depth ζ is assigned to center x of the sensitivity profile as the depth of the measurement. The integration over the samples thickness D results in a convolution of the sensitivity function with the density profile $\rho(\zeta)$ of the respective chemical element:

$$\Phi(\mathbf{x}) = \Phi_0 \sigma_{\mathsf{F}} \int_0^D \eta(\zeta - \mathbf{x}) \rho(\zeta)$$
$$\times \exp\left(-\int_0^\zeta \overline{\mu}_{\mathsf{lin}}(\zeta) d\zeta\right) d\zeta \tag{3}$$

For each of the chemical elements detected, such an equation can be introduced. Hence, following this approach, quantitative evaluation of depth sensitive measurements implies the treatment of a system of integral equations which are coupled via the attenuation term.

The complete treatment of this system of equations is still to be carried out. As a first step, we developed a model for the sensitivity η [5]. The resulting analytical representation will be useful for the solution of the convolution problem in Eq. (3). The development and the solutions for elementary cases provide fundamental insights into the properties of three dimensional X-ray fluorescence analysis. The analytical model for the sensitivity function $\eta(x)$ is derived on the basis of the properties of the X-ray optics used.

One of these properties, the flux density distribution in the focal region of glass capillary lenses have been investigated widely. Most authors point out that a Gaussian profile is a suitable to good description of the flux density. For the modelling of the sensitivity η , it is further assumed that the acceptance at the entrance side of a polycapillary lens can also be consid-



Fig. 3. Intensity of a thick sample. The sketch illustrates the fundamental parameter approach for the primary intensity of depth sensitive measurements. The sample surface is seen at the left side. The depth of the measurement is assigned to the maximum of the sensitivity profile. The approach is made for a thin layer in the depth ζ .

ered as Gaussian. As shown in detail in [5], a description of the three dimensional sensitivity $\eta(\mathbf{r})$ is obtained by the product of both Gaussians.

$$\eta(\mathbf{r}) = \frac{T_{\rm E}T_{\rm D}\Omega\varepsilon}{8\pi^2\sigma_{\rm E}^2} \times \exp(-(a_{11}x^2 + a_{22}y^2 + a_{33}z^2 + bxy))$$
(4)

where T is the transmission of the X-ray optics in the excitation and in the detection channel (subscripts E and D), Ω signifies the solid angle of detection, and ε is the detector's quantum efficiency, $\sigma_{\rm F}$ is the characteristic width of the (Gaussian) flux density distribution of the optic in the excitation channel. The shape of the sensitivity is determined by the exponential term. x, y, and z are the coordinates of the position vector **r**. The parameters a_{11} , a_{22} , a_{33} and b depend on the characteristic width of the optics and on the angle between excitation and detection. The term in the exponent represents an ellipsoid. With the angle between the beams being 90°, b vanishes, and the extension along the ellipsoids main axes, where the sensitivity drops to half of its maximum, equals the full width of half maximum of the respective X-ray lens.

At this point, we obtain a clear idea of what is called the 'probing volume' or 'confocal volume'. We can describe it as a sensitivity distribution, which decreases exponentially with increasing distance from its center. The iso-surfaces have the shape of ellipsoids.

In order to obtain the sensitivity profile, that was introduced in the intensity equations Eq. (2) and Eq. (3), one has to integrate the three dimensional sensitivity $\eta(\mathbf{r})$ over the targets sur-

face plane. It can be shown, that this results in a Gaussian function for any orientation of the target surface.

Finally, we can characterise the sensitivity for depth sensitive measurements with two parameters: the characteristic width σ_x and the integral sensitivity $\tilde{\eta}$, both of which can in principle be traced back to the properties of the X-ray lenses:

$$\eta(\mathbf{x}) = \frac{\tilde{\eta}}{\sqrt{2\pi\,\sigma_{\mathbf{x}}}} \exp(-\mathbf{x}^2/2\sigma_{\mathbf{x}}^2) \tag{5}$$

With Eq. (5) an analytical expression for the primary fluorescence intensity of a homogeneous layer of a certain thickness D is obtained, when it is combined with Eq. (3):

$$\Phi(\mathbf{x}) = \frac{\Phi_0 \tilde{\eta} \sigma_{\mathsf{F}}}{2} \rho_i \exp\left(\frac{(\overline{\mu}_{\mathsf{lin}} \sigma_{\mathsf{x}})^2}{2}\right) \exp(-\overline{\mu}_{\mathsf{lin}} \mathbf{x})$$
$$\times \left[\exp\left(\frac{D + \overline{\mu}_{\mathsf{lin}} \sin_{\mathsf{x}}^2 - \mathbf{x}}{\sqrt{2} \sigma_{\mathsf{x}}}\right) - \exp\left(\frac{\overline{\mu}_{\mathsf{lin}} \sigma_{\mathsf{x}}^2 - \mathbf{x}}{\sqrt{2} \sigma_{\mathsf{x}}}\right) \right]$$
(6)

It is possible to compare the shape of the intensity profile obtained with a scan of a homogeneous glass reference material with the predicted curve. In Fig. 4 the intensity profile for Sr is depicted. For the theoretical curve, the parameters sensitivity $\tilde{\eta}$, characteristic width σ_x and the overall density ρ were used as free parameters for fitting the measured curve. The calculated curve matches the measurement quite well, supporting the correctness of the model. Although the theoretical profile agrees well with the measurement, one should note that the sensitivity profiles found in experiments might deviate from a Gaussian. Woll *et al.* for example, who applied a single bounce monocapillary with a long focal distance on the excitation side, report a skewness of their profile [11].

In any case, where the model of the sensitivity is valid, the procedure introduced above can be applied for the calibration of the 3D micro-XRF spectrometer. It facilitates a calibration based on thick multielement reference materials.

A preferable analytical case is that the dimensions of the structure of the specimen are larger than the typical width of the probing volume. Then both error functions in Eq. (6) take the value 2. Two absorption terms are left. One is a plain Lambert-Beer term. However, one should recall, that Eq. (6) stands for a homogeneous bulk sample. For inhomogenous samples, $\bar{\mu}_{lin}x$ must be replaced by the integral from the surface to the position measured. The second exponential term represents the self absorption inside the probing volume. If the 'mean free path' $1/\bar{\mu}_{lin}$ is small compared to the width of the sensitivity profile σ_x (around 10 μ m), it may be neglected and only the Lambert-Beer absorption term is left. The development of a quantification, based on this equations seems to be a promising next step.

However, it should be stressed that there is a general limitation for quantitative 3D XRF. In Eq. (6) the density ρ_i is the parameter describing the sample. It represents the local density of the element *i*, not the density the element has as an



Fig. 4. Theoretical and experimental intensity profiles for glass reference material. The squared symbols depict the intensities measured. The intensity of Sr increases from the left to the right, when the micro volume moves from outside the sample into the material and decreases again due to absorption. The theoretical profile, obtained by fitting agrees well with the experimental values.



Fig. 5. Intensity profile of a two layer system. The sample consists of a layer of chrysocolla, a green siliceous pigment with copper as main constituent, and a second layer of white lead. The shift of the profiles indicates two separate layers of around 10 and 20 μ m thickness, respectively.

atomic property. This is a basic property of 3D micro-XRF. The count rate detected for a specific element depends on its local density in the specimen and not on its weight fraction. Basically this is due to the fact, that the mass of the atoms seen by the detector determines the count rate. In the case of confocal XRF, this is the mass inside a volume defined by the spectrometer.

In order to obtain weight fractions of the elements the overall local density of the sample must be known. The intensity of the scattered radiation is a measure for that. However, its quantitative treatment is challenging, in particular in the case of excitation with synchrotron radiation, which is polarised.

4. Indian Mughal Paintings—An Application Example

The application example presented in the following was part of a study of the composition and structure of Indian paintings from the Mughal period, which started midth of the 16th century and ended with the beginning of the 19th century [6]. These paintings, showing souvereigns or other important personalities, were produced by a specific technique in particular workshops. The paint layers were applied successively and each was polished to confer a particular gloss. The objective of the study was to increase the up to now only scarce knowledge of the painting techniques and the pigment palette used by the artists of this period.

A typical count rate profile obtained is depicted in Fig. 5. The shift of the profiles indicates a succession of two layers, one with ca. 10 μ m thickness, the other one with around 20 μ m. The sample was prepared for a feasibility study in advance to the application of the new method to the precious Mughal paintings. The measurement was carried out with tube excitation, whereas the following results were obtained at a wavelength shifter beamline at BESSY II.

One of the miniatures investigated is the portrait of Abdallah Zakhmi (Fig. 6), dated to the end of the 17th century. However, the dating is doubtful, because Sn-white and Zn-white was used. These pigments were found in prior measurements using PIXE. In Europe, artists applied Zn-white not earlier than in the 19th century. However, for India this is still disputed, because Zn was mined there already before the beginning of the Mughal period.

At several points on the turquoise background, on the orange skirt, and on the white dagger depth scans were carried out. One of the intensity profiles obtained for the white dagger is depicted in Fig. 7. Not only at the background but also at the skirt and even at the small dagger, which is only a few mm large, the depth scans always revealed only one single layer. This was quite unexpected from the view-point of art-history. In order to make sure, that the profiles actually represent single layers, and that the results are not due to strong absorption hiding the deeper structure, an estimation of its thickness was necessary. As by now, and at the time of the investigation of the Mughal paintings, a quantification which treats the system of integral equations (6) is not yet developed, a simplified way was chosen. The sensitivity function which was determined with a glass reference material, was convoluted with a rectangular function for each chemical element separately. The width of the rectangular function represents the thickness of the paint layer, whereas the height is the local density of the re-



Fig. 6. Mughal painting 'Abdallah Zakhmi', Museum of Indian Art, Berlin. In order to investigate the succession of layers, measurements were taken at the three labelled points. The painting is dated to the end of the 17th century. However, the dating is doubtful, because Sn and Zn was used as a pigment.

spective element. Self absorption is thereby neglected. For the two main components Zn and Sn, layer thicknesses of 16 μ m for Zn and 12 μ m for Sn were calculated. The densities obtained were 330 mg/cm³ and 950 mg/cm³. The layer thicknesses have about the size of the resolution limit and therefore the deconvolution produces results with high uncertainty. A more reliable quantity is the product of thickness and mass density, i.e., the mass deposition of the respective chemical elements. This is sufficient for the determination of the attenuation of radiation which might originate from an underlaying paint layer. It is thereby possible to prove that in particular lead from the skirt of the portraved Abdallah Zakhmi would be detected with considerable count rate if present. Through this calculation the finding that there is only one single paint layer present could be confirmed.

Another example from the same investigation demonstrates the capabilities to reconstruct complex layer systems. In Fig. 8, the count rates of Rayleigh and Compton scatter peaks are plotted. The intensity of the scattered radiation reflects the overall density of the matrix. The right peak is caused by the pigments of the paint layer. For the other three peaks, no corresponding fluorescence was detected. The reason for these oscillations in the detected scatter intensity is a succession of lime and paper. The painters of the Mughal period prepared their painting cardbord by liming sheets of paper upon each other. This preparation included intermediate polishing and pressing. Obviously, with the measurement of Fig. 8, a spot was hit where this polishing was not carried out with



Fig. 7. Count rate profile obtained at the dagger. The count rate profiles are normalised to one. The maximum count rates in units of $(s nA)^{-1}$ are included in the legend (nA is the current of the ionisation chamber, monitoring the incoming flux). The profiles clearly indicate a single paint layer.



Fig. 8. Scattered intensity. The graph depicts the profile of the intensity of the scattered radiation. The peak at the right side is due to the pigment layer, the other peaks are due to lime between the paper sheets. Depicted as well is the calculated intensity profile, obtained by the reconstruction of the density profile of the sample as it is shown in Fig. 9.



Fig. 9. Reconstructed density profile. The reconstruction was obtained by fitting the position and the thickness of a given number of layers. Only the convolution with the sensitivity profile was calculated, absorption was not taken into consideration (see Eq. (3)).

care. In Fig. 9, the result of a reconstruction of the thickness of the structures with the same method as described above is shown. The theoretical count rate profile is plotted in Fig. 8. The reconstruction in Fig. 9 gives an impression of the capabilities to reconstruct the structure of stratified materials. The independently found layer succession coincides well. However, the shoulder at the paint layer might also be an artefact. To discriminate reliable results from unreliable ones will be one of the tasks in the course of the development of quantitative analysis for 3D micro-XRF.

5. Summary

Within the three years since the first confocal micro-XRF setup has been built up the new method was applied in various fields of research. The first application was in archaeometry. Meanwhile, samples from geology, life science and materials science were investigated. 3D micro-XRF experiments have been carried out at various synchrotron radiation facilities, e.g. Bessy II, ESRF, Hasylab, CHESS. At Bessy and at CHESS, 3D micro-XRF spectroscopy will be made available as a standard tool. Confocal micro-XRF setups using an X-ray tube as source have been built up as well and a few applications are known.

A field of current research is the development of quantification methods for 3D micro-XRF. The first steps towards quantification revealed basic properties of the method. The correction of absorption effects and the calculation of the sample composition based on fundamental parameter methods will be feasible. However, there will be foreseeable limitations in precision for the latter, because such calculations must include the treatment of the scattered excitation.

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References

- B. Vekemans, L. Vincze, F. E. Brenker and F. Adams: Journal of Analytical Atomic Spectrometry, **19** (2004), 1302–1308.
- [2] B. Kanngieser, W. Malzer and I. Reiche: NIM, B211 (2003), 259–264.
- [3] B. Kanngießer, W. Malzer, A. F. Rodriguez and I. Reiche: Spectrochim. Acta, B60 (2005), 41–47.
- [4] K. Janssens, K. Proost and G. Falkenberg: Spectrochim. Acta, B59 (2004), 1637–1645.
- [5] W. Malzer and B. Kanngieser: Spectrochim. Acta, B60 (2005), 1334–1341.
- [6] I. Reiche, R. Gadebusch, O. Hahn, U. Reinholz, B. Kanngießer and W. Malzer: Proceedings of the 34th International Symposium on Archaeometry, submitted.
- [7] Z. Smit, K. Janssens, K. Proost and I. Langus: NIM, B219–220 (2004), 35–40.
- [8] L. Vincze, B. Vekemans, F. E. Brenker, G. Falkenberg, K. Rickers, A. Somogyi, M. Kersten and F. Adams: *Anal. Chem.*, **76** (2004), 6786–6791.
- [9] A. R. Woll, D. H. Bilderback, S. Gruner, N. Gao, R. Huang, C. Bisulca and J. Mass: *Mater. Res. Soc. Symp. Proc.*, **852** (2005), 281–290.
- [10] G. J. Havrilla and N. Gao: 51st Annual Denver X-ray Conference, Denver, USA, (2002).
- [11] A. R. Woll, J. Mass, C. Bisulca, R. Huang, D. H. Bilderback, S. Grunder and N. Gao: *Appled Physics A*, submitted.