Recent developments at the TwinMic beamline at ELETTRA: an 8 SDD detector setup for low energy X-ray Fluorescence

A Gianoncelli¹, G Kourousias¹, A Stolfa¹, B Kaulich¹²
¹ ELETTRA Sincrotrone Trieste ScpA, S.S. km 14 in Area Science Park, 34149 Basovizza, Trieste (Italy)
² Now: Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, United Kingdom
E-mail: alessandra.gianoncelli@elettra.trieste.it

Abstract. The present manuscript reports the characteristics of a novel Low Energy X-ray Fluorescence (LEXRF) system installed at the TwinMic X-ray Microscopy station operated at Elettra synchrotron (Trieste, Italy). The setup has been recently upgraded to an 8 large area Silicon Drift Detectors (SDD) system able to collect the XRF fluorescence emitted by the specimen in the 180-2200 eV energy range. The LEXRF system in an X-ray microscope has allowed combining chemical specificity of the specimen with the morphological information acquired in transmission at submicron length scales. Distinct advances of the new set-up are related to software system that has introduced new algorithms and methods.

1. Introduction
X-ray fluorescence is a spectroscopic technique that can be applied in a large variety of fields, spanning over biology [1], food science [2], and forensics [3]. Many synchrotron radiation facilities [1,3] and commercial laboratory and portable XRF systems use high-energy X-ray sources (> 2 keV) [4]. Low-energy XRF (LEXRF) systems are still relatively unexplored due to i) the low fluorescence yield, ii) the strong absorption of low energy XRF photons by air and iii) the small working distances determined by the short focal lengths of the X-ray optics at such photon energies. Nevertheless LEXRF is attracting increasingly more attention since it allows elemental mapping of light elements, namely C, N, O, Mg, Na, that are the main constituents of life matter. Therefore LEXRF can provide important information for studying biochemical processes. Nowadays even if there exist a few in-vacuum operation LEXRF instruments available at synchrotron facilities [5], to our knowledge the TwinMic LEXRF prototype system [6] has been the first one combined with transmission X-ray microscopy capable to detect emission lines down to B (Figure 1). The present paper reports on the recent upgrade of the system, showing the new setup in addition to recent results and the choice of a new HDF5-based data structure [7] that enables a better insight to the data.

2. Experimental setup
TwinMic is a soft X-ray transmission microscope working in the 400-2200 eV energy range that combines full-field imaging and scanning X-ray microscopy in a single instrument [8]. It can provide versatile contrast modes including absorption/brightfield and phase contrast imaging. The LEXRF system is used when TwinMic is operated in Scanning X-ray Microscopy mode (SXM), where the microprobe down to sub-100 nm size is provided by a zone plate diffractive optics and the sample is raster scanned with respect to the microprobe. The transmitted X-rays are collected by a Fast
Readout CCD camera through a X-rays-visible light converting system [9] while the emitted XRF photons are recorded by the LEXRF system. This provides simultaneously the morphological information through absorption and phase contrast images, and elemental maps generated by the LEXRF system.

2.1 The LEXRF setup
The current state of the LEXRF system consists of 8 windowless Silicon Drift Detectors (SDDs) from company PNsensor [10] disposed circularly around the sample (Figure 2). The SDDs are located on a copper support provided with a pipe system allowing circulating water to bring away the heat produced by the hot side of the Peltier cooler. This permits to cool down the SDDs to -15 °C. The SDDs have an active area of 30 mm² and FWHM of 135eV at 5.9 keV and 69eV on the C Kα line. They are windowless in order to reduce the absorption of B and C line; nevertheless it was noticed that after sometime the surface of the detector could get contaminated from the sample. Therefore customized protection caps based on a Si₃N₄ window with 75 nm thickness have been applied on the SDDs case in order to minimise the degradation of the detectors. The SDD axes are at 20 degrees in respect to the specimen surface and the SDDs are at around 28 mm distance from the focal point of the zone plate optics. The total solid angle acceptance is therefore 2.4 sr.
A customised pulsed reset preamplifier and MCA FPGA-based processing electronics was built by XGlab [11]. The biasing board and the preamplifier are located inside the TwinMic vacuum chamber (10⁻⁶ mbar). More details are available in [9].

2.2 Software upgrade for large data
The amount of data that the 8 detector setup produces is very large (i.e. a single 100x100 scan, using 8 SDDs of 8192x16bit channels each, produces 1.311GB). The main control is through a LabView solution that manages the synchronisation of the STXM with the LEXRF acquisition. Recent software developments have resulted to the Spectrαrithmetics platform [13] that is an add-on to the acquisition workflow. The platform realises an XRF specialised data structure relying on the HDF5 data format [7,11] and various techniques for fast data pre-processing (i.e. energy calibrated SDD sums) in a modular and expandable way. The 8 detector system coupled with the software updates permits faster and more efficient processing than any previous setup.

3. Results
3.1 Elemental mapping
The TwinMic LEXRF can provide 100 nm spatial resolution elemental mapping [8] (Figure 4), the limitation in the lateral resolution being the intensity of the XRF signal. The microprobe size is chosen as a compromise between reasonable spatial resolution and good XRF statistics.
The developed LEXRF has been successfully applied in several experiments for elemental mapping of different chemical elements [15]. Relevant studies include: electrodeposition and corrosion of metals electrodes for fuel cells applications [16], investigation of chemical elements involved in asbestos toxicity in human lung tissues [17], elemental distribution of physiologically important elements in food samples [17,18], cellular distribution and degradation of CoFe2O4 nanoparticles (NPs) in fibroblast cells [19]. For instance by mapping Co and Fe distribution (by monitoring their L emission lines) in cells exposed to different concentration of NPs the latter study allowed revealing that the NPs are mainly clustering in the perinuclear region (Figure 3). For more details see reference 19.
Beside qualitative elemental distribution, procedures and suitable standards for quantitative XRF mapping are under development. XRF quantification at low energy is still poorly exploited due to the difficulty of getting suitable standards and the degree of uncertainty of XRF parameters below 1 keV.

Figure 3. Absorption image (a), Co and Fe elemental maps in a fibroblast cell exposed to 500 µM concentration of CoFe2O4 NPs (74.5µm x 32µm, 93x40 pixels, 450nm spot size) (Courtesy of G. Ceccone). The XRF intensity is in counts normalised by acquisition time and ring current.

Figure 4. Ni XRF maps obtained on a Ni Siemens Star. The images show the Ni counts collected by 4 SDDs located at 90 degrees one from the other (10µm x 10µm, 100x100 pixels, 100nm spot size).

3.1 New imaging modes in development
The SDDs are installed as single detector elements in order to better match the mechanical constraint of the TwinMic sample compartment. For ordinary XRF mapping it is typically used the sum signal from the 8 SDDs. This gives a total response that is equivalent to a single SDD with bigger active area, therefore higher count rate. Nevertheless the spectra collected by the single SDDs are separately saved. In this way the signal recorded by the different detectors can be monitored and processed independently. As previously mentioned the SDDs are installed in a relatively grazing configuration in respect to the sample surface. Therefore the specimen surface can create shadowing effects for the SDDs and the different detectors may record a different count rate for specific scanning points, even though the XRF emitted by the sample is isotropic. Preliminary tests made on a Ni Siemens star with a 4 SDDs system clearly show the different response of the detectors (Figure 4). A depth map of the sample surface, could be retrieved by differentiating the signals coming from the different detectors. We expect that a topographic map will complement the information currently provided during the scanning. Such type of imaging has very high demands in terms of data access and raw processing.
power. This is work in progress and its algorithmic and software side are part of the Spectrarithmetics platform [11] and will be the subject of a future communication.

Conclusions and Future Perspectives
The reported TwinMic LEXRF developments have resulted to substantial capabilities for elemental mapping of light elements. TwinMic in the latest LEXRF mode has been successfully used in multiple research fields. The development and installation of a monolithic array of multielement Si detector is under evaluation since it may provide a bigger solid angle of detection allowing the reduction of the acquisition time and the potential increase of the detection limits. Further future improvements to the current setup may be achieved through the development of faster and lower noise electronics for more efficient processing of the XRF signal, aiming at better signal to noise ratio and faster data acquisition.

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