Signal alignment problems on multi-element X-ray Fluorescence detectors

Francesco Guzzi[1,2], George Kourousias[2], Fulvio Billè[2], Gioia Di Credico[3], Alessandra Gianoncelli[2], and Sergio Carrato[1]

[1] Image Processing Laboratory, University of Trieste, Italy
[2] Elettra Sincrotrone Trieste, Basovizza, Italy
[3] Department of Statistics, University of Trieste, Italy
Corresponding author: francesco.guzzi@elettra.eu

Abstract. X-ray fluorescence (XRF) is a spectroscopic technique with applications in several fields, such as biology, food science and forensics. Often setups have multi-element detectors in order to improve the signal-to-noise ratio. The relative set of produced spectra have to be aligned to a reference spectrum, in a procedure that is referred to as energy calibration, which is necessary for the fitting. Automated methods fail and a manual procedure is typically employed instead. In this paper, we discuss the signal alignment problem of such systems and we illustrate the preliminary results of a new automated method for linear XRF spectra alignment, which potentially can be used also for other time-series like data.

Keywords: LEXRF, Signal alignment, Energy calibration, SDDs

1 Introduction

X-ray fluorescence (XRF) is a spectroscopic technique that is currently applied in a large variety of fields [1], spanning from biology, cultural heritage, food science and space exploration [2]. XRF spectra are commonly exploited to gather information on the composition of a specimen, as the X-ray fluorescent emissions appear at specific photon energies, making elemental identification a complex but definitely solvable inverse process. Due to its nature, the Low-Energy variant of the technique (LEXRF) poses many more experimental difficulties [3] but is crucial for the identification of light elements. Silicon Drift Detectors (SDD) [4] are currently the most employed to measure the photon energy for each detected photon as it arrives; indeed, the amount of photo-produced electrons is a function of the pair creation energy and the incident photon energy, which can then be calculated by measuring the total accumulated charge of the signal pulse [4]. If a micro-focused X-ray beam (Fig. 1 a) is raster-scanned onto a sample surface (Fig. 1 b) [5], the elemental information (provided by the acquired spectra) is also spatially dependent, producing an "elemental map" of the specimen itself (Scanning Fluorescence X-ray Microscopy). The spectroscopic information is sometimes correlated with the outcome of another imaging technique, such as Scanning Transmission X-ray Microscopy (STXM) that instead provides the sample absorption information (Fig. 1 e) [2]. Setups such as the ones employed

at the TwinMic spectro-microscopy beamline [5] of the Elettra Sincrotrone Trieste synchrotron facility are specially designed to simultaneously perform both the experiments, by employing a transverse XRF detector geometry (Fig. 1). Being the produced XRF radiation isotropic, in order to increase the counting efficiency (but also to acquire topographic information [6]) it is mandatory to increase the observation solid angle, preferably not by enlarging the detector area, but by increasing the number of channels [7] (Fig. 1 c1), arranging many small detectors around the specimen (Fig. 1, panel c2). Thus, to obtain meaningful information, especially for low counts spectral lines, each spectrum needs to be summed channelwise. High pixel count planar ring configurations [8] have been superseded by a slanted design with many SDDs suspended around the sample. As a result, both the detector capacity (and thus the Equivalent Noise Charge) and the risk of pile up are reduced. TwinMic currently employs 8 SDDs which cover a solid angle of 0.255 sr, meaning that 4% of the isotropically emitted photons are collected [5]. New detectors and instrumentation design are under active development and will provide a total surface area that covers 22.4% of the entire hemisphere; the proposed solution will employ a total of 32 detectors [7]. Even more complex design with 64 channels are under development [9].
A set of quantised spectra (Fig. 1 d) is the starting point for the data analysis (element fitting). Unfortunately, due to the heterogeneity in the signal processing chain, the effective value of each energy bin for each channel is slightly different, meaning that no channel-wise operation (e.g. summation/average) can be directly carried out on the raw spectra. The spectra are not only energy-shifted but a scale transform is also required for the x-axis to correctly align the signals. Many automatic techniques can be fooled [10]: being collected from different viewpoints, each spectrum is only similar to the others and possesses only few common features. Manual alignment is thus currently the preferred method, which however becomes more tedious and error-prone as the number of channels increases.
In this paper, we describe the problems of multi-channel energy calibration and present the preliminary results obtained by employing an automatic multi-stage technique that is promising for our class of signals.

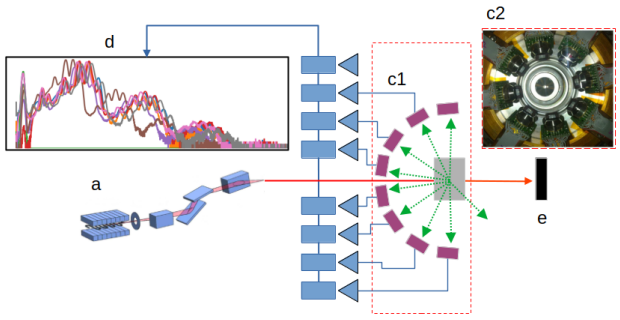

Fig. 1: Transverse geometry spectro-microscopy beamline: an X-ray beam is produced, focused (a) and projected onto a sample (b). X-ray fluorescence is partially detected by the detector arrangement (c1, c2). The processed signals are raw spectra which require an energy calibration procedure (d) prior to fitting. The absorption image is recorded on a different detector (e).

2 Alignment problem and state of the art solutions

Mono-dimensional signal alignment, or in this context *energy calibration*, is a problem that is faced in many fields, from speech processing to time series analysis. As for image registration, the degrees of freedom define the underlying correction model. In our context, we are interested in a transformation of the form [11]:

$$f'_k = a \cdot f_k + b \tag{1}$$

where f_k is the *kth* energy bin in the original axis, f'_k is the bin in the transformed axis, a is a scaling parameter and b controls the shift. The amount of recent work in the literature related to spectra alignment is the measure of how the problem is not completely solved yet [10]. Indeed, even in the case of commercial multi-channel systems, the acquisition software provides a GUI for semi-automatic methods, which rely on the human-made selection of features in the signals (peaks). Similar reasoning is applied also for open-source solutions, such as PyMCA [12], a widely used software for XRF processing. From this perspective it is apparent that a common approach to signal alignment is based on three phases: 1) peak detection; 2) peak matching among different signals and 3) transform parameters estimation from the peaks list. Manual intervention is obviously required only in the first two phases where the user is asked to select corresponding features among many spectra. However, automatic methods following the same reasoning are also reported, e.g. in [13]; a second common solution to signal alignment is referred to as "Dynamic Time Warping" [14], a non-linear warp procedure that is typically employed in speech processing. The method is designed to align two signals by creating a warping path in the 2D synthetic space of the x coordinates, which describes the joint coordinates transformation that makes the two signals appear more similar. Unfortunately, this approach is not very suitable for our purpose as it is designed for a pairwise alignment and no fixed reference is maintained. A second major drawback is the severe deformation of the signals (staircase artefact, Fig. 2 panel e). A third common way to align the signals is to formalise the process in an optimisation framework, where a loss function such as MSE or a form of correlation is iteratively minimised (maximised). In [11] the authors propose the Pearson correlation as a loss function and employ a windowed non-linear refinement near the peaks. A different type of iterative process is instead used in [15] which is a hybrid technique, where an artificial signal is generated by finding the locations of the peaks on the reference signal and parameters of (1) are then iteratively searched to maximise the correlation between any other spectra with this artificial reference signal.

3 Proposed method

In this paper we propose the use of a two-step procedure which employs two different iterative processes. Similarly to an image registration procedure [16], the main alignment step is carried out within an optimisation framework which uses a multi-resolution approach, from the coarsest to the finest resolution. This pyramidal approach is essential to capture the global envelope of each spectrum and avoid local minima in the loss function, notwithstanding the differences

among the curves. Additionally we propose the use of the Normalised Mutual Information (NMI) as the optimisation function [17], which measures how a given function value in s_1 can be predicted by the corresponding value in s_2. It can be calculated by (2):

$$NMI(s_1, s_2) = \frac{H(s_1) + H(s_2)}{H(s_1, s_2)} \tag{2}$$

where $H(s_1)$ and $H(s_2)$ are respectively the entropies of the two signals s_1 and s_2, while $H(s_1, s_2)$ is the joint entropy. The minimisation can be carried out by negating (2). For each channel (detector), all the acquired spectra at any pixel are summed up to produce the cumulative spectra to align. The algorithms starts by choosing one signal of the set as the common reference. This choice can be made upon the number of features in a spectrum, or by choosing the spectrum with highest energy. To prepare for the second step, a peak finding routine is used on the per-channel mean, helping to reject false positives for the peaks. The actual second alignment uses the peaks-made synthetic signal as described in [15], exploiting a grid search approach. Each pairwise alignment is carried out independently from each other trough a multi-process parallel software architecture. This is crucial for a large number of spectra such as in [7].

4 Results

The proposed algorithm was tested on a set of two cumulated XRF scans [18] which we released online [19]. The spectrum obtained at each pixel is summed to create the cumulated signal for each channel-detector. Fig. 2 shows how the raw signals in panel a are aligned cascading the two algorithms as described in the previous section (panel b). Algorithm [15] alone is easily fooled by signal variations, leading to an incorrect alignment for one of the pairs (panel c). Conversely, the iterative algorithm we formulated is more capable of finding a coarser transform which can be sufficient in some cases (panel d). It has to be noted that the signal of channel 2 (Fig. 2) is composed only by one peak, the first. Fig. 2 panel e shows instead how a DTW-based algorithm fails in correctly aligning the two signals, as it fits the single peaks on the signal of detector 2 on the entire envelope of the two central peaks centered around bin 1000.
Fig. 3 panel a shows the output of the alignment procedure for the dataset 2; as can be seen in panel c the alignment is even better than the one done manually (panel b), which has been carried out by selecting only the most visible peaks. Even if the procedure is iterative, the alignment of an entire dataset of 8 spectra takes less than 5 s on a PC equipped with 8 (threaded) cores (Intel Xeon e3-1245), running Ubuntu 18.04, Python 3.8, Numpy 3.20.2 and SciPy 1.6.2.

5 Conclusions

In this paper we presented the problem of energy calibration, a crucial preprocessing step in LEXRF analysis, especially in the case of a multi-detector system. We described the elements that typically fools many automated procedures and finally propose a method, whose preliminary results are really promising. As we encourage the signal processing community to work on this problem,

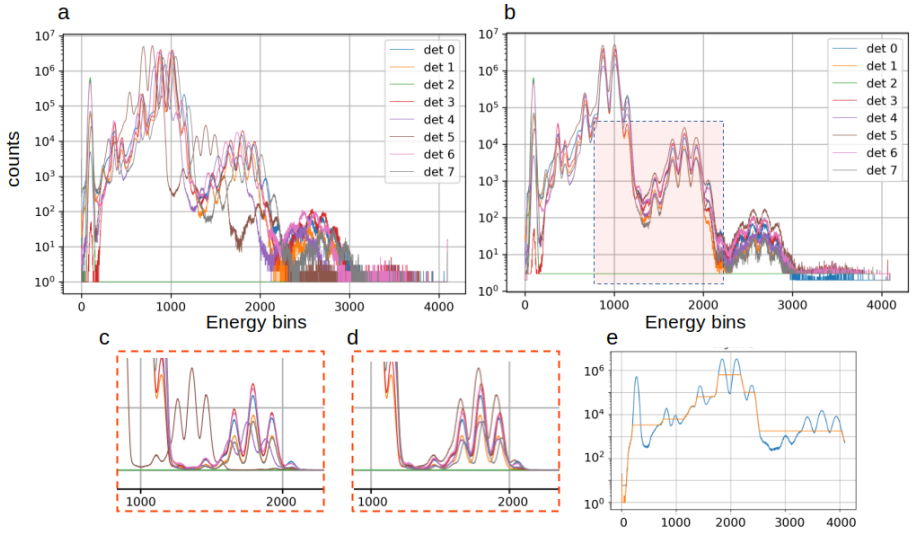

Fig. 2: Alignment of dataset 1. (a): raw spectra; (b) output of the automatic alignment; (c) and (d): output of the two algorithms if used singularly; (e): failing DTW procedure for detector 2.

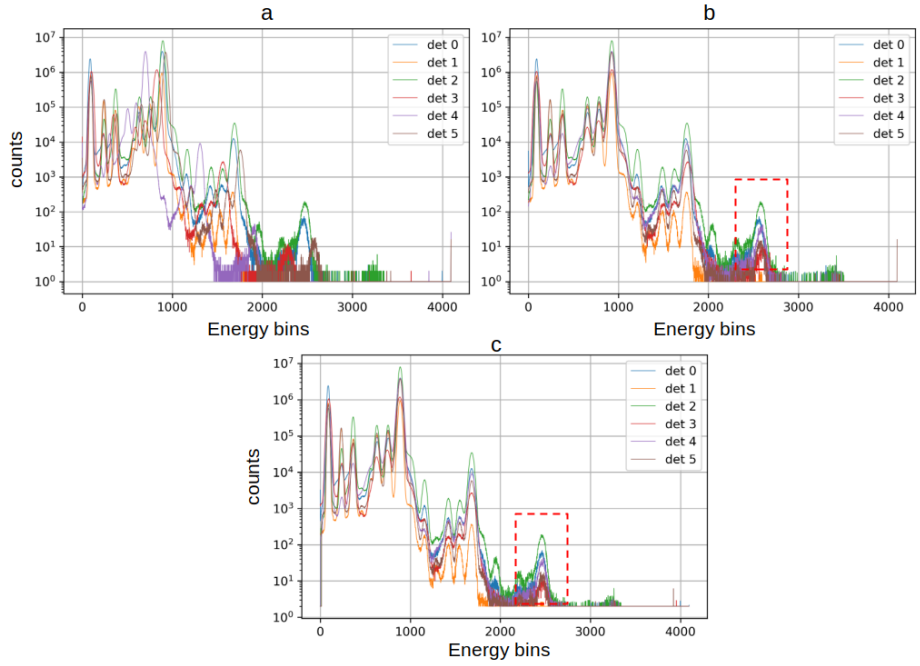

Fig. 3: Alignment of dataset 2: (a) raw spectra; (b): manual alignment; (c): proposed procedure, which better fits the data than (b).

we release two dataset [19] acquired during a real LEXRF experiment performed with synchrotron radiation light.

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