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Chemical speciation using high energy resolution PIXE spectroscopy in the tender X-ray range

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ABSTRACT

High energy resolution X-ray emission spectroscopy employing wavelength dispersive (WDS) crystal spectrometers can provide energy resolution on the level of core-hole lifetime broadening of the characteristic emission lines. While crystal spectrometers have been traditionally used in combination with electron excitation for major and minor element analysis, they have been rarely considered in proton induced X-ray emission (PIXE) trace element analysis mainly due to low detection efficiency. Compared to the simplest flat crystal WDS spectrometer the efficiency can be improved by employing cylindrically or even spherically curved crystals in combination with position sensitive X-ray detectors. When such spectrometer is coupled to MeV proton excitation, chemical bonding effects are revealed in the high energy resolution spectra yielding opportunity to extend the analytical capabilities of PIXE technique also towards chemical state analysis. In this contribution we will focus on the high energy resolution PIXE (HR-PIXE) spectroscopy in the tender X-ray range performed in our laboratory with our home-built tender X-ray emission spectrometer. Some general properties of high energy resolution PIXE spectroscopy in the tender X-ray range are presented followed by an example of sulfur speciation in biological tissue illustrating the capabilities as well as limitations of HR-PIXE method used for chemical speciation in the tender X-ray range.

1. Introduction

Proton Induced X-ray Emission (PIXE) analytical technique [1] is commonly applied to determine elemental constituents of the target (including elements in trace amounts) and determine quantitatively the elemental composition of the investigated sample. The PIXE technique provides with high sensitivity absolute, quantitative concentrations for elements between Mg and U without using any internal or external standards. Since it is multi-elemental, non destructive, pretty fast and require very little sample preparation it has been established as a routine analytical tool in a variety of research fields. The development of PIXE technique was triggered in the seventies by the development of the semiconductor detectors. Also today the method is based on the energy dispersive (EDS) solid state X-ray detectors with high collection efficiency combined with a good enough energy resolution to resolve characteristic X-ray emission lines of different elements. While the use of EDS detectors enables analysis of elemental composition the energy resolution is not high enough to observe also effects of chemical bonding. Consequently, chemical speciation of elements in the sample cannot be performed and this is one of the drawbacks of the method.

Besides elemental composition, chemical speciation is extremely important in various research fields. At the moment, the information of electronic structure and chemical state of the element in bulk materials is most commonly provided by the X-ray absorption spectroscopy (XAS) being performed routinely at the synchrotron facilities [2]. XAS technique probes the unoccupied states above the Fermi level and relies on the use of tunable monochromatic synchrotron radiation. Complementary to XAS, also X-ray emission spectroscopy (XES) can be used to study the electronic structure [2]. In this case we are measuring the relaxation of the core ionized atom by a radiative transition from the occupied electronic states below the Fermi level. In XES spectroscopy the emission spectrum is recorded with energy resolution comparable to the one provided by a monochromator of a typical third generation synchrotron beamline reaching $\Delta E/E \sim 10^{-4}$ level. Compared to energy resolution of the Silicon Drift Detectors (SDD), employed most commonly in X-ray analysis this value is approxi-

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mately two orders of magnitude lower. At the moment this can only be achieved by a wavelength dispersive Bragg crystal spectrometer which is therefore required to perform XES analysis. Most importantly, XES is based on a relaxation of core-ionized state and is therefore not restricted to synchrotron facilities, solely. If we couple a high energy resolution wavelength dispersive spectrometer with a MeV proton excitation, PIXE spectra can be recorded with energy resolution on the level of lifetime core-hole broadening, providing the opportunity to expand the capabilities of PIXE technique also towards chemical speciation.

At the moment, XES spectroscopy performed at the synchrotron beamlines is mainly based on hard X-ray spectrometers with energy resolution similar to the resolution of the beamline monochromator. These are multiple analyzer focusing crystals in different geometries [3,4] typically operating in air due to large target-detector distances employed to achieve high resolving power. Consequently, the in-air absorption sets their low energy working limit and they are not applicable for chemical speciation of low-Z elements with emission energies in the tender X-ray range (2–5 keV) which requires a full in-vacuum spectrometer. Such in-vacuum installation is more applicable for PIXE and can be coupled directly to the beamline of the MV proton accelerator providing MeV proton beam. High energy resolution PIXE spectrometers have been therefore constructed to perform chemical state analysis in this energy range [5] and recently used also in combination with proton microbeam to explore in addition also spatial resolution and perform point analysis of the chemical state [6,7].

At the Microanalytical Center of the J. Stefan Institute (JSI) in Ljubljana hosting a 2 MV Tandem accelerator we are using a complete in-vacuum crystal spectrometer in Johansson geometry to perform PIXE measurements in the 2–6 keV energy range with sub natural line-width energy resolution [8]. The spectrometer has been used successfully to study chemical effects in PIXE spectra of low-Z elements [9–11] and also 3d transition metals [12,13]. Recently, a systematic experimental and theoretical study of electronic structure of phosphorus, sulfur, and chlorine in a series of compounds covering the full range of oxidation states and different local symmetries has been performed using HR-PIXE [14–16]. In this contribution some of the most important results, which are directly applicable to the chemical state analysis of these elements in different samples, are highlighted. Finally, an example of sulfur speciation in a biological tissue is presented demonstrating the capability of HR-PIXE technique in the tender X-ray range for chemical speciation.

2. Chemical speciation

Generally, high energy resolution X-ray emission spectra are probing the local occupied electronic states reflecting the chemical environment of the X-ray emitting atom. The technique is sensitive to the oxidation state, valency and molecular symmetry. In this chapter we will present briefly the most important features of the emission spectra of low-Z elements, namely phosphorus, sulfur and chlorine, which can be used to perform chemical speciation. We will split the discussion into two parts, the first one deals with the analysis based on the $K\alpha$ core-to-core and the second one with the $K\beta$ valence-to-core X-ray emission spectra.

2.1. Oxidation state analysis using $K\alpha$ emission line

The $K\alpha$ line corresponds to the electron transition between deep atomic like 2p and 1s orbitals and is the most intense line in the K X-ray emission spectrum. Since the emitted spectrum corresponds to core-to-core electron transition, the spectral shape exhibits a typical Lorentz-shaped atomic-like $K\alpha_{1,2}$ doublet structure as seen in Fig. 1 for the case of sulfur. The model spectrum consisting of two Voigt functions, which is a convolution of the natural Lorentzian shape with the Gaussian function corresponding to the instrumental function of the spectrometer, can be almost perfectly fitted to the measured spectrum as also presented in Fig. 1 for the case of sulfide sample. The characteristic $K\alpha_{1,2}$ doublet spectral shape is not affected by the chemical environment apart from small changes in the $K\alpha_1/K\alpha_2$ intensity ratio already observed before in synchrotron radiation induced spectra [17]. On the other hand, clear energy shifts are observed in the measured spectra depending on the oxidation state of the element. At such high experimental energy resolution on the level of natural core-hole lifetime broadening, the influence of the valence orbital electron population screening the nuclear potential is revealed as tiny energy shifts of the measured $K\alpha$ lines. As demonstrated in our recent study [15], the $K\alpha$ emission energy is correlated with the formal oxidation state and even better with the effective local charge of the central atom determined by the quantum chemical calculations based on the density functional theory (DFT). Due to the relatively simple and narrow line shape, the energy shift can be determined with very high precision and HR-PIXE measurements of $K\alpha$ emission line can be used effectively as a clean and robust merit of the oxidation state and effective electronic charge of third-row elements in different samples.

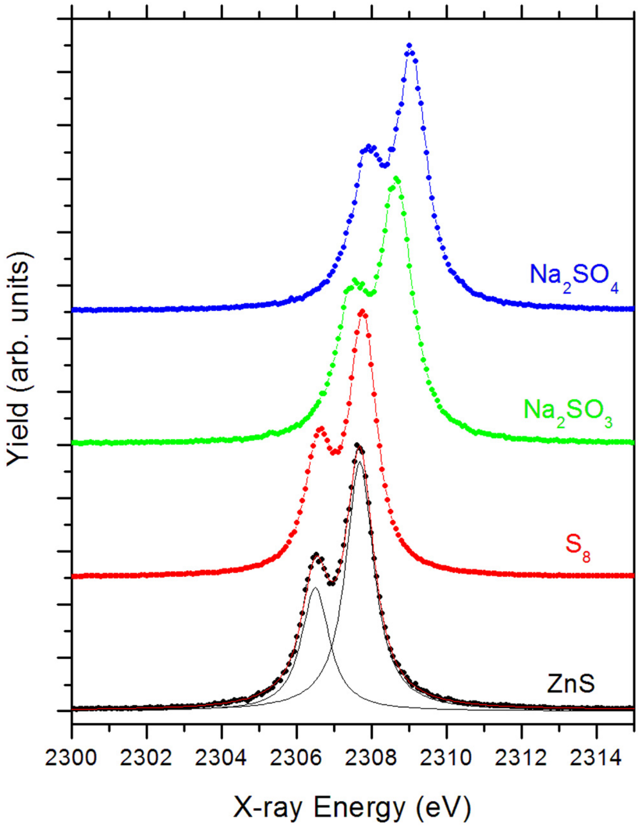

Fig. 1. High energy resolution proton induced $K\alpha_{1,2}$ spectra of several sulfur compounds with different oxidation states. The spectra were induced by 2 MeV protons and recorded by our spectrometer providing energy resolution of ~0.5 eV. For the Na$_2$SO$_4$ the spectrum is fitted with two Voigt profiles in order to determine with high precision the absolute energy of the emission line.

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