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In-lab X-ray fluorescence and diffraction techniques for pathological calcifications

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ABSTRACT

If imaging by physical methods is probably the best well-known link between physics and medicine, other ways such as X-ray fluorescence and diffraction techniques give significant information to clinicians. In this contribution, we would like to assess different results obtained through such techniques on three main problems in urology namely Randall's plaque, brushite kidney stones and phase conversion between weddellite and whewellite. Randall's plaque is a mineral deposit at the surface of the renal papilla which is responsible for the prevalence increase of kidney stones among young people. X-ray fluorescence suggests that an inflammation process is related to Randall's plaque. X-ray fluorescence shows that brushite stones, well known to be related to some pathologies or biochemical disorders, could also be related to unexpected conditions as suggested, for example, by the high content of Br found in several brushite stones. Such results deserve further investigations to explain the origin of that element in the stones. Regarding the phase conversion from weddellite to whewellite, X-ray fluorescence data suggest that trace elements initially present in the stone remain for the major part in situ during the conversion process, which may be clinically relevant to relate the crystalline phase and etiology. X-ray fluorescence and diffraction experiments can thus give significant clues to the clinicians. These examples as well as other investigations assessed in this contribution underline a typical scientific transfer between a physics laboratory and hospital.

1. Introduction

Since their discovery, X-ray related techniques have gained wide acceptance in materials science. Among them, X-ray fluorescence (XRF) [1–4] and X-ray diffraction (XRD) [5–8] are two well-established and powerful tools for a non-destructive analysis of materials with broad applications in science and industry. In medicine, numerous investigations of biological entities have also been performed with these techniques [9–15]. It is also possible to combine both XRF and XRD on the same experimental set-up to obtain simultaneously elemental and structural information on the sample. Furthermore, technical developments in X-ray laboratory sources, optics and detectors in recent years have allowed performing measurements at a local scale with micrometric X-ray beams (~10 μm in diameter) to investigate possible heterogeneities. The fact that such measurements combining XRF and XRD are now available in the laboratory offers a significant

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advantage, albeit the weaker X-ray intensity, over similar experiments on synchrotron radiation facilities for which experimental access is scarce. XRD and XRF techniques can also be implemented at the hospital to help to characterize pathologies or for disease diagnosis through in vivo experiments [16].

In this contribution, we would like to underline through different kinds of XRF and XRD experiments, that chemical and structural characteristics of pathological calcifications [17–19] give invaluable information to clinicians. For example, most of the XRF experiments in medicine deal with trace elements which are intrinsic components of numerous biological systems, since a third of all known proteins contain metal cofactors as catalytic components [20]. Moreover, some trace elements are directly related to a specific disease (aluminum to Alzheimer's disease [21]; copper accumulation to Wilson disease [22]) or are present in therapeutic drugs or diagnostic agents (*cis*-platin in chemotherapy [23], gadolinium in magnetic resonance imaging [24] as well different kinds of nanoparticles [25]). After a brief description of the principles of XRF and XRD techniques, we will present a set of experimental data collected on such in-lab facilities.

2. Basics of XRD and XRF techniques

2.1. Interaction of X-rays with matter

X-rays considered as an electromagnetic radiation possess the duality of being both electromagnetic waves with short wavelength λ ranging typically from 0.1 to 1 Å and massless non-charged particles named photons with energies E from 1 to 100 keV. X-ray photons can interact with the electrons in matter by three different mechanisms as shown in Fig. 1: (i) the photo-electric effect when matter absorbs the incident X-ray photon and then emits electrons or X-ray photons, (ii) Compton scattering, where the scattering of the incident X-ray photon is accompanied by some energy transfer to the electron (inelastic scattering) and (iii) Thomson (elastic) scattering where the scattered X-ray photons have the same energy as in the incident beam. Note that at low energy, the photoelectric effect is more important than Compton scattering.

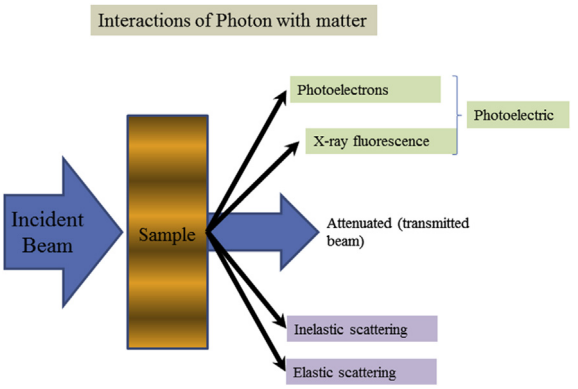

Fig. 1. Schematic representation of the different interactions between X-rays and matter.

The photo-electric effect is responsible for the XRF and Auger photoelectron phenomena whereas XRD is related to the Thomson scattering process. Note that photoelectron spectroscopy is usually subdivided according to the source of exciting radiation into X-ray Photoelectron Spectroscopy (XPS) which uses soft X-rays (with a photon energy of 200–2000 eV) to examine core-levels and Ultraviolet Photoelectron Spectroscopy (UPS) which is based on UV radiation (with a photon energy of 10–45 eV) to examine valence levels.

2.2. X-ray fluorescence

In the photoelectric absorption process, incident photons with quantum energy ($h\nu$) interact with an absorber atom and completely disappear. In their place, photoelectrons are ejected from one of the bound shells of the atom with energy equal to $h\nu - E_b$ (where E_b represents the binding energy of the photoelectron in its original shell, see Fig. 2a). During the atomic relaxation, the filling of the inner shell vacancy can produce X-ray fluorescence radiation with characteristic energies of the atom and also other photoelectrons named Auger electrons [26,27].

The characteristic energies of the X-ray fluorescence radiation emitted from a sample enable us to identify unambiguously and quantify the different elements present. Such experiments can be performed on solid, liquid or thin-film samples. Finally, note that X-ray fluorescence can be also induced by gamma-emitting radioisotopes (^{241}Am,

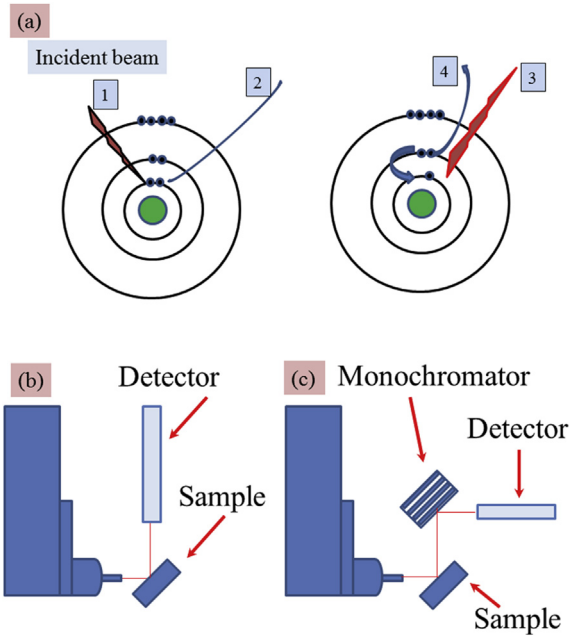

Fig. 2. (a) Simple representation associated with the X-ray fluorescence process: 1 – incident X-ray photon, 2 – emitted photoelectron, 3 – X-ray fluorescence photon or 4 – Auger electron (b, c) schematic experimental set-ups corresponding to (b) energy-dispersive (ED) and (c) wavelength-dispersive (WD). For the ED experimental device, the energy resolution is given by using the detector (around 150–200 eV) while for the WD one, the energy resolution is defined by using the monochromator (around 1–2 eV).