Educational X-ray experiments and XRF measurements with a modified, mobile system adapted for characterization of Cultural Heritage objects

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Abstract

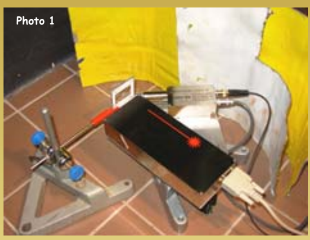
It is common to modify valuable, sophisticated equipment, which has been originally acquired for other purposes, in order to adapt it for the needs of additional educational experiments, with greater didactic effectuality. The present project concerns a setup, developed from components of a portable system for X-ray fluorescence spectroscopy (XRF), aiming at: i) the formation of familiar and conventional laboratory exercises, like the verification of Moseley's law, Compton's law and Lambert-Beer's law; ii) the calibration of the XRF with reference materials, aiming on quantitative measurements of the elemental composition of objects of cultural interest. Using the calibrated experimental setup indicative measurements of metal objects are demonstrated, in order to discuss their spectra and their qualitative and quantitative analysis.

The system and the applied experiments are designed as an educational package of laboratory exercises on the one hand for students in physical sciences and on the other hand it is especially adapted for the education of students who will work in the field Cultural Heritage, such as conservation science or archaeological science. The material characterization of ancient artefacts and art objects via analytical equipment is important in many respects, such as in terms of sustainable conservation planning or in terms of investigating ancient technologies.

Materials and Methods

The detector used is an Amptek XR-100CR, semiconductor diode (Si-PIN), optimized to detect X-ray photons direct in the energy range of 1 to 30 keV. The pre-amplified signals are processed with an end-amplifier and a multichannel analyzer (MCA of Phywe or 8000A of Amptek), sorting them in 4k addresses (channels), according to their energy. The multichannel analyzer is connected to a computer on which the data are presented in form of spectra and graphs. The spectral lines are assigned to the specific elements by using the software PMCA and the quantitative analysis software XRF-FP, both of Amptek, while the data acquisition is proceeded with the software Measure of Phywe and Origin of OriginLab Co. The X-ray beam is generated with a mini mobile X-source (Amptek Laser-X) providing a low intensity radiation beam (10 μA) with a maximum energy of 35 keV. The system is provided with two mini diode Laser, mounted under the constructive board, in order to define the exact excitation point of the sample. In this way the distance of the sample to the X-ray source and the detector remains constant.

The experimental set up, an in-house construction, which is used for the presented XRF measurements of different objects and standardreference materials and for a series of educational experiments, like the verification of the Compton effect, is shown in Photos 1, 2 and 3. In Figures 1 and 2 the schematic experimental XRF setup is presented for analysis samples and for investigating Compton scattering in a Plexiglas plate, respectively. For the calibration procedure and the verification of the Moseley's law a multi-component standard in form of a pellet and series of metal reference standards are used. For the verification of the validity of Lambert-Beer's law simple Aluminium foil is used as an absorber material, appropriately folded, in order to achieve different values of surface densities.



Photos of the experimental set up used for indoor XRF measurements (**photos 1, 2**) and for the Compton effect experiment (**photo 3**)

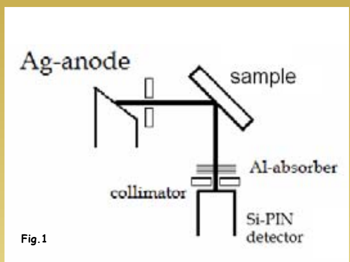


Fig.1: A schematically draw of the experimental set up for XRF experiments is shown, where the standard sample was excited by the beam of a X-ray source with an Ag-anode. A collimator was used in order to define the beam, while a series of Al foils has been placed between the standard sample and the detector, in order to attenuate sequentially the intensity of the X-ray beam.

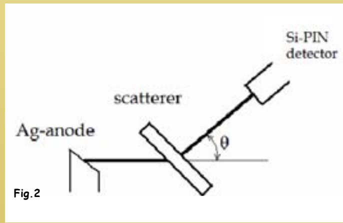


Fig.2: A schematically draw of the set up for the Compton experiment (photo 3), is shown, in which a plate of Plexiglas was used as a scatterer intervened to the X-ray beam between the source and the detector, positioned at different angles of scattering.

XRF applications on cultural heritage objects

During the last decade portable EDXRF systems became a standard method for non-destructive elemental analysis of materials in the field of Cultural Heritage, allowing even for *in-situ* measurements (Photo 4, 5). Educational experiments for students of archaeological science or conservation science will focus on imparting basic knowledge about the characteristics of the technique. Therefore, example objects representing different materials are measured (Photo 6) and the XRF spectra are evaluated (Figure 3, 4).

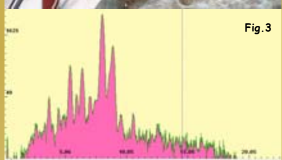


Fig. 3: XRF spectrum of a spot on the arm of the bronze monument in photo 4.

Photo 4: Outdoor bronze monument (Victoria Square, Athens, Greece), **Photo 5:** In-situ measurement on site. **Photo 6:** Analysis of a fragment of a pipe recovered from the 'Patris' shipwreck

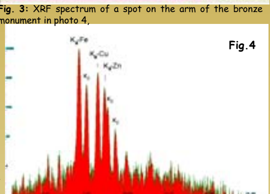


Fig. 4: XRF spectrum of the pipe fragment in photo 6 (Major element peaks are identified).

Conclusions

A setup has been developed, composed of parts of a portable system for XRF spectroscopy, in order to be used for educational purposes. The realization of a number of familiar and conventional laboratory exercises, like the verification of Moseley's law, Compton's law and Lambert-Beer's law, with an satisfactory success and additionally the conception of the instructive procedure of XRF calibration constitutes an helpful educational package of laboratory exercises for students in physical sciences. Additionally, the system is especially adapted for the education of students who will work in the field of Cultural Heritage, such as conservation scientists and archaeometrists.

Measurements and Results

a) Calibration

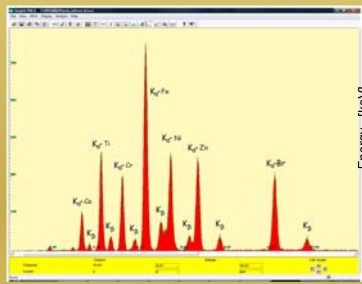


Fig.5.: A characteristic XRF spectrum of the multi-component standard sample used for the energy calibration of the system.

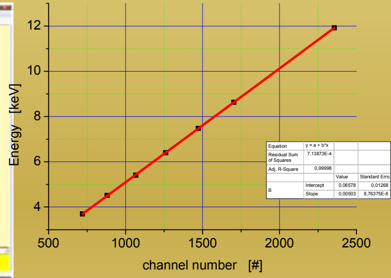


Fig.6: A calibration plot, based on the data of the components' energies contained in the standard multi-component sample and the channel number of the corresponded X-ray lines in XRF spectrum (fig.5)

b) Moseley's law

The energy E_{mn} of each transition on the atomic level of the elements is proportional to the quadrate of their atomic number, as expressed in the equation, most known as the Moseley's law

$$E_{mn} = R_H (Z-\sigma)^2 \left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

where R_H and σ is the Rydberg constant and the shield constant of the atom.

for m = 2 $\sqrt{E_{21}} = \sqrt{\frac{3}{4} R_H} \cdot (Z-\sigma)$

for $B = \sqrt{\frac{3}{4} \cdot R_H}$ $\Rightarrow$ $\sqrt{E_{21}} = B \cdot Z - B \cdot \sigma$

From the linear fit to the data (Fig.7) follows an good approach of the experimental to the theoretical values (Table 1).

	Theoretical value	Experimental value
$R_{HK\alpha}$ [eV]	13.6	13.90 ± 0,20
$R_{HK\beta}$ [eV]	13.6	13.53± 0,10
$\sigma_{K\alpha}$	1,0	1,23 ± 0,10
$\sigma_{K\beta}$	1,0	1,78 ± 0,10

Table 1

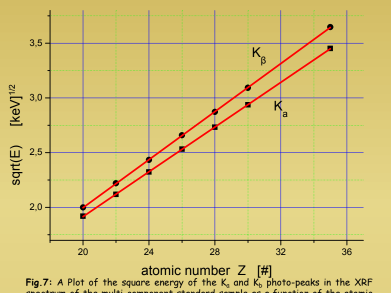


Fig.7: A Plot of the square energy of the K_a and K_b photo-peaks in the XRF spectrum of the multi-component standard sample as a function of the atomic number their corresponded elements.

c) Lambert-Beer's law

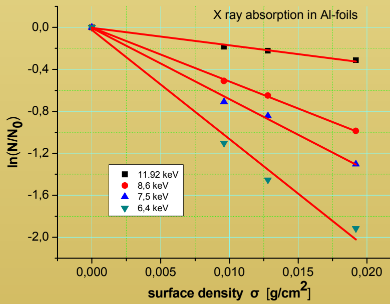


Fig.8: Plot of the absorption of four characteristic energies of a standard, constructed with the data calculated from XRF spectra, obtained with Al-foils of various surface densities. From the slope of the fitted lines the absorption coefficient was directly derived.

The attenuation of the X ray intensity after transmitting through a material, as a result of interactions, is a function of thickness of the material (often expressed by the surface density σ). and of a material constant μ, called absorption coefficient. This is the main content of the Lambert-Beer's law, as formulated in the following relation:

$$N = N_0 \cdot e^{-\mu \cdot \sigma}$$

where N and N_0 the number of counts, proportional to the X-ray intensity in a certain depth and at the begin, before has introduced into the material.

$$\Rightarrow \quad \ln\left(\frac{N}{N_0}\right) = -\mu \cdot \sigma$$

E [keV]	μ_{theo} [cm^2/g]	μ_{exp} [cm^2/g]
6,40	91,7	104±14
7,47	57,5	68±7
8,63	38,9	51±4
11,92	15,1	17±2

Table 2

In the table 2 values of μ for Aluminium at the certain energies are listed, as such energies, originated from the fluorescence radiation, with which the absorbing material, in our case the Al foils, was irradiated.

The corresponded experimental values of μ, as calculated from a series of XRF spectra, seem to follow the expected theoretical trend, taking into account that the foils used in this experiment was not pure Al-material.

The constant μ depended from the energy of the X-ray photons, characterizes the absorber and defines the expected permeability grad of the X ray photons with a difference in energy, in a almost remarkable way.

d) Compton effect

The spectral shift, which corresponded to the difference of energy of the X ray photon, after the collision with an electron within the scattered material, is known as the Compton effect and was described by a simple equation below. The spectral shift at 90° angle is a constant with a value of λ = 2.5 pm. The experimental value of λ= 2.26 ± 0.30 pm obtained from the spectra, the slope of the linear curve in fig. 9, approximate enough the theoretical value and it is an acceptable result for educational purposes.

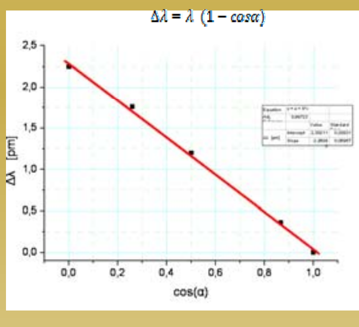


Fig.9: A Plot of spectral shift of the characteristic line (Ag-K_a), of the anode material of the X-ray source, versus the cos(a), The obtained data from the spectra at different angles (s. fig 10), showed α satisfactory approach to the theoretically expected results.

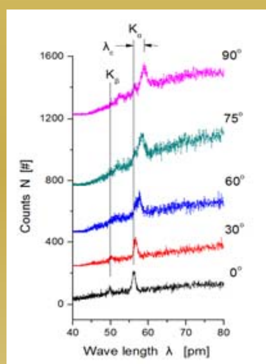


Fig.10: A serial of XRF energy spectra, which was measured at different angles, obtained from the X-ray source, after scattering on the Plexiglas plate. The wavelength was calculated from the corresponded energies, after an appropriate calibration. A blue spectral shift of the wavelength for Ag-K_a (inelastic scattering) is shown, while the elastic scattering is just observable.

References

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