

X-Ray fluorescence and Raman spectroscopy

Advanced physics laboratory (2nd part) – 4CFU

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Abstract

In this paper we report about two different experiences: X-ray fluorescence and Raman spectroscopy. Our starting aim was to discover the composition of two samples using fluorescence technique and performing both qualitative and quantitative analysis. A specimen results to be composed of Ga, Sb, Bi, whereas the other one of Pt and Fe. Then we examined different Raman spectra in order to understand the behaviour of some parameters varying the front entrance slit width of the spectrometer. It arises that the wider the slit the greater the detected photons number up to a limiting value.

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1.1 Experimental setup

In this experiment we work with energy-dispersive spectroscopy setup. As X-ray source we use a Coolidge tube with a molybdenum water cooled anode. The outgoing beam passes through a monochromator and is further focused by optical components. The sample emitted radiation is collected by a solid-state detector (a thick silicon junction PIN diode) coupled with standard multi-channel electronics. Both the Coolidge tube and the detector have a beryllium window in order to maintain the internal vacuum. Moreover in the second case it is useful also to protect the solid-state device which is cooled down up to $-55\text{ }^{\circ}\text{C}$ by Peltier effect. Unfortunately this window is one of the limitations of this kind of detector since its transmission depends on the photons energy and does not allow to detect elements lighter than calcium.

1.2 Data analysis

1.2.1 Qualitative analysis

Our data are expressed in terms of photons counts vs channels, so at the beginning we calibrated them in order to have energy on the x-axis, obtaining the two spectra in fig. 1a and fig. 1b. Once we fitted each peak with a gaussian, we found its centroid which represent the corresponding emission line energy. Then we compared these energies with the values collected in our reference handbook [1], in order to find the corresponding element. From this analysis we discovered that sample 1 is made of gallium, bismuth and antimony, whereas

X-Ray fluorescence (XRF) is a non-invasive technique used to determine the composition of a specimen. The sample is irradiated with an X-ray beam (primary excitation) which ionize the atoms. As a consequence these atoms return to the ground state re-emitting characteristic X-rays (secondary excitation), according to the atomic number of each component.

Given the XRF spectrum two kinds of analyses can be carried out: a qualitative one, that allows the identification of the components, and a quantitative one through which their concentrations can be determined.

sample 2 consists of platinum and iron.

1.2.2 Quantitative analysis

Knowing the components of our samples we can get a first estimation of their weight fraction, considering the peaks relative intensity and the fact that not each line has the same fluorescence yield nor the detector collects with the same efficiency photons at different energies. Making use of:

$$\text{weight fraction} \propto \frac{\text{rel. intensity}}{\text{fluo. yield} \times \text{det. efficiency}}$$

it turns out that sample 1 is composed of 68% Ga, 21% Bi, 11% Sb and sample 2 of 97% Pt, 3% Fe.

In order to determine exactly their relative amount we can perform a more accurate quantitative analysis. Without loss of generality, we can assume the source to be monochromatic and the sample to have an infinite thickness, so that the following formula applies:

$$I_i(E_i) = \frac{\eta(E_i)}{4\pi \sin(\psi_1)} \frac{Q_{if}(E_0) I_0(E_0)}{\mu(E_0) \csc(\psi_1) + \mu(E_i) \csc(\psi_2)}$$

where:

- E_0 is the energy of the incident radiation,
- E_i is the energy of the emitted radiation,
- $I_i(E_i)$ is the fluoresced intensity at energy E_i ,
- $\eta(E_i)$ is the efficiency of the detector at energy E_i ,
- $Q_{if}(E_0)$ contains all the fundamental parameters associated with the characteristic XRF from i -element¹,
- $\mu(E_0)/\mu(E_i)$ is the total mass attenuation factor at energy E_0/E_i ²,
- ψ_1 is the incident angle of X-rays,
- ψ_2 is the angle of emitted X-rays.

Plugging in all the variable values we finally get that sample 1 is a mixture of 69,33% Ga, 21,14% Sb, 9,53% Bi, whereas sample 2 contains 96,54% Pt, 3,46% Fe.

¹ $Q_{if}(E_0) = W_i \tau_i(E_0) \omega_i f$, where W_i is the weight fraction of i -element, $\tau_i(E_0)$ is the total photoelectric mass absorption coefficient of i -element at energy E_0 , ω_i is the fluorescence yield and f is the relative intensity of the emission line.

² $\mu = \sum_m W_m \mu_m$, where W_m and μ_m are the weight fraction and the mass attenuation factor of the m -element, respectively.

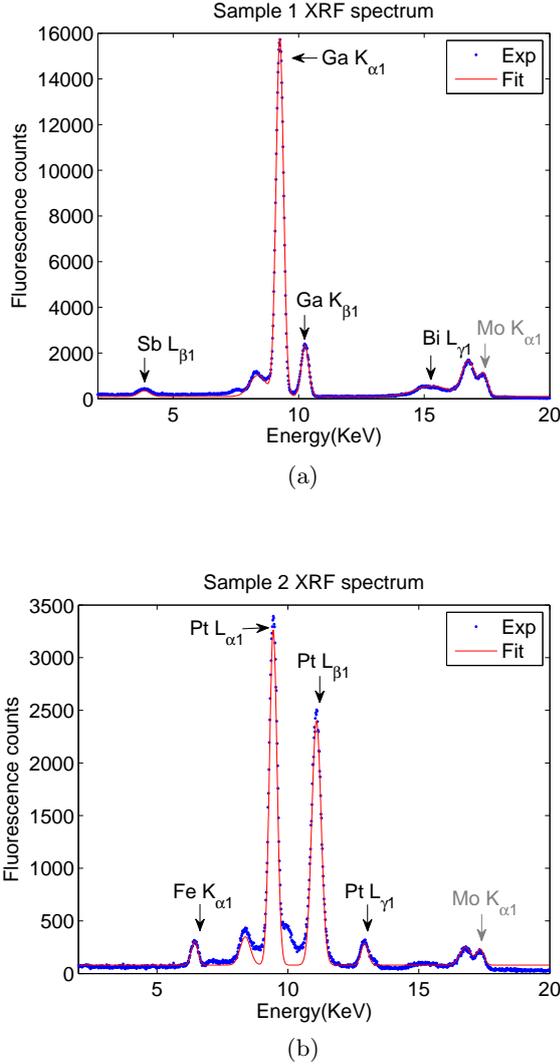


Figure 1: Blue dots are the experimental data, red line is the fitting curve. Black arrows refer to the element and the emission line of each peak, while the grey one deals with the radiation due to Mo anode. (a) Sample 1. (b) Sample 2.

2 Raman Spectroscopy

Raman spectroscopy is based on the so called Raman effect. When photons interact with atoms different reactions can take place. Specifically, referring to scattering processes, the elastic one is the most probable (Rayleigh scattering), i.e. scattered photons have same energy of the incident beam. But a small fraction of incoming photons can be scattered with a different wavelength (Raman effect): if outgoing radiation has an energy greater than the incoming one anti-Stokes Raman scattering happens, otherwise the process is named Stokes Raman scattering.

2.1 Experimental setup

In our experiment we used a micro Raman technique. Our experimental setup is composed of a laser which enters into a microscope via optical fiber. The beam can be focused onto the sample by different objectives. The outgoing radiation goes into the spectrometer by means of a second optical fiber, passing through the front entrance slit of the instrument. Photons are then collected by a CCD. A dedicated software (LabSpec Raman software) elaborates the data giving as a result a spectrum, where only Stokes part is taken into account because the anti-Stokes peaks would be less intense. Moreover Rayleigh peak is cut by a filter, since otherwise it would have overcome the signal which we are interested in.

2.2 Measures

Our purpose is to measure Raman shift of photons irradiated from a silicon sample which is illuminated by a red laser beam ($\lambda=632,83 \text{ nm}$). In order to focus it, 100x objective has been used. In particular we want to compare the spectra obtained varying only the front entrance slit width, while the following acquisition parameters are held fixed:

- grating: 1800 g/mm^3 ,
- acquisition time: 30 sec ,
- accumulation: 10,
- range: $(0-1500) \text{ cm}^{-1}$.

2.3 Data analysis

We performed 9 measurements with front entrance slit widths of 40, 70, 100, 150, 200, 250, 300, 400, 600 (μm) respectively. To make a quick comparison, we first plotted all the data in the same graph

³This grating has been chosen over 600 g/mm in order to have a better resolution.

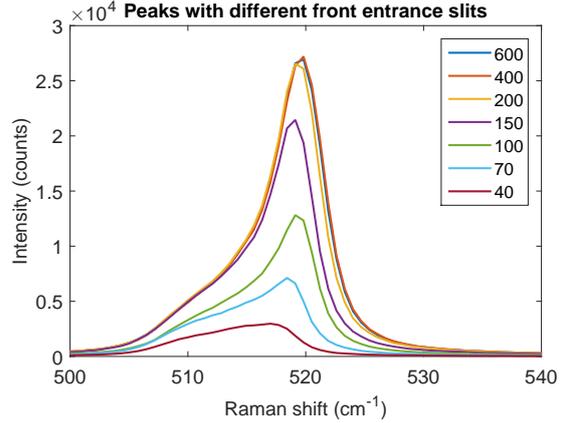


Figure 2: One-phonon peak for different front entrance slit widths.

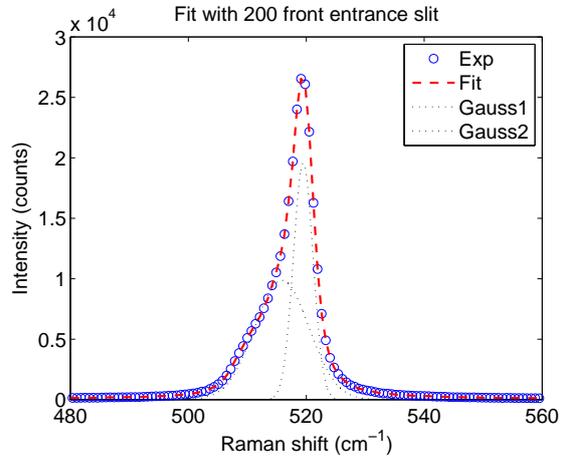


Figure 3: Blue dots correspond to the experimental data, dashed black lines are the two gaussians used to perform the fit and the dashed red line is the fitting curve.

zooming in on the one-phonon peak, as shown in fig. 2. We can notice that the larger the slit the higher and the sharper the peak.

To get quantitative information we fitted each one-phonon peak with two gaussians (cf. fig. 3); in particular we calculated areas and centroids of these gaussians. Then we averaged the centroids using as weights the area under the corresponding gaussian. All the parameters resulting from the fit are reported in app. A.

From these fitting curves we found the centroids performing a weighted average. We report them in tab. 1.

To be sure of the physical significance of the spectra we calculated the ratio between the two gaussians FWHM for each peak (cf. fig. 4). Notice that there is only one ratio out of the confidence interval: it is the red point referring to the $40 \mu\text{m}$ front entrance slit width.

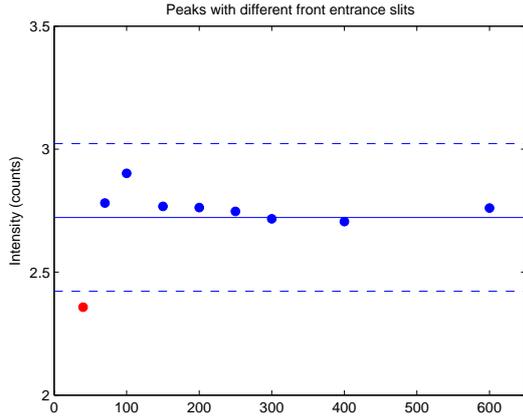


Figure 4: Dots are the ratio between FWHMs (the red one refers to $40 \mu m$ slit), continuous line is the average of the ratios, while dashed lines represent the confidence interval.

3 Conclusions

For what concerns XRF from the quantitative analysis it results that sample 1 is composed of 69,33% Ga, 21,14% Sb, 9,53% Bi and sample 2 of 96,54% Pt, 3,46% Fe. Making a comparison with the compositions obtained from the initial rough approximation we can guess that geometry of the experiment, source and detector features are more significant in the case of the first specimen.

As regards Raman spectroscopy we can state that increasing the front entrance slit width we detect a greater and greater number of photons. Moreover it seems that the Raman shift found out slightly depends on the same varying parameter, since the one-phonon peak centroids move to the right as the width raises. These results apply to widths up to $200 \mu m$, whereas from this value on both the centroids position and the number of detected photons are almost constant. Therefore we deduce that choosing a width less than $200 \mu m$ not all the signal reaches the spectrometer. In particular the $40 \mu m$ slit is not suitable for measuring Raman shift because the spectrum is rather different from all the others, in addition the ratio between FWHMs of the two fitting gaussians is the only one out of the confidence interval.

A Fitting parameter

In tab. 1 are shown all the parameters resulting from the fit of each phonon peak.

width(μm)	peak 1		peak 2		centroid (cm^{-1})
	\bar{x}_1 (cm^{-1})	$2\sigma_1$ (cm^{-1})	\bar{x}_2 (cm^{-1})	$2\sigma_2$ (cm^{-1})	
40	517,5	3,8	513,3	9,1	514
70	518,5	3,5	514,1	9,7	515
100	519, 3	3,5	515,3	10,1	516
150	519,0	3,7	514,9	10,3	517
200	519,5	3,9	515,9	10,8	517
250	519,7	4,0	516,2	11,1	517
300	519,7	4,0	516,1	11,0	517
400	519,8	4,0	516,4	10,9	518
600	519,7	4,1	516,2	11,2	517

Table 1: Centroids, FWHMs and centroids weighted average of the two gaussians fitting each one phonon peak in correspondance to different front entrance slit widths.

References

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