

EXPLORING CULTURAL HERITAGE WITH PIXE

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I. Centazzo¹, L. A. Charawi², A. Curcu³, A. D'Alessandro⁴, S. Ginocchietti⁵, C. Maugeri⁶

¹*I. I. S. Evangelista Torricelli, Maniago (Pordenone), Italy.*

²*L. S. Gaetana Agnesi, Milano, Italy.*

³*L. S. S. Leonardo Da Vinci, Trento, Italy.*

⁴*I. I. S. Enrico De Nicola, Sesto S. Giovanni (Milano), Italy.*

⁵*L. S. S. Primo Levi, Roma, Italy.*

⁶*L. S. S. Gian Battista Grassi, Saronno (Varese), Italy.*

ABSTRACT

This report presents the results of measurements conducted using the Particle Induced X-ray Emission (PIXE) technique at the INFN National Laboratories of Legnaro (Padua) as part of the Programma INFN per Docenti 2023 (PID 2023). The purpose of these measurements was to investigate the elemental composition of pigments and hard stones, with a focus on their application in cultural heritage studies. Building on this experience, the present article aims to propose an interdisciplinary teaching activity for high school, combining modern physics with art history and archaeology, using the PIXE technique as a foundation.

KEYWORDS: PIXE, X-ray, accelerator, proton beam, cultural heritage, teaching activity.

INTRODUCTION

PID (Programma INFN per Docenti) is a training course offered by the INFN (National Institute for Nuclear Physics) at its National Laboratories. Each course lasts five days and includes both theoretical and experimental lessons, covering topics in nuclear and astroparticle physics, as well as accelerator physics. Special emphasis is placed on the interdisciplinary aspects of research. In particular, this paper concerns the workshop activity entitled “Nuclear physics applied to cultural heritage: PIXE” carried out by the authors as part of the 2023 edition of PID at the Legnaro National Laboratories, under the guidance of Dr. Andrea Gozzelino [1].

Particle Induced X-ray Emission (PIXE) is a non-destructive analytical technique used primarily

in material science, archaeology, biology, and environmental studies to determine the elemental composition of samples. PIXE relies on bombarding a material with high-energy charged particles, typically protons, which induce the emission of characteristic X-rays from the atoms within the sample. PIXE technique is better suited for relatively high atomic number elements ($Z > 11$). PIXE is less effective at detecting elements with an atomic number below 11. These elements emit low-energy X-rays that can be easily absorbed before reaching the detector, making their detection difficult. For more details, the reader can refer to textbooks as [2] and [3].

The paper is structured as follows:

1. basics of X-ray spectrometry and PIXE technique, using an approach suitable for students with notions of electromagnetism and atomic models;
2. description of our activity at AN2000 accelerator laboratory, including the experimental setup, materials supplied;
3. our results, using PIXE in order to recognize the elemental composition of known specimen;
4. outline of an educational activity suited for final or fourth year secondary order students.

BASIC PRINCIPLE OF PIXE

The fundamental principle of PIXE is based on atomic excitation. When a sample is irradiated with a beam of charged particles, usually generated by a particle accelerator, the incident protons interact with the atoms in the sample. This interaction causes the ejection of inner-shell electrons, named as K , L , M , N and so on, creating a vacancy. Electrons from higher energy levels then fall into these vacancies, releasing energy in the form of X-rays, as shown in FIG. 1. The energies of the emitted characteristic X-rays uniquely identify elements present in the sample, while the amplitude of the X-ray emission is proportional to the concentration of those elements.

The X-ray spectrum is simply determined by the energy levels of the electrons in the atom. The energy level diagram of a medium-heavy element with the X-ray transitions is shown in FIG. 2. The transitions going to the K shell are indicated as K X-rays. When the vacancy is filled by an electron coming from the L shell the transition is denoted as K_{α} , and when it comes from the M shell, K_{β} . Similarly, the transitions to the L shell are indicated as L X-rays, and these have some

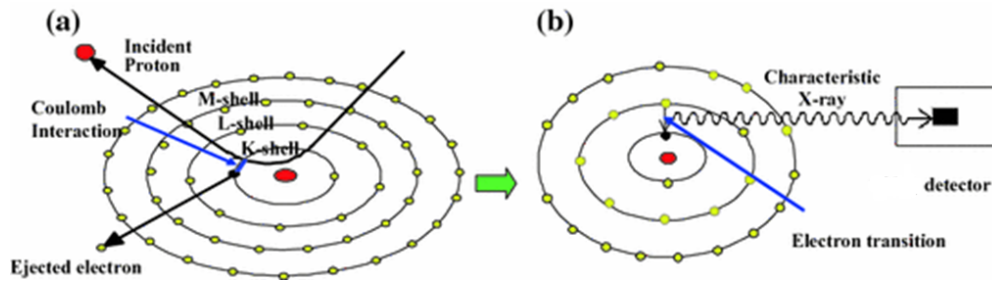


FIG. 1. Basic principle of PIXE. (a) Indicates proton interaction with inner shell electron. (b) Indicates emission of electron, fall of upper shell electron and radiation of X-ray. [4]

components, especially for heavy elements. Generally, the light and medium-heavy elements are identified by their *K* X-rays and the heavy elements by *L* X-rays due to the effective detection of the *K* X-rays which can be obtained in the range $20 < Z < 50$ and of the *L* X-rays for $Z > 50$.

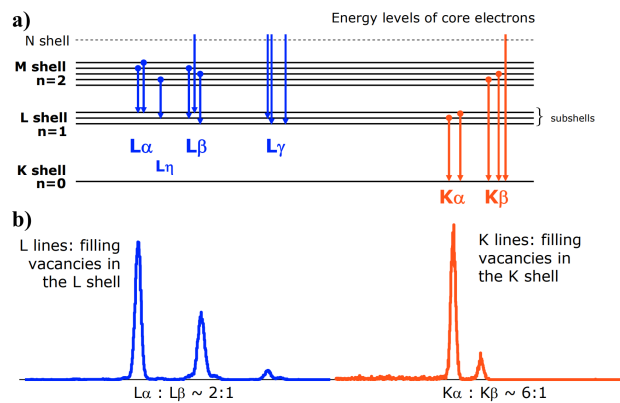


FIG. 2. Energy levels and X-ray transitions in medium-heavy element.

The energy of characteristic X-ray is equal to the difference between the vacant shell electron binding energy and the donor shell electron binding energy. Using X-ray spectrum, energy level diagram and knowing X-ray energies, it can be possible to determine the elemental composition of the specimen.

EXPERIMENTS

PIXE measurements were carried out using 2 MeV proton beam ($90^\circ / 0^\circ$ beamline) from the 2.0 MeV AN2000 Van de Graaff accelerator (FIG. 4). This accelerator uses a continuous moving belt in a high pressure tank to maintain a terminal at a voltage of typically 2 MV. Therefore,

the accelerator can supply 2 MeV energy per proton. Several tens of microamperes are generated by this machine. Such amounts of currents are relatively high for PIXE analysis, which generally uses a few tens of nanoamperes.

Proton beam, focused and deflected by a system of magnets (FIG. 3), hits the sample target in a vacuum chamber. Emitted X-rays are detected by a 100 mm² cooled High-Purity Germanium (HPGe) detector.

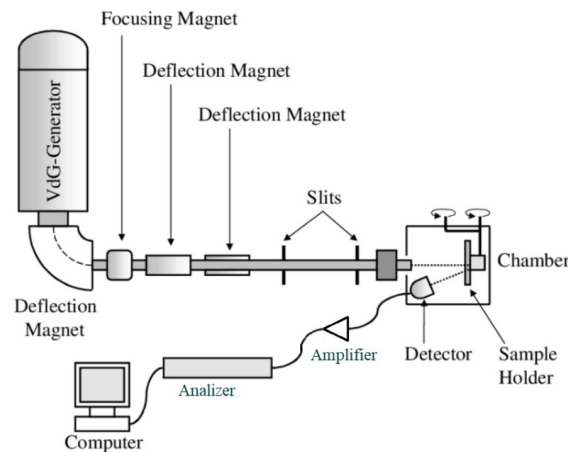


FIG. 3. Van De Graaff accelerator scheme. (Available from [6])

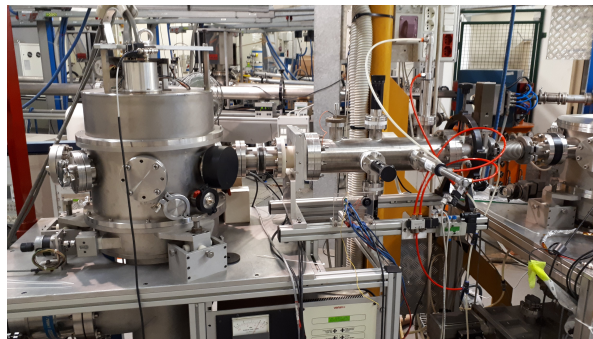


FIG. 4. AN2000 accelerator line at LNL [7]

The electrical impulses coming out of the detector are suitably amplified, sampled with a 11-bit analogue-to-digital converter (ADC), finally catalogued by a multi-channel analyser (2048 channels) according to their amplitude. Each channel represents a specific energy range in the spectrum, so the number of signals for each channel represents the spectral intensity of the radiation for the corresponding energy range. Finally a histogram (PIXE spectrum) is visualised at the front-end panel of the data acquisition system. In a typical PIXE spectrum the *x*-axis reports energies while the *y*-axis the intensity of the peaks in counts.

The raw data of the spectrum can be stored in the computer memory for off-line analysis using GUPIXWIN software; otherwise the list of y -coordinates can be saved as a *.txt* file. In this way it will be always possible to reconstruct the histogram using a spreadsheet editor.

The analysis of the spectrum can give both qualitative and quantitative information. Firstly, elements present in the target are identified from the energies of the characteristic peaks in the X-ray emission spectrum. Secondly, the elemental abundances are determined by normalising the peak counts by the total charge.

To obtain channel-to-energy conversion factor, it is necessary to perform an energy calibration, analysing known materials with well-defined energy emissions. In our experiments we used samples collected on a support of alumina: on one side there was an array of thirteen standard Kremer pigments ([9]), arranged as in FIG. 5, while on the other side there was a sample of lapis lazuli.

The coarse positioning of samples is controlled by a PC software package under LabView, allowing x - y - z movements and rotations along the z -axis. Movements can be continuously monitored on the PC display through a sample positioning microscope equipped with a TV camera. A multiple sample holder, like that we used, avoids opening the vacuum target chamber in order to replace the sample.

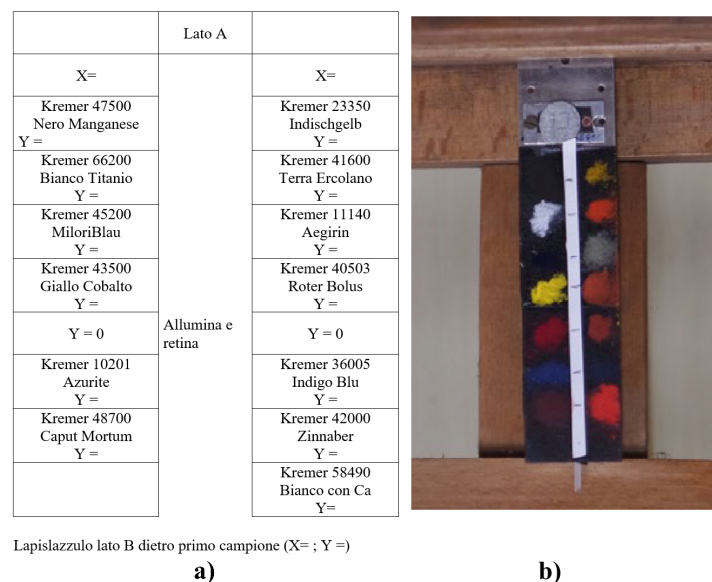


FIG. 5. a) lab sheet: scheme of pigments array; b) sample array from [5] similar to the one used in our activity

In our experimental activity, we performed the calibration measurements with three known pigments: Cobalt Yellow (Kremer 43500), Titanium White (Kremer 46200) and Cinnabar (Kremer 42000). The consulted list of the main *K*, *L* and *M* X-ray emission energies (in keV) for sodium to uranium elements (FIG. 6) is available at this site [8].

NA	Element	Z	K	L	L ₁	L ₂	L ₃	M	M ₁	M ₂	M ₃
11	Na	11	0.280	0	0	0	0	0	0	0	0
12	Mg	12	0.281	0	0	0	0	0	0	0	0
13	Al	13	0.477	0	0	0	0	0	0	0	0
14	Si	14	0.848	0	0	0	0	0	0	0	0
15	P	15	1.041	0	0	0	0	0	0	0	0
16	S	16	1.254	0	0	0	0	0	0	0	0
17	Cl	17	1.482	0	0	0	0	0	0	0	0
18	Ar	18	1.740	0	0	0	0	0	0	0	0
19	K	19	2.010	0	0	0	0	0	0	0	0
20	Ca	20	2.957	0	0	0	0	0	0	0	0
21	Sc	21	2.622	0	0	0	0	0	0	0	0
22	Ti	22	2.952	0	0	0	0	0	0	0	0
23	V	23	3.187	0	0	0	0	0	0	0	0
24	Cr	24	3.122	0	0	0	0	0	0	0	0
25	Mn	25	2.952	0	0	0	0	0	0	0	0
26	Fe	26	2.952	0	0	0	0	0	0	0	0
27	Co	27	2.952	0	0	0	0	0	0	0	0
28	Ni	28	2.952	0	0	0	0	0	0	0	0
29	Cu	29	2.952	0	0	0	0	0	0	0	0
30	Zn	30	2.952	0	0	0	0	0	0	0	0
31	Ga	31	2.952	0	0	0	0	0	0	0	0
32	Ge	32	2.952	0	0	0	0	0	0	0	0
33	As	33	2.952	0	0	0	0	0	0	0	0
34	Se	34	2.952	0	0	0	0	0	0	0	0
35	Br	35	2.952	0	0	0	0	0	0	0	0
36	Kr	36	2.952	0	0	0	0	0	0	0	0
37	Rb	37	2.952	0	0	0	0	0	0	0	0
38	Sr	38	2.952	0	0	0	0	0	0	0	0
39	Y	39	2.952	0	0	0	0	0	0	0	0
40	Zr	40	2.952	0	0	0	0	0	0	0	0
41	Nb	41	2.952	0	0	0	0	0	0	0	0
42	Mo	42	2.952	0	0	0	0	0	0	0	0
43	Tc	43	2.952	0	0	0	0	0	0	0	0
44	Ru	44	2.952	0	0	0	0	0	0	0	0
45	Rh	45	2.952	0	0	0	0	0	0	0	0
46	Pd	46	2.952	0	0	0	0	0	0	0	0
47	Ag	47	2.952	0	0	0	0	0	0	0	0
48	Cd	48	2.952	0	0	0	0	0	0	0	0
49	In	49	2.952	0	0	0	0	0	0	0	0
50	Sn	50	2.952	0	0	0	0	0	0	0	0
51	Sb	51	2.952	0	0	0	0	0	0	0	0
52	Te	52	2.952	0	0	0	0	0	0	0	0
53	I	53	2.952	0	0	0	0	0	0	0	0
54	Xe	54	2.952	0	0	0	0	0	0	0	0
55	Ba	56	2.952	0	0	0	0	0	0	0	0
56	La	57	2.952	0	0	0	0	0	0	0	0
57	Ce	58	2.952	0	0	0	0	0	0	0	0
58	Pr	59	2.952	0	0	0	0	0	0	0	0
59	Nd	60	2.952	0	0	0	0	0	0	0	0
60	Pm	61	2.952	0	0	0	0	0	0	0	0
61	Sm	62	2.952	0	0	0	0	0	0	0	0
62	Eu	63	2.952	0	0	0	0	0	0	0	0
63	Gd	64	2.952	0	0	0	0	0	0	0	0
64	Tb	65	2.952	0	0	0	0	0	0	0	0
65	Dy	66	2.952	0	0	0	0	0	0	0	0
66	Ho	67	2.952	0	0	0	0	0	0	0	0
67	Er	68	2.952	0	0	0	0	0	0	0	0
68	Tm	69	2.952	0	0	0	0	0	0	0	0
69	Yb	70	2.952	0	0	0	0	0	0	0	0
70	Lu	71	2.952	0	0	0	0	0	0	0	0
71	Hf	72	2.952	0	0	0	0	0	0	0	0
72	Ta	73	2.952	0	0	0	0	0	0	0	0
73	W	74	2.952	0	0	0	0	0	0	0	0
74	Re	75	2.952	0	0	0	0	0	0	0	0
75	Os	76	2.952	0	0	0	0	0	0	0	0
76	Ir	77	2.952	0	0	0	0	0	0	0	0
77	Pt	78	2.952	0	0	0	0	0	0	0	0
78	Au	79	2.952	0	0	0	0	0	0	0	0
79	Hg	80	2.952	0	0	0	0	0	0	0	0
80	Tl	81	2.952	0	0	0	0	0	0	0	0
81	Pb	82	2.952	0	0	0	0	0	0	0	0
82	Bi	83	2.952	0	0	0	0	0	0	0	0
83	Po	84	2.952	0	0	0	0	0	0	0	0
84	At	85	2.952	0	0	0	0	0	0	0	0
85	Rn	86	2.952	0	0	0	0	0	0	0	0
86	Fr	87	2.952	0	0	0	0	0	0	0	0
87	Ra	88	2.952	0	0	0	0	0	0	0	0
88	Ac	89	2.952	0	0	0	0	0	0	0	0
89	Th	90	2.952	0	0	0	0	0	0	0	0
90	Pa	91	2.952	0	0	0	0	0	0	0	0
91	U	92	2.952	0	0	0	0	0	0	0	0

FIG. 6. list of energies (in keV) of the principal *K*, *L* and *M* X-ray emission lines for elements from sodium to uranium, hung on the AN2000 control room.

RESULTS

CALIBRATION

In the following pictures (FIG. 7-9) we report collected PIXE spectra of our standard samples. Each histogram in this work is built using the .txt files containing raw data from each test run, including the counts per channel and a data acquisition time (at least 600 seconds).

The Cobalt Yellow spectrum (FIG. 7) shows two distinct peaks that can be referred to as K_{α} and K_{β} Co lines at the 307 and 340 channels. In the range of channel 143-150 we observe the K_{α} and K_{β} overlap of potassium (*K* element).

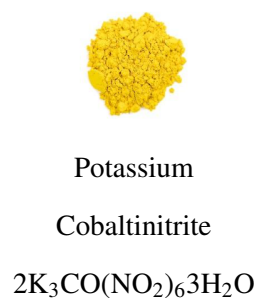
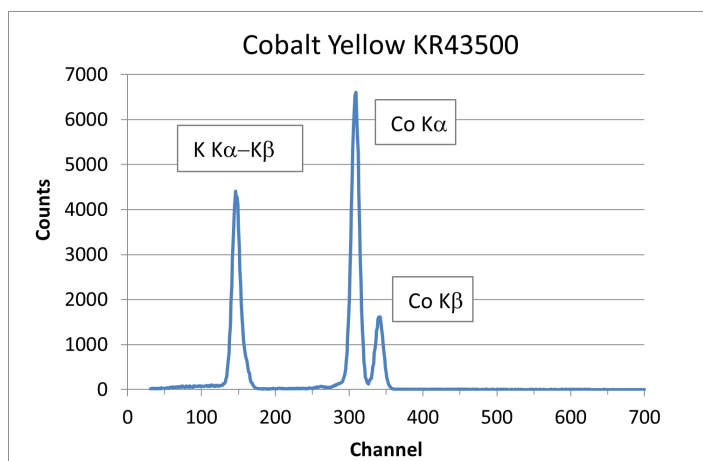


FIG. 7. PIXE spectrum of Cobalt Yellow pigment

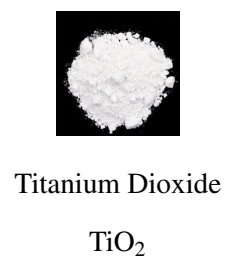
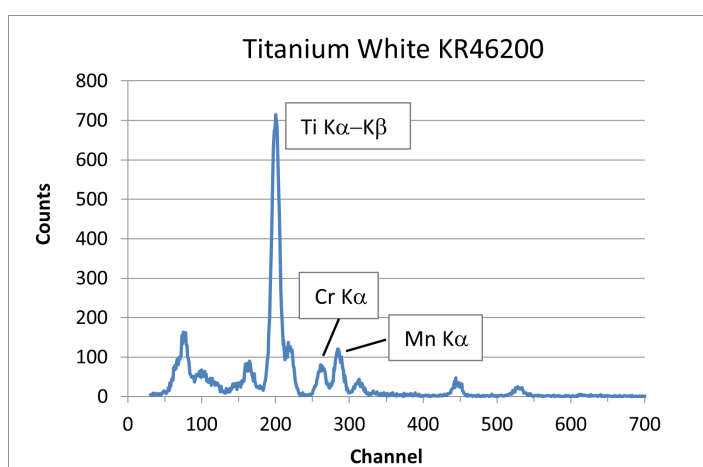


FIG. 8. PIXE spectrum of Titanium White pigment

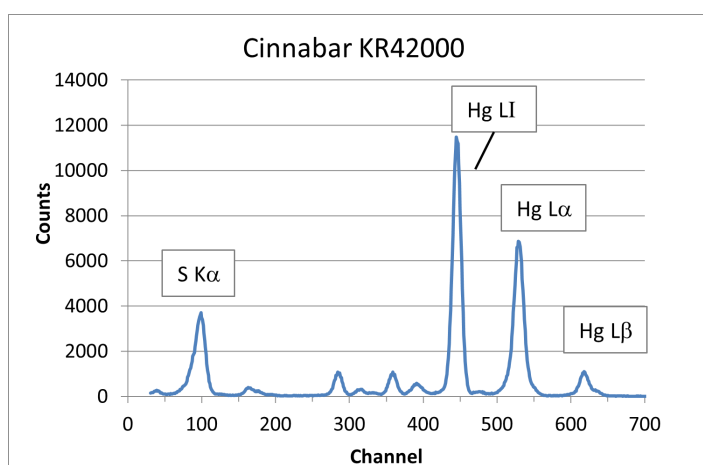


FIG. 9. PIXE spectrum of Cinnabar pigment

In Titanium White spectrum FIG. 8, we distinguish the K_α and K_β Ti lines, with the second one overlapping the K_α peak tail. Other elements were identified after the calibration.

Finally, we clearly identify *L* Hg lines and the K_{α} S line in the Cinnabar PIXE spectrum FIG. 9.

TABLE I lists the energies (in keV) corresponding to the identified lines, and the linear regression fit in FIG. 10, based on these data, reveals the following relationship:

$$E(\text{keV}) = 0,0176(\text{keV}/\text{ch}) \cdot \text{channel} + 1,05(\text{keV})$$

Sample	Channel	E (keV)	Element	Line
Kr 43500	307	6.923	Co	K_{α}
Kr 43500	340	7.648	Co	K_{β}
Kr 46200	200	4.508	Ti	K_{α}
Kr 46200	217	4.932	Ti	K_{β}
Kr 42000	98	2.307	S	K_{α}
Kr 42000	445	8.722	Hg	L1
Kr 42000	530	9.989	Hg	L_{α}
Kr 42000	618	11.908	Hg	L_{β}

TABLE I. Data for the calibration

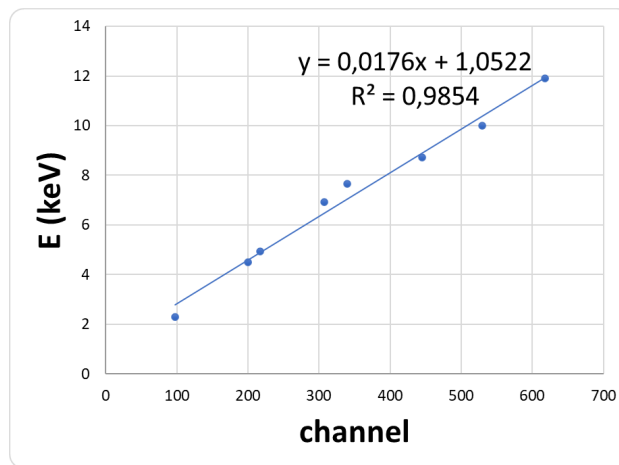


FIG. 10. Energy calibration curve for PIXE analysis

ANALYSIS OF SAMPLES

Fixed the channel to energy calibration, we analysed other samples in order to identify the elemental composition and check the validity of our calibration. We show the following PIXE spectra (FIG. 11-13) with recognized X-rays energies of some elements.

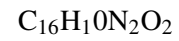
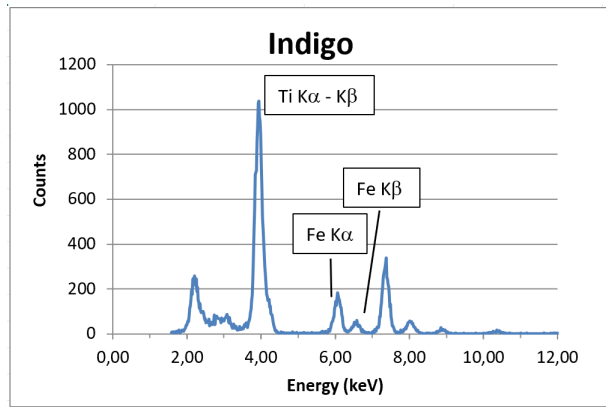
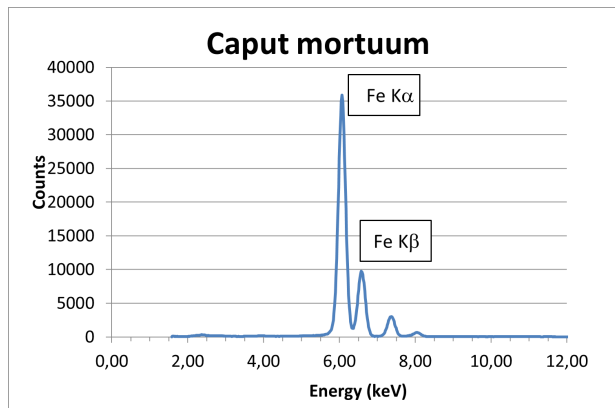


FIG. 11. PIXE spectrum of Indigo pigment



Mixture of Fe_2O_3 ,
 MgO , Al_2O_3 , TiO_2 ,
 $MgSO_4$, SiO_2 (from
 Safety Data Sheet at
 Kremer website [9])

FIG. 12. PIXE spectrum of Caput Mortuum pigment

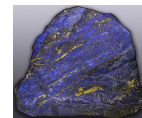
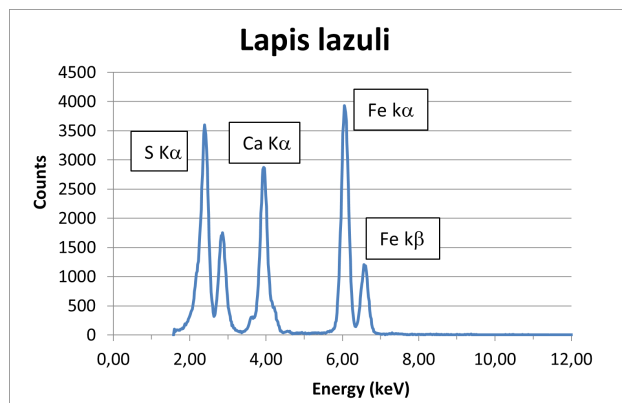


FIG. 13. PIXE spectrum of lapis lazuli

Although the calibration process enables us to convert the channel number, where a peak is detected on the graph, into the corresponding energy of the detected X-ray, we encountered difficulties in identifying certain peaks with sufficient confidence. Despite the calibration, some peaks remained ambiguous or uncertain. This could be due to factors such as overlapping peaks, low signal-to-noise ratios, limited resolution of the detector, or an inaccurate calibration. If the

calibration isn't precise, even small deviations can lead to uncertainties in identifying the exact energies of the peaks.

The lapis lazuli sample appeared visually heterogeneous, for this reason it was tested in multiple locations. However, the data collected depict the same histogram .

RESOLUTION

PIXE spectrum usually consists of two basic parts, background and signal peak of a specific element. Energy resolution is the ability of the detector to separate closely spaced X-ray peaks. Limited resolution of the detector may cause nearby peaks to blur together.

The signal peak can be approximated as a Gaussian shape and the resolution R is the ratio between the full width at half maximum $FWHM$ (expressed in eV) and the energy E corresponding to the centre of the Gaussian

$$R = \frac{FWHM}{E}$$

The $FWHM$ of the Gaussian is mathematically expressed by

$$FWHM = \Delta E = 2.35 \cdot \sigma$$

where σ is the standard deviation.

We calculated the energy resolution at the first peak of L Hg lines of the Cinnabar spectrum FIG. 14. We detected 10 channels $FWHM$, corresponding to 0,176 keV, at 8,7 keV (LI Hg), as shown in FIG. 9. In this way we obtained a resolution of 2%, confirming that the HP-Germanium detector has a good resolution.

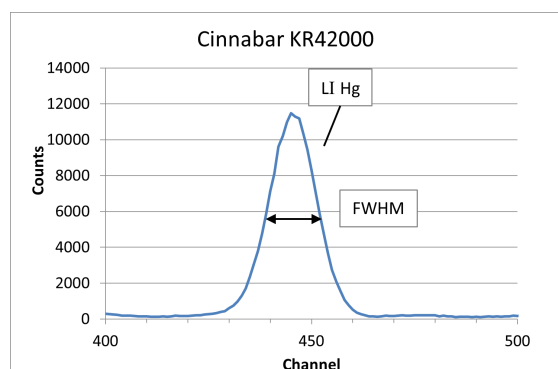


FIG. 14. Close up of Cinnabar spectrum to calculate $FWHM$ at LI Hg line

TEACHING ACTIVITY: "EXPLORING CULTURE HERITAGE WITH PIXE"

We are proposing an interdisciplinary teaching activity, designed for last or fourth year high school students and that integrates physics, chemistry, and art. It demonstrates how modern physics, through PIXE analysis, can be applied to solve real-world problems in the study of cultural heritage. The objectives are the following.

- Introduce students to the principles of atomic physics and spectroscopy.
- Explore the application of PIXE in the analysis of cultural heritage.
- Engage students in analysing real-world data from PIXE experiments.
- Foster collaboration between physics and art history classes.

ACTIVITY OUTLINE

Introduction to Atomic Physics and PIXE. The lesson begins with a physics teacher introducing the basics of atomic structure, focusing on Bohr's atomic model, energy levels, and the concept of atomic spectra. The teacher will explain how PIXE works: a proton beam is directed at a sample, ejecting inner-shell electrons and causing X-ray emissions that are characteristic of the elements present.

Art history and Pigment Composition. An art history teacher will discuss the evolution of painting techniques and pigments through the centuries. This segment will focus on the chemical composition of specific pigments used by famous artists. Historical information about pigment production will provide context for the PIXE analysis.

Visit to the LABEC (Laboratorio di Tecniche Nucleari per i Beni Culturali). Visiting LABEC, a laboratory specialising in nuclear physics applied to cultural heritage conservation, could be a highly educational experience, in order to enhance the students' understanding of how nuclear techniques, including PIXE, are applied in real-world settings. Located in Sesto Fiorentino (Florence), LABEC offers cutting-edge equipment and expertise in the analysis of artworks and historical materials.

Hands-on analysis Students will be divided into groups. Each one will be provided with .txt files containing a list of counts per channel, derived from the same session of PIXE tests on pigments, whose compositions are similar to those of some famous artworks. Actually, students

are required to carry out the same analysis as outlined in the previous section. Besides, each group will receive a case study to analyse, such as determining the authenticity of a painting based on pigment composition.

Data Interpretation Students will interpret the spectra by comparing the energy peaks in their data with reference tables that provide the characteristic X-ray energies of various elements. Through this process, they will identify the elements present in the pigments and draw conclusions about the authenticity or historical context of the artwork.

Group Presentation Each group will present their findings in a collaborative session. In addition to interpreting the scientific data, students will discuss the broader implications of their findings in terms of art history, conservation, and cultural heritage. For example, they may explore how knowledge of pigment composition can help conservators restore paintings without damaging them.

CONCLUSIONS

This interdisciplinary teaching activity provides a unique opportunity for students to apply scientific principles to real-world problems, bridging the gap between the sciences and the humanities. By analysing PIXE data, students gain hands-on experience with modern physics techniques and explore their application in the field of cultural heritage. This activity encourages critical thinking, collaboration, and the practical application of classroom knowledge, offering a glimpse into how science can inform and preserve the world's artistic legacy.

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