DEVELOPMENT OF NON-DESTRUCTIVE TECHNIQUES USING PROTON BEAM ACTIVATION FOR HERITAGE OBJECTS.

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Presentation outline

- Background
- Arronax cyclotron
- Problematic
- Objectives
- Application of the method to a heritage object
- Conclusion and persepctive

Background

Heritage objects are made of ancient metals (gold, copper, iron, lead, tin, and silver) and bear the mark of their history. (A. Jambon, 2017).

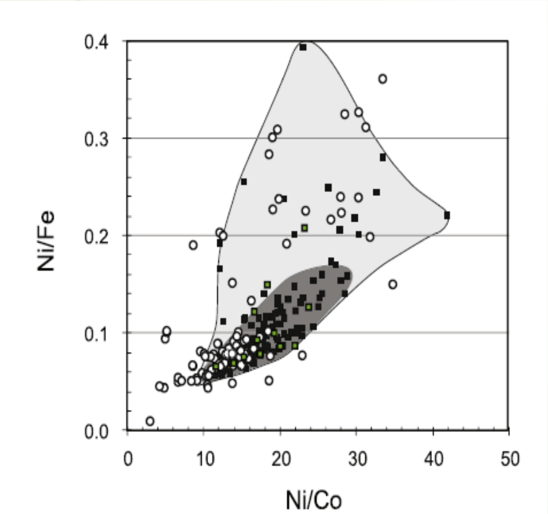


Fig. 1. Ni/Fe vs Ni/Co in iron meteorites.

Photo 1: Bronze Age iron knife

The analysis of heritage objects allows us to study their origin and manufacturing techniques.

Background

Scientists have developed analytical methods that enable the characterization of the materials that make up objects (Vladimir I et al, 2019).

NON-DESTRUCTIVE METHODS.

Based on the detection of radiation (X or γ) emitted after the excitation/activation of matter by ionizing radiation or charged particles.

XRF: X-Ray Fluorescence.

Methods are based on the interaction of an X-ray beam with a sample.

ION BEAM ANALYSIS METHOD.

Methods based on the interaction of a beam of charged particles (protons, deuterons, or alpha particles) with a sample.

Background

NON-DESTRUCTIVE METHODS.

ION BEAM ANALYSIS METHOD.

- Ion Beam Analysis (IBA) is a set of methods derived from nuclear physics (Jeynes, 2011).

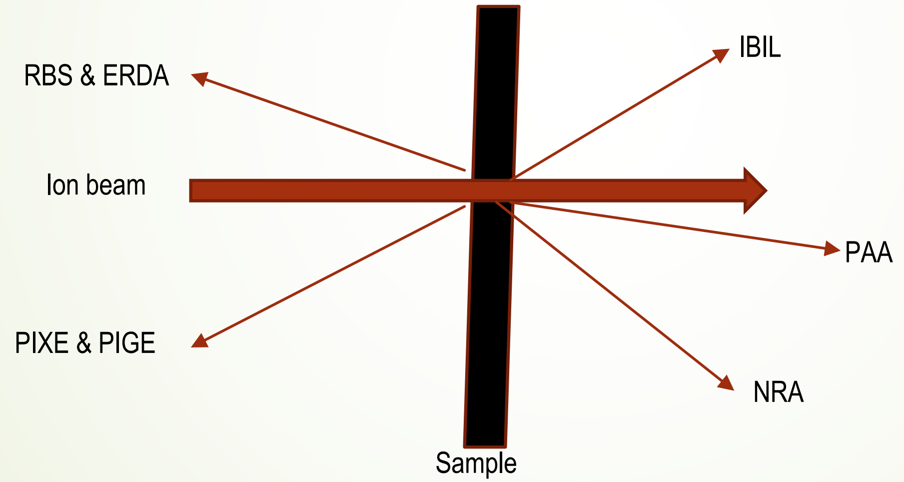


Fig 2: Differents techniques of ion beam.

- Detection of the characteristic radiation or particles induced by this interaction enables the elements to be identified and quantified.

Background

ION BEAM ANALYSIS METHOD.

HE-PIXE analysis method

PIXE is based on the excitation of the electronic pattern by ionization of the inner atomic layers (K, L...), de-excitation produces the emission of a characteristic X-ray.

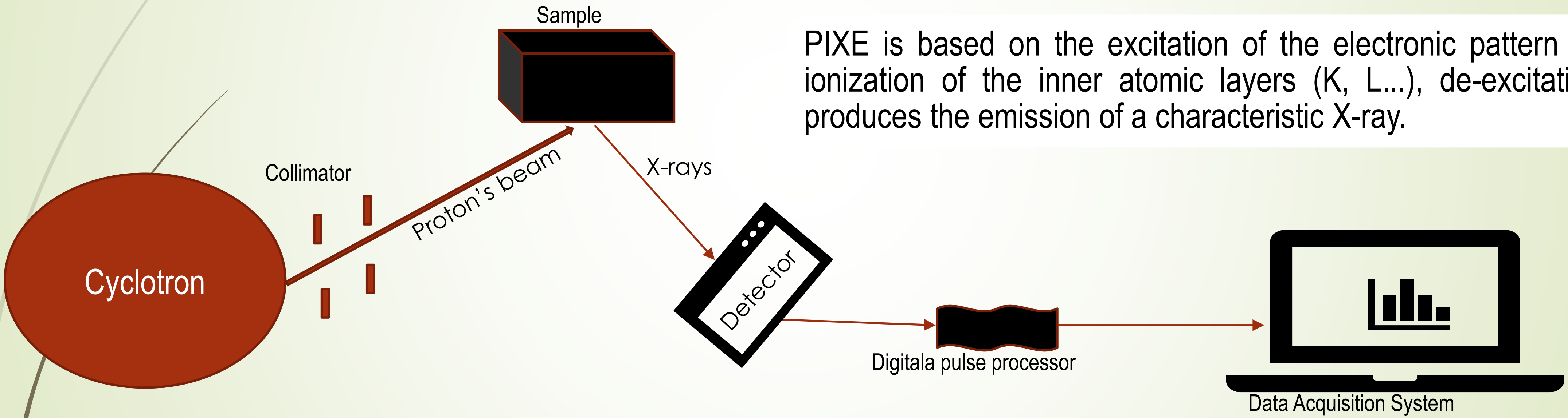


Fig. 3: Diagram representing the HE-PIXE method

Background

ION BEAM ANALYSIS METHOD

Proton activation analysis (PAA) methods.

- They are based on irradiating the sample with a beam of protons, causing nuclear reactions that produce specific radionuclides

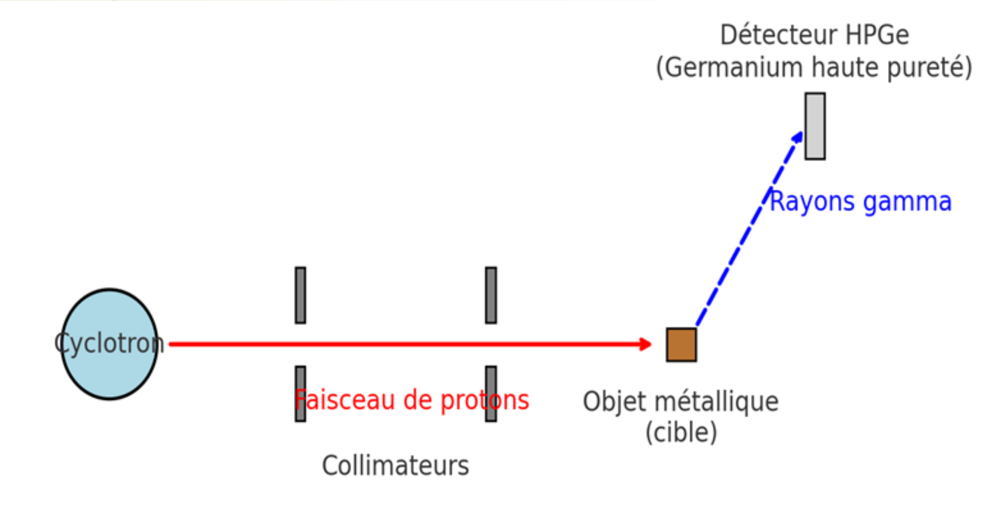


Fig. 4: Diagram representing the PAA method

Detecting their gamma radiation allows the elements present to be identified and quantified.

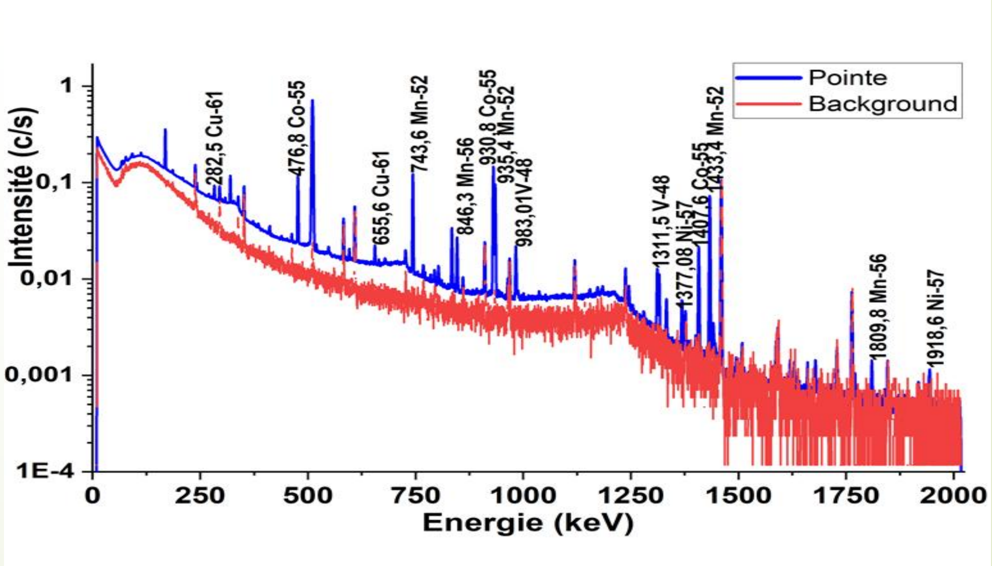


Fig. 5: Gamma spectrum

- The PAA method, which is based on nuclear reactions, has less matrix effect on the surface and allows for deeper analysis that is less affected by corroded layers.

Arronax cyclotron

- ARRONAX (Accelerator for Research in Radiochemistry and Oncology at Nantes-Atlantique) is a high-energy (70 MeV), high-intensity cyclotron (750 µA of proton and 35 µA of alpha particles) (J. Martino, 2007).

Photo 2: Arronax cyclotron

Faisceaux	Particule accélérée	Energie (MeV)	Intensités
Protons	H-	30 - 70	1 pA – 350 µA
	HH+	17,5	1 pA – 50 µA
Deutérons	D-	15 - 35	1 pA – 50 µA
Particules α	He++	70	1 pA – 35 µA

Table 1: Arronax cyclotron energy

- ARRONAX's main objectives are to produce innovative radioactive isotopes for nuclear medicine.

To carry out research into the interaction of particles with matter, including radiolysis, radiobiology and the high-energy proton-induced X-ray emission analysis method (HEPIXE).

Arronax cyclotron

ARRONAX ion beam analysis methods.

High-energy proton-induced X-ray emission (HEPIXE) analysis method: Measuring the concentration of trace elements in heritage objects.

Measurements of gold concentrations in coins, which are in the order of hundreds of µg/g, were carried out to differentiate the origin of silver coins.

Photo 3: Coinage (16th century).

However, it was not possible to quantify indium precisely because its concentrations are below this detection limit.

Problématic

ARRONAX HE-PIXE (High Energy Proton Induced X-ray Emission) analysis method.

Difficulty quantifying elements with low concentrations below the detection limit. Example of quantifying indium in coins.

It is impossible to eliminate the background noise generated by the interaction between the beam and the target without disturbing the signal of interest.

Difficult for analyzing objects with a thick layer of surface corrosion.

Objectives

- **The main objective is to develop ion and neutron activation methods within ARRONAX for heritage objects.**

- Optimization of activation analysis device for short- and long-lived elements.

- Implementation of a specific neutron method device to convert protons from the cyclotron into neutrons.

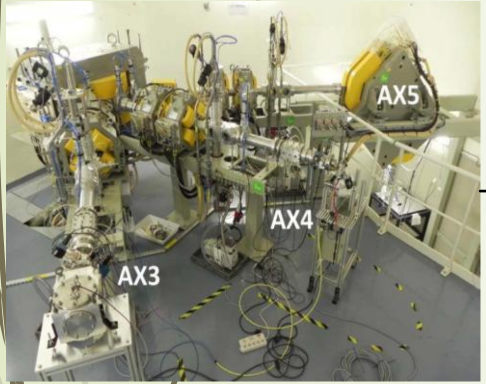
- Complementarity between ion beam techniques developed at ARRONAX and Arc'Antique laboratory analysis techniques (pXRF method).

- Optimization of detection (µg/g) and in-depth quantification of trace elements in objects.

Application of the method to a heritage object

Materials.

- The PAA consists of irradiating a 3 mm thick iron knife and a standard of 80% Fe and 20% Ni with a beam of 50 MeV, 1 nA for 3 minutes.



50 MeV proton beam AX5 line

Iron knife

HPGe gamma detector

Data acquisition system.

- The objective of analyzing the Bronze Age iron knife is to determine the origin (terrestrial or meteoritic) of the iron.

Application of the method to a heritage object

Methodology

- The irradiation energy was chosen in relation to the sample thickness and taking into account the production of the radioisotopes of interest. The different cross sections were determined by Tendl-2025.

Ni-58(p, pn)Ni-57

Fe-56(p, 3n2p)Mn-52

Photo 4 Shart of radionucleide (NuDat 3.0)

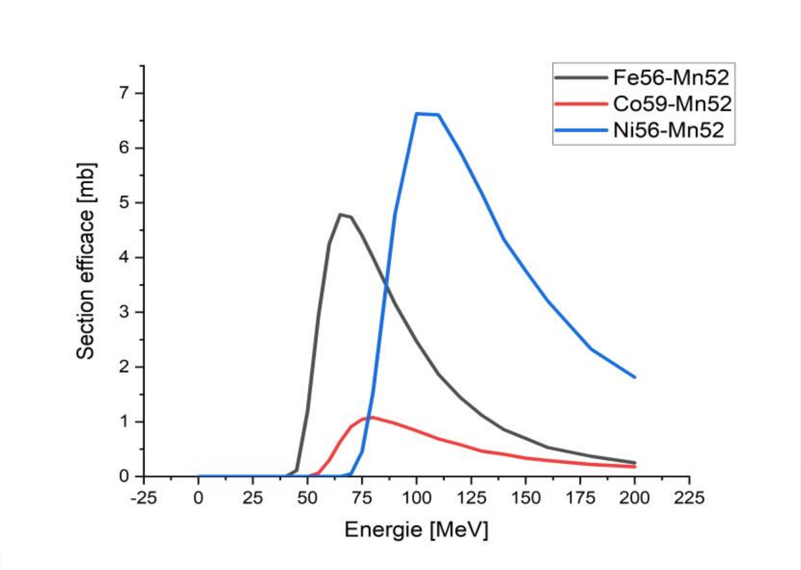


Fig. 6: Courbe de section efficace

Application of the method to a heritage object

Methodology.

- **Spectrum processing**
- The spectra were analysed using ORIGIN software, which identifies the peaks and processes the spectrum to calculate the peak's areas.

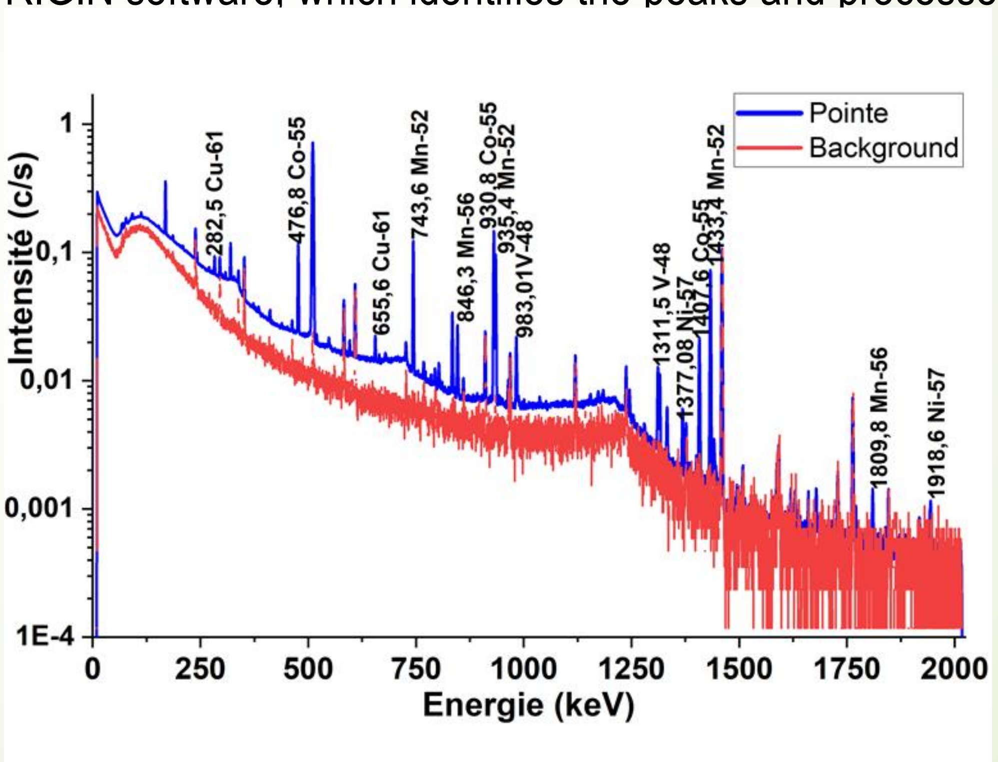


Fig. 5: Gamma spectrum

Application of the method to a heritage object

Methodology

- **Determination of peak areas**.
- The peak's areas were dertmineted using the integration and fiting methods in ORIGIN.

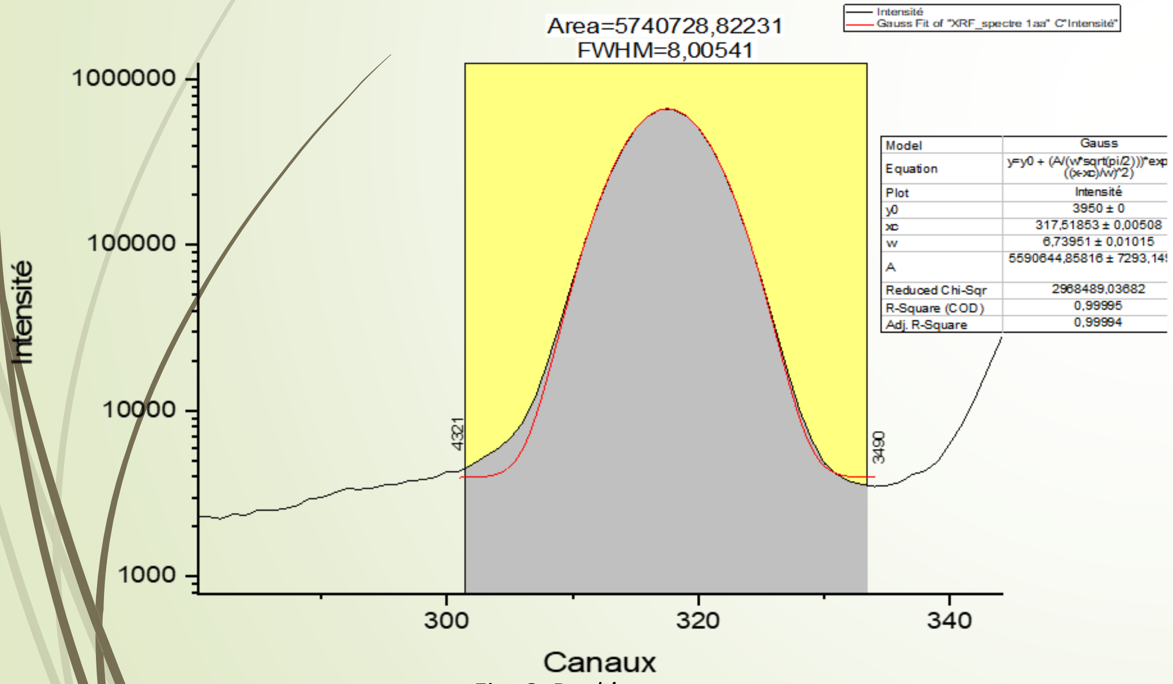


Fig. 6: Peak's area

- Intégration method.

$$Aire_{nette} = Aire_{brute} - Fond_{résiduel}$$

- The ratio was calculated from the areas of each peak.

$$Ratio\left({}^{Ni}/_{Fe}\right) = \frac{A_{Ni}}{A_{Fe}}$$

Application of the method to a heritage object

Methodology.

- Subtraction of background noise; in case the same peak appears in the background noise.

$$Aire_{nette} = Aire_{mesuré} - \left(Aire_{bruit-fond} * \frac{Temps_{sp-mes}}{Temps_{sp-bf}}\right)$$

- Correction for radioactive decay to trace back to production activity.

$$A_0 = \frac{A}{e^{-\lambda(t_{EOB})} * \left(1 - e^{-\lambda(t_{Comptage})}\right)}$$

The Ni mass concentration was calculated by comparing the object ratio with that of the standard

$$Ratio\left(\frac{Ni}{Fe}\right)_{cor} = \frac{\left(Ratio\left(\frac{Ni}{Fe}\right)\right)_{objet}}{\left(Ratio\left(\frac{Ni}{Fe}\right)\right)_{standard}}$$

$$C_{Ni} = 20\% Ratio_{cor}$$

Application of the method to a heritage object

Results and discusion

- In this work, the mass fraction of nickel obtained is 0.28%, which is lower than the theoretical value.

- Compared to the result obtained with pXRF, which is 0.5% nickel in iron.

- Our measurement point is in the lower part of the Ni/Fe ratio of the various study data compiled by A. Jambon on the origin of meteorite iron.

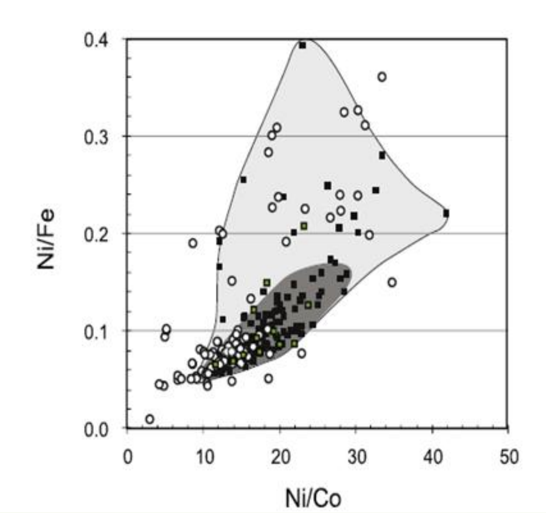


Fig. 1. Ni/Fe vs Ni/Co in iron meteorites (A. Jambon, 2017).

Conclusion and perspectives

- The PAA method was satisfactory in measuring low concentrations of Ni relative to iron in a complex object.
- Our results seem to indicate that the iron is meteorite, and to confirm this, we will need to find the Ni/Co ratio.
- For the coming time, we plan to set up an acquisition chain with a shielded HPGe detector to measure the gamma rays emitted by short-radioisotopes in the reaction's casemate.
- Multiply several points on the knife with pXRF and HEPIXE
- The irradiation of other heritage objects such as a medieval lead pipe.

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Acknowledgements

- General Commission for Atomic Energy, in particular Commissioner General Professor Steve MUANZA, for agreeing to finance my studies;
- Subatech for accepting me into one of its research teams (PRISMA);
- General Manager of ARRONAX for accepting me in the installations.
- Thesis Director Ferid HADDAD for his guidance and for accepting this onerous task.
- My supervisors Charbel KOUMEIR and Charlène Pele-Meziani for their guidance and presence at all times.
- All the staff of SUBATECH and GIP ARRONAX and all the PhD students.

THANK YOU FOR YOUR ATTENTION