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Proton Activation Analysis of medieval lead pipes

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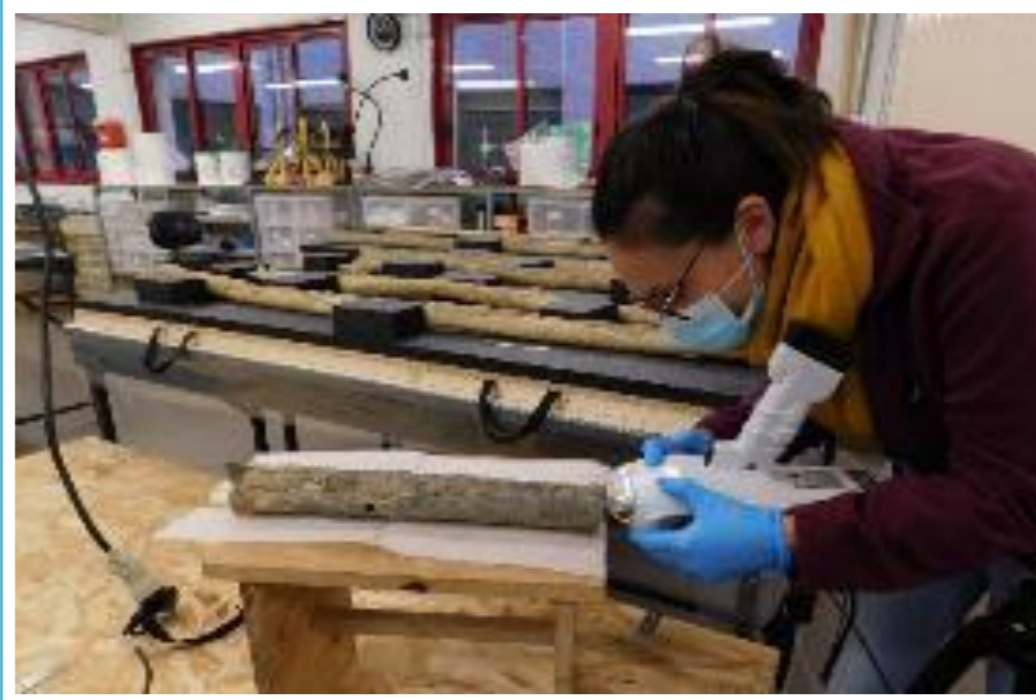
Historical context and questions about the object

We studied a 13th and 14th century water supply system for the kitchens of the castle of Suscinio, Morbihan, France. Several sections of pipes have been extracted from the excavation. There were shaped by bending lead sheets of about 7mm thick. The edges were joined longitudinally by the addition of a brazing material, a tin-lead alloy. The study of the brazing elemental composition can improve the understanding of the manufacturing technique used in the case of lead pipes [1].



13th – 14th century water supply system for the kitchens of the castle of Suscinio, FR

Specific concerns related to the object:
 Is the concentration of tin in the lead homogeneous throughout the thickness of the solder?
 Is the eutectic ratio of the tin-lead alloy reached, 66% Pb – 33% Sn?
 Can the analysis of the chemical composition of the pipes be used to determine the period in which they were made, by comparing them to other lead elements present in the castle, such as the stained glass windows?
 Can identification of trace elements lead to the distinction of specific sources of supply of raw material?



Lead pipe, Arc'Antique laboratory, Loire Atlantique, France

Tin-lead brazing:

The Romans are famous for their extensive production and copious use of lead, especially for their water systems (“fistulae”). Due to the high resistance of lead to corrosion, finds of artefacts of lead are plentiful [2]. Romans used tin for soldering the join, lead pipe matrix could also have tin impurities. They used so-called “tertiarium”, an alloy with two parts of lead and one part of tin, the reason lies in fact that this alloy is eutectic and it melts at temperature which is lower than each of the separate metals. Liquid tin is generally oxidized (SnO₂) and lead can also present a thick layer of corrosion (PbCl₂, PbCO₃). Lead pipes have continued to be used to this day even though lead contamination of water is toxic to humans.



Pipe cross-section



Zoom on the pipe

Analytical strategy and methods used

Proton Activation Analyses (PAA)

ARRONAX cyclotron delivers high energy beam up to 70MeV allowing non-destructive materials analyses with PAA [3]. We measure the secondary radiations emitted after irradiation realized with proton beam. Excitations in material are of atomic or nuclear nature. PAA consists in analyzing γ -ray spectra of radioisotopes produced by nuclear reactions with the target nuclei. This analysis is performed off-line with a Ge crystal detector.

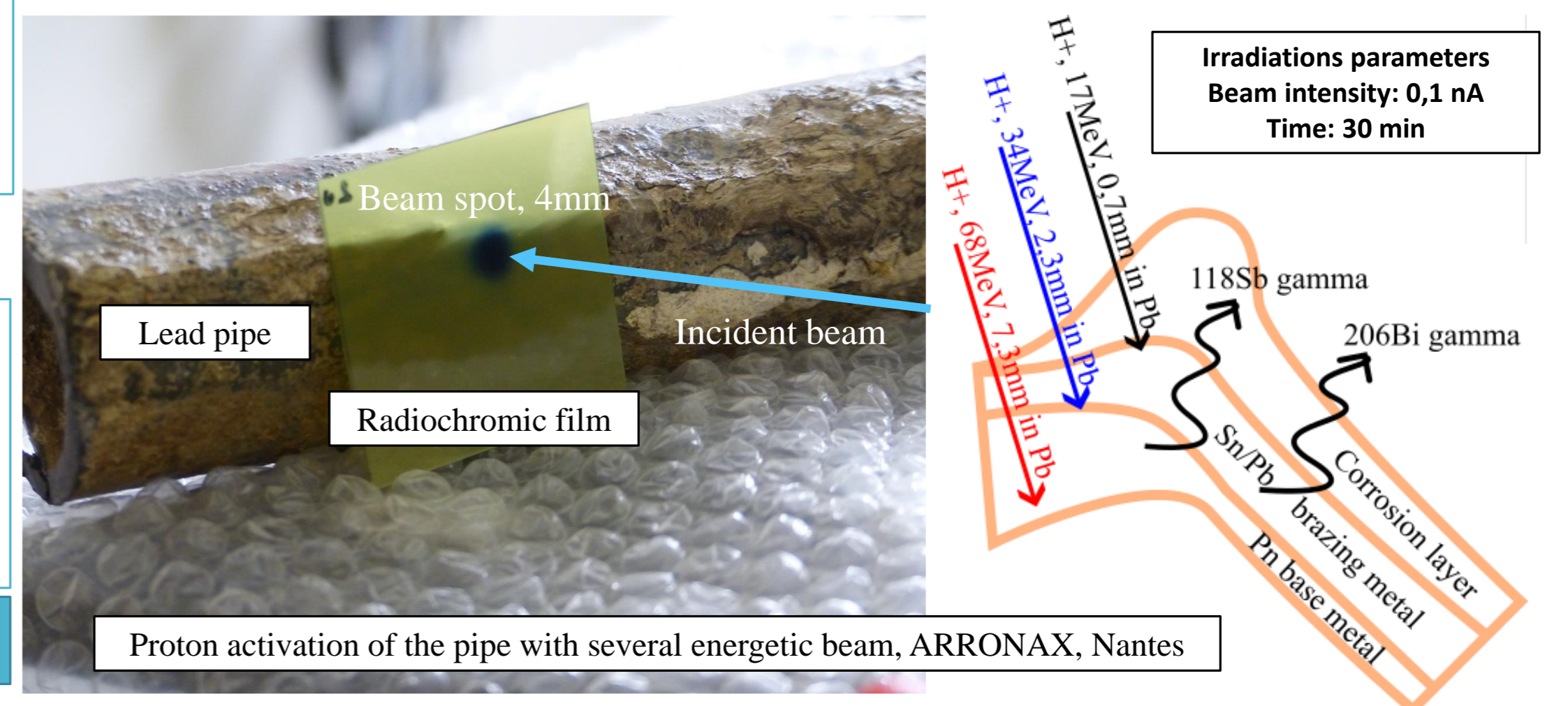


PAA induced radio-isotopes decay, object must be kept in quarantine from few hours to several days

In-depth Pb/Sn distribution

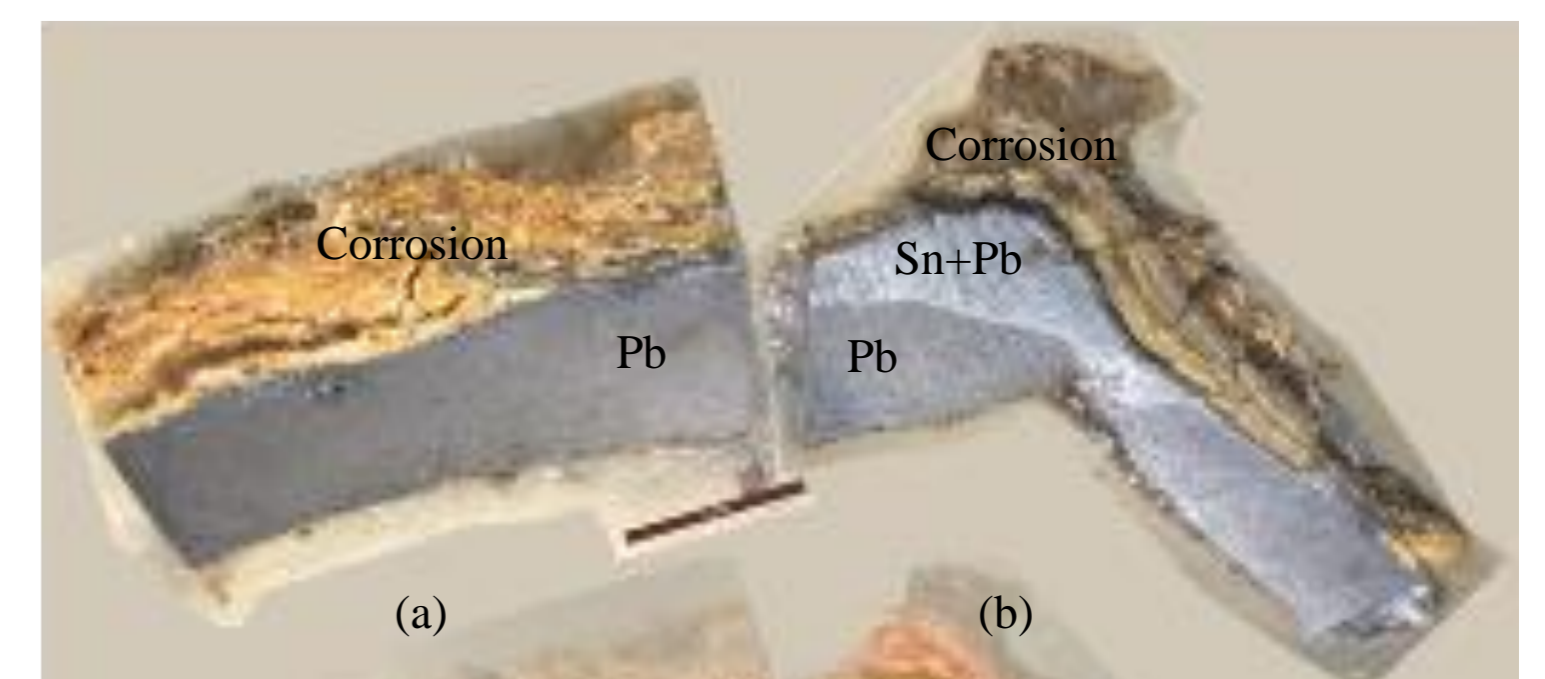
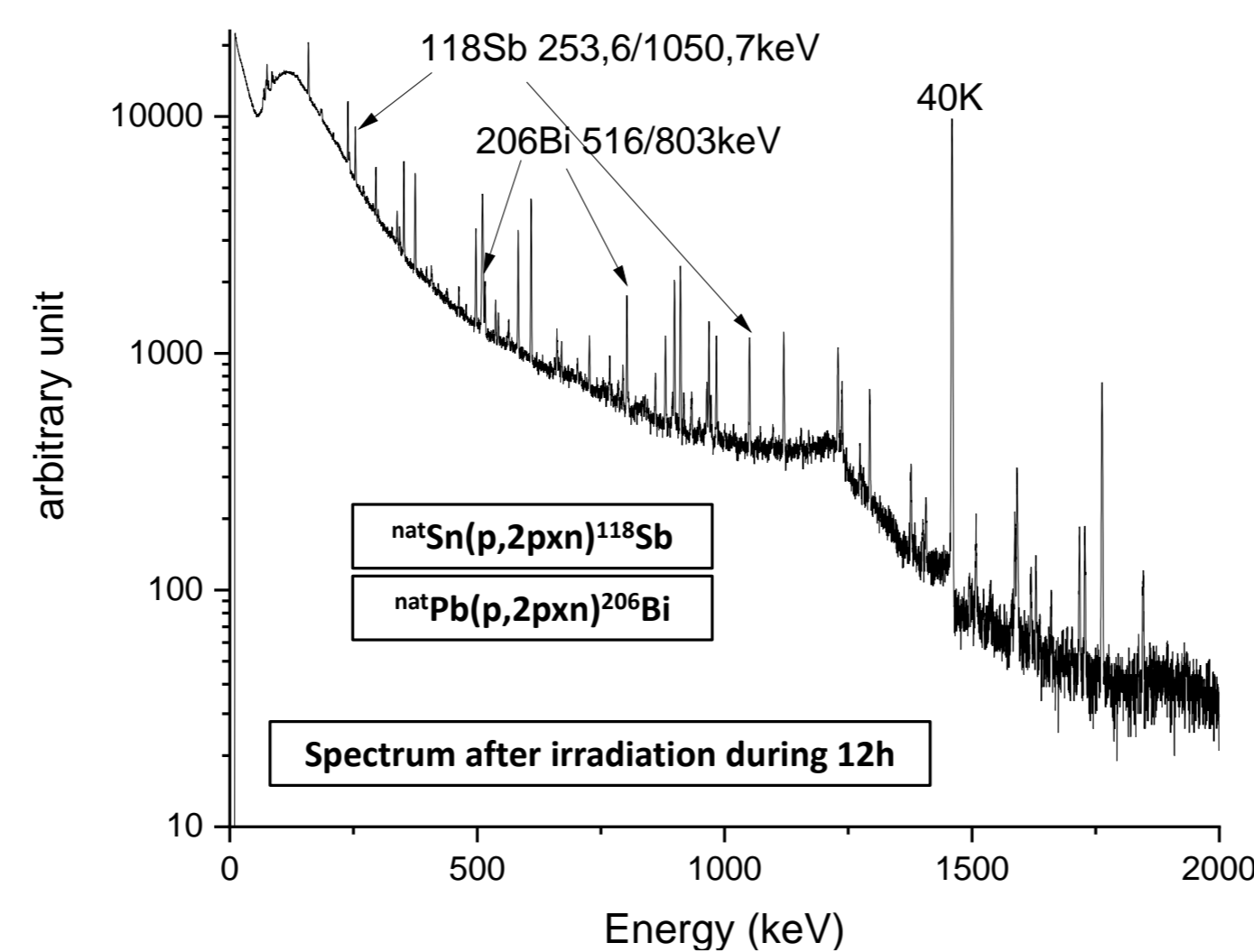
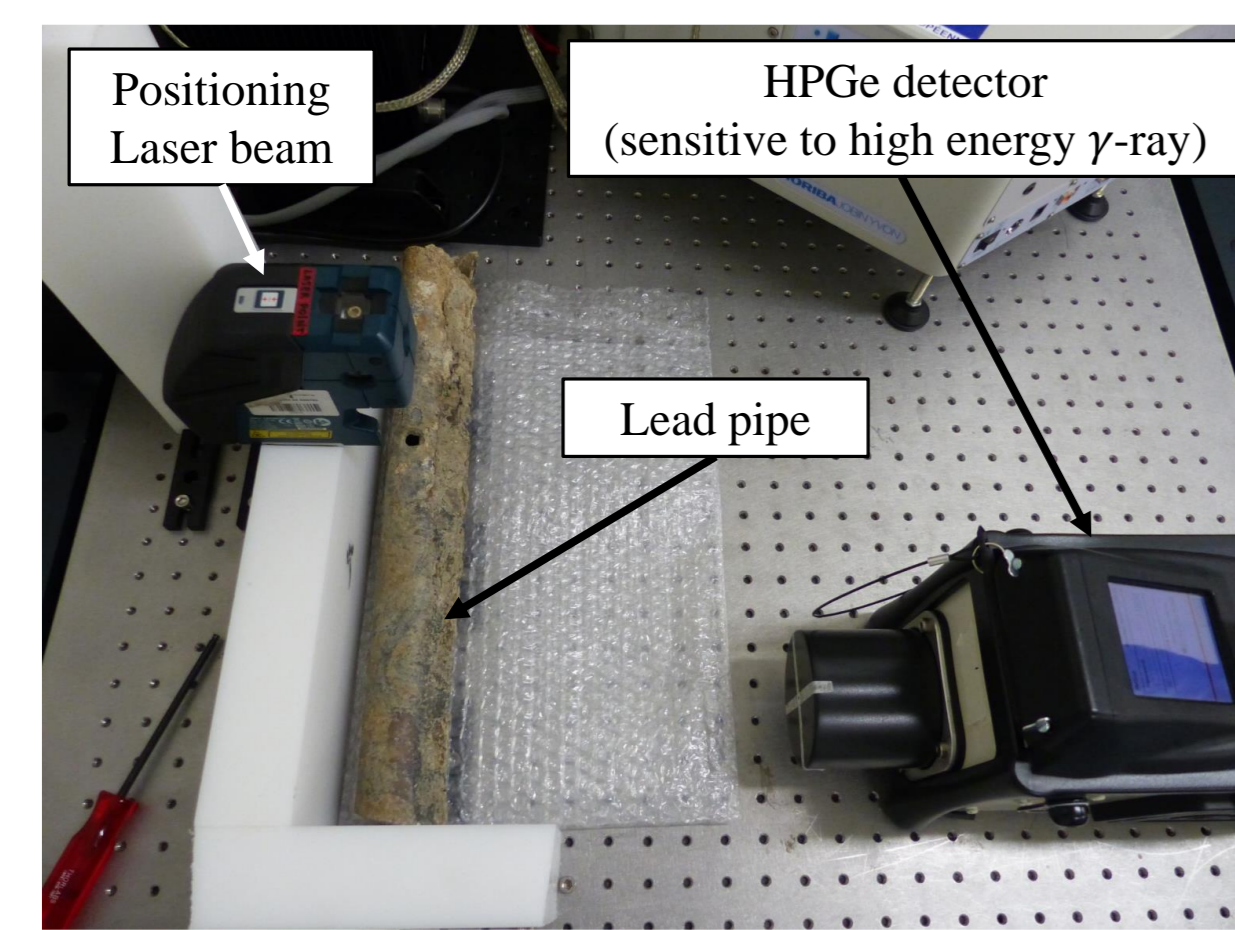
With PAA, we can probe heavy materials (high Z elements) with a thick multilayer structure, such as a soldered and corroded lead pipe. Proton range in such material can reach several millimeter depending on their energy. Moreover, γ rays emitted by Pb and Sn radioisotopes are energetic enough to be detected in all the proton range. Finally, in-depth distribution profile could be made in the brazing zone as well as in the base material.

Analytical set up



Irradiations parameters
 Beam intensity: 0,1 nA
 Time: 30 min

γ -ray spectra – 34MeV proton beam



Cross-section of the pipe, (a) curve edge; Pb + corrosion (b) brazing joint; base material (Pb) + Sn + corrosion layer

The radioisotopes 118Sb and 206Bi are used because they have a couple of γ -rays quite distant in energy. Differential attenuation of γ lines (118Sb 253,6/1050,7 and 206Bi 516/803) helps to evaluate the equivalent thickness corresponding to Sn and Pb depth detection.

PAA Results

Sn at 34MeV (2mm range in Pb):

The experimental value of 118Sb ratio is 3.27 (profile of tin in 2mm). Assuming that tin has a homogeneous distribution, the ratio tends to the value 3.27 for a depth of 1mm. So the experimental value corresponds to a tin profile with a high concentration in the first mm.

Sn at 68MeV (7mm range in Pb):

The experimental value of 118Sb ratio is 2.29 (profile of tin in 7mm). Assuming that tin has a homogeneous distribution, the ratio tends to the value 2.29 for a depth of 3.5mm. So the experimental value corresponds to a tin profile with a high concentration in the first 3.5 mm.

Pb at 68MeV:

The experimental value of 206Bi ratio is 0.5 (profile of lead in 7mm). Assuming that Pb has a homogeneous distribution, the ratio tends towards the value 0.5 for a depth of 7mm. So the experimental value shows that the lead is present in all the proton range, which is in agreement with lead sheet thickness.

Complementary X-ray spectroscopic analyses

MEB-EDS analyses

Base material composition: 95-98%w Pb + <0,5%w Cu/Sn
 Brazing composition: 56%w Pb + 58%w Sn

P-XRF analyses

Base material composition: Highly variable values (6 points, 0-66%w Sn and 34-100%w Pb)
 Brazing composition: Highly variable values (10 points, 2-64%w Sn and 36-68%w Pb, only one point with an eutectic concentration)

Analytical outlooks

- PAA can be used to probe lead pipe in depth.
- First results have to be confirmed by using several beams between 17 and 68MeV to scan the whole irradiated area with a step of 1mm in-depth
- Looking at other radioisotopes could be interesting even to detect trace elements (related to provenance concerns)
- MEB-EDS and XRF analyzer are also used to get precise profile concentration values on a cross-section of the pipe

[1] Ernesto Papparazzo, Surface and interface analysis of a Roman lead pipe “fistula”: microchemistry of the soldering at the join, as seen by scanning Auger microscopy and X-ray photoelectron spectroscopy, Applied Surface Science 74 (1994) 61-72

[2] A. Wyttenbach and P. A. Schubiger, Trace element content of roman lead by neutron activation analysis, Archaeometry 15, 2 (1973). 199-207. Printed in Great Britain

[3] C. Koumeir et al., A new facility for High energy PIXE at the ARRONAX Facility, https://arxiv.org/abs/1011.4057 (2010)