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Proton Activation Analysis of medieval lead pipes

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].

Specific concerns related to the object:

Is the homogeneity 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 raw material?

First results have to be confirmed by using several beams between 17 and 68MeV to scan the pipes. Such experiments have been set up in ARRONAX, Nantes. 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.

γ-ray spectra – 34MeV proton beam

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 3.5mm. 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.

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.

Analytical set up

Irradiations parameters
Beam intensity: 0.1 μA
Time: 30 min

Beam spot: 4mm

Positioning Laser beam
HPGe detector (sensitive to high energy γ-ray)

Lead pipe

PAA analytical off-line bench in ARRONAX, Nantes

Complementary X-ray spectroscopic analyses

MEB-EDS analyses
Base material composition: 95-98%/w Pb + <0.5%/w CuSn
Brazing composition: 56%/w Pb + 58%/w Sn

P-XRF analyses
Base material composition: Highly variable values (6 points, 0.66–100%/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.