Applications to Cultural Heritage II - Diffraction

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Summary:

Three examples of Neutron Diffraction applied to Cultural Heritage:

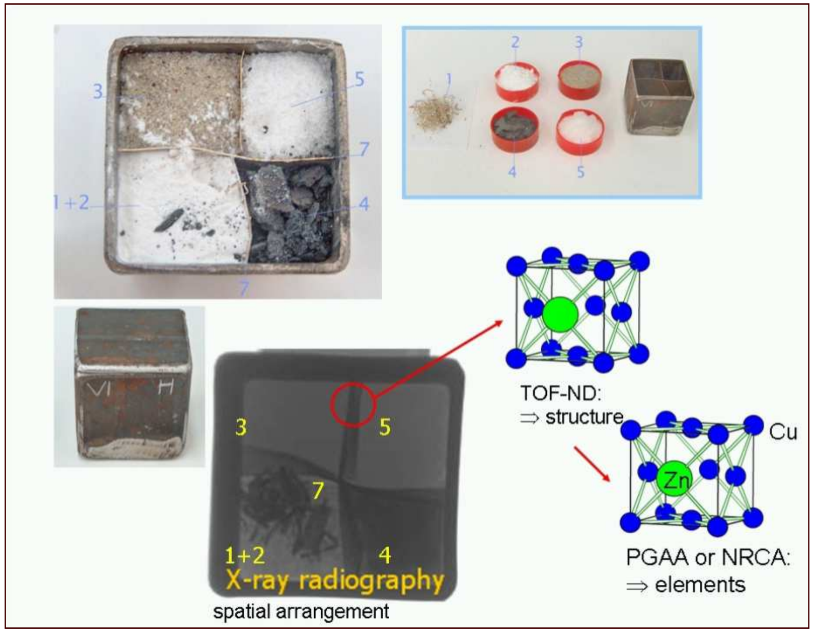
1) **Black Boxes study**
Aim: identify strengths and weaknesses of Neutron Diffraction to analyze archaeological objects.

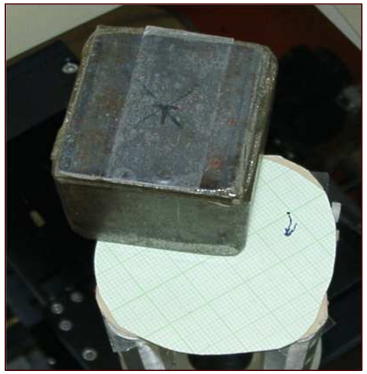
2) **Ghiberti Head Neutron Diffraction study performed at Engin-X**
Aim: identify cavities and inhomogeneity in the bulk of the sample, phase composition and residual strain distribution.

3) **Neutron and Musical heritage**
Aim: Simultaneous and integrated neutron-based techniques for material analysis of a metallic ancient flute (diffraction, NRCA and radiography)

Black Boxes study:

- **Neutron diffraction** applications for the study of archaeological objects
- Develop a **best practice for combined use of neutron analysis methods** for different combinations of materials (PGAA, TOF-ND, NT)
- 17 samples: **closed cubes** containing **2D and 3D geometrical arrangements of materials** (metals, minerals, ceramics, and organic matter)
- Measurements on ROTAX, GEM, and INES at the ISIS Facility (UK)





Black Boxes study - time of flight neutron diffraction

Powerful for investigating the crystal structure to the samples

TOF: determination of neutrons' energy for a 'white beam' measuring their time of flight

$$E = \frac{1}{2} m_n v^2 = \frac{1}{2} m_n \left(\frac{L}{TOF} \right)^2$$

Bragg's Law

$$(TOF)_{hkl} = \frac{2m_n}{h} L d_{hkl} sin\theta_0$$

m_n = neutron mass
L = flight length between the moderator to the sample
TOF = employed time to cover the L distance

ROTAX

3 detector banks in horizontal plane

fast acquisition, medium resolution

Flight path 14.0 m

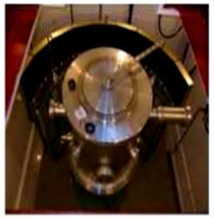
GEM

6 detector banks

fast acquisition, high resolution

Flight path 17.0 m

INES



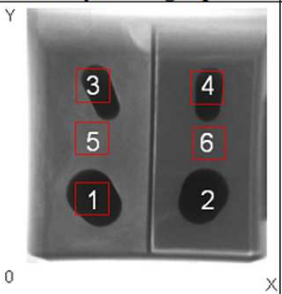
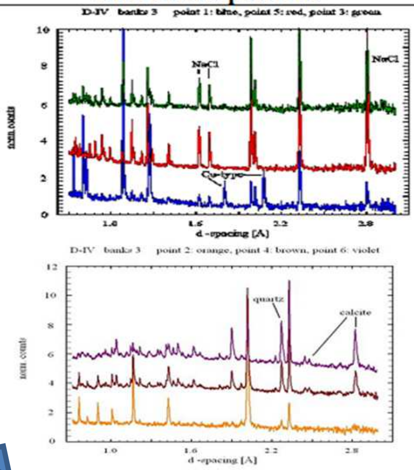
9 detector banks in horizontal plane

slow acquisition, high resolution

Flight path 22.8 m

Black Boxes study

Table 2 (a). TOF Neutron Diffraction results on D-IV

Box no.	X-ray radiograph	Set-Up	Diffraction patterns	ND results
D-IV		**Instrument: ROTAX** beam size 10x10 mm; beam along z box alignment: P1-P6 aligned with incident beam; no offset		**Point 1**: NaCl, Cu-type (fcc) a=3.592 Å, steel (Fe) or copper (Cu) **Point 2**: bcc a=2.845 Å, ferrite (Fe) + cementite (Fe_3C), in clay=calcite+quartz **Point 3**: NaCl, small fcc peaks a=3.6 Å, steel (Fe) or copper (Cu) **Point 4**: calcite, quartz, bcc a=2.845 Å, ferrite (Fe) **Point 5**: NaCl **Point 6**: calcite (75wt%), quartz (25 wt%)

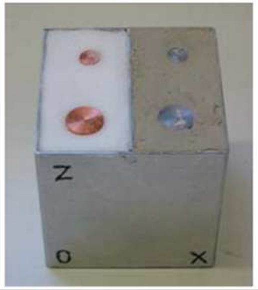
Tomography and measurements points

Diffraction patterns with phases identification

ND results as function of measurement point: crystal structure and phase identification

Black Boxes study

Table 2 (b). *Comments on TOF-ND results on D-IV*

Box no.	Box content from TOF-ND	Complementary info	Reality Check
D-IV	- Two compartments with different filling materials: salt (NaCl) and clay consisting of quartz (25 wt% SiO_2) and calcite (75wt% $CaCO_3$). - The **objects** in the two chambers are made of different materials: **1**: fcc-structure, Cu-type (fcc structure); lattice parameter (a=3.592 Å) is closer to steel (3.594 A) than to copper (3.615 A) **2**: Bcc lattice, ferrite (Fe); extra cementite (Fe_3C) peaks; clay peaks are small compared to the Fe peaks; **3**: fcc-structure, Cu-type (fcc structure); lattice parameter (a=3.592 Å) indicates steel **4**: The rod material is bcc-Fe (ferrite)	- **PGAA** identifies fcc-metal as **Cu** for points (1) and (3) - **PGAA** identifies **Al** as separator material. 	Cu and Iron rods, embedded in halite (NaCl) and clay (51% calcite, 20% quartz, 12% muscovite, 17% kaolinite) - The main components are identified by TOF-ND. - PGAA is required to decide on the fcc-material: copper. - For the clay the two main components were identified with approximately the correct proportions. - After disclosure of the content, kaolinite is identified in the pattern. - Muscovite was not detected by TOF-ND. - The lattice parameters of Cu and Fe are systematically shifted towards lower values. This is probably due to absorption (i.e. apparent shift of the material towards the neutron source.) - **Extra phase**: Cementite is observed in the ferrite. - The second wall of the box is not visible for both filling materials. The Cu rod in position 3 was almost missed by the neutron beam due to misalignment of the box on the instrument.

Box content from ND

Prompt gamma activation analysis as complementary: elemental analysis

Check with the real content of the box

Black Boxes study

Conclusions:

- PGAA, ND and radiographies provide complementary information
- Radiographies guide ND, PGAA measurements
- PGAA: Distinction between Cu alloys and Cu
- ND: Distinction between compounds of the same element (cementite (Fe_3C) identified in iron rods, distinction between FeO, Fe_2O_3, Fe_3O_4)
- ND: Distinction between different crystal structures (alpha brass (fcc), beta-brass (bcc))
  – Difficulties to distinguish different lattice parameters and same crystal structure – effect of peak shift (Cu: a=3.6145 Å, steel: a= 3.608 Å or Al: 4.048 Å, Ag: a=4.086 Å, Au: 4.078 Å indistinguishable) → PGAA fundamental

Publication:
- *G. Festa, W. Kockelmann, A. Kirfel and the Ancient Charm Collaboration*, 'Neutron Diffraction Analysis of 'Black Boxes'', *Archaeometry Workshop*, N. 1 (2008)

The 'Lorenzo Ghiberti' relief

Object: prophet head
Author: Lorenzo Ghiberti
Period: 1425-1452
Owner: Opera di S. Maria del Fiore, Firenze
Site: *Porte del Paradiso - Battistero di Firenze*
Material: gilded bronze
Dimensions: diameter = 13 cm, height = 7 cm

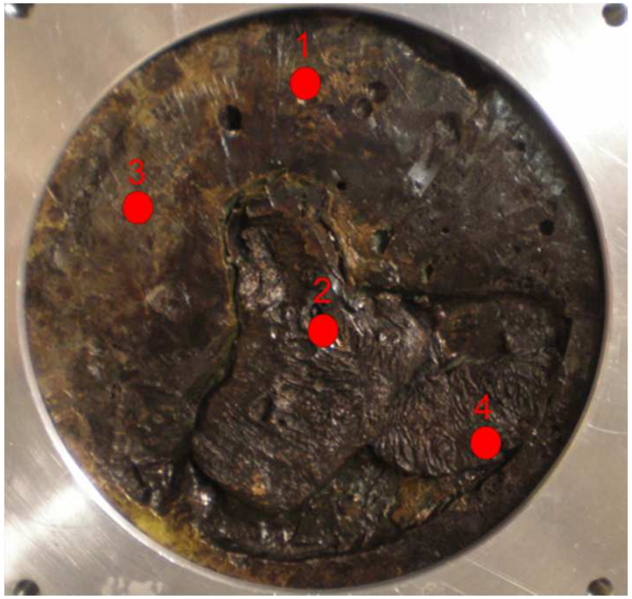
- After the flood of 1967, the gates were removed from the *Battistero* and preserved in the *Museo dell'Opera del Duomo*
- Restoration was made in the laboratory '*Bronzi ed Armi Antiche*'
- Restoration was made with different methods: chemical bath in the Rochelle salt solution, laser cleaning

Ghiberti Head critical aspects

A. Gilding state

B. Extension of the secondary melting

C. Study of the two melting about composition and working methods



Ghiberti Head Neutron Diffraction study:

Prompt Gamma Activation Imaging (PGAI)

↓

Gilding state

Neutron Diffraction

↓

Difference between two meltings: composition and working methods

Neutron Radiography + Neutron Diffraction

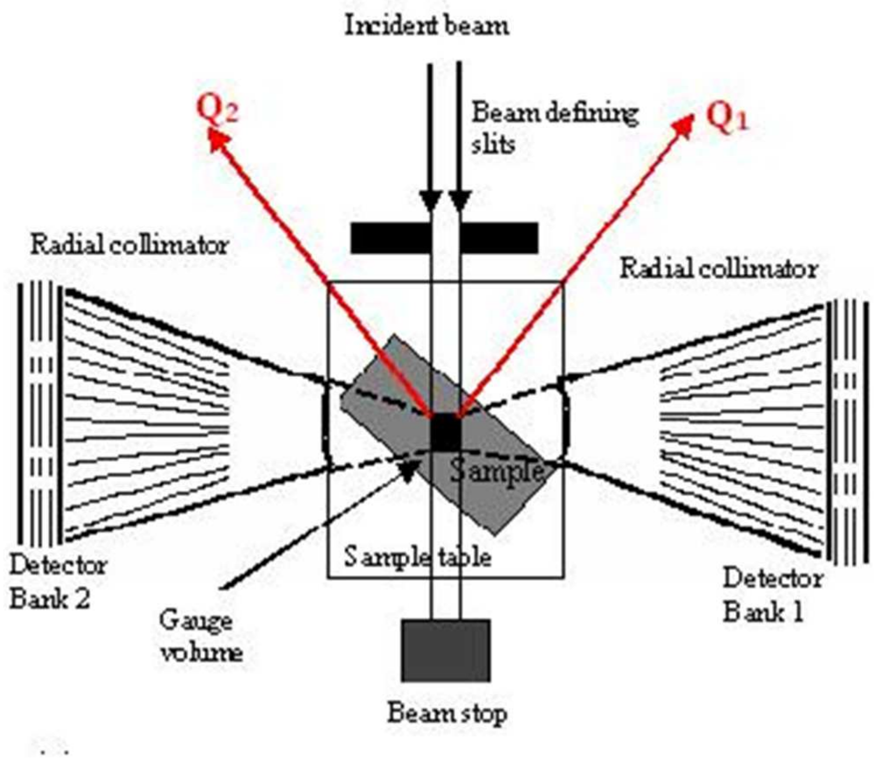
↓

Extension of the secondary fusion

→ **Measurements performed at ISIS - UK (ENGIN-X instrument)**

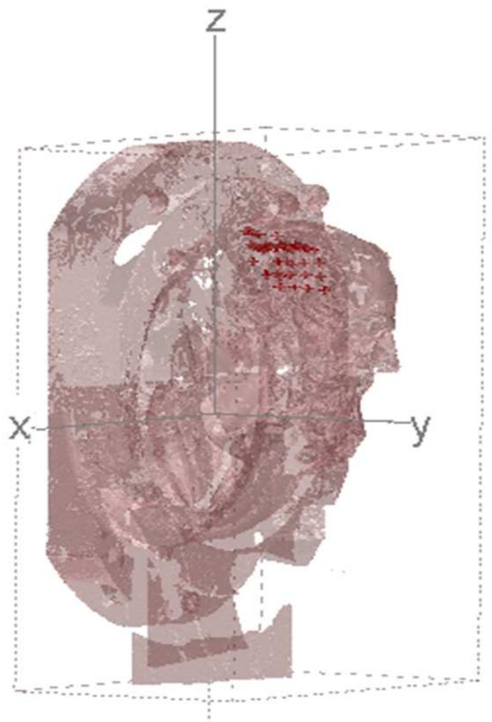
Ghiberti Head Neutron Diffraction study:

Study performed at ENGIN-X instrument: two 90^0 detector banks

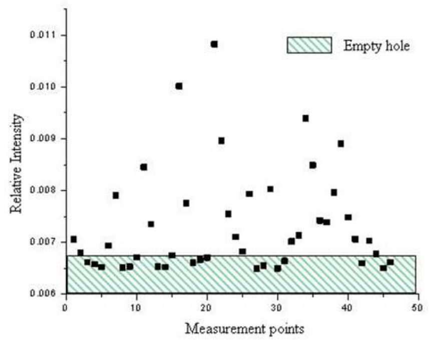


- It could defined a small measurement volume (gauge volume) in the sample of a few millimeters – trough collimation of incident beam and radial collimator in front of detectors).
- A laser scanning system and a dedicated software to identify gauge volume in the sample was used.

Extension of the secondary melting



3D view of the 50 measurement points inside the bronze relief

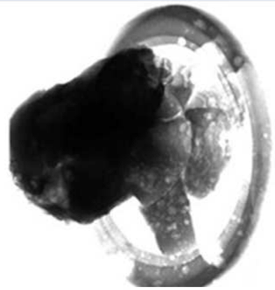


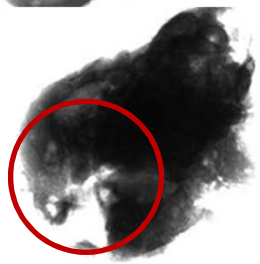
- Diffraction measurements **to identify cavities or inhomogeneous zone** in the relief → ND used to test the absence of bronze α phase peaks

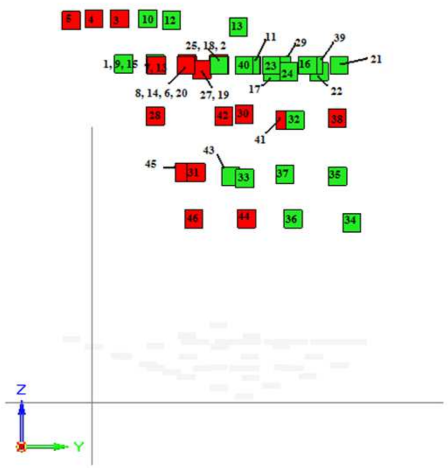
- Region of interest identified through previous neutron radiographies

- A large d-spacing window (0.21-2.7 Å) to enable any potential peaks of clays used during casting

No other diffraction peaks → hollow volume, excluded fusion clays. The hollow volume is located in the area from the base of the neck to the occipital lobe.







3D view of the 50 measurement points inside the bronze relief: red=filled (bronze peak), green=hollow (no bronze peak)

Difference between two meltings: composition and working methods

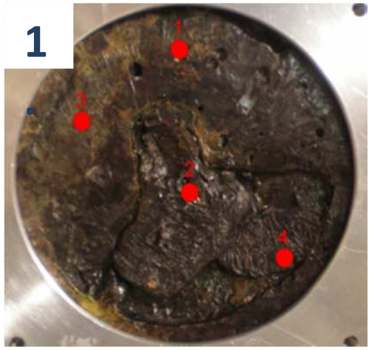
Neutron diffraction → crystal structure

In the present case was used to:

1. **Study the composition of the two melting:** measurements performed in the back area (red points in the figure) → to analyze differences in peak position and shape between first and second melting
2. **Study the residual strain distribution:** vertical and horizontal scans to study the bronze peak-broadening and its strain trends

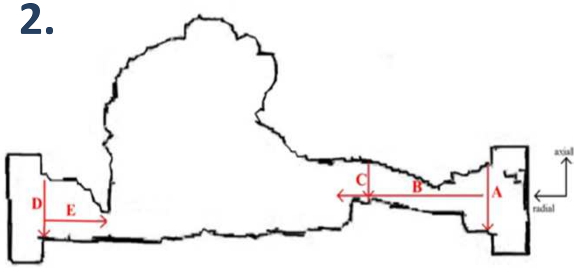
Strain is the response of a system to an applied stress. When a material is loaded with a force, it produces a stress, which then causes a material to deform → Crystal structure deformations

1



Compositional analysis

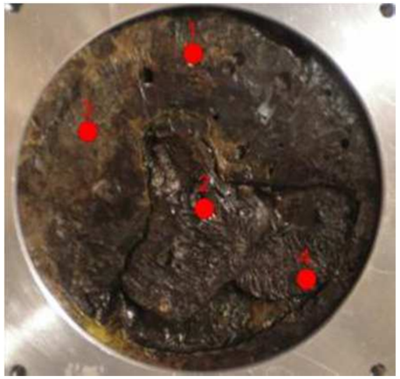
2.

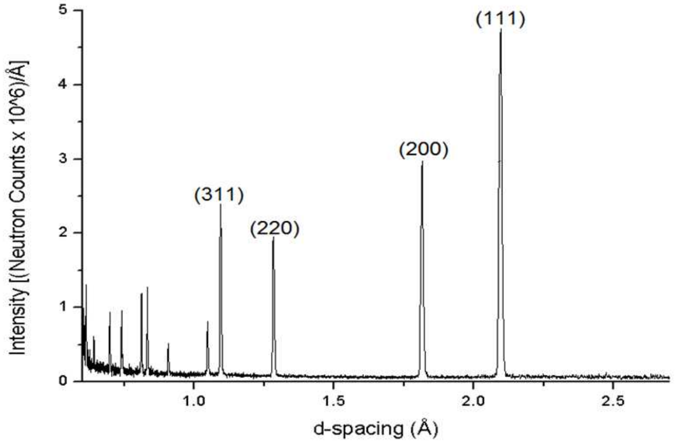


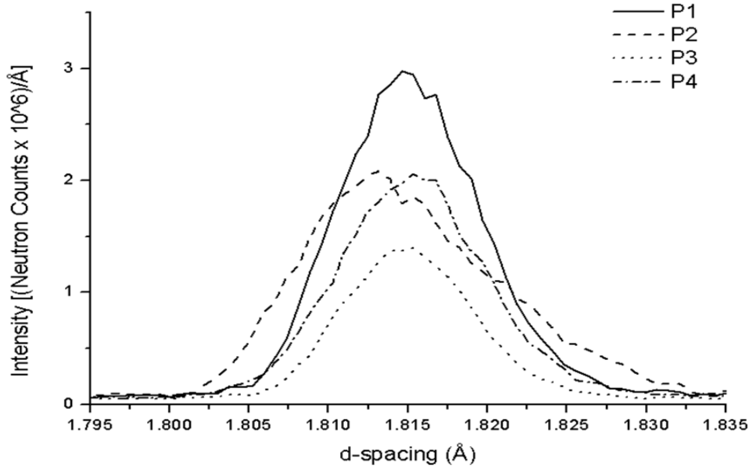
Residual strain analysis

Composition of the two meltings

- ✓ Measurements on the back area of the relief (1mm from the surface).
- ✓ Analyze differences in peak position and shape between first and second melting (P2=remelting; P1, P2, P4=primary melting).





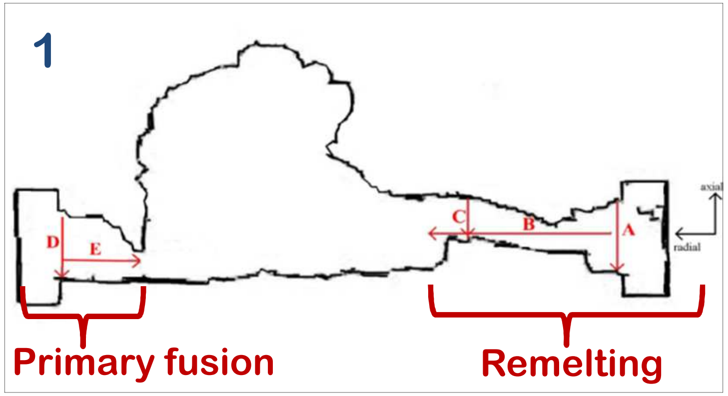


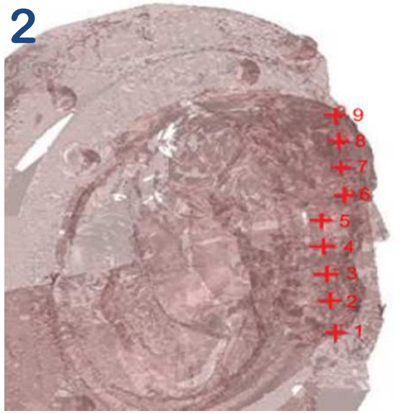
RESULTS:

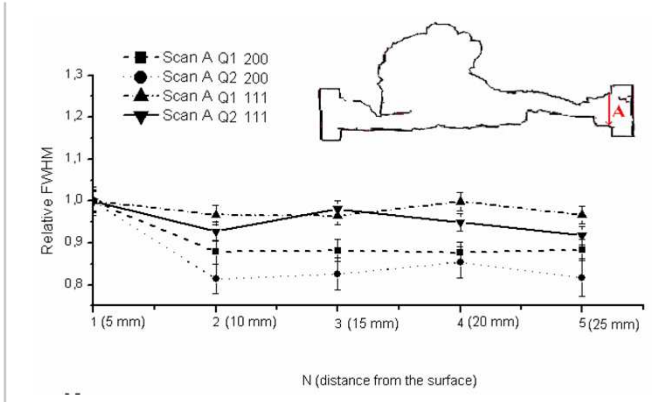
A) **Primary melting** – regular peak (homogenization treatments)

B) **Remelting** – broader and irregular reflection peaks (dendritic segregation typical of as-cast alloy and higher cooling rate – only a filler material without any treatment)

Residual strain distribution:







1. **Strain scans along horizontal and vertical directions to study peak broadening and strain ((d-d$_0$)/d$_0$) trends**
2. **Strain scans along face and beard (aim: comparing strain trends - this area is part of the first fusion or re-melting?)**

NO REFERENCE sample→ RELATIVE measurements (d$_0$ = arbitrary)

RESULTS:

- **Same strain trends of 1ª and 2ª fusion: horizontal direction → crystal planes compression, vertical direction → widening of crystal planes**
- **Remelting scans (beard/face and remelting) have larger strain variation → related to the absence of some homogenization process → beard and face areas are part of the remelting and superface was treated with hand tools to realize the facial features.**

Ghiberti Head conclusions:

Conclusions:

1) Second fusion and empty volume inside:
Definition of an hollow volume and detection of the extension of the secondary melting
2) Treatments:
First fusion → thermal treatments
Second fusion→ without treatments

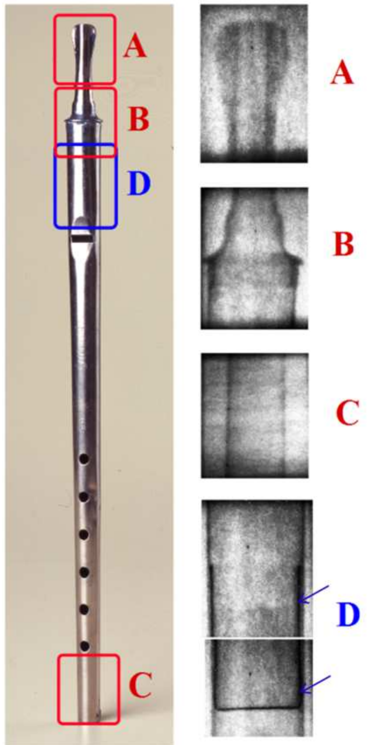
Related publications:

- G. Festa, C. Andreani, M. P. De Pascale, R. Senesi, G. Vitali, S. Porcinai, A. M. Giusti, R. Schulze, L. Canella, P. Kudejova, M. Mühlbauer, B. Schillinger and the Ancient Charm Collaboration *'A non-destructive stratigraphic and radiographic neutron study of Lorenzo Ghiberti's reliefs from Paradise and North doors of Florence Baptistery'*, Journal of Applied Physics, 106, N.4 (2009)
- G. Festa, R. Senesi, M. Alessandroni, C. Andreani, G. Vitali, S. Porcinai, A. M. Giusti, T. Materna, A. Paradowska, *'Non destructive neutron diffraction measurements of cavities, inhomogeneities and residual strain in bronzes of Ghiberti's relief from the Gates of Paradise'*, Journal of Applied Physics, 109, n.6 (2011)

Neutrons and Music:

Simultaneous and integrated neutron-based techniques for material analysis of a metallic ancient flute

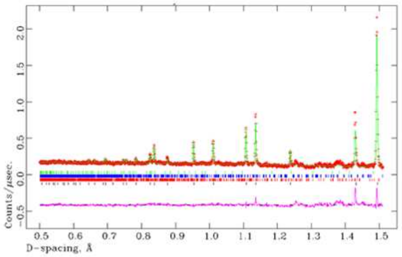
A metallic 19th century flute instrument coming from '*Accademia Nazionale di Santa Cecilia*' was studied by: Neutron Diffraction, Neutron Radiative Capture Analysis and Neutron Radiography.



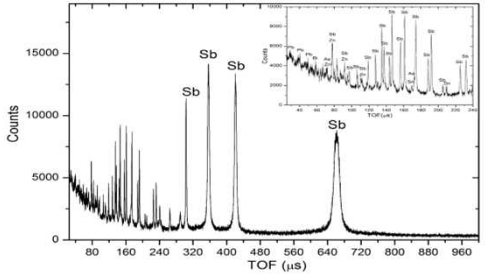
The aim of this study was to show the potential application of multiple and integrated neutron-based techniques approach for musical instruments and derive information of cultural heritage interest .

Neutron-based techniques for material analysis of a metallic ancient flute:

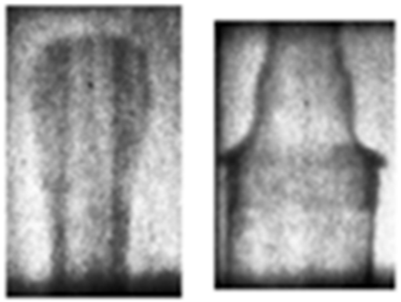
Neutron Diffraction:
phase analysis



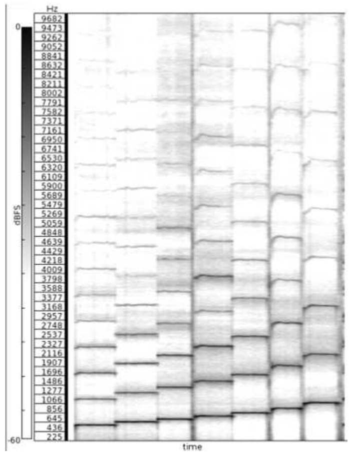
Neutron Resonance Capture Analysis:
elemental characterization



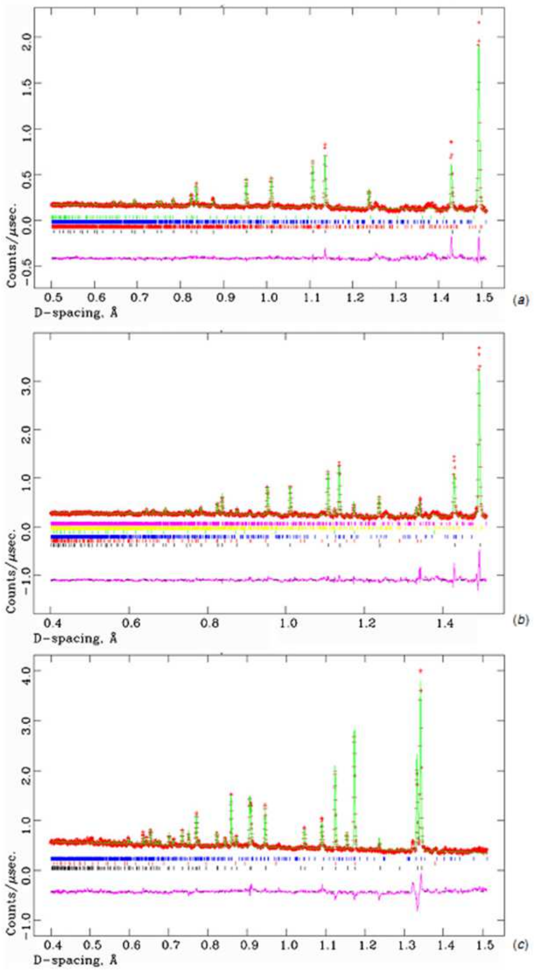
Sound Analysis:
quality of the emitted sound



Neutron Radiography:
internal morphological structure

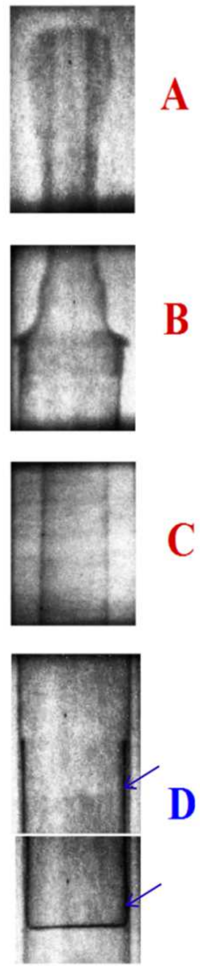


Neutrons and Music:



Diffraction spectra of the flute. Best fit of data is also shown, with the peak position of the different components, and residue is reported in violet.

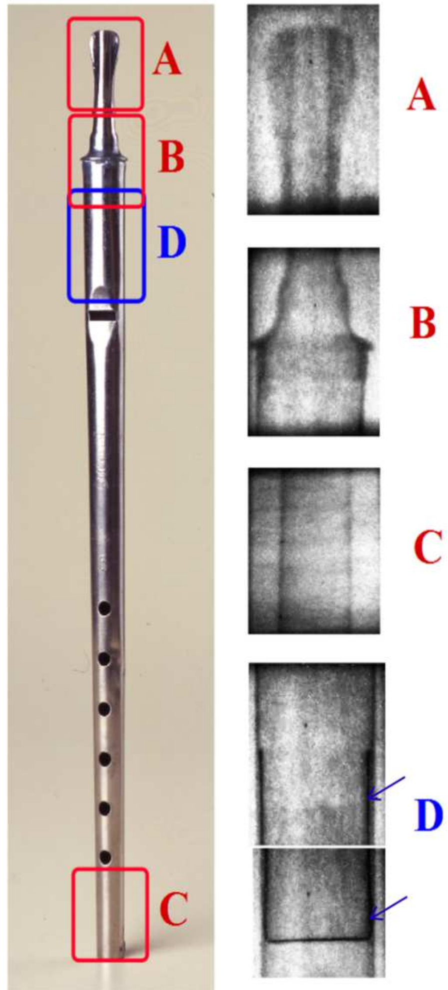
- **Mouthpiece**: peaks labeled as lead = black, tin (II) sulphate = red, lead tetroxide = blue, zincite = green;
- **welded region**: peaks labelled as lead = black, zinc = red, herzenbergite = blue, palladium = green, tin (II) sulphate = yellow, lead tetroxide = red;
- **body region**: peaks labelled as zinc = black, palladium = red and herzenbergite = blue.



Neutrons and Music:

Results and conclusions:

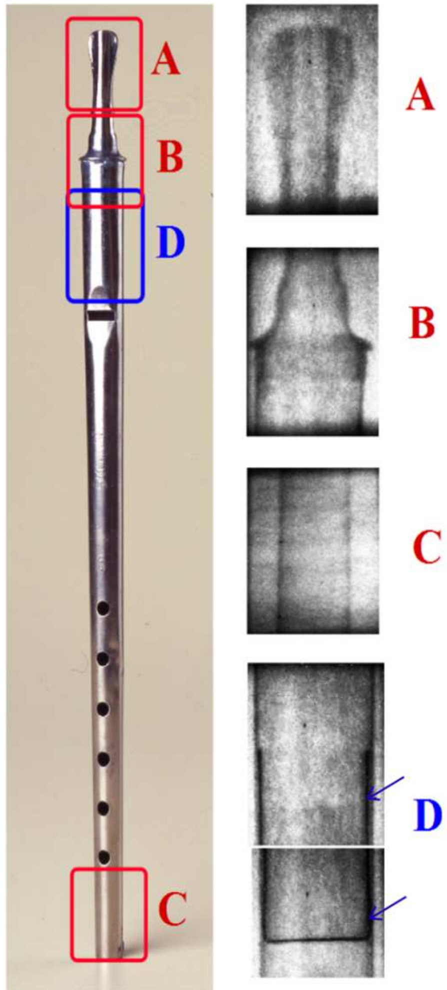
- Integrated and simultaneous neutron analyses performed on a small metallic duct flute from *Accademia Nazionale di Santa Cecilia* Musical Instruments Collection, providing unique **information on its composition and manufacture**, in a completely non-destructive manner.
- A **non homogeneous composition** of the flute.
- **Elemental and phase compositions**: the body of the instrument is mainly composed of zinc covered by palladium (generally used for larger organ pipes), mouthpiece mainly composed by lead (material typically used for organ pipes of small dimensions).



Neutrons and Music:

Results and conclusions:

- Additional advantage: **simultaneity of the measurements** resulted in a very low residual activation of the sample.
- **Sound analysis** revealed difficulty on this instrument of playing notes from the second register through overblowing, rough positioning of the holes
- It can be likely concluded that the flute was intended for popular and amateur use.



Related publication:

- G. Festa, A. Pietropaolo, F. Grazzi, L.F. Sutton, A .Scherillo, L. Bognetti, A. Bini, E. Barzagli, E. Schooneveld and C. Andreani
'Simultaneous and integrated neutron-based techniques for material analysis of a metallic ancient flute', Meas. Sci. Technol. 24 (2013) 095601 (9pp).

Thanks for your attention!