Design and use of portable X-ray fluorescence devices for the analysis of heritage materials

M. Chiti, D. Chiti, F. Chiarelli, R. Donghia, A. Esposito, A. Gorghinian | LNF - INFN

M. Ferretti | CNR - ISPC

High Precision X-ray Measurements 2023 conference
Laboratori Nazionali di Frascati dell'INFN
June 23th, 2023

INFN Istituto Nazionale di Fisica Nucleare Laboratori Nazionali di Frascati

Consiglio Nazionale delle Ricerche

ISPC ISTITUTO di SCIENZE del PATRIMONIO CULTURALE

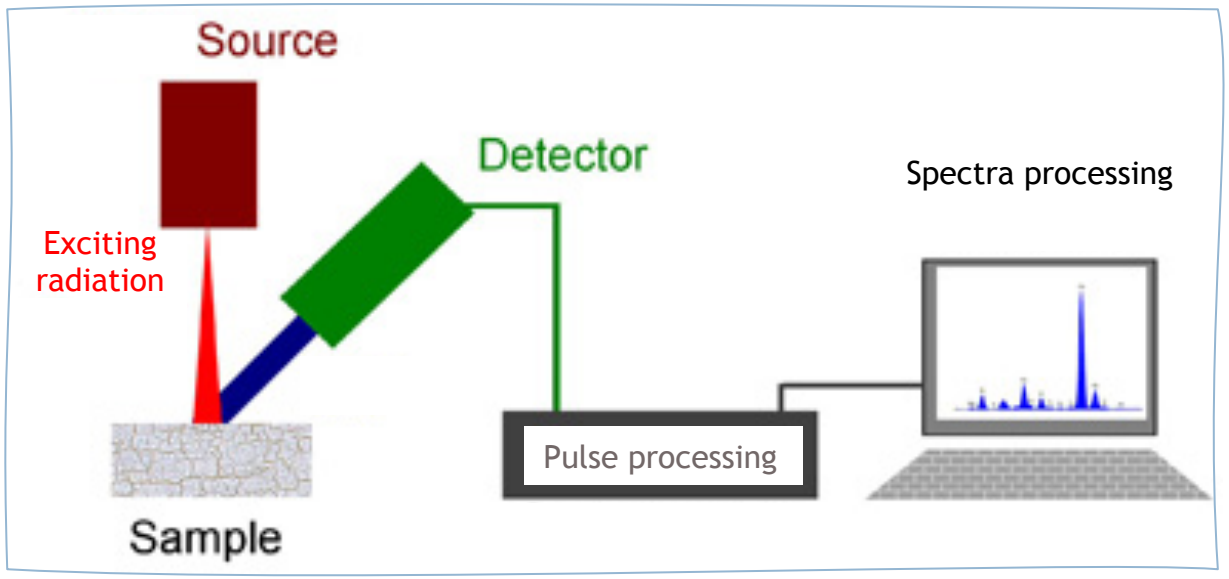
Outline

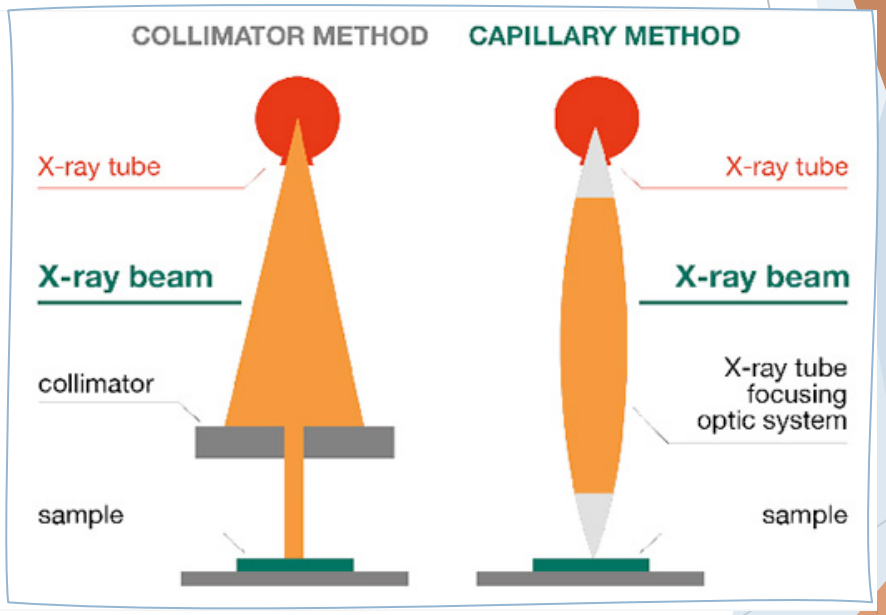
- XRF for cultural heritage
- Experimental setup
  - With and without beam focusing
  - Application-tailored spectrometers
- Analytical performances
- Case studies
  - Iron Age glass beads
  - Pre-historical copper-based artefacts

XRF for cultural heritage

Heritage artefacts	XRF
Elemental composition can be significant of provenance, fabrication technology, autenticity	Performs multi-elemental analysis
Should not be damaged	Non-invasive
May be too big or too fragile to be moved	Portable

XRF setup – beam focusing





Authors' design devices (1)

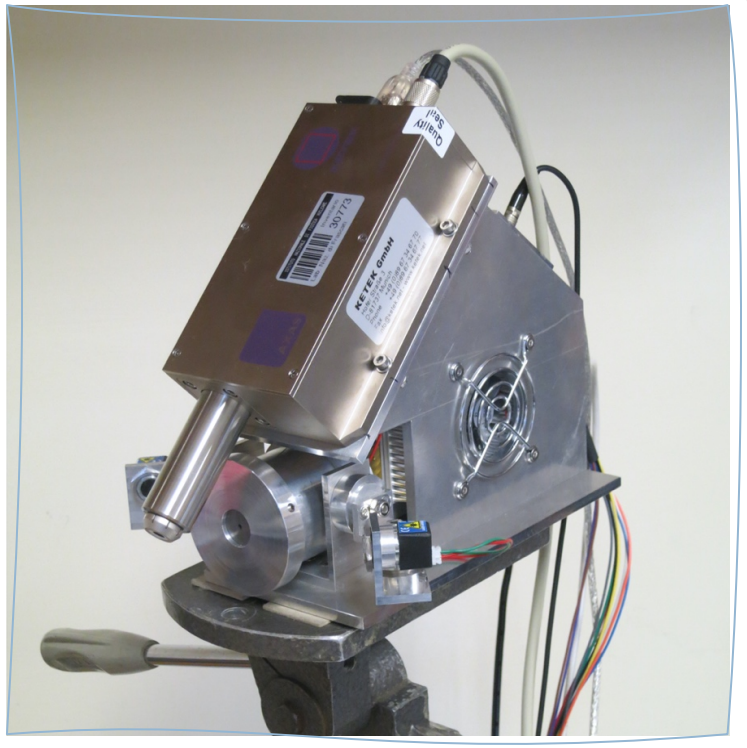
FRANKIE

- Front-window X-ray tube - W anode
- **HV = 50 kV**; I = 200 μA
- SDD - area = 20 mm^2; thickness = 450 μm
- **Polycapillary lens** - focal spot of 300 μm

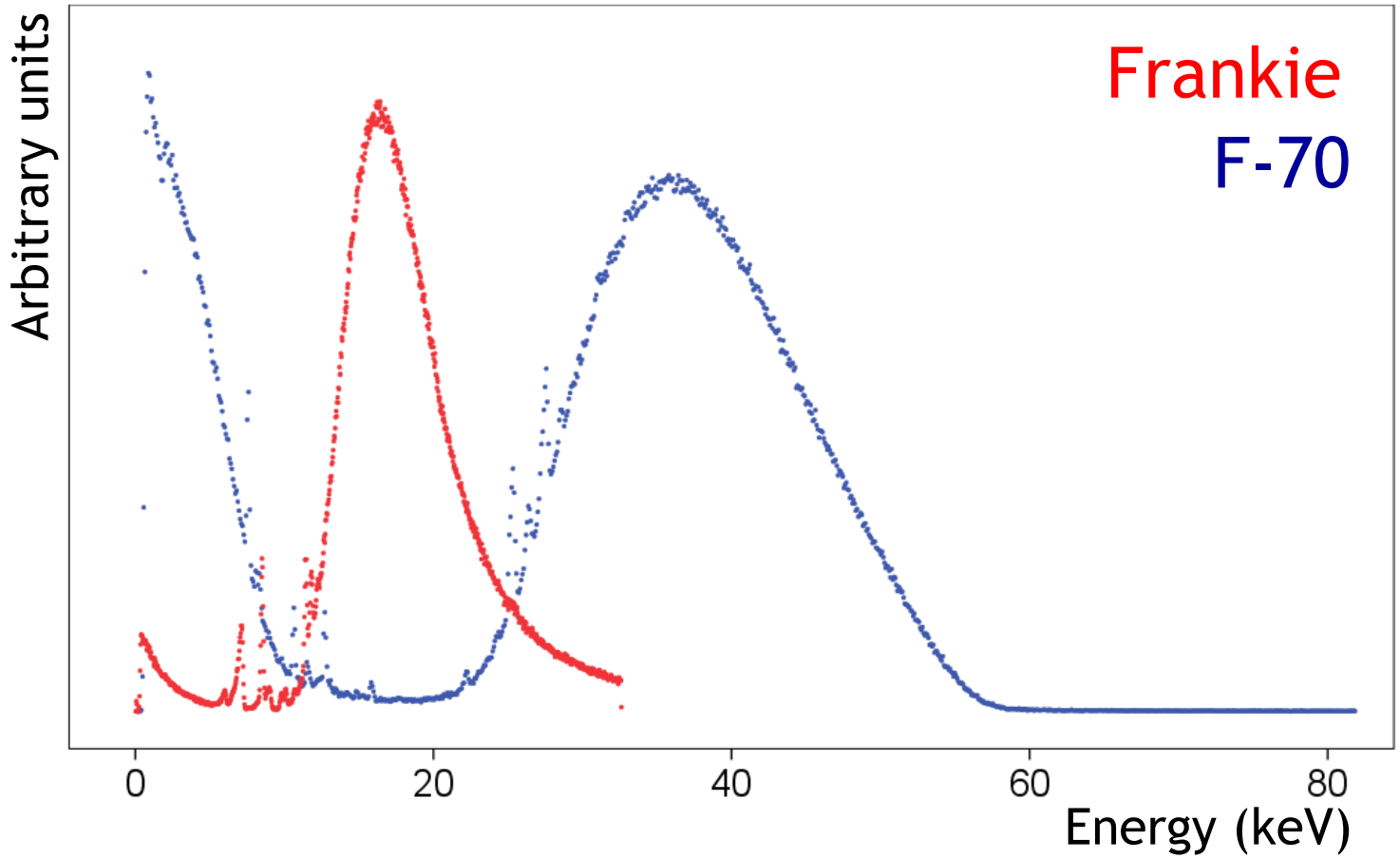
Authors' design devices (2)

F-70

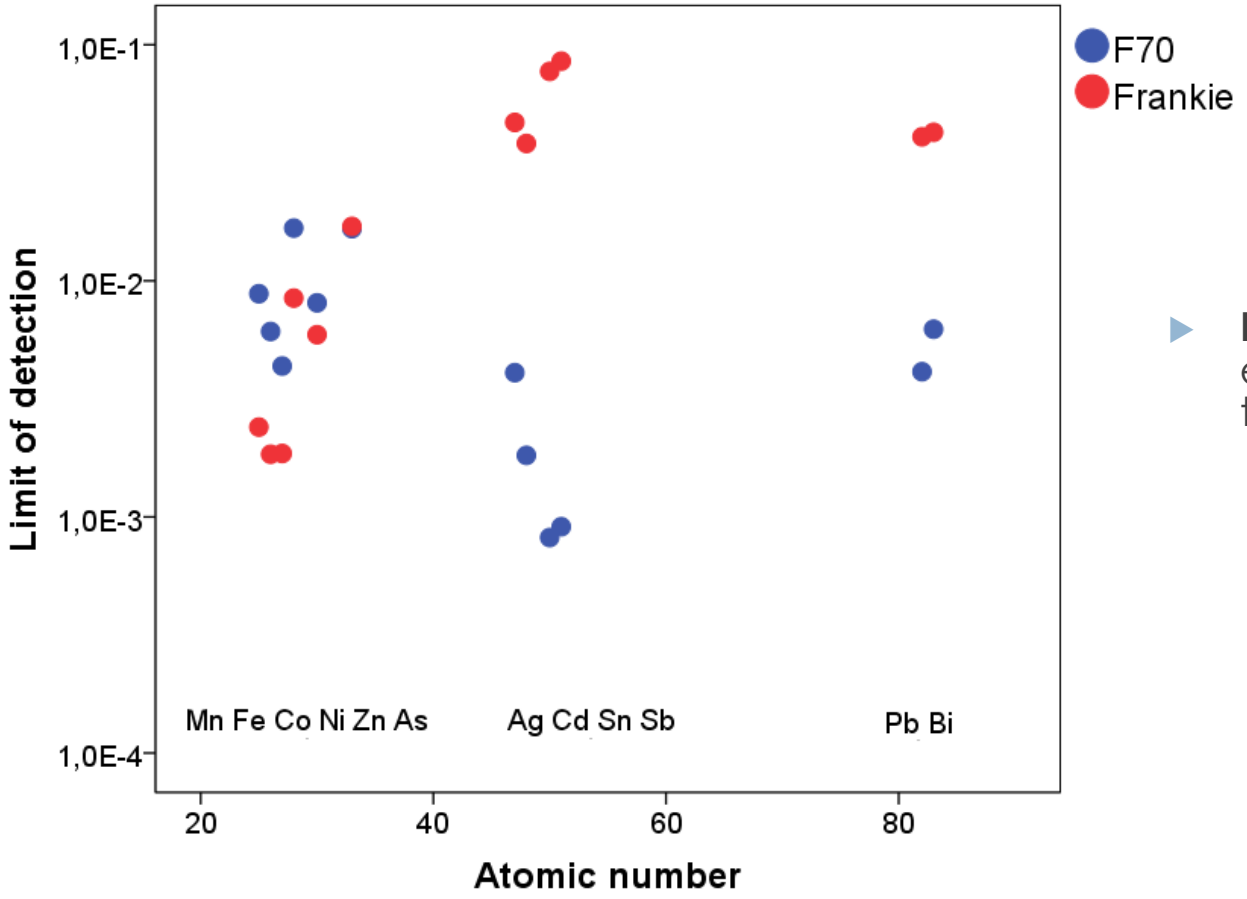
- Front-window X-ray tube W anode;
  - **HV = 70 kV**; I = 170 μA
- SDD - area = 20 mm^2; thickness = 450 μm
  - **No beam focusing**



Energy distribution of the exciting radiation



Limits of detection in copper-based alloys



- **LOD:** minimum concentration of an element necessary for its fluorescent lines to be distinguished from bg (C.L. 95%)

$$LOD = \frac{2.33 \cdot C_{std} \cdot \sqrt{B}}{P}$$

B: bg area
P: peak area
C_{std}: element concentration in the reference material

The devices are designed for specific applications

Frankie: analysis of small details, for example enamelled plates

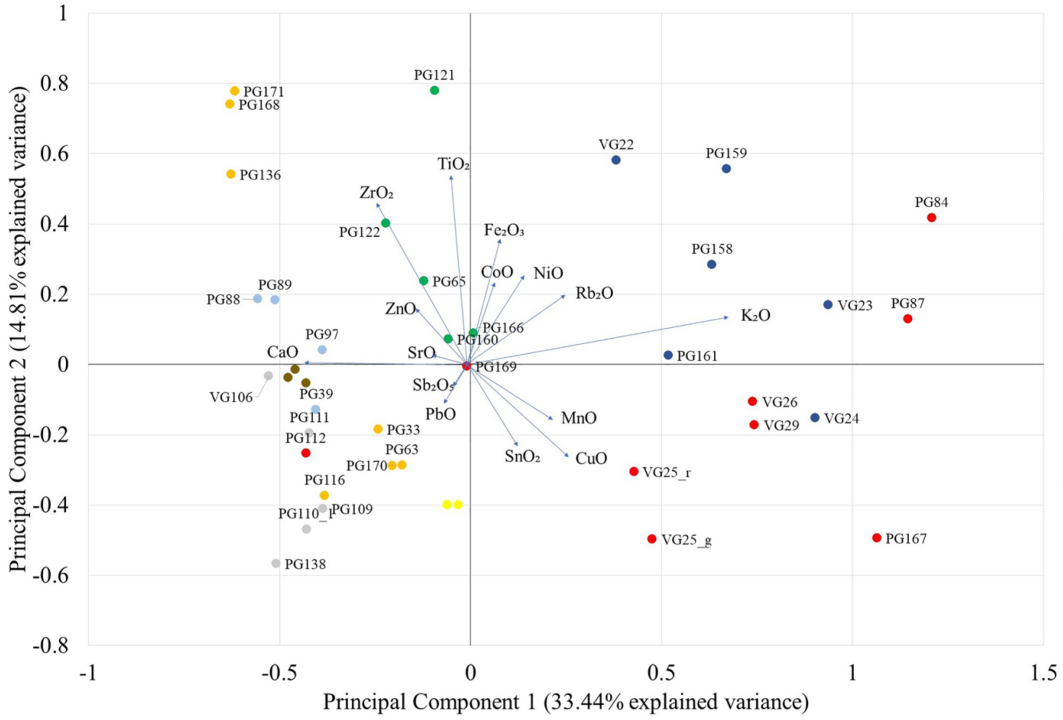
F-70: analysis of minor and trace elements, for example in copper-based artefacts

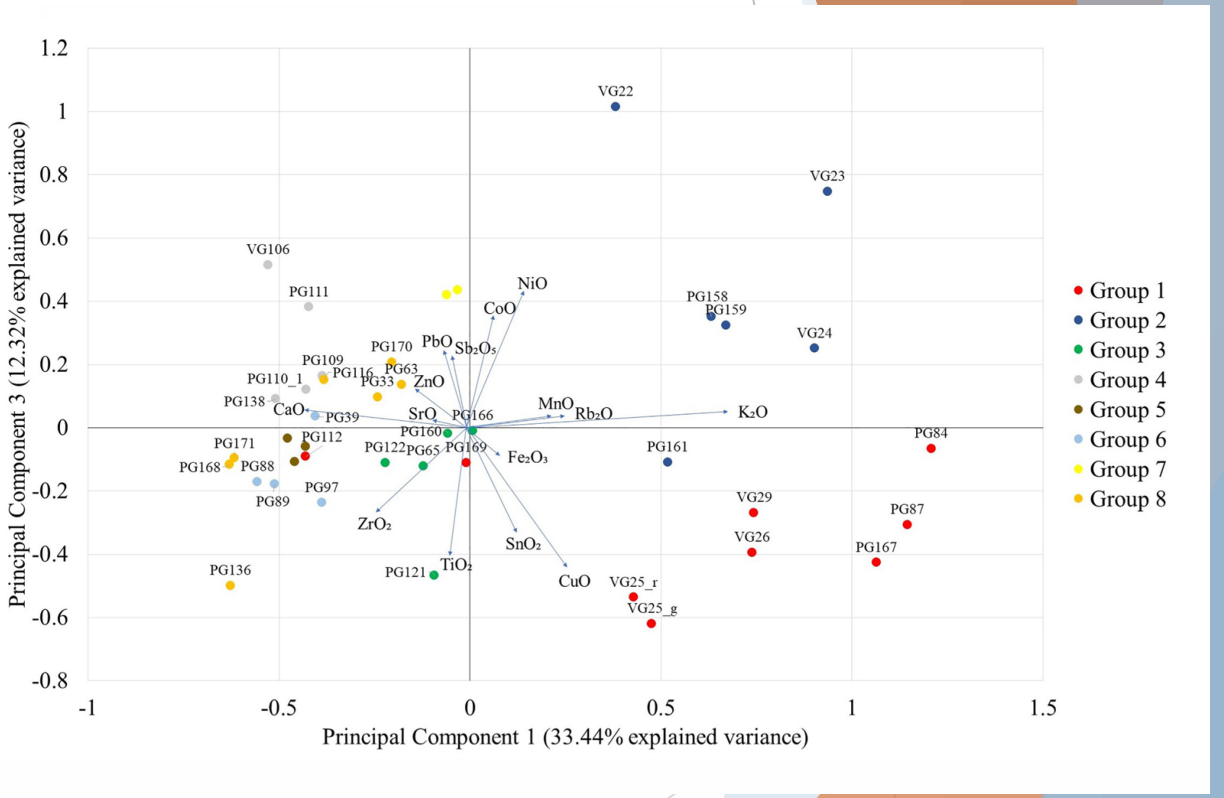
Iron Age glass beads

- Artefacts of Villa Giulia museum
- XRF w Frankie
- Spectra analysis w PyMCA→ element concentration

O. Yatsuk, L. Koch , A. Gorghinian, G. Fiocco, P. Davit, L.C. Giannossa, A. Mangone, S. Francone, A. Serges, A. Re, A. Lo Giudice, M. Ferretti, M. Malagodi, C. Iaia and Monica Gulmini, *An archaeometric contribution to the interpretation of blue-green glass beads from Iron age Central Italy*, Heritage Science (2023) 11:113. https://doi.org/10.1186/s40494-023-00952-1

Iron Age glass beads: fabrication contexts





Iron Age glass beads: colourants and opacifiers

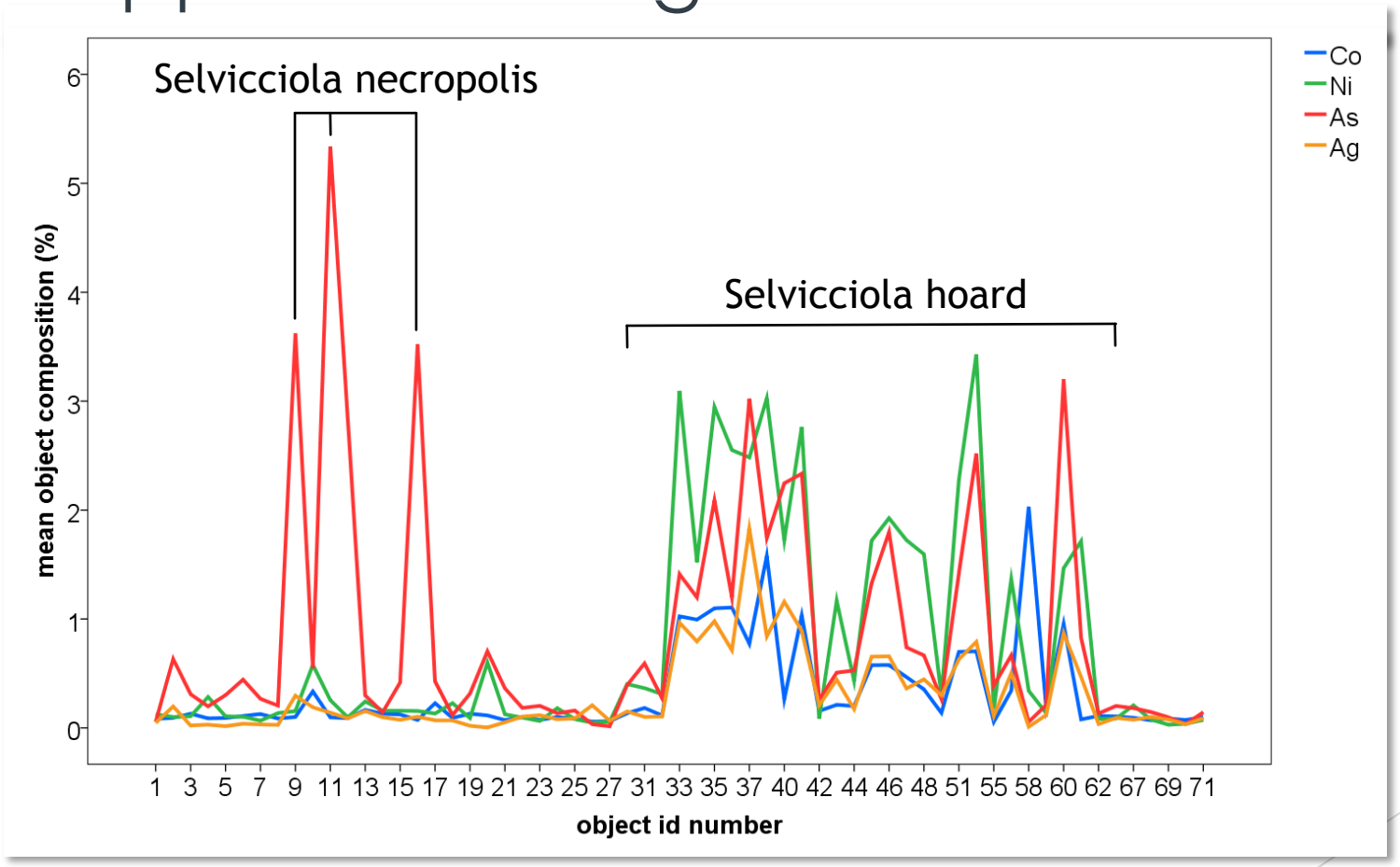
	Samples	Chromophore(s)/Opacifier	Technique for confirmation
RED	VG24, 25, 26, 29	Cu^{0}	FORS, p-XRF
DARK-GREEN	VG25	Cu^{2+}, Fe^{3+}	FORS, p-XRF, LA-ICP-MS
BLUE	VG28	Cu^{2+}, Fe^{3+}	FORS, p-XRF, LA-ICP-MS
Co–Cu BLUE	VG106	Co^{2+}, Cu^{2+}, Fe^{3+}, Fe^{2+}	FORS, p-XRF, LA-ICP-MS
DARK	VG22, 2359,	Co^{2+}, Fe^{2+}, Fe^{3+}	FORS, p-XRF, LA-ICP-MS
WHITE 1	VG 106	$CaSb_2O_6$	p-XRF, SEM–EDS, μ-Raman, LA-ICP-MS
WHITE 2	VG25, 26, 29	Fine bubbles	OM, p-XRF, μ-Raman, LA-ICP-MS

Pre-historical copper-based artefacts

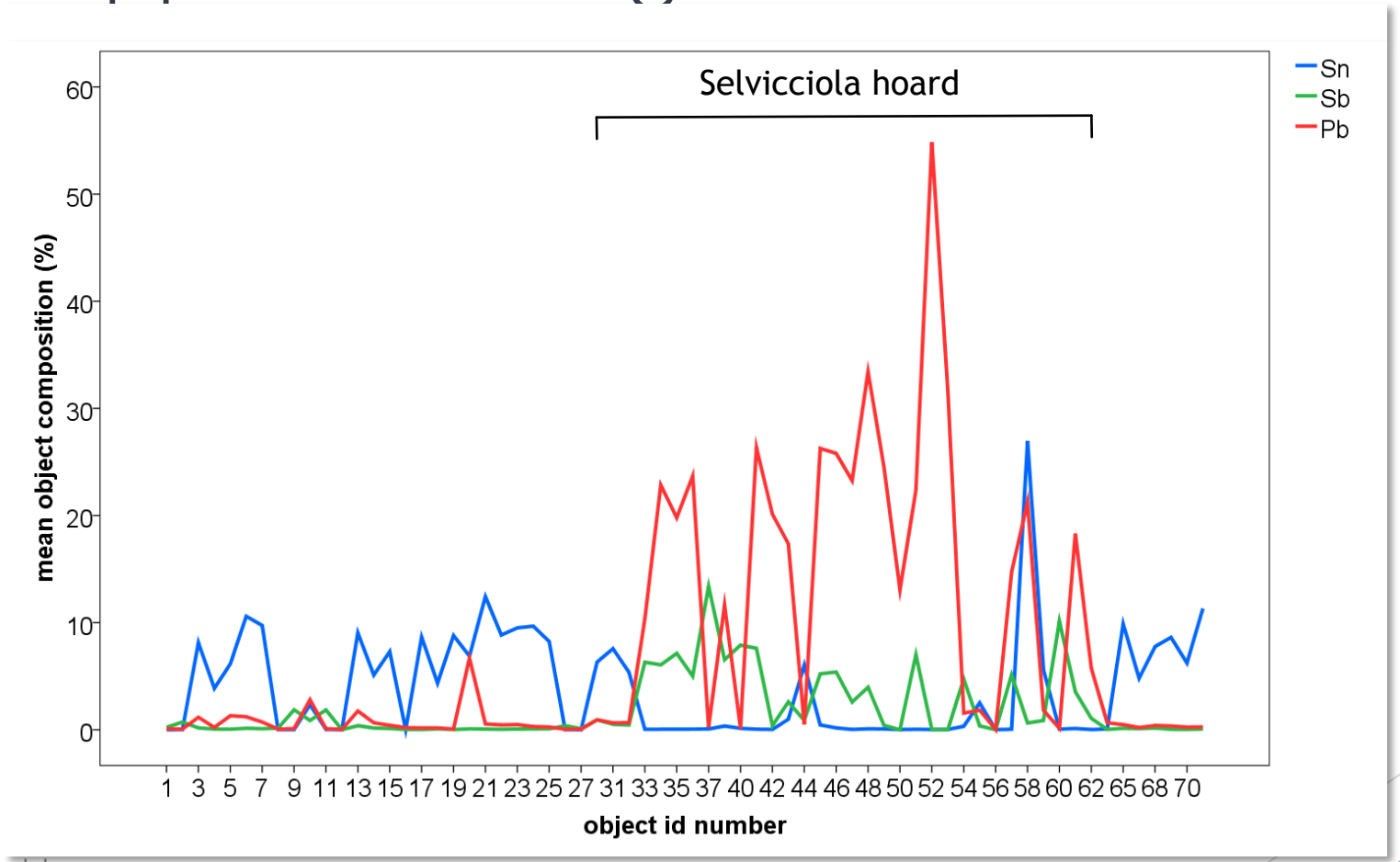
- pre – and proto-historic metallic findings from areas in the provinces of Rome and Viterbo (Central Tyrrhenian Italy).
- XRF w F-70
- element concentration analysis w PyMCA

A. Esposito, P. Petitti, M. Ferretti, A. Gorghinian, F. Rossi, *The production of metal artefacts in Southern Etruria (Central Italy): case studies from Copper to Iron Age*, STAR: Science & Technology of Archaeological Research (2019). DOI:10.1080/20548923.2019.1660496.

Pre-historical copper-based artefacts: changes in minor elements composition from Copper to Iron Age



Pre-historical copper-based artefacts: changes in main elements composition from Copper to Iron Age



Conclusions

- Polycapillary optics are essential to obtain intense primary beam with focal spot sizes of tens to hundreds of μm
  - but they are detrimental for the limits of detection of elements with absorption edges beyond 20 keV

- For instruments not using polycapillary optics, the parameter that mostly affects the limits of detection is the tube voltage, especially for elements with Z~50 (i.e. Ag, Cd, Sn, Sb)

Thanks for listening!

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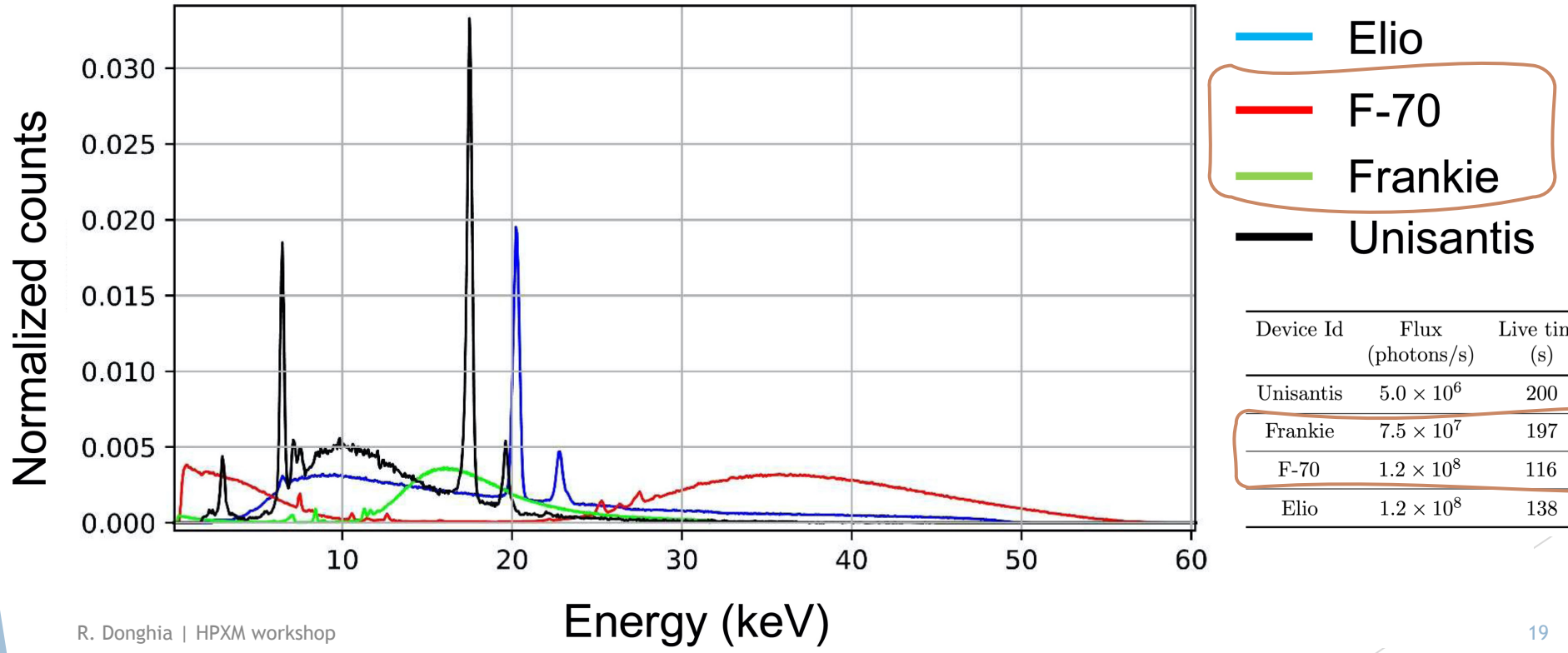
Backup slides

Comparison

- Spectra acquired by using a low-Z and highly scattering material as target
- Total areas normalized to 1
- Compton shift - intrinsic detectors efficiency - fluorescent lines from surrounding materials



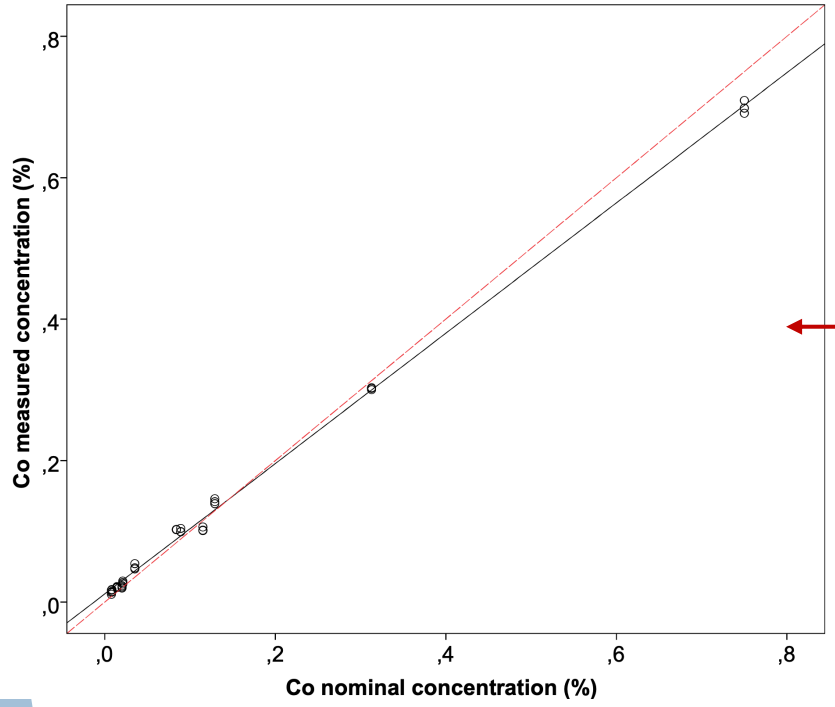
Device Id	Flux (photons/s)	Live time (s)	Integrated flux (photons)
Unisantis	5.0×10^6	200	1.0×10^9
Frankie	7.5×10^7	197	1.5×10^{10}
F-70	1.2×10^8	116	1.4×10^{10}
Elio	1.2×10^8	138	1.7×10^{10}

Analysis and Figure of merit

- **LOD:** minimum concentration of an element necessary for its fluorescent lines to be distinguished from bg (C.L. 95%)

$$LOD = \frac{2.33 \cdot C_{std} \cdot \sqrt{B}}{P}$$

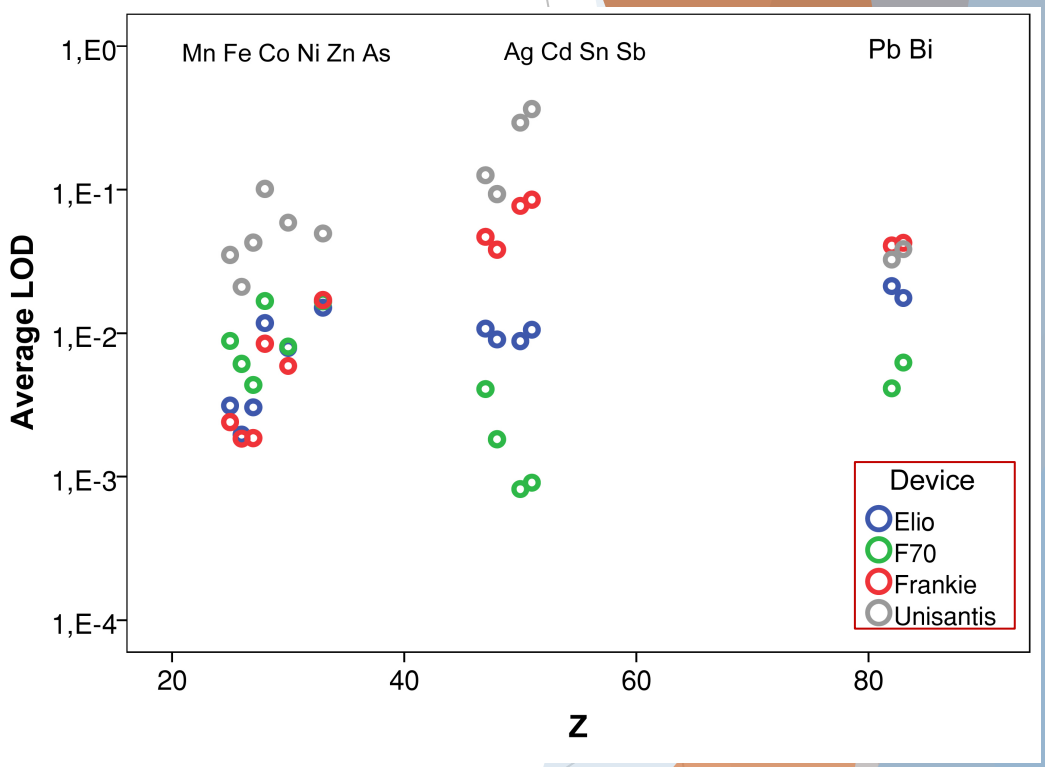
B: bg area
P:peak area
C_{std}: element concentration in the reference material



- **LOQ**: represents the minimum measurable concentration
- Standard Error of Regression **(SER):** standard error of the least square regression of the measured (PyMCA) versus the nominal concentration, defined as the root mean square distance of the data points from the line → deviation estimate from the regression line.
- Systematic errors are supposed to be removed by calibration, the SER accounts for the remaining random errors.

LOD results

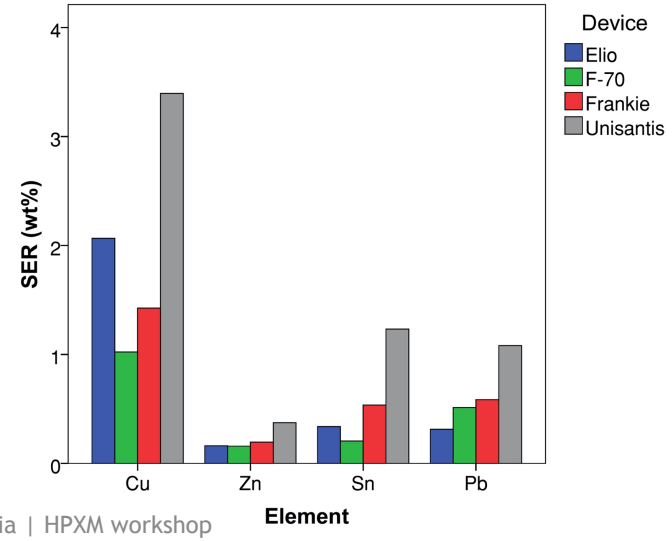
- **1' group** → similar performances (0.002 wt% ÷0.02 wt%)
- **2' group** → affected by different excitation conditions. F-70 is the best performing device for copper alloys studies, with 0.002 wt%, followed by Frankie with 0.06 wt%
- **3' group** → F-70 has a larger part of the primary spectrum above the absorption edges, compared to Frankie. Performances not so different among devices (0.006 wt% and 0.04 wt%, respectively)

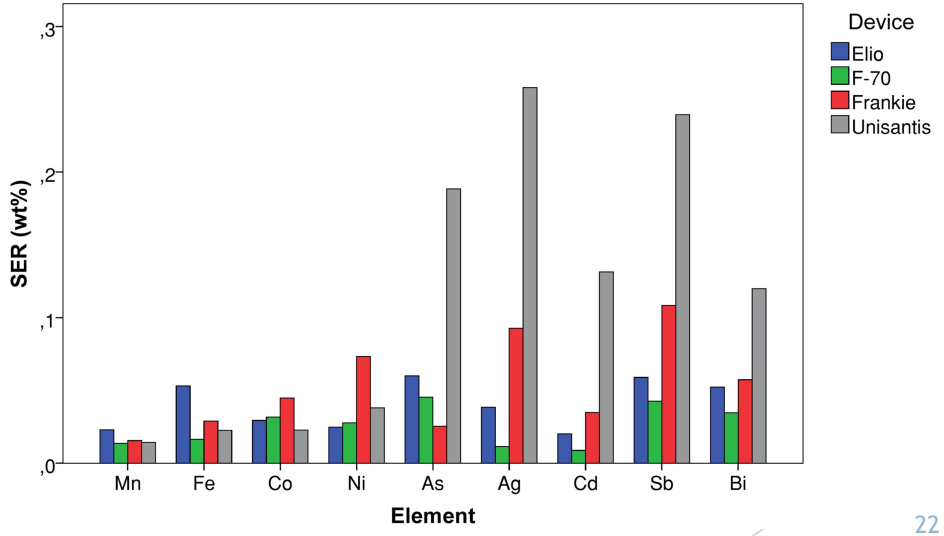


SER – results (1)

- The best SER does not necessarily correspond to the best LOD

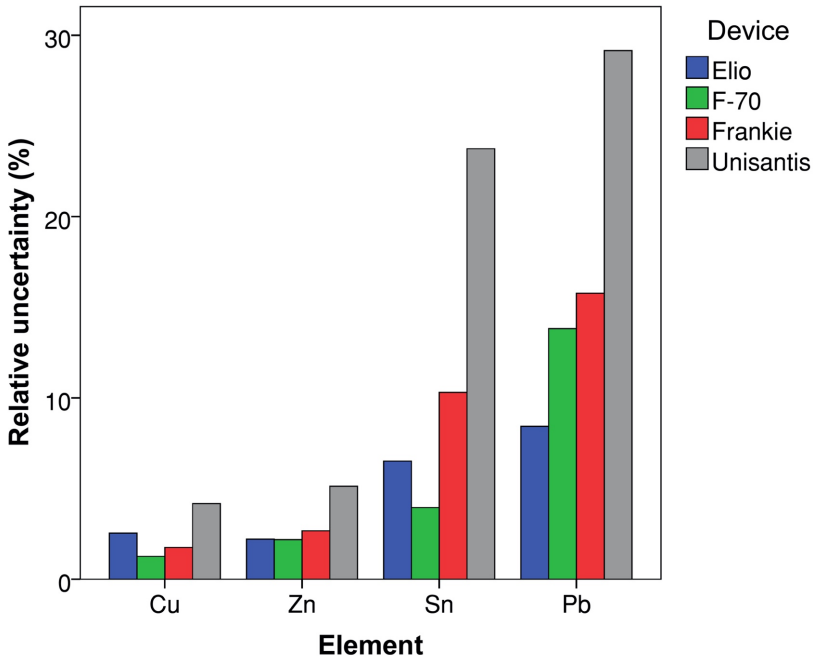
- Both F-70 and Frankie are characterized by SER values in the range of
  - a few wt% for Cu (the most abundant element in all samples)
  - tenths of wt% for the other major elements (Zn, Sn and Pb)
  - hundreds of ppm for the minor elements

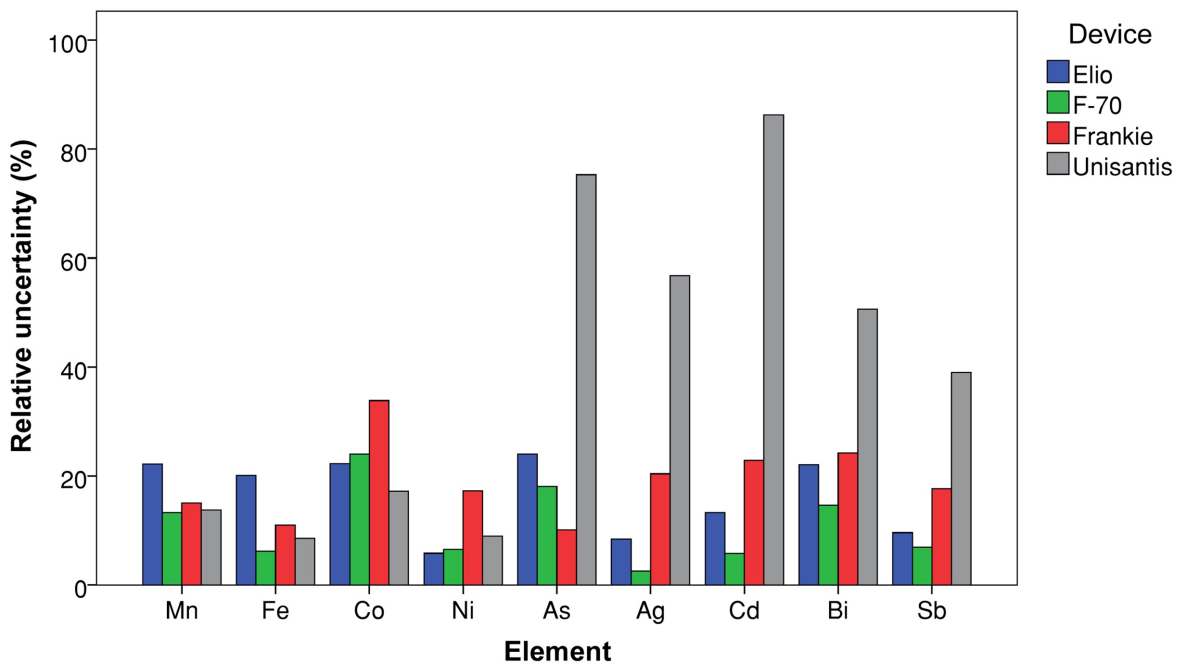




SER – results (2)

- Relative uncertainties: calculated dividing the SER by the average nominal concentration of the element
- Results are below 15% for all major elements, with Pb reaching the highest values, and below 30% for minor elements, with the exception of Frankie





Frankie

The polycapillary lens allows to perform study on micro spot

→ detecting element trace on each color

Enamel plates of 4th century

F-70

- Intense photon beam → fast measurements or higher statistyc
- The good performance shown demonstrates the use of X-ray tubes working **above 60 kV may improve the excitation conditions to analyze copper alloys**
- No beam focusing do not cut the spectra