Portable XRF spectometer use for archaeometrical studies in Romania – a review

Bogdan Constantinescu

National Institute for Nuclear Physics and Engineering, Bucharest, Romania

Due to its mobility, portable X-Ray Fluorescence (pXRF) spectrometer is probably the most adequate elemental analyzer for archaeologists. pXRF analysis can be performed not only directly in museums or collections but even in archaeological sites, immediately artifacts are discovered. We report on some spectacular cases related to illegal excavations based on metal detectors in the area of Sarmizegetusa, the ancient Dacian capital, situated in an isolated mountain region (Orăştie) in the heart of Transylvania. The analyzed artifacts – gold jewelry as one kilo each spiraled armbands, silver adornments as torques and brooches, gold and silver ancient coins as “Koson” and pseudo-Lysimachus staters - were recuperated by Romanian authorities from treasure hunters. We also present pXRF applications on wall paintings and icons in two churches.

Several hoards containing at least twenty four gold spiral bracelets and few thousands of gold coins (staters) of pseudo-Lysimachus and Koson types (Koson with and without monogram) have been unearthed in the time frame between 1999 and 2001, by organized gangs of illegal treasure hunters, in five different spots in the area of Sarmizegetusa Regia, in the Orăştie Mountains, Romania.

Sarmizegetusa Regia - The Sacred Zone

B. Constantinescu, E. Oberlander-Tarnoveanu, R. Bugoi, V. Cojocaru, M. Radtke, *The Sarmizegetusa Bracelets*, Antiquity Journal (London) 84 Issue 326 (2010)1028-1042.

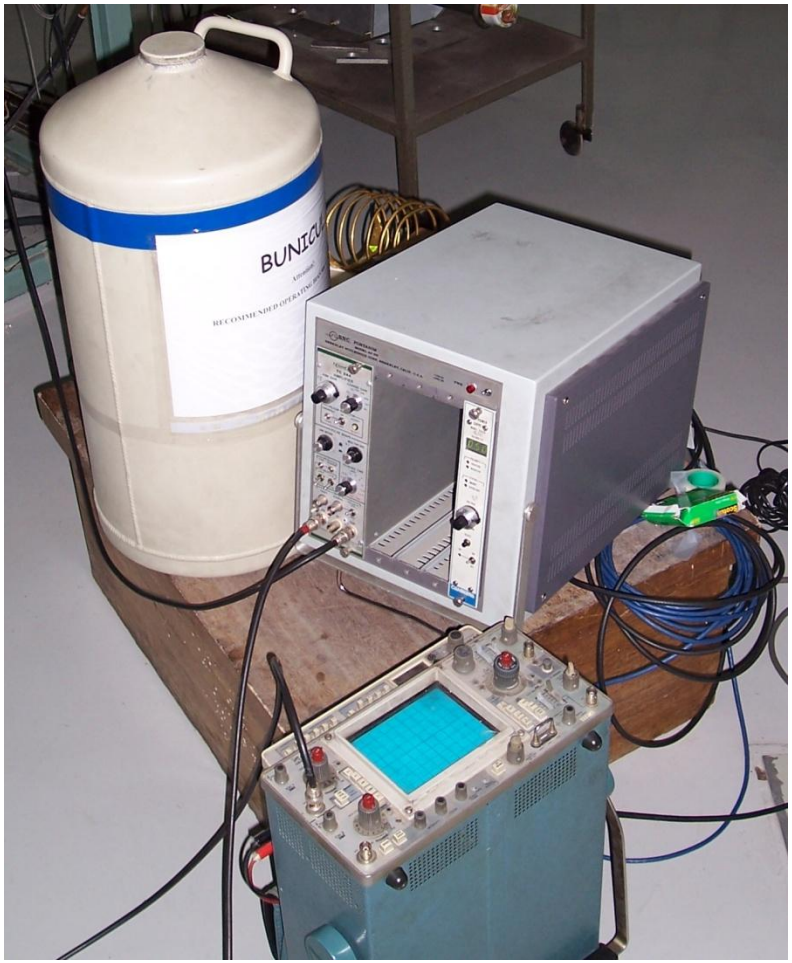
Dacian Koson a) with and b) without monogram

In the compositional studies of archaeological gold artifacts, besides the ratios between the three main components of gold alloys (Au-Ag-Cu) which can be used in their authentication, trace elements might bring significant clues. Trace-elements which can be found in native gold are the Platinum Group Elements (PGE) - Pt, Ir, Os, Ru, Rh, Pd, but also Sn, Sb, Te, Hg, Ti, Zr, As, Bi, Fe.

From Antiquity to the Middle Ages, the most important gold source consisted of placer deposits. Alluvial gold is derived from weathered rocks containing vein gold deposits. The overall silver and copper content of the alluvial gold is somewhat lower than the one of the initial vein gold from which it had originated.

X-Ray Fluorescence (XRF) analysis

X-Ray Fluorescence set-up



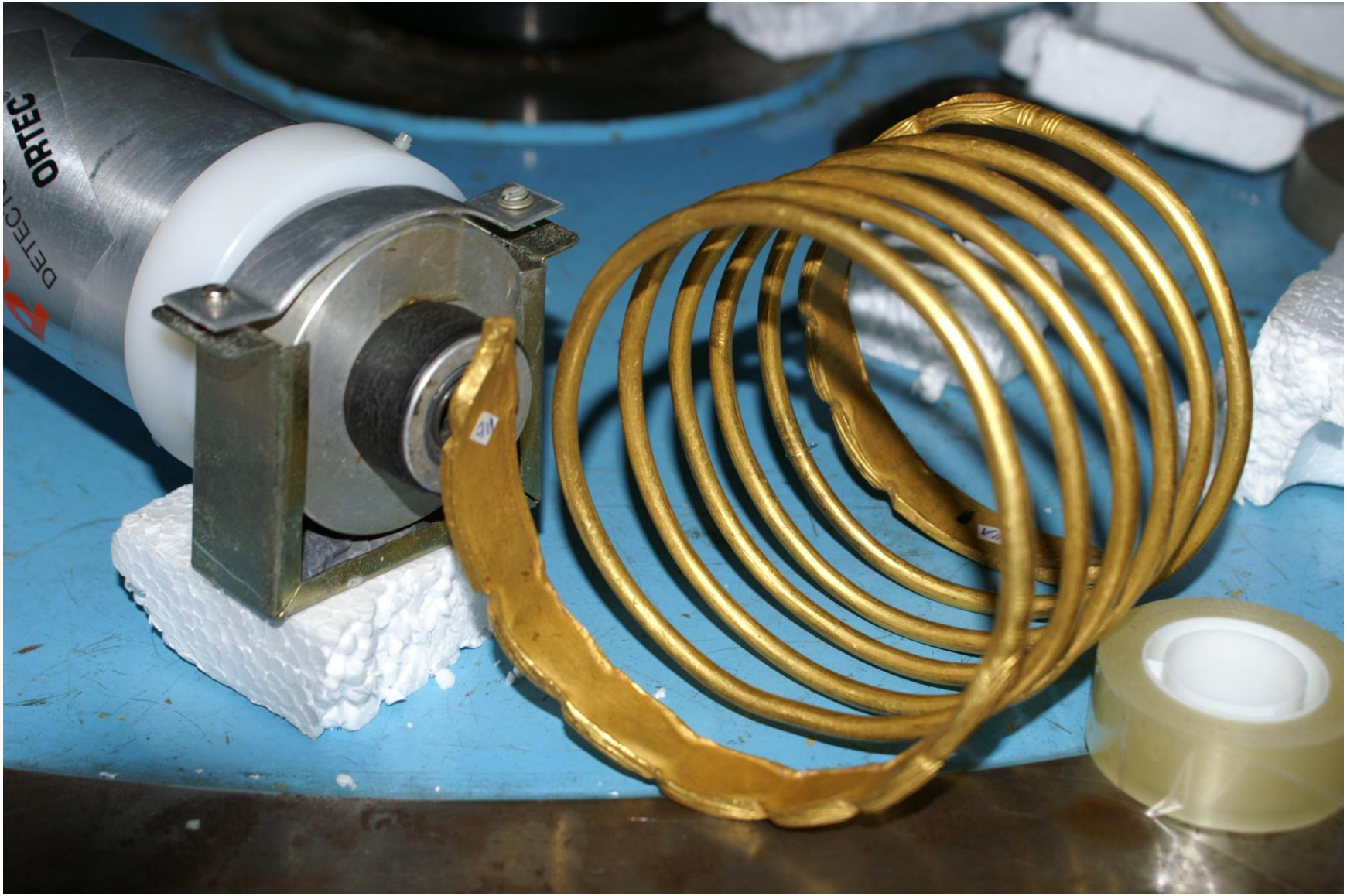
- **Multielemental**
- **Non-destructive**
- **Inexpensive**
- **Sensitive (detection limits: tens of ppm)**
- **Analyzed area: the whole coin surface**
- **Analyzed depth: tens of microns**

<u>Spectrometric chain</u>

- **30 mCi ^{241}Am source**
- **HPGe horizontal detector (FWHM~200 eV @ 5.9 keV)**

Electronics:

- **Charge sensitive preamplifier**
- **Amplifier**
- **MultiChannel Analyzer**

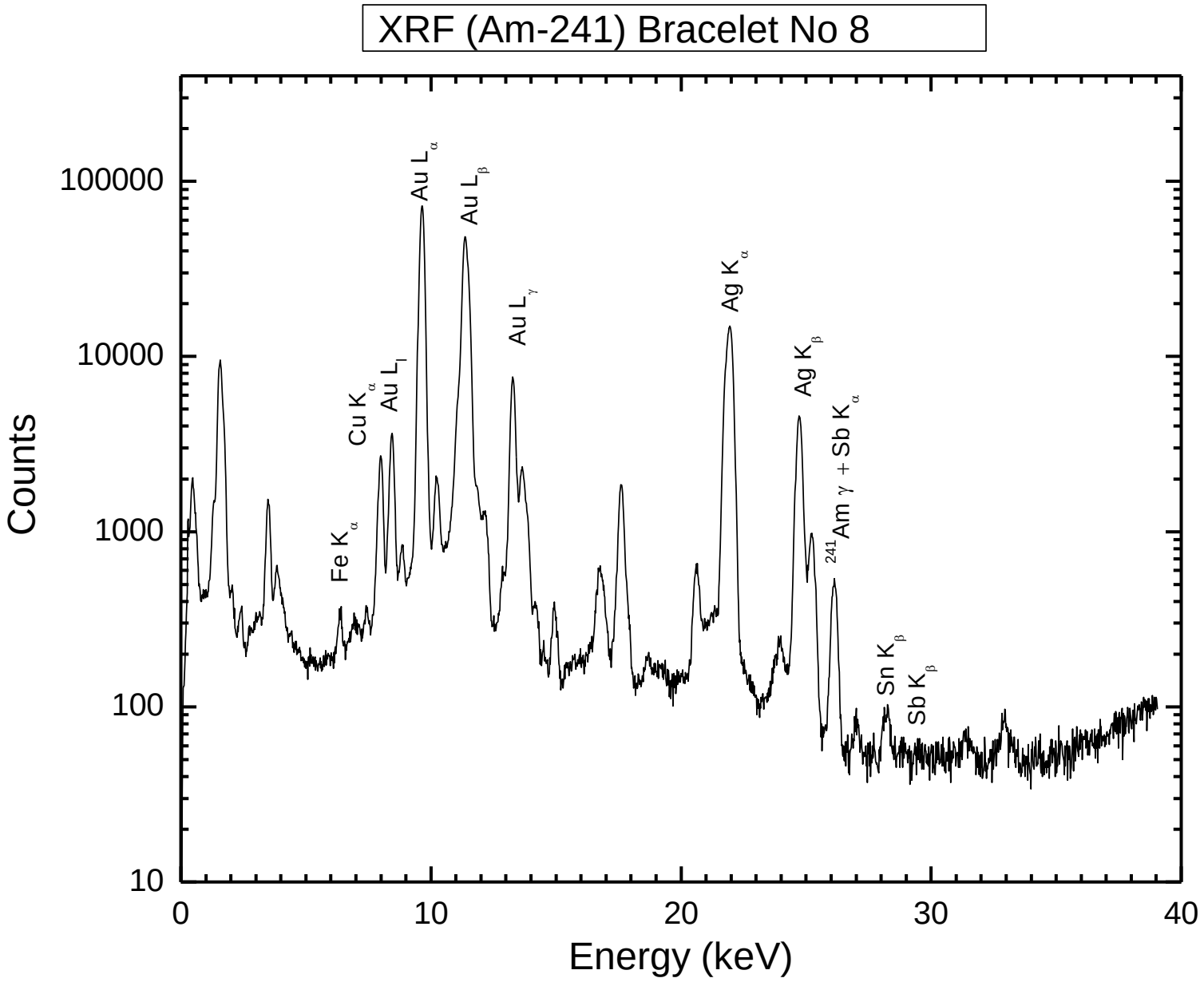

ORTEC

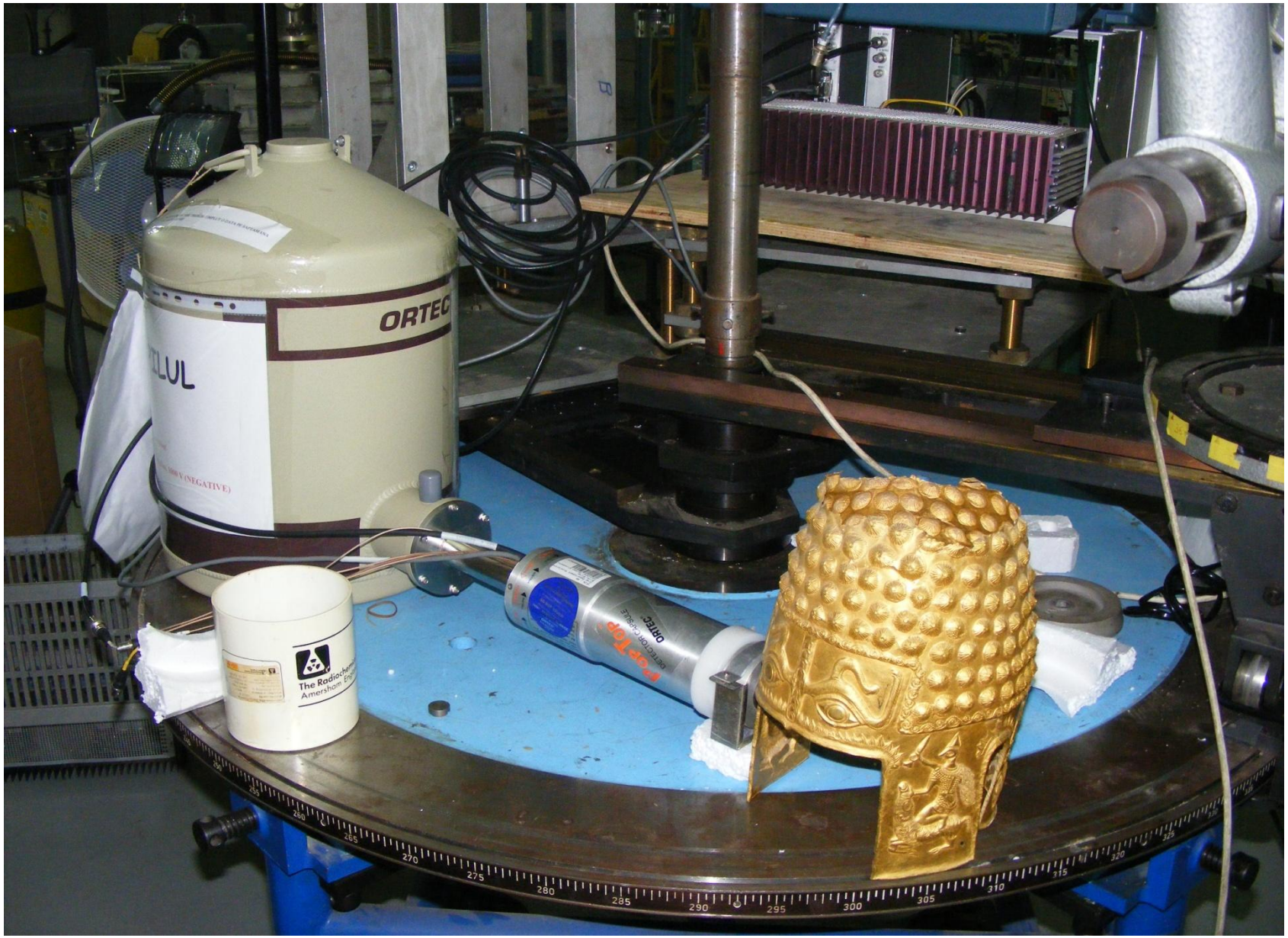
Am-241 based XRF – Dacian bracelets composition

Bracelet no.	Weight (g)	Au (wt%)	Ag (wt%)	Cu (wt%)	Sn ($mg \cdot kg^{-1}$)
1	982.2	89.8	9.5	0.6	200
2	1076.72	78.2	20.3	1.5	60
3	1115.31	82.4	16.2	1.4	360
4	927.98	91.5	8.1	0.4	125
5	764.95	92.8	6.9	0.3	<MDL*
6	1062.55	92	7.1	0.9	230
7	1196.03	92.9	6.3	0.7	<MDL *
8	1136.06	85	12.8	2.1	1500
9	682.3	87.1	12.2	0.6	120
10	1047	88.7	10.3	0.9	425
11	825	86.1	12.6	0.7	400
12	884.37	83.5	14.3	1	500
13	933.4	84.8	14.6	0.6	<MDL *

*MDL – Minimum Detection Limits

Bogdan Constantinescu, Daniela Cristea-Stan, Angela Vasilescu, Rolf Simon, Daniele Ceccato, *Archaeometallurgical Characterization of Ancient Gold Artifacts from Romanian Museums Using XRF, Micro-PIXE and Micro-SR-XRF Methods*, The Publishing House of the Romanian Academy – Proceedings of the Romanian Academy, Series A, 13(1), (2012) 19-26.


XRF (Am-241) Bracelet No 8
Counts
Energy (keV)
100000
10000
1000
100
10
0
10
20
30
40
Fe Kα
Cu Kα
Au Lℓ
Au Lα
Au Lβ
Au Lγ
Ag Kα
Ag Kβ
241Am γ + Sb Kα
Sn Kβ
Sb Kβ



Cotzofenesti helmet – 3rd Century BC


EDWARDS
BOC EDWARDS
Active Gauge Controller
EDWARDS
BOC EDWARDS
ATENȚIE!
MANIPULAREA SAU UTILIZAREA LUI REMUS SE VA FACE DOAR SUB SUPRAVEGHEREA UNUI MEMBRU AL GRUPULUI DE FIZICĂ ATOMICĂ !

Cucuteni – Baiceni bracelet (Moldova) – 3rd Century BC

X-Ray Fluorescence analysis – XRF

X-MET 3000TX PORTABLE XRF SPECTROMETER

X-Ray tube – Rh anode

PDA computer

X-Ray detector: Si PIN diode, Peltier cooled

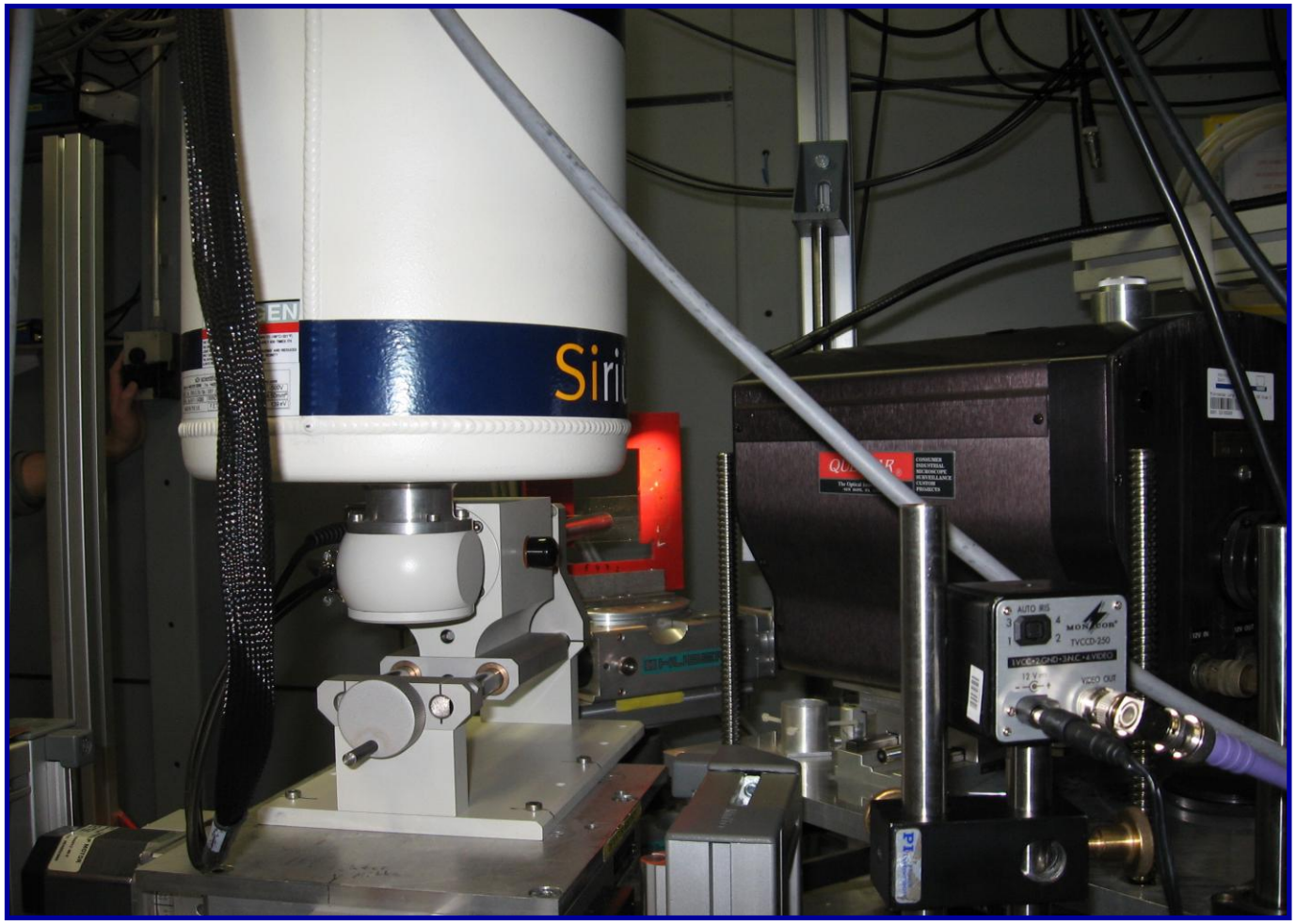
Kapton window


X-MET3000TXR
K49994

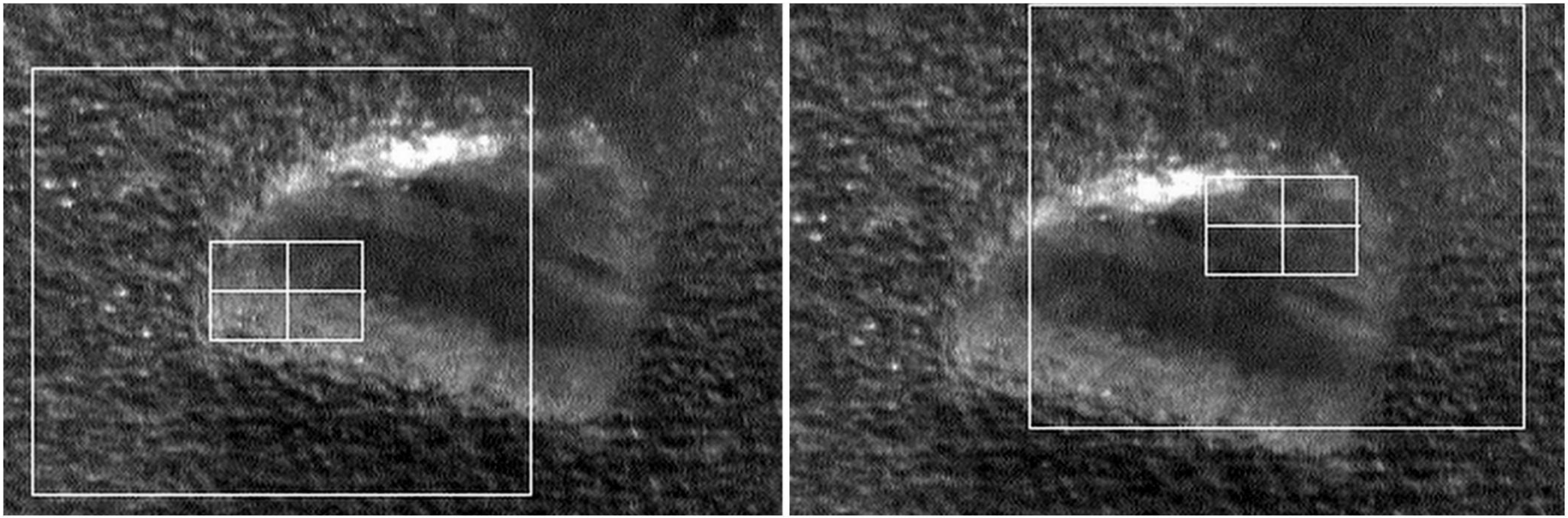

X-MET3000TXR+
OXFORD INSTRUMENTS

Crown of Queen Mary – 1922
Ruby – Chromium Red Garnet – Manganese, Iron

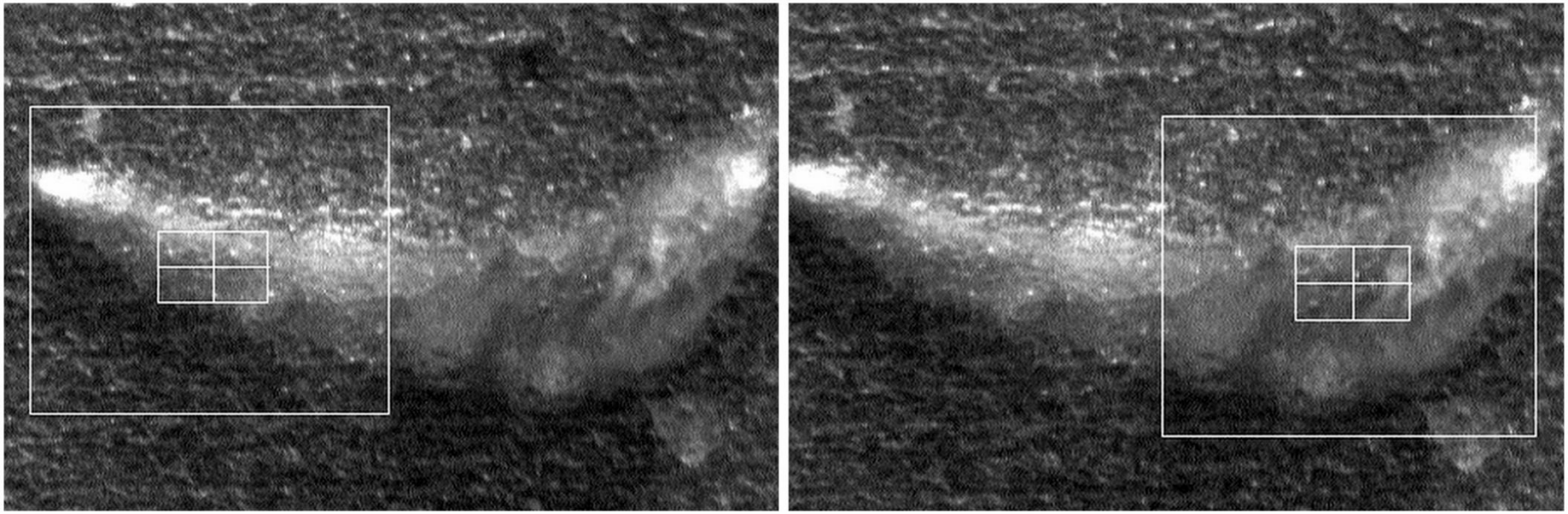
In early 2011, we obtained the permission of the Romanian authorities to take two sets of very small (1-2 mg) samples from the extremities of the bracelets and from 17 Koson and pseudo-Lysimachus staters to separately analyze them by micro-SR-XRF at BESSY and by micro-PIXE at AGLAE Paris.



Micro-SR-XRF at BESSY Synchrotron, Berlin, Germany



BESSY micro-SR-XRF Koson without monogram



BESSY micro-SR-XRF Bracelet 4 head B

The same aspects were revealed after the analyses of similarly small fragments (less than 100 microns in diameter) from 13 Dacian gold bracelets. We illustrate with bracelet no 2, where the XRF measurement in three areas (approx. 2 cm^2 each) gave the average composition of Au 81.2% Ag 16.2% Cu 1.6% Sn 60 ppm.

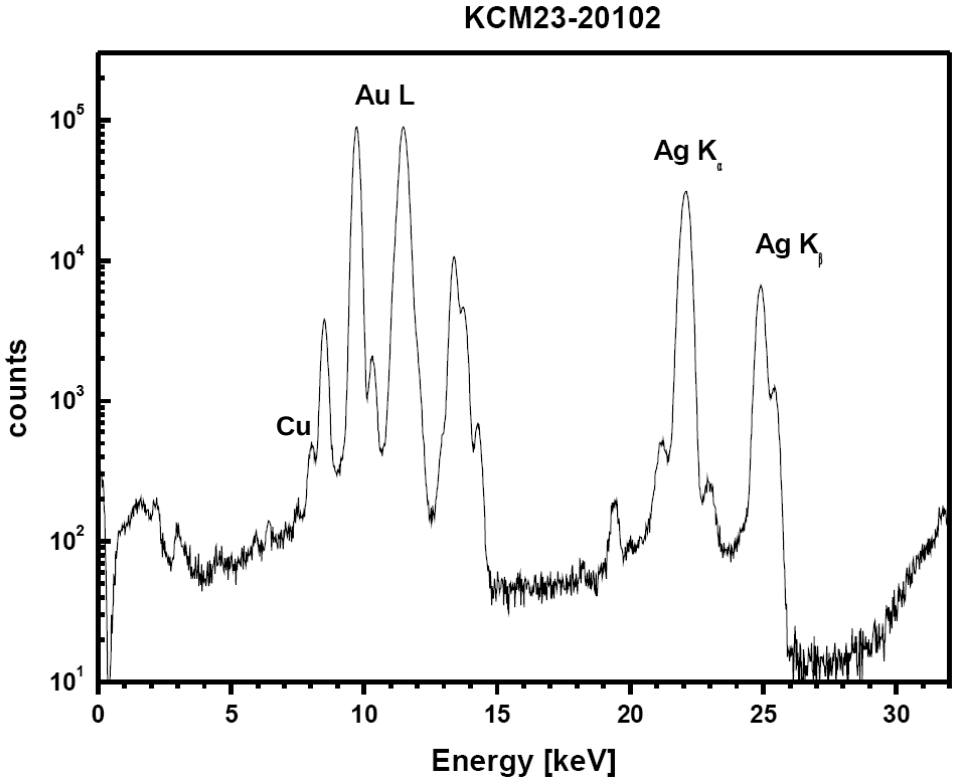
Table 3 presents results of the SR-XRF measurements on 2 micro-samples of the same bracelet, head A and B.

SR-XRF results on bracelet no.2

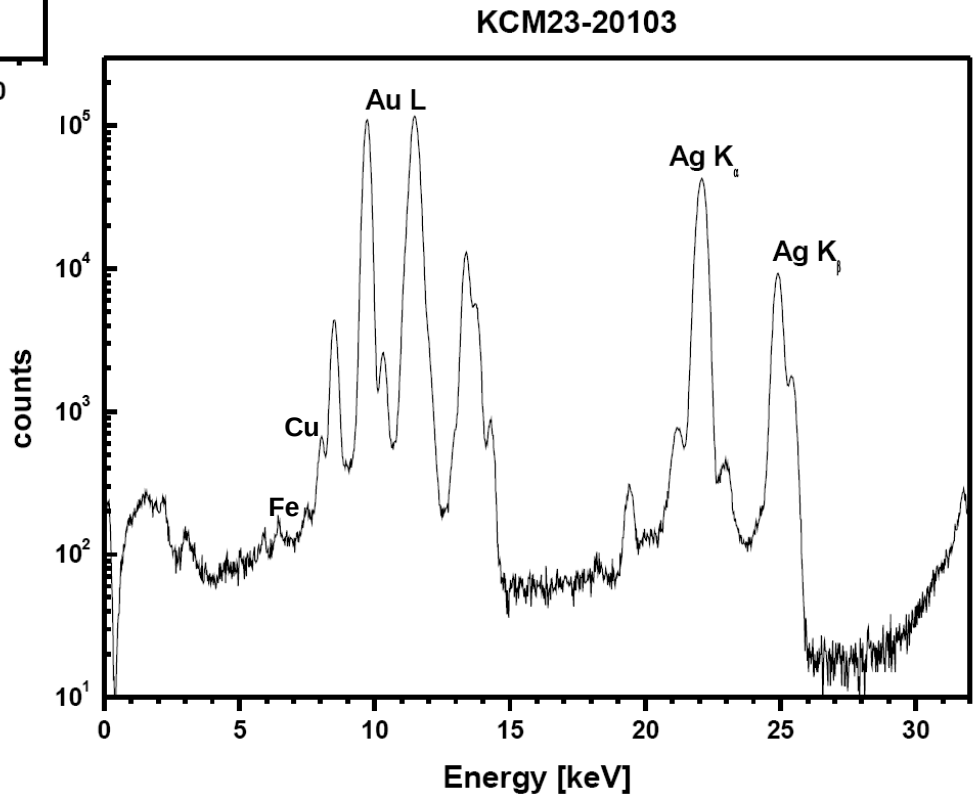
Head A					
Measurement	Au [%]	Ag [%]	Cu [%]	Fe [%]	Sn [ppm]
1	77.78	19.53	2.43	0.25	52
2	80.78	17.06	1.46	0.68	109
3	81.01	16.87	1.45	0.65	88
Head B					
1	77.72	18.53	3.71	0.030	52
2	78.15	18.69	3.11	0.039	49

The differences are significant not only between the two “heads”(ends) of the bracelets (a “huge” item for gold jewelry: weight 1076.72 g, length 2.69 m, external diameter 112 mm, 8 spires), but also for the same fragment in the case of “head” A, indicating the use of small grains (“gold sand”) of alluvial gold melted partly or at all.

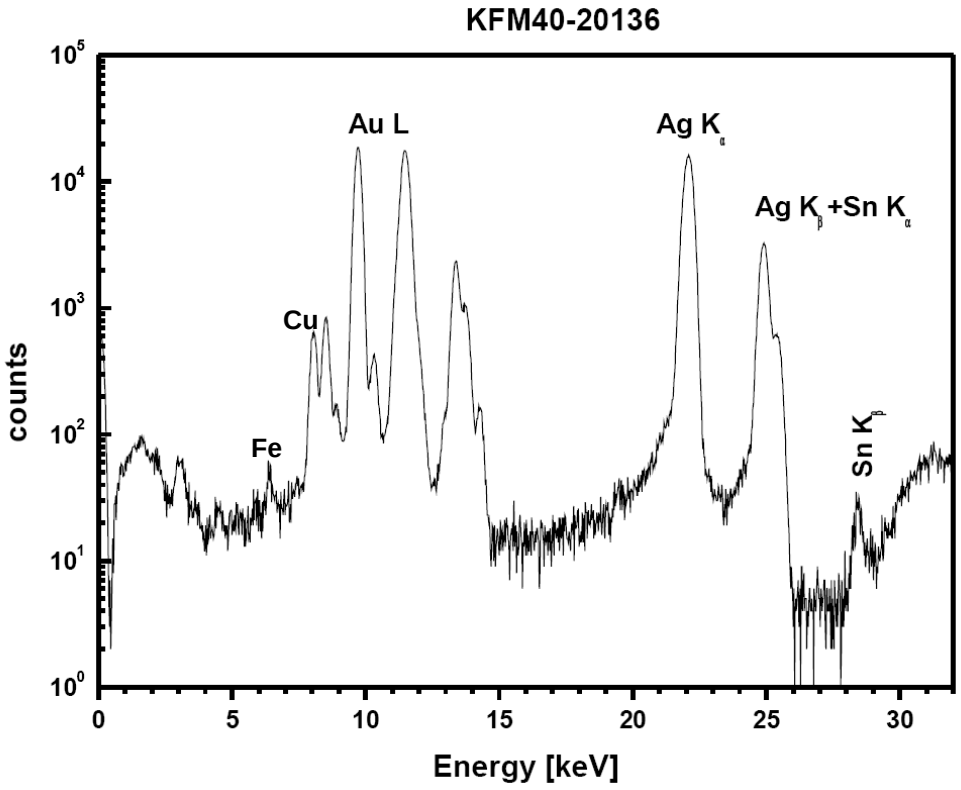
Dacian Koson with monogram



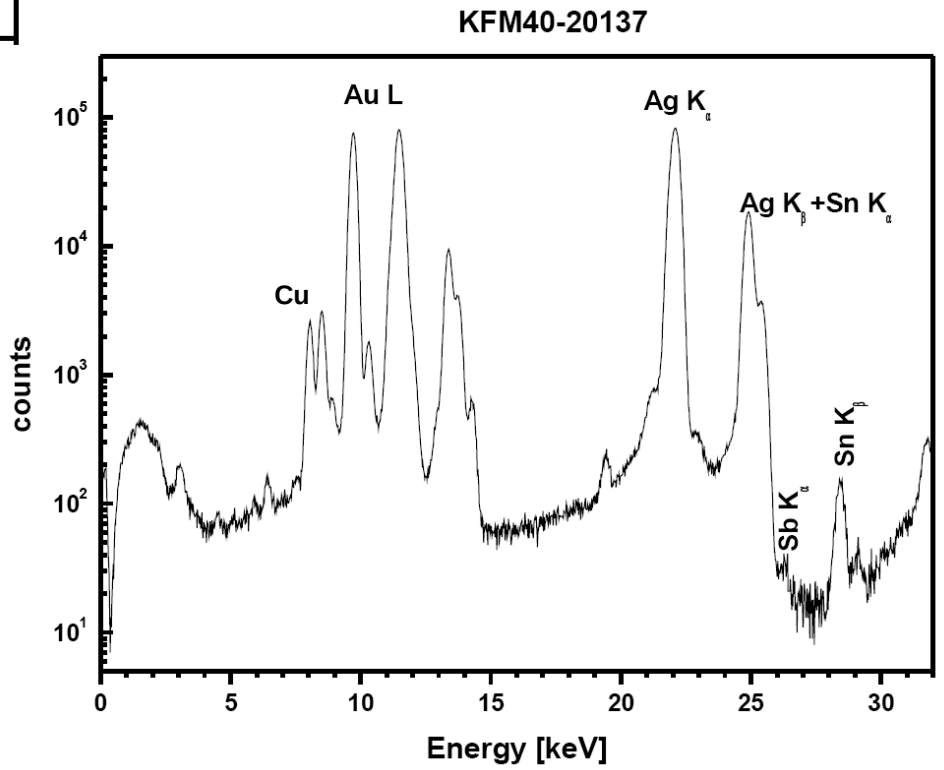
Koson with monogram no.23



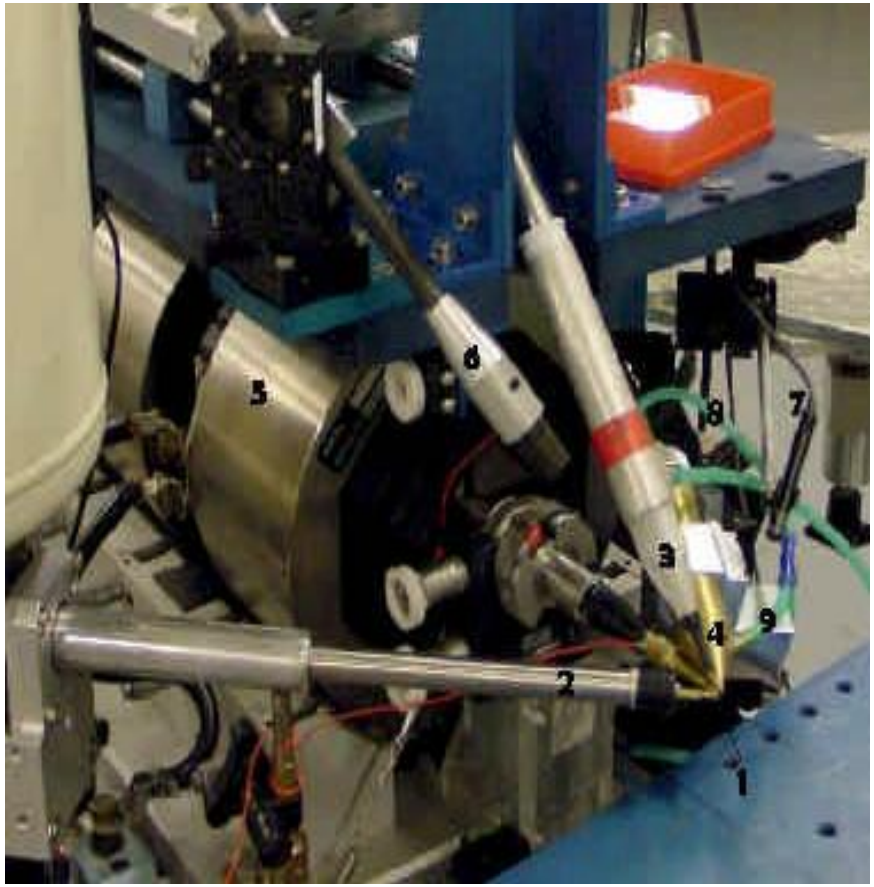
Dacian Koson without monogram



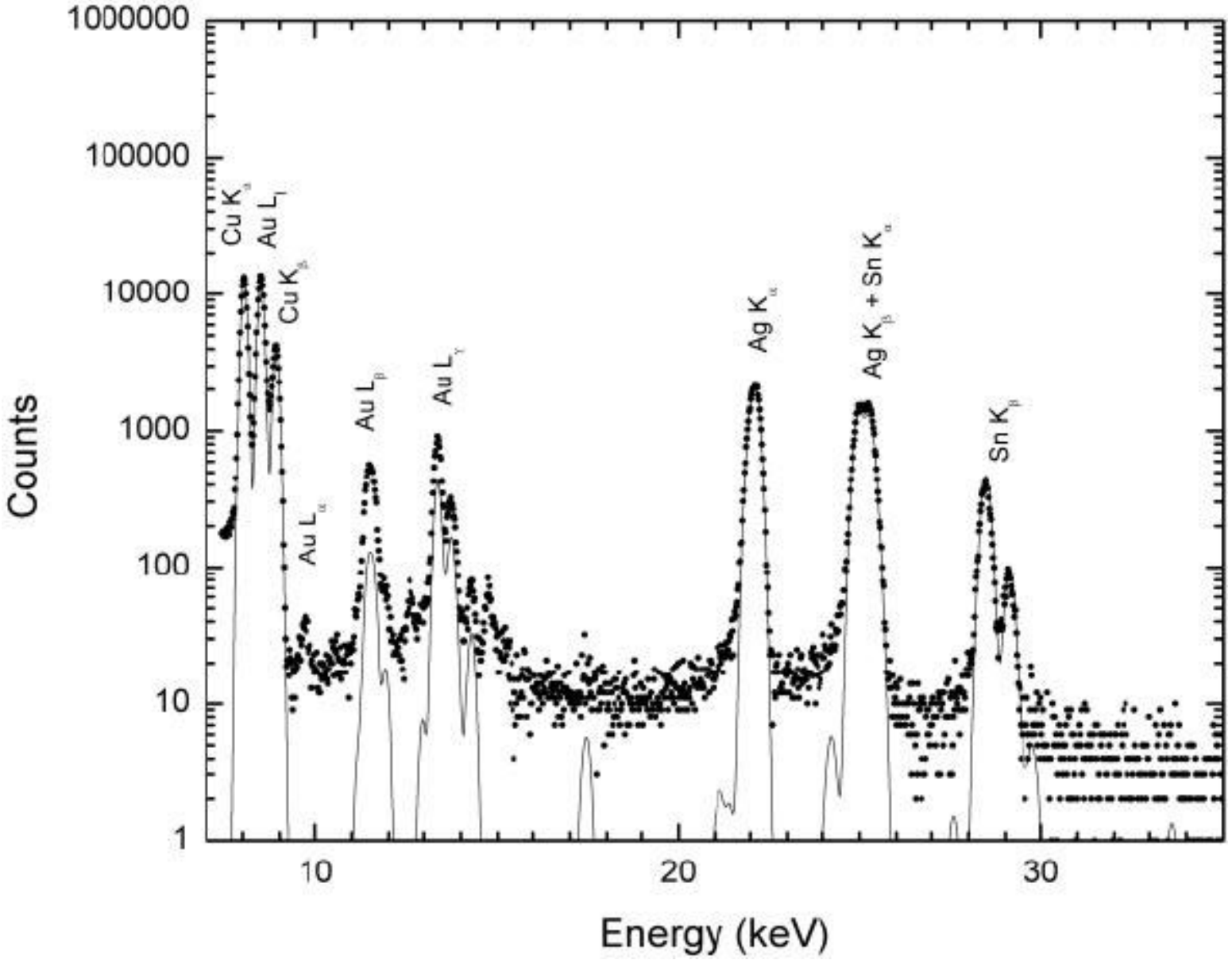
Koson without monogram no.40



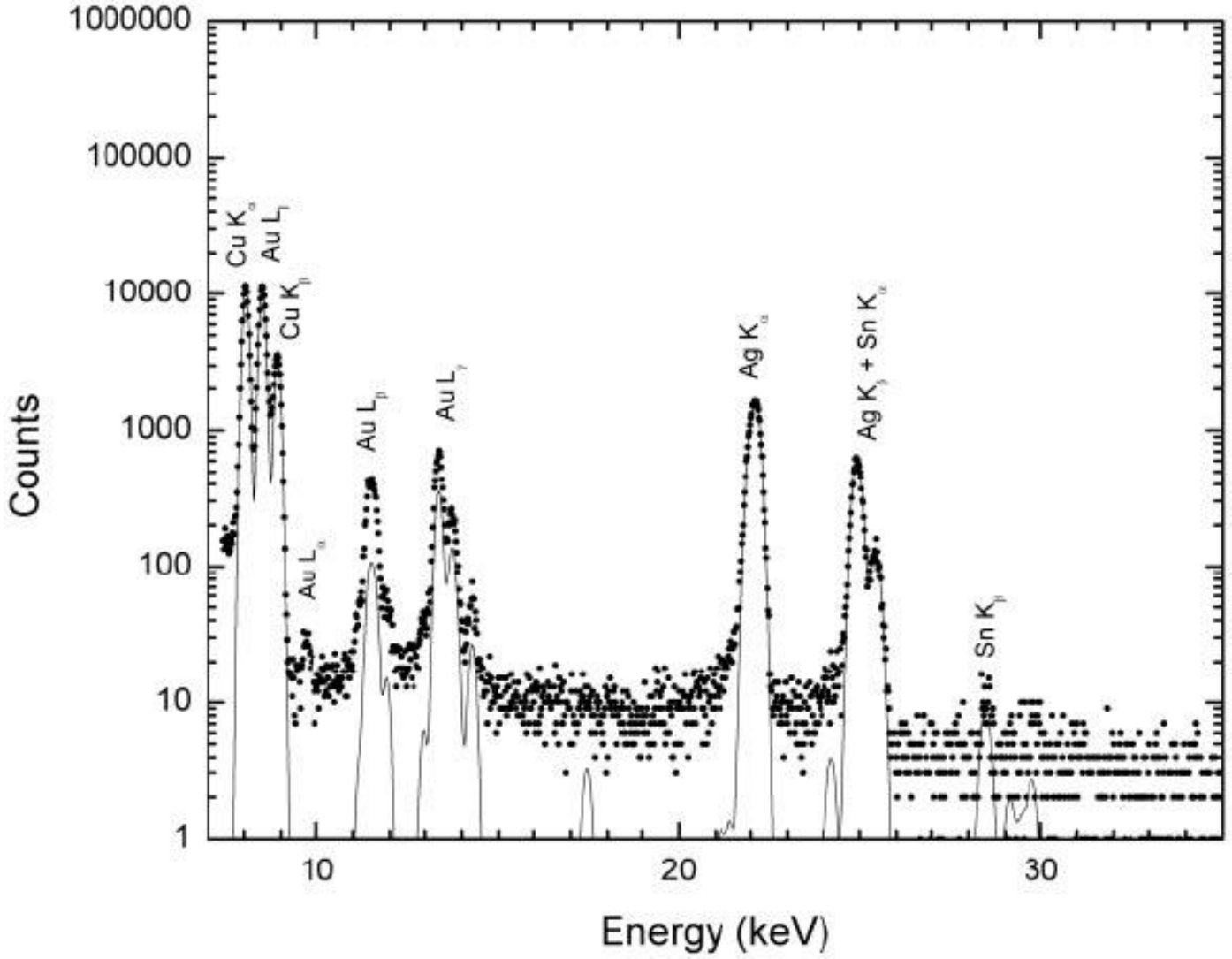
Micro-PIXE at AGLAE accelerator of CNRS-Musee du Louvre, Paris, France



- 3 MeV proton micro-beam (roughly 50 μm diameter) extracted into air
- irradiation with a 10 nA beam current for about 15 minutes
- two Si(Li) detectors: low-energy (1-10 keV) - for the determination of matrix elements (Au, Ag, Cu) and high-energy (5-40 keV) – for trace-elements (Sn, Sb, Te)
- to reduce the high contribution of Au L X-ray lines in the X-ray spectra and the sum peaks interfering with the signals of elements neighboring Ag K X-ray lines, the measurements were performed using a 75 μm Cu filter in front of the high-energy Si(Li) detector



Micro-PIXE spectrum of a minute fragment of a koson without monogram (first analyzed area) – the high tin signal is to be noted.



Micro-PIXE spectrum of the same fragment of a koson without monogram, but measured in a different spot (the second analyzed area) – a strong decrease in the tin signal (as compared with the previous spectrum) can be observed.

A most trustful hypothesis is that the Koson staters with monogram – the original coins – were minted somewhere in the neighbouring Roman provinces (in the Balkans) from refined, "coined" gold and the Koson staters without monogram are "Barbarian" copies made in Dacia (Transylvania) from native gold using a primitive metallurgy incapable to completely melt the small pieces of alluvial gold.

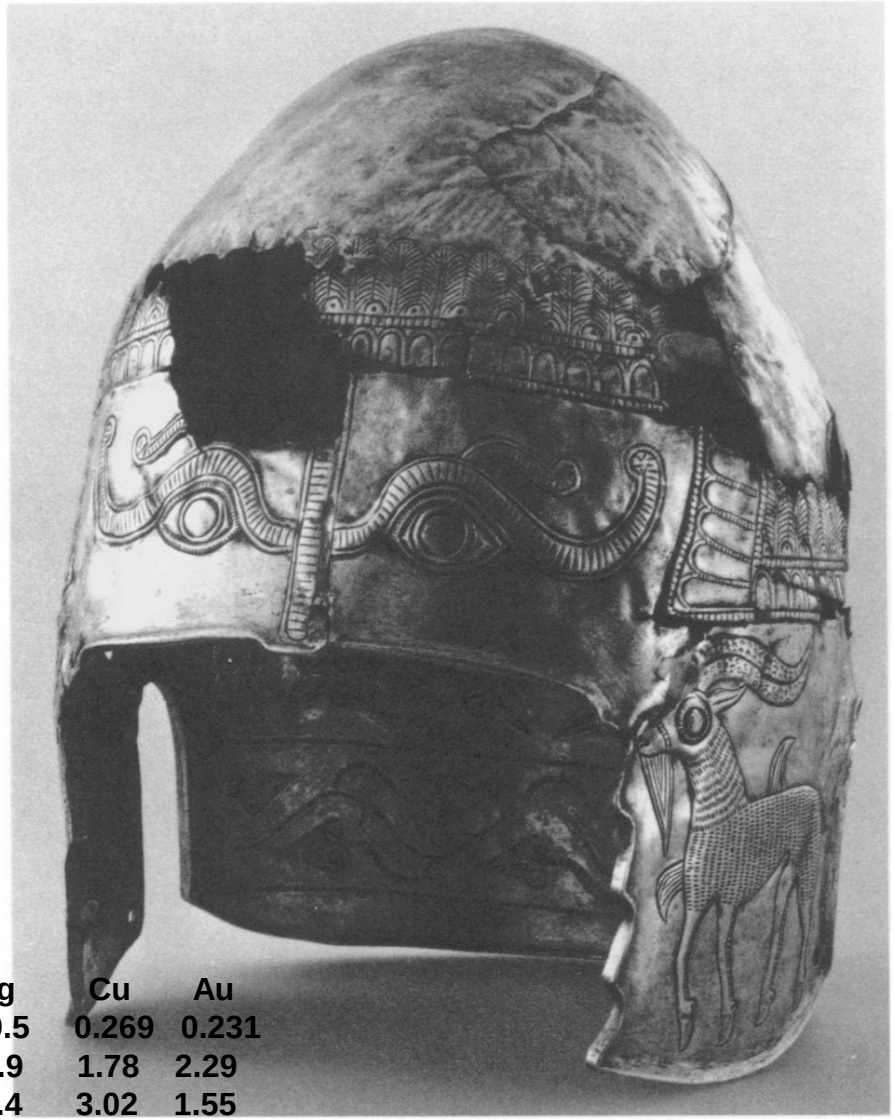
Bogdan Constantinescu, Angela Vasilescu, Daniela Stan, Martin Radtke, Uwe Reinholz, Guenter Buzanich, Daniele Ceccato and Ernest Oberlaender-Tarnoveanu *Studies on archaeological gold items found in Romanian territory using X-Ray-based analytical spectrometry,* Journal of Analytical Atomic Spectrometry, Vol. 27. No. 12, (2012) 2076-2081.

Poroina Rython 3rd Century BC

Agighiol hoard (Dobroudja) - 5th Century BC

Element	Ag	Cu	Au
Helmet %	99.5	0.269	0.231
Helmet – rivet	95.9	1.78	2.29
Helmet – foil (repaired)	95.4	3.02	1.55

Helmet Thracian
Photo Detroit Institute of Arts

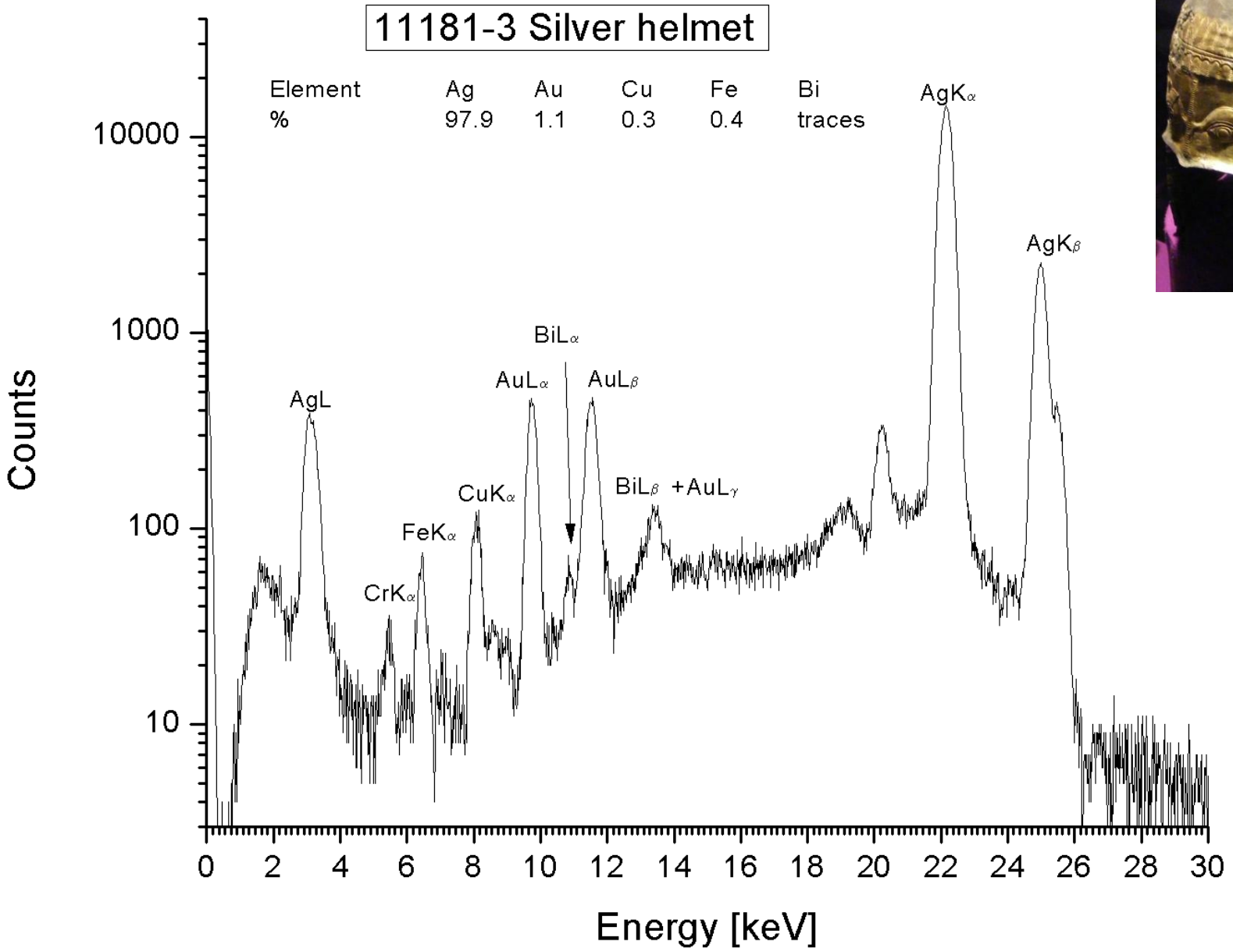


Helmet Thracian
– photo Detroit Institute of Arts

(Meyers, *Pieter*, "*Three Silver Objects from Thrace*: A Technical Examination," METROLPOLITAN MUSEUM JOURNAL, vol 16, 1982, pp 49-54)

11181-3 Silver helmet

Element	Ag	Au	Cu	Fe	Bi
%	97.9	1.1	0.3	0.4	traces




Silver beaker – Metropolitan Museum of Art New York
(Photo: Bogdan Constantinescu)
V.Griessmeier – 1936; P.Jacobsthal – 1944; Goldman, Berciu, Farkas si Meyers

Thracian Cup photo – Metropolian Museum of Arts

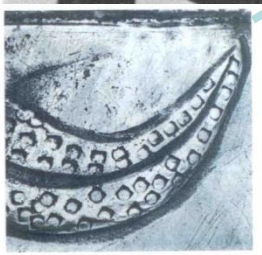
(Meyers, *Pieter*, "*Three Silver Objects from Thrace*: A Technical Examination," METROLPOLITAN MUSEUM JOURNAL, vol 16, 1982, pp 49-54)

Element	Ag	Cu	Au
%	99.7	0.065	0.242

Thracian silver Cup (Beaker) no.1 - Agighiol hoard

Element	Ag	Cu	Au	Fe	Bi
%	98.9	traces	0.5	0.4	0.05

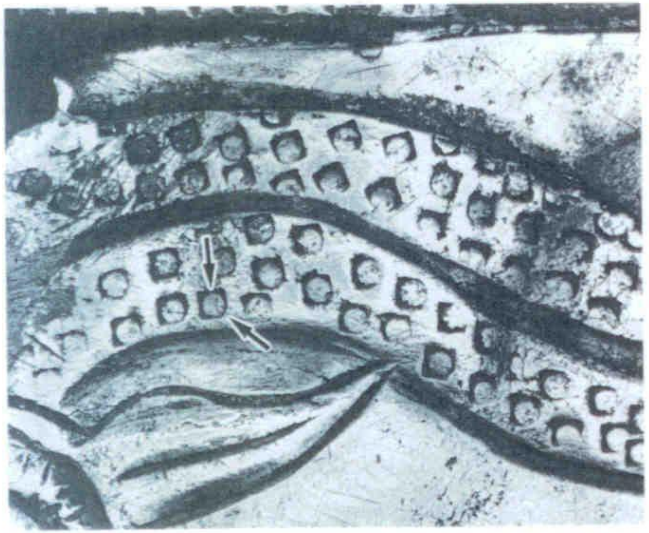
Silver helmet - gilded, nr. Inv. 11181

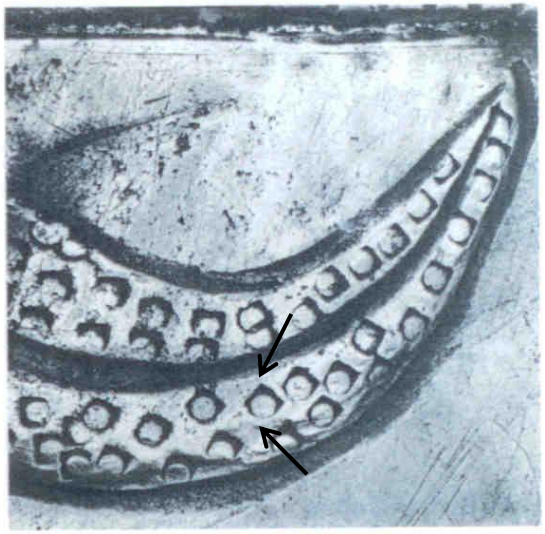


Helmet Thracian
Photo Detroit Institute of Arts

Helmet Thracian
– photo Detroit Institute of Arts

(Meyers, *Pieter*, "*Three Silver Objects from Thrace*: A Technical Examination," METROLPOLITAN MUSEUM JOURNAL, vol 16, 1982, pp 49-54)





Helmet Thracian -The Detroit Institute of Arts,

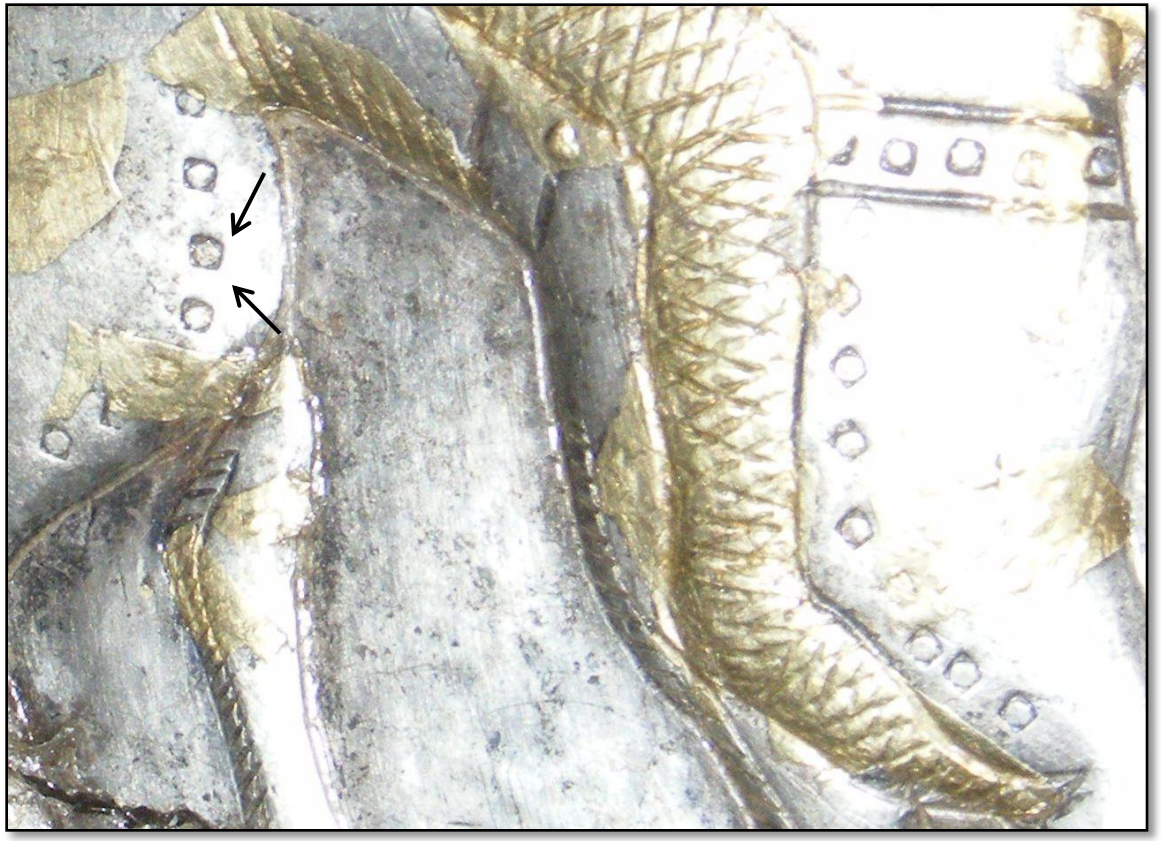
Details of animal horns
- chasing tool

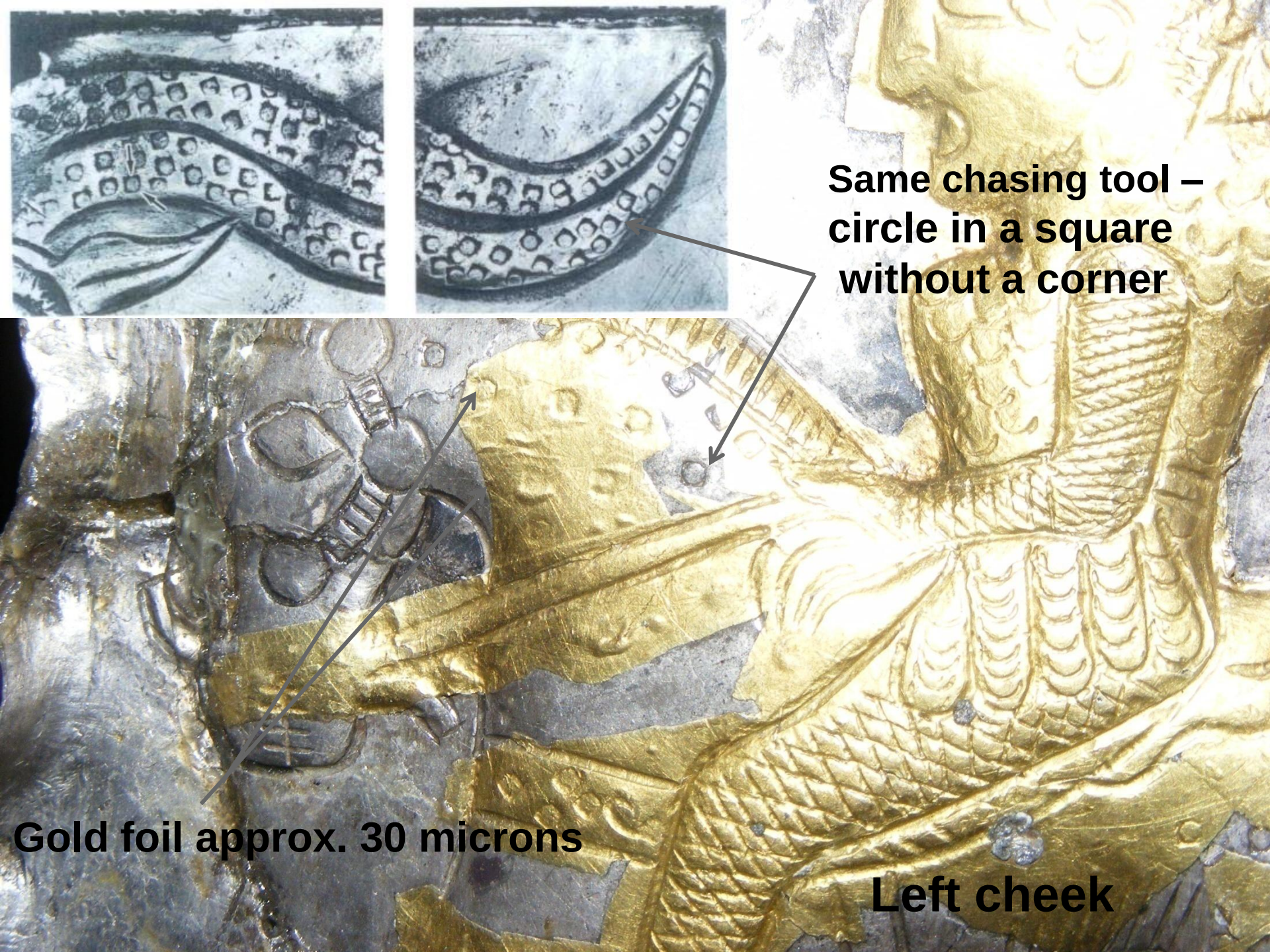
- *(Meyers*, *Pieter*, "*Three Silver Objects from Thrace*: A Technical Examination," METROLPOLITAN MUSEUM JOURNAL, vol 16, 1981, pp 49-54)

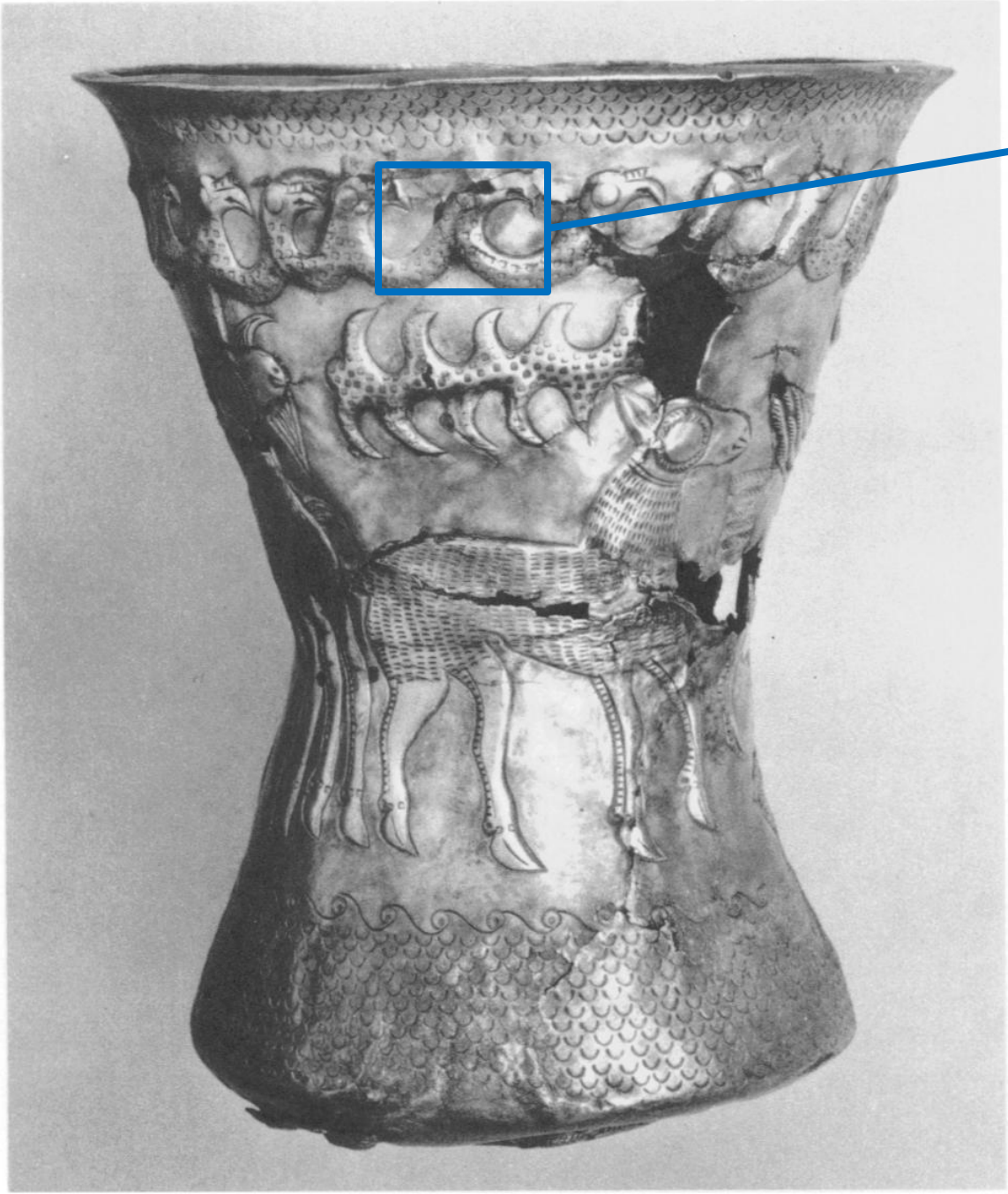
Thracian Helmet -
Agighiol Hoard
- Bucharest

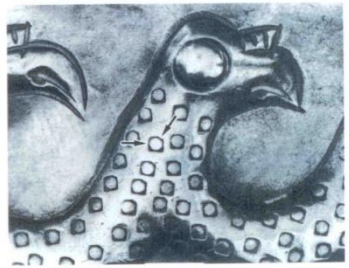
The helmet detail (right cheek) – chasing tool

Model punch - circle in a square without a corner




Same chasing tool – circle in a square without a corner
Gold foil approx. 30 microns
Left cheek



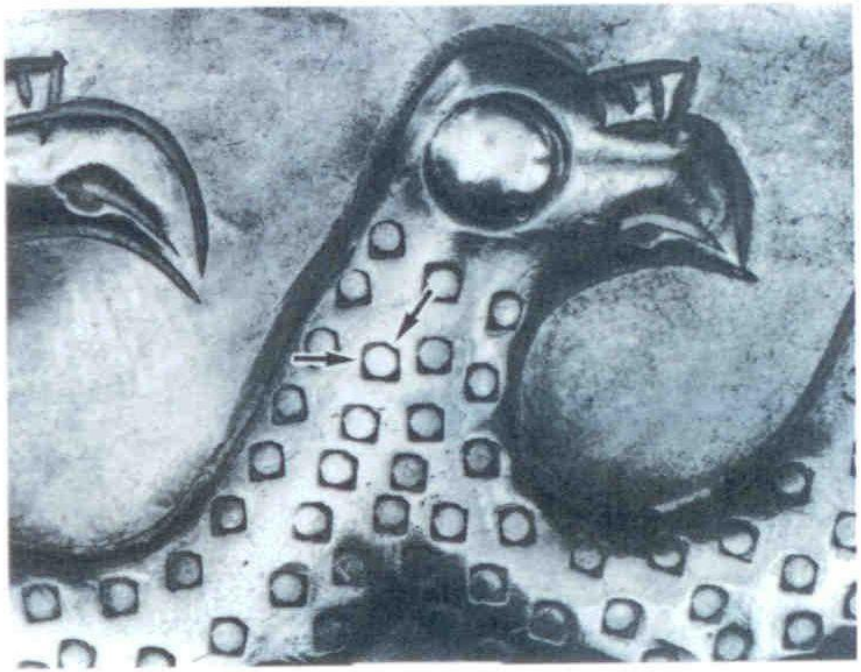


Thracian Cup
photo – Metropolian Museum of Arts

(Meyers, *Pieter*, "*Three Silver Objects from Thrace*: A Technical Examination," METROLPOLITAN MUSEUM JOURNAL, vol 16, 1982, pp 49-54)

Thracian Cup – Agighiol Hoard - Bucharest

Detail

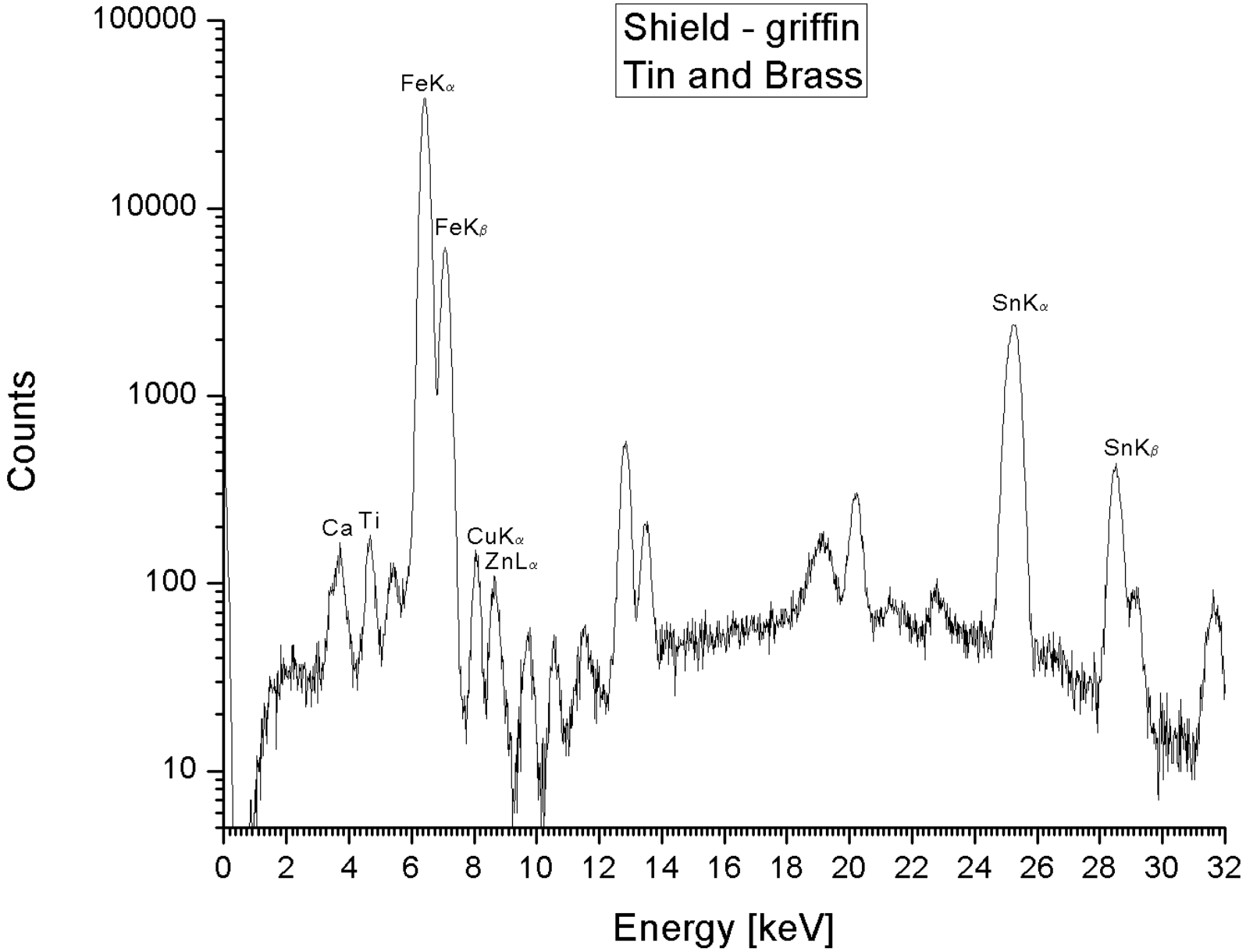


Silver Thracian cup - Metropolitan Museum of Art - New York
Detail - chasing tool

Silver Thracian Cup – Agighiol Hoard – Bucharest
Detail - chasing tool

(Meyers, *Pieter*, "*Three Silver Objects from Thrace*: A Technical Examination," METROLPOLITAN MUSEUM JOURNAL, vol 16, 1981, pp 49-54)

Iron shield – Dacian? Roman?


Shield - griffin
Tin and Brass
Counts
Energy [keV]
100000
10000
1000
100
10
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
FeKα
FeKβ
Ca
Ti
CuKα
ZnLα
SnKα
SnKβ

Roman shield
of a Signifer

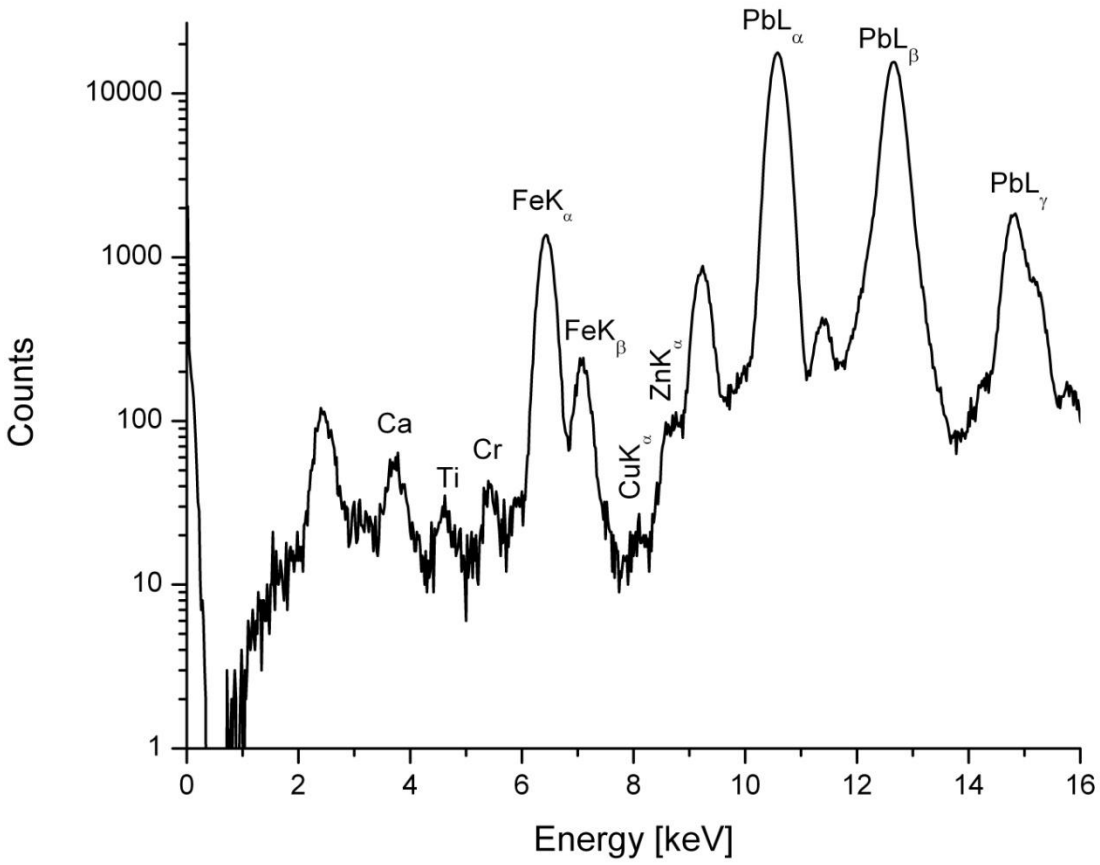
Tinning
Brass foil

The XRF elemental analysis method is completely nondestructive and can be performed directly in situ.

In our "in-church" study, by scanning of specific areas, we identified inorganic pigments containing Fe, Co, Cu, Zn, As, Pb, Hg, Ag, Au, Sn, Sb, Ba.

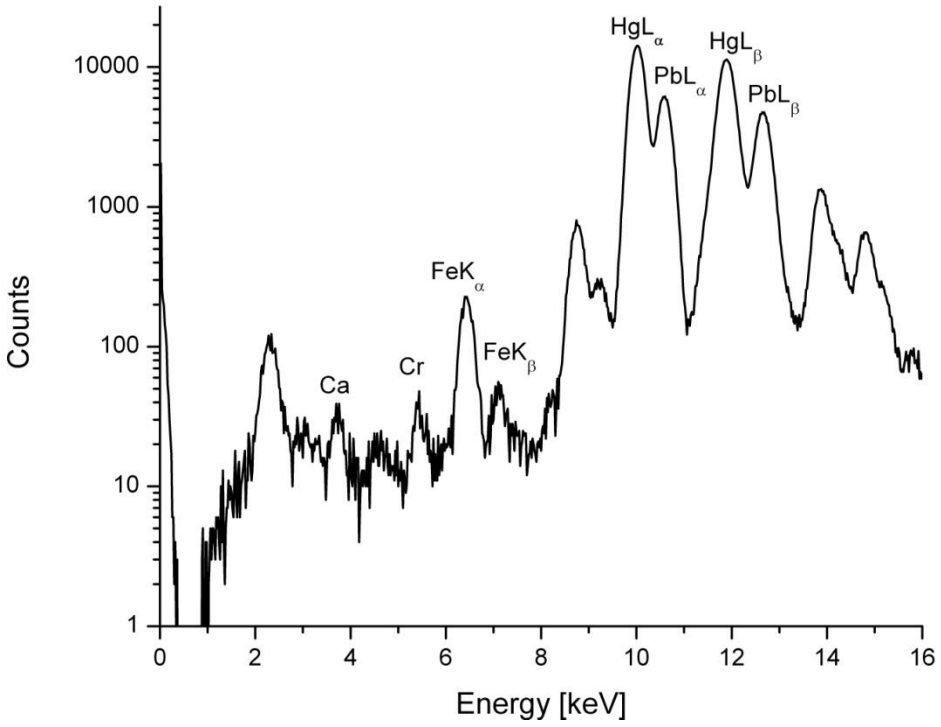
In order to be easily identified, areas were photographed and marked with letters. For St. George wall picture, we measured the area of his legs: carnation, golden shoes, red jacket and blue mantle.

St. George's leg area

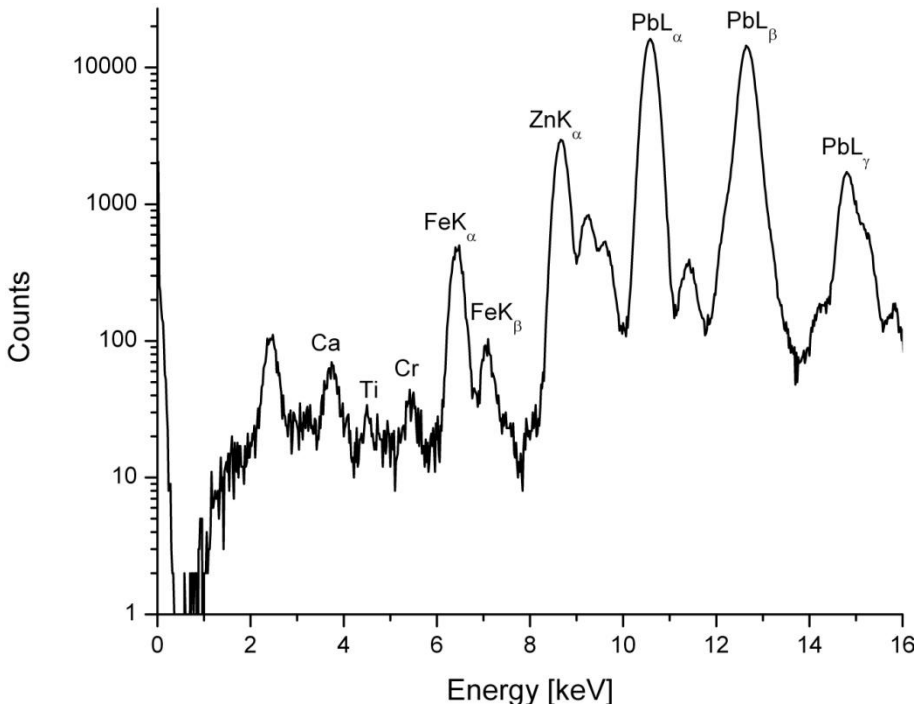


XRF spectrum - yellow area
(no. 2 in St. George's leg area)

Yellow pigment - was probably made from a mixture of chrome-yellow + ochre.



XRF spectrum - red area
(no. 3 in St. George's leg area)



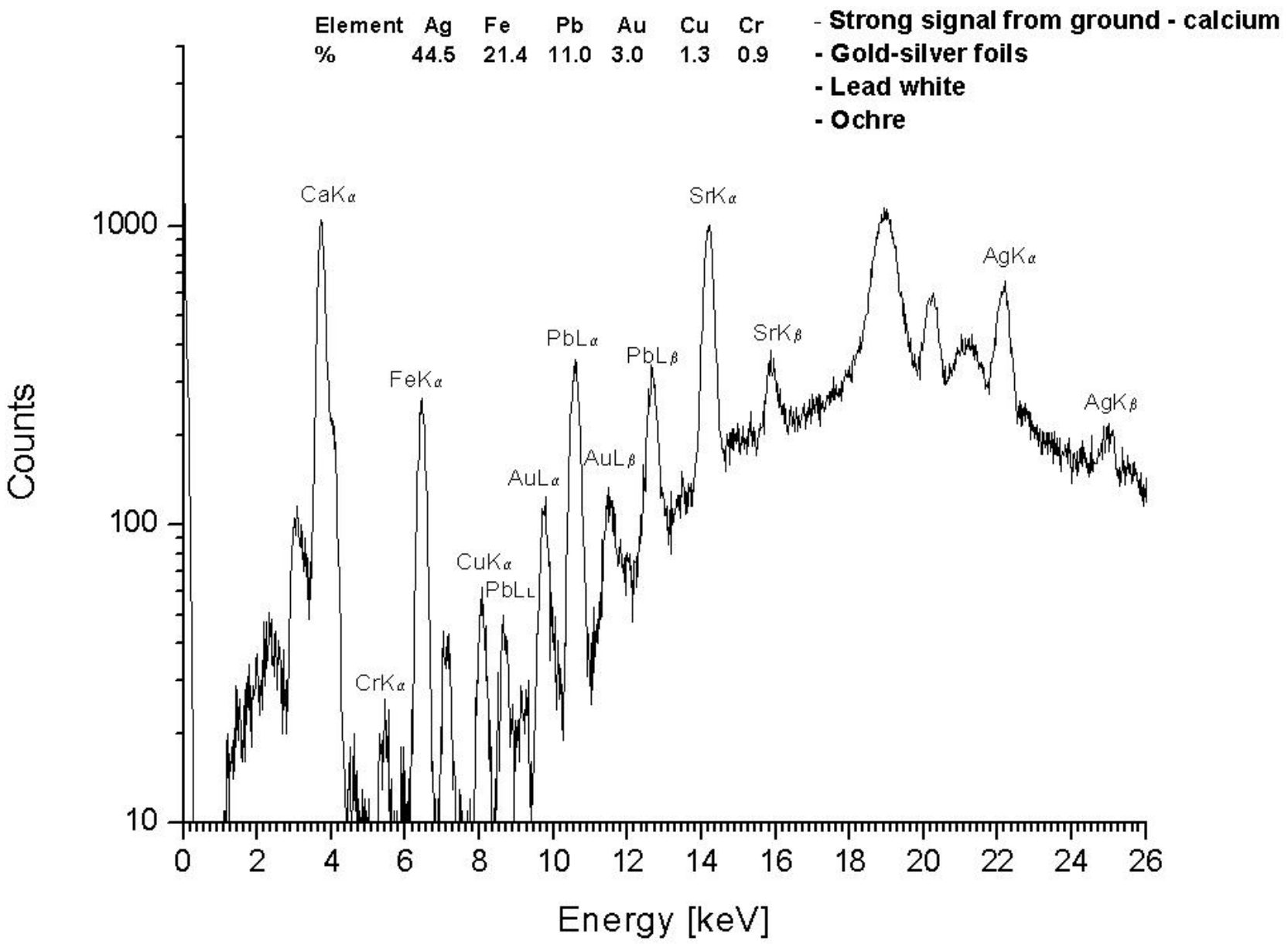
XRF spectrum - blue area
(no. 4 in in St. George's leg area)

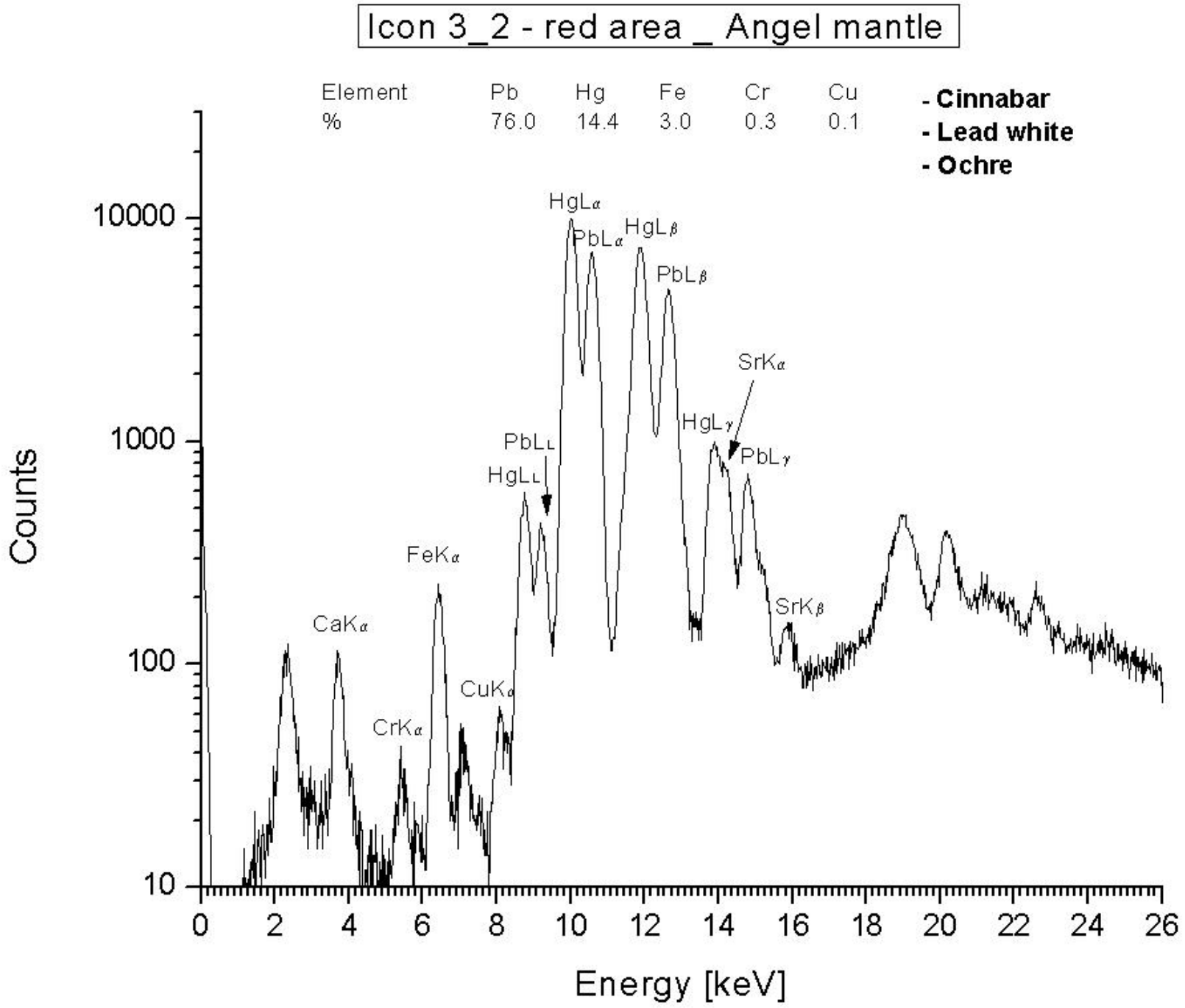
Red is still on a mercury-based pigment (probably cinnabar) which is found in small quantities also in carnation.

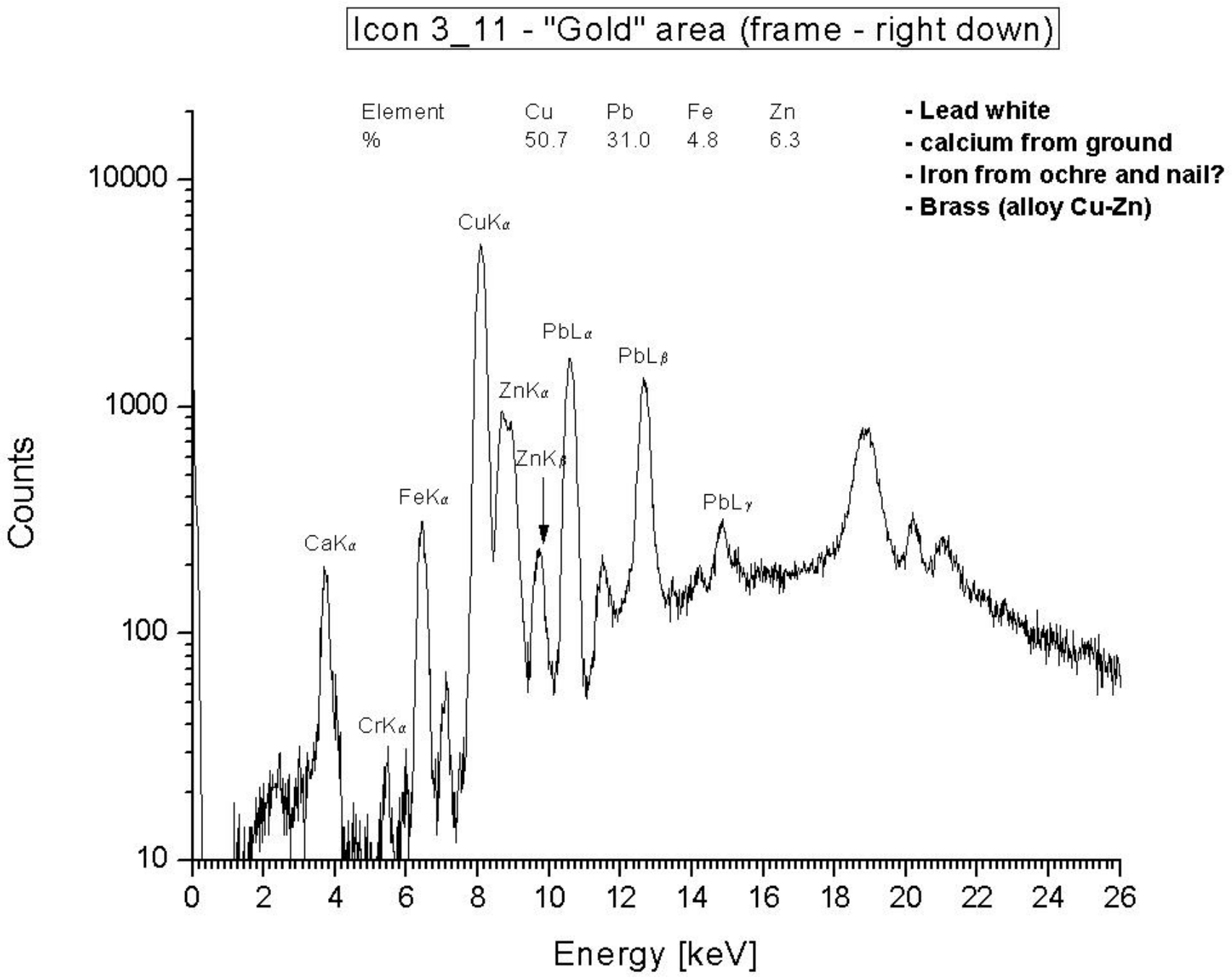
Blue is an iron-based pigment (Prussian blue?). Note the presence of chrome yellow in all areas and the presence of iron - an indicator of ochre - in all colors. In the blue we detected a relatively high zinc content which means a later repainting, covering the original lead white layer (20th Century?) because in Church's icons Tattarescu used only white lead.

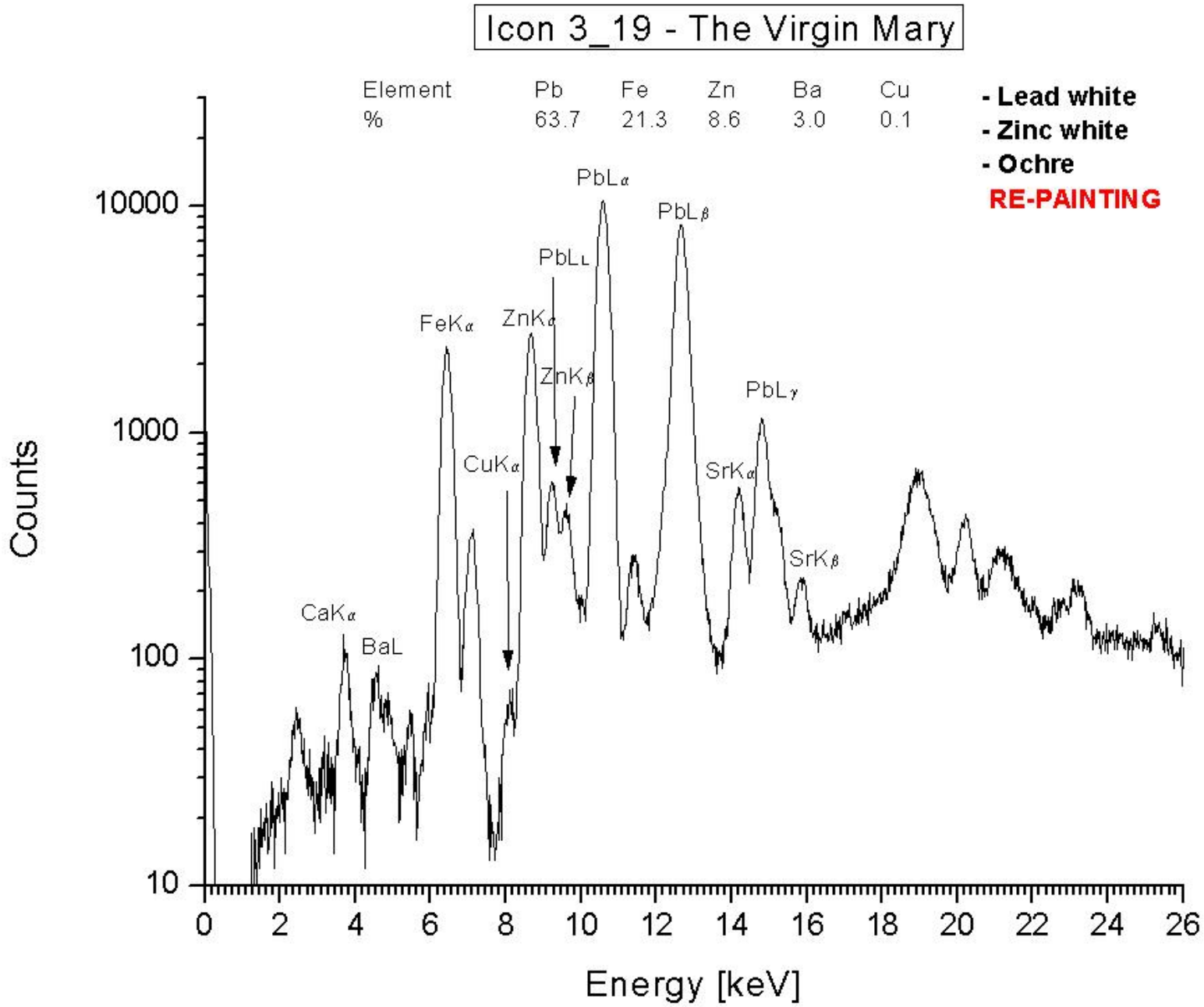

3.12
3.14
3.1
3.23
3.24
3.19
3.18
3.5
3.2
3.3
3.17
3.4
3.21
3.10
3.11

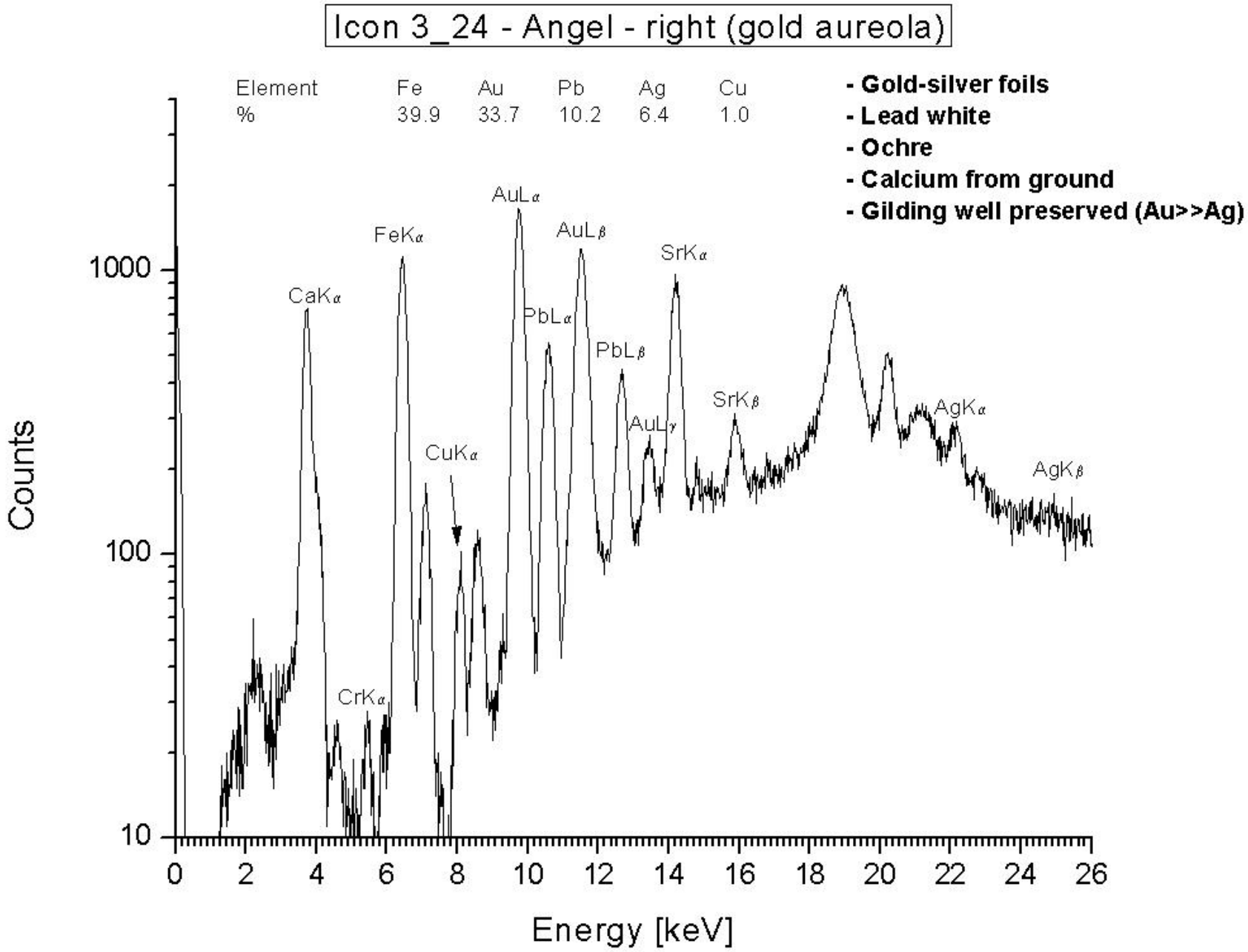
Icon 3_1 - The Virgin Mary (off-white aureola)




Icon 3_2 - red area _ Angel mantle
Element Pb Hg Fe Cr Cu
% 76.0 14.4 3.0 0.3 0.1
- Cinnabar
- Lead white
- Ochre
HgLα
PbLα
HgLβ
PbLβ
SrKα
HgLγ
PbLγ
PbLL
HgLL
FeKα
CaKα
CrKα
CuKα
SrKβ
Counts
10000
1000
100
10
0 2 4 6 8 10 12 14 16 18 20 22 24 26
Energy [keV]


Icon 3_11 - "Gold" area (frame - right down)
Element Cu Pb Fe Zn
% 50.7 31.0 4.8 6.3
- Lead white
- calcium from ground
- Iron from ochre and nail?
- Brass (alloy Cu-Zn)
CuKα
PbLα
PbLβ
ZnKα
ZnKβ
FeKα
CaKα
CrKα
PbLγ
Counts
Energy [keV]
10000
1000
100
10
0
2
4
6
8
10
12
14
16
18
20
22
24
26


Icon 3_19 - The Virgin Mary
Element Pb Fe Zn Ba Cu
% 63.7 21.3 8.6 3.0 0.1
- Lead white
- Zinc white
- Ochre
RE-PAINTING
PbLα
PbLβ
PbLℓ
FeKα
ZnKα
ZnKβ
PbLγ
CuKα
SrKα
SrKβ
CaKα
BaL
Counts
10000
1000
100
10
0 2 4 6 8 10 12 14 16 18 20 22 24 26
Energy [keV]


Icon 3_24 - Angel - right (gold aureola)
Element Fe Au Pb Ag Cu
% 39.9 33.7 10.2 6.4 1.0
- Gold-silver foils
- Lead white
- Ochre
- Calcium from ground
- Gilding well preserved (Au>>Ag)
CaKα
FeKα
CrKα
CuKα
AuLα
PbLα
AuLβ
PbLβ
AuLγ
SrKα
SrKβ
AgKα
AgKβ
Counts
1000
100
10
0 2 4 6 8 10 12 14 16 18 20 22 24 26
Energy [keV]

Acknowledgement

Romanian National Scientific Research Agency ANCS grant PN-II-ID-PCE-2011-3-0078 is gratefully acknowledged.

Thank you for attention!