School on Synchrotron Light Sources and their Applications 13-24 January 2025

Synchrotron multi-modal micro-analyses for cultural heritage: Application to the study of inks composition in Egyptian papyri

Presentation and tutorial on the use of PyMca software

Marine Cotte

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Li-Hill, 2019, Grenoble

19 PARTNER COUNTRIES

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France	27.5 %
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(Denmark, Finland, M	Norway, Swedei
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6 Scientific Associate Countries:

Israel	1.75 %
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Poland	1.0 %
Portugal	1.0 %
Czech Republic	0.6%
South Africa	0.30 %



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NATURAL AND CULTURAL HERITAGE AT THE ESRF

Distribution of shifts (8hrs) delivered on beamlines during the scheduling year 2018, by scientific area





 \bigcirc

Heritage studies via user program





Non-manufactured objects: evolution of Life.

Natural processes involved at all time scales:

- days-months (e.g. embryonic development),
 - months-years (e.g. growth from child to adult),
 - centuries-millenia (e.g. species domestication),
 - 1M-1B years (life evolution)

Manufactured objects: evolution of technologies.

Physical and chemical processes during and after creation:

- Creation of artworks : evolution of technologies in space •
 - and time, choice and combination of materials, formulations. Authentication



Degradation, preservation, conservation



Structure, morphology



Chemistry



NATURAL AND CULTURAL HERITAGE AT THE ESRF

Cultural Heritage



Natural Heritage





SOME ARTEFACTS ANALYZED AT THE ESRF IN 2016-2023 (NOT EXHAUSTIVE)



Inks on Papyri Carlsberg Collection, Copenhagen, Christiansen Herculaneum, Brun



Cimabue's Maestà of Ming porcelains Santa Maria dei Servi Institute (15th-16th C.), (1280 - 1285),L. Monico, Ph. Sciau, Perugia Toulouse



Ultramarine pigment Beijing Archaeological in Girl with a Pearl Earing, Mauritshuis, (1665), A. Gambardella, Amsterdam



Van Gogh's Sunflowers van Gogh Museum, (1888 - 1889),L. Monico, Perugia, Antwerp



Munch's Scream, Munch Museum (1910), L. Monico, Perugia



(1908-1913),

J. Langlois,

Paris



Miro's Femme dans la rue (1973), M. Ghirardello, Milano Today

Antiquity



Hellenistic Egyptian Blue Kos, (1st C. BCE) A. Kostomistopoulo, Oslo



Bamiyan Buddhist Leonardo da Vinci's paintings last Supper Afghanistan, (6th-9th C.) Santa Maria Delle Grazie Y. Taniguchi, (1495 - 1498)M. Cotte, Tokyo ESRF



Rembrandt's Night watch Rijksmuseum (1642), V. Gonzalez, Delft



Caspar David Friedrich's Wanderer above the Sea of Fog Hamburger Kunsthalle, (1818), I. Reiche, Paris



Porcelains. Sèvres manufacture End 19th Beg. 20th C. L. Verger, Paris





Picasso's Femmes Foundation Beyeler, (1907), M. Ghirardello, Milano

Ducos du Hauron early color photographs, 1870's, M. Cotte, ESRE ESRF The European Synchrotron

WHICH TECHNIQUES TO STUDY WHICH MATERIALS?







Revealing nature of ancient Egyptian inks



In collaboration with Thomas Christiansen¹, Poul Erik Lindelof ², Kell Mortensen², Kim Ryholt¹, Sine Larsen³

 Department of Cross-Cultural and Regional Studies (ToRS), Section of Egyptology, University of Copenhagen, Karen Blixens Plads 8, 2300 Copenhagen S, Denmark
 Niels Bohr Institute (NBI), University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark
 Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark

Papyrus from the P. Carlsberg collection, University of Copenhagen Tebtunis temple library, 1st - 3rd century CE Pathyris, late 2nd and early 1st century BCE





RESEARCH ARTICLE | ANTHROPOLOGY | 👌

Insights into the composition of ancient Egyptian red and black inks on papyri achieved by synchrotron-based microanalyses



Thomas Christiansen 🖾 , Marine Cotte 💿 🖾 , Wout de Nolf, 🖬 and Sine Larsen 💿 Authors Info & Affiliations

Edited by Katherine Faber, California Institute of Technology, Pasadena, and accepted by Editorial Board Member Tobin J. Marks September 21, 2020 (received for review March 10, 2020)

October 26, 2020 117 (45) 27825-27835 <u>https://doi.org/10.1073/pnas.2004534117</u>

SCIENTIFIC REPORTS

OPEN The nature of ancient Egyptian copper-containing carbon inks is revealed by synchrotron radiation based X-ray microscopy

Received: 31 August 2017 Accepted: 31 October 2017 Published online: 10 November 2017

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Thomas Christiansen^{1,7}, Marine Cotte^{2,3}, René Loredo-Portales⁴, Poul Erik Lindelof⁵, Kell Mortensen⁵, Kim Ryholt¹ & Sine Larsen⁶

SCiEnTiFiC REPORTS | 7: 15346 | DOI:10.1038/s41598-017-15652-7



2- INK COMPOSITION IN EGYPTIAN PAPYRI

WORKS LED BY

Thomas Christiansen, Sine Larsen, University of Copenhagen

SAMPLES

12 fragments of papyri from the Carlsberg Collection (Tebtunis temple library, 1st-3rd C. CE), with both red and black inks

QUESTIONS

Which are the components present in inks? A unique recipe? Iron and lead identified with laboratory techniques. Which compounds?





Part 1: how to obtain element maps?



X-RAY FLUORESCENCE (XRF)

To determine elemental composition





X-RAY FLUORESCENCE SPECTROSCOPY



Ejected electron



=> identification of elemental composition



X-ray fluorescence emission energies (eV)

Element	Kα ₁	Ka2	Kβı	La ₁	Lα ₂ Lβ ₁	ı Ц3 ₂	LY 1	Mα ₁	
3 Li	54.3								
4 Be	108.50								
5 B	183.3								
6 C	277								
7 N	392.4								
8 O	524.9								
9 F	676.8								
10 Ne	848.6	848.6							
11 Na	1,040.98	1,040.98	1,071.1						
12 Mg	1,253.60	1,253.60	1,302.2						
13 A1	1,486.70	1,486.27	1,557.45						
14 Si	1,739.98	1,739.38	1,835.94						
15 P	2,013.7	2,012.7	2,139.1						
16 S	2,307.84	2,306.64	2,464.04						
17 C1	2,622.39	2,620.78	2,815.6						
18 Ar	2,957.70	2,955.63	3,190.5						
19 K	3,313.8	3,311.1	3,589.6						
20 Ca	3,691.68	3,688.09	4,012.7	341.3	341.3	344.9			
21 Sc	4,090.6	4,086.1	4 460.5	395.4	395.4	399.6			
22 Ti	4,510.84	4,504.86	4,931.81	452.2	452.2	458.4			
23 V	4,952.20	4,944.64	5,427.29	511.3	511.3	519.2			
24 Cr	5,414.72	5,405.509	5,946.71	572.8	572.8	582.8			
25 Mn	5,898.75	5,887.65	6,490.45	637.4	637.4	648.8			
26 Fe	6,403.84	6,390.84	7,057.98	705.0	705.0	718.5			
27 Co	6,930.32	6,915.30	7,649.43	776.2	776.2	791.4			
28 Ni	7,478.15	7,460.89	8,264.66	851.5	851.5	868.8			
29 Cu	8,047.78	8,027.83	8,905.29	929.7	929.7	949.8			
30 Zn	8,638.86	8,615.78	9,572.0	1,011.7	1,011.7	1,034.7			
31 Ga	9,251.74	9,224.82	10,264.2	1,097.92	2 1,097.92	1,124.8			
32 Ge	9,886.42	9,855.32	10,982.1	1,188.00) 1,188.00	1,218.5			
33 As	10,543.72	10,507.99	11,726.2	1,282.0	1,282.0	1,317.0			
34 Se	11,222.4	11,181.4	12,495.9	1,379.10) 1,379.10	1,419.23			
35 Br	11,924.2	11,877.6	13,291.4	1,480.43	1,480.43	1,525.90			
36 Kr	12,649	12,598	14,112	1,586.0	1,586.0	1,636.6			
37 Rb	13,395.3	13,335.8	14,961.3	1,694.13	1,692.56	1,752.17			
38 Sr	14,165	14,097.9	15,835.7	1,806.56	6 1,804.74	1,871.72			
39 Y	14,958.4	14,882.9	16,737.8	1,922.56	6 1,920.47	1,995.84			
40 Zr	15,775.1	15,690.9	17,667.8	2,042.36	6 2,039.9	2,124.4	2,219.4	2,302.7	
41 Nb	16,615.1	16,521.0	18,622.5	2,165.89	2,163.0	2,257.4	2,367.0	2,461.8	
42 Mo	17,479.34	17,374.3	19,608.3	2,293.16	2,289.85	2,394.81	2,518.3	2,623.5	
43 Tc	18,367.1	18,250.8	20,619	2,424	2,420	2,538	2,674	2,792	
44 Ru	19,279.2	19,150.4	21,656.8	2,558.55	2,554.31	2,683.23	2,836.0	2,964.5	
45 Rh	20,216.1	20,073.7	22,723.6	2,696.74	2,692.05	2,834.41	3,001.3	3,143.8	
46 Pd	21,177.1	21,020.1	23,818.7	2,838.61	2,833.29	2,990.22	3,171.79	3,328.7	
47 Ag	22,162.92	21,990.3	24,942.4	2,984.31	2,978.21	3,150.94	3,347.81	3,519.59	
48 Cd	23,173.6	22,984.1	26,095.5	3,133.73	3,126.91	3,316.57	3,528.12	3,716.86	
49 In	24,209.7	24,002.0	27,275.9	3,286.94	3,279.29	3,487.21	3,713.81	3,920.81	
50 Sn	25,271.3	25,044.0	28,486.0	3,443.98	3,435,42	3,662.80	3,904.86	4,131.12	
51 Sb	26,359.1	26,110.8	29,725.6	3,604.72	3,595.32	3,843.57	4,100.78	4,347.79	
52 Te	27,472.3	27,201.7	30,995.7	3,769.33	3,758.8	4,029.58	4,301.7	4,570.9	
53 I	28,612.0	28,317.2	32,294.7	3,937.65	3,926.04	4,220.72	4,507.5	4,800.9	
54 Xe	29,779	29,458	33,624	4,109.9	_				
55 Cs	30,972.8	30,625.1	34,986.9	4,286.5	4,272.2	4,619.8	4,935.9	5,280.4	
56 Ba	32,193.6	31,817.1	36,378.2	4,466.26	4,450.90	4,827.53	5,156.5	5,531.1	
57 La	33,441.8	33,034.1	37,801.0	4,650.97	4,634.23	5,042.1	5,383.5	5,788.5	833
58 Ce	34,719.7	34,278.9	39,257.3	4,840.2	4,823.0	5,262.2	5,613.4	6,052	883
59 Pr	36,026.3	35,550.2	40,748.2	5,033.7	5,013.5	5,488.9	5,850	6,322.1	929





FIT OF XRF SPECTRA : PYMCA

PyMca

Faq

References SOURCE FORGI

Home Introduction Documentation

Welcome to the PyMca X-ray Fluorescence Toolkit Home Page. License Download



http://pymca.sourceforge.net/

Principles:

ESRF

• fit with constraints on the fitting parameters (detector characteristics,

detection geometry, matrix composition, excitation energy, etc.)

• complete emission line series (i.e., M, L or K series)





ADVANTAGES OF SYNCHROTRON SOURCES FOR XRF MAPPING





3- Beam energy (ies)



Elemental mapping







DEMO 1: MACRO-XRF MAPPING



Sample9 unfocused Cl map1 124*69 steps of 100µm

• Open the .edf files in sample9_CI_unfocussed (select one file; PyMca opens all)



ADVANTAGES OF SYNCHROTRON SOURCES FOR XRF





- 1- Flux = speed
- 2- Beam size
- 3- Beam energy (ies)



THE ID21 SCANNING X-RAY MICRO-SPECTROSCOPY END-STATION



Beam focussed with Kirkpatrick Baez mirrors (or Zone plates) Beam size: 0.3μm ver. × 0.7μm hor. Flux 10¹⁰ ph/s Energy range: 2.0-11keV



ZOOMING-IN THE SAMPLE

Macro and µXRF mapping at ID21



Egypt, 1st-2nd CE, P. Carlsberg 89



Beam size 0.3×0.7μm² Pixel size 0.5×0.5μm²

Beam size 0.3×0.7µm² Pixel size 4×4µm²

Beam size \varnothing 100µm Pixel size 100×100µm²



At the ESRF, beamlines offer beam size from ~1mm² down to 30×30nm²

T. Christiansen, M. Cotte, R. Loredo-Portales, P. E. Lindelof, K. Mortensen, K. Ryholt and S. Larsen, "**The nature of ancient Egyptian copper**containing carbon inks is revealed by synchrotron radiation based X-ray microscopy", *Scientific Reports, 7, 15346 (2017)*.



Part 2: how to obtain identification and location on organic compounds (binder)?



HOW TO IDENTIFY ORGANIC COMPOUNDS?

Towards the identification of lead compounds How to identify organic molecular groups?



µFTIR map on a fragment of ink



Infrared spectro-microscopy





FTIR ANALYSIS OF A FRAGMENT FROM PAPYRUS



Part 3: how to obtain identification and location on crystallized compound?



High lateral resolution X-ray diffraction (ID13, ex ID21, ID16B, ID11...)

- Micro-beam ($\leq 1 \times 1 \ \mu m^2$)
- 2D mapping for phase identification and localization

High-lateral resolution XRD ID13, ESRF

13 keV 2 x 2 µm² beam



Differentiate each micrometric layer
Qualitative only because of orientation effects



CaCO₃ PbCO₃ Pb₃(CO₃)₂(OH)₂

Towards the identification of lead compounds

How to identify and map crystalline phases?







The European Synchrotron



RESEARCH ARTICLE | ANTHROPOLOGY | 👌

Insights into the composition of ancient Egyptian red and black inks on papyri achieved by synchrotron-based microanalyses



Thomas Christiansen 🖾 , Marine Cotte 💿 🖾 , Wout de Nolf, 🖬 and Sine Larsen 💿 Authors Info & Affiliations

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SCiEnTiFiC REPORTS | 7: 15346 | DOI:10.1038/s41598-017-15652-7























GETTING BEAMTIME AT A SYNCHROTRON FACILITY: THE PEER-REVIEW PROCESS

Idea



High tech instruments



THE "HISTORICAL MATERIALS" BLOCK ALLOCATION GROUP: A NEW SHARED ACCESS



13 European teams + Metropolitan Museum

- ENS Paris-Saclay (former Rijksmuseum): V. Gonzalez
- Rijksmuseum (ex University of Antwerp, KIKIRPA): F. Vanmeert
- CNR-SCITEC: L. Monico
- ESRF, LAMS: M. Cotte, C. Holé, G. Robertson
- Courtauld Institute of Art: A. Nevin, A. Burnstock
- Politecnico di Milano: D. Comelli
- Rijksmuseum: K. Keune
- IRCP/C2RMF: I. Reiche
- Universitat Politècnica de Catalunya: N. Jiménez
- IRCP: G. Wallez
- TU Delft: M. Alfeld
- ISPC-CNR: A. Suzuki
- AXES: K. Janssens
- Metropolitan Museum (ex Univeristy of Cambridge): E. Purdy

https://www.esrf.fr/BAG/HG172



Heritage-bag@esrf.fr

Access to ID22 and ID13 ONLY! Twice a year at the 2 beamlines





First ring: partners of the initial BAG proposal Second ring: indirect partners through collaborations



ID22 : High-angle resolution XRD

- Energy: ~35 keV
- Scan range 2θ: 3 20°
- Analysis time: ~20 min/powder;~2 h/historical sample
- Instrumental function 2θ (FWHM of (111) Si peak) ~ 0.0027°
- Samples in capillaries
- ⇒ precise and sensitive detection of crystalline phases, their identification, and the characterization of their microstructural and structural properties



ID13 : High-lateral resolution XRD

- Energy: ~13 keV
- Analysis time: ~10 min -2 h/map (15ms/ pixel)
- Beam size ~ $2 \times 2 \mu m^2$
- Samples as thin sections (preferable) or cross-sections
- \Rightarrow stratigraphical distribution of crystaline phases at the micrometer scale



4 days every 6 months Local contact : Manfred Burghammer burgham@esrf.fr



THE "HISTORICAL MATERIALS" BLOCK ALLOCATION GROUP: A HIGH THROUGHPUT!

The success of the BAG relies on the capacity to analyze tens of samples per experiment.



The European Synchrotron | ESRF

THE "HISTORICAL MATERIALS" BLOCK ALLOCATION GROUP: A VERY EFFICIENT WAY TO TRAIN NEW USERS



Croatia, 1_USA, 2_UK, 1 Indonesia, 1 Spain, 3 Switzerland, 3 The Netherlands, 5 Belgium, 10 Italy, 17



A total number of 120 partners

TRAINING THROUGH EXPERIMENTS, COURSES AND TUTORIALS









SOME RECENT OUTCOMES OF THE HISTORICAL MATERIALS BAG

molecules

MDPI

Article

The "Historical Materials BAG": A New Facilitated Access to Synchrotron X-ray Diffraction Analyses for Cultural Heritage Materials at the European Synchrotron Radiation Facility

Marine Cotte ^{1,2,*}, Victor Gonzalez ^{3,*}, Frederik Vanmeert ^{4,5,*}, Letizia Monico ^{4,6,7,*}, Catherine Dejoie ¹, Manfred Burghammer¹, Loïc Huder¹, Wout de Nolf¹, Stuart Fisher¹, Ida Fazlic^{1,8}, Christelle Chauffeton^{9,10,11}, Gilles Wallez^{9,11,12}, Núria Jiménez¹³, Francesc Albert-Tortosa¹³, Nati Salvadó¹³, Elena Possenti¹⁴, Chiara Colombo 14, Marta Ghirardello 15⁽¹⁰⁾, Daniela Comelli 15⁽¹⁾, Ermanno Avranovich Clerici ^{4,16}(1), Riccardo Vivani ¹⁷, Aldo Romani ^{6,7}, Claudio Costantino ^{6,7}, Koen Janssens ^{4,8}, Yoko Taniguchi ¹⁸ Joanne McCarthy ¹, Harald Reichert ¹ and Jean Susini ^{1,†}

ACS

Lead(II) Formate in Rembrandt's Night Watch: Detection and Distribution from the Macro- to the Micro-scale

Victor Gonzalez",* Ida Fazlic", Marine Cotte", Frederik Vanmeert, Arthur Geste Steven De Meyer, Fréderique Broers, Joen Hermans, Annelies van Loon, Koen Jansse Petria Noble, and Katrien Keune



Since first beamtime in 2020-II:

- 18 publications •
- >25 oral presentations •
- >15 posters •



M. Ghirardello, Microscopy and micro analysis

> Cadmium yellow degradation in Miro's paintings, N. Gomez Lobon, Heritage Science

aint lave



Carbonation of fresco paintings, N. Oriols, Cement

and Concrete Research

[Mg²⁺]/[Ca²⁺

[Ca2*] [Mg2

SH105184-11



Black stains on the passepartout of **Codex Atlanticus Folio 843 by** Leonardo da Vinci, N. Guarnieri, Scientific Reports



SH105193-15

Architectural Bricks from **Khorsabad and Susa Sites:** Characterization of Black Glazes, E. Beauvoit, *Heritage*





X-ray and Infrared Microanalyses of Mona Lisa's Ground Layer and

Victor Gonzalez,* Gilles Wallez, Elisabeth Ravaud, Myriam Eveno, Ida Fazlic, Tiphaine Fabris,

Significance Regarding Leonardo da Vinci's Palette

Austin Nevin, Thomas Calligaro, Michel Menu, Vincent Delieuvin, and Marine Cot

- Unique insight accessible thanks to synchrotron-based techniques
- Most of the analyses are done on fragments, rarely on objects
- Most of the analyses track chemical composition (rather than morphology)
- Chemistry records track of original manufacturing processes and later degradation phenomena
- Often, different techniques are combined (portable/ lab / ESRF, X-rays/ infrared/ UV- vis...) as they offer various contrasts and information





Thank you for your presence and your attention!

Particular thanks to all colleagues involved in beamlines development and maintenance, in the operation of the ESRF and to all users, ESRF colleagues and services making this research possible

https://www.esrf.fr/BAG/HG172

Heritage-bag@esrf.fr cotte@esrf.fr



Li-Hill, 2019, Grenoble