ESRF	**Experiment title:** PIGMENT COMPOSITION AND 'PAINT POTS' BY COMBINAITION OF COMPLEMENTARY MICROANALYSIS TECHNIQUES	**Experiment number**: CH1777
Beamline: ID21 ID 18F ID22	**Date of experiment**: from: to: ID21 20 - 24 September 2004 (10 shifts) 13-19 July 2005 (18 shifts) ID22 09-12 March 2005 (10) and 17-21 November 2005 (14) ID18F 13-16 April 2005 (9)	**Date of report**: 01/02/06
Shifts: 61	**Local contact(s)**: Marine Cotte, Pierre Bleuet, Jean Susini	*Received at ESRF:*

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Report:

In this project, we aim at understanding the variation in the pigment composition used for ancient cosmetics or paintings and to introduce the notion of "*paint pot*" in the archaeological research: For determining the geographical origin of the minerals and their preparation (chemical/mechanical transformation, heating…), complexity and dissimilarities in composition can be possibly related to several sources of raw materials or different preparation processes. Consequently the analytical examination of the pigments makes it possible to characterise a "paint pot" as used for a short period in a workshop to prepare cosmetics or paintings. From all the data collected, we show in this report several striking results:

- **Trace elements in lead-based Greco-Roman make-up** were analysed at the beamlines ID18F and ID22. The powdered cosmetics made of isolated grains were analysed to identify their trace element signature. A focused X-ray micro-beam was successively tuned at 12 keV, below the L_{III} absorption edge of Pb, and 28 keV for global characterisation of the metal impurities. The X-ray fluorescence signal integrated over each single grain was detected against the X-ray micro-diffraction pattern collected in transmission with a bi-dimensional detector. From this signature we tried to identify provenances of the mineral ingredients in the make-up and distinguish between natural ores and synthesised products. We note the various compositions with very small amounts of silver, iron and cooper.

- **Identification of Mn-oxides in Greco-Roman make-up** : The main ingredients in a large proportion of black make-up are galena and carbon black. In the other cases, previous SEM observations have shown the presence of manganese oxides in cosmetics from Bactrian (2^{nd} millinium BC) and Georgia (Greek period). XAFS analyses with the micro focused beam at ID21 enabled us to identify the pyrolusite (MnO2) as the most frequently used Mn-pigment. A striking fact is that its optical properties are similar with those of galena. We can assume that pyrolusite was sometimes used in make-up in replacement of the traditional galena, giving the final product the same colour and metallic tune.

- **The pigments in the Matthias Grünewald's palette.** The physico-chemical signatures of the pigments, preparation layers and binding media are necessarily related with relevant practices and know-how of the artists. Measurements on ID21 and ID22 help us understand the uses of pigments in Northern European paintings at the beginning of the Renaissance (samples mainly from Grünewald). As the quantity of precious samples is so small and the mixtures are most complex, a microfocussed beam was necessary to characterise the various components. Our experience showed that not one analytical technique can achieve an unambiguous answers. Thus, combination of complementary and quantitative synchrotron µ-XRF, µ-XRD and µ-XANES techniques enabled us to identify the minerals, the trace elements and the chemistry and possible modification during ageing. Similarities and differences found in the study of ten samples brought to light the artist's know-how: what the artist's choice intended for special pigments, probably it was related to the respective different working properties: colour, adherence, stability, hardness? This work will continue during the second period of the LTP to obtain more data and try to answer to two main questions: Where did the artists get the pigments (in relation with a possible import/export trade market) ? What were the preparation processes discussed in details in early treatises (Pliny the Elder in Antiquity, Alberti, Cennino Cennini or Agricola in the XVth - XVIth century) ?

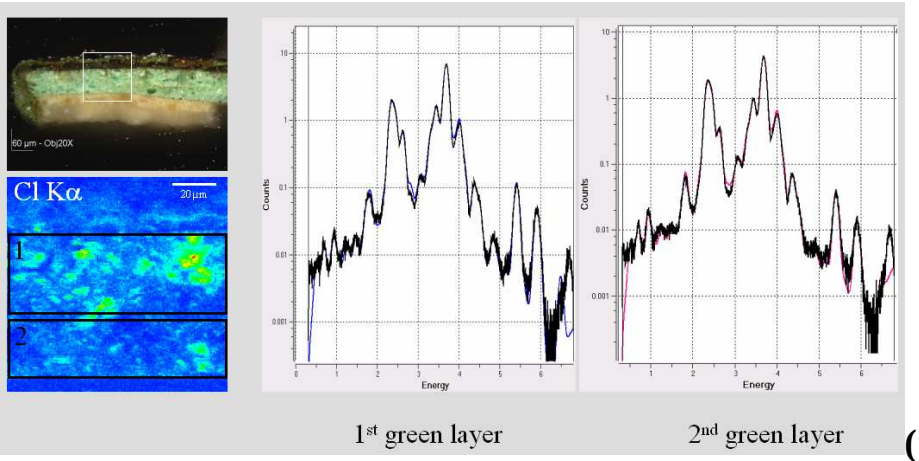
- **The Stibnite, an unexpected pigment in the Grünewald's palette**: Characterisation of pigments from Issenheim Altarpiece and another Grünewald's painting from the Bale Museum points out the presence of a specific pigment, the antimony sulphide stibnite. It was detected by XRF and identified by XANES measurements on ID21. Small grains of stibnite have been used to obtain a dark grey painting with a metallic shade, for the representation of an eagle or of armour. In that case, the main problem with the XRF imaging technique is the overlap of emission peaks: example S(K)+Pb(M); Sn(L)+Sb(L)+Ca(K). The identification of these pigments needs suitable deconvolution software. Armando Solé, BLISS Group ESRF, has developed the software PyMCA including a fitting program with all L and M lines and the automatic analysis of XRF map

Publications :

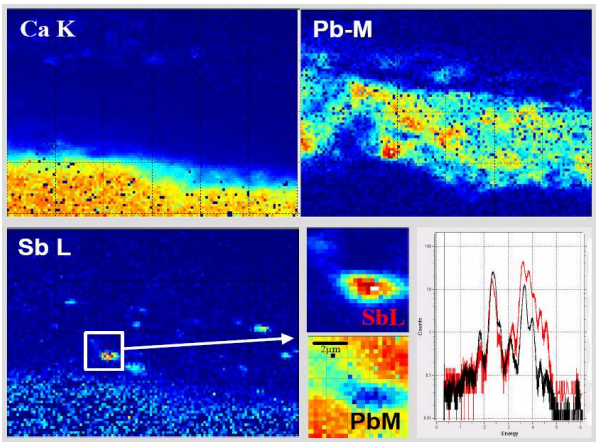
- WELCOMME E., WALTER Ph., VAN ELSLANDE E., TSOUCARIS G., (2006) – Investigation on white pigments used as make-up during the Greco-Roman period. To release in *Applied Physics A – Materials Science & Processing.*
- Techne (to be published)

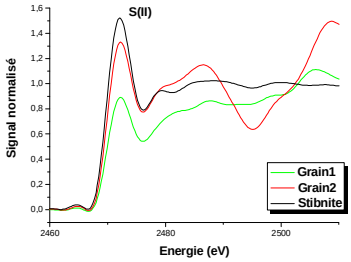
Communications :

- Identification of the painting techniques in Northen Europe at the beginning of the Renaissance by Synchrotron microimaging, Ph. Walter, E. Welcomme, E. Laval, M. Menu, A. Principaud, E. Van Eslande, M. Cotte,F. Fauth, A. V. Sole, J. Susini, E. Dooryhee, J.L. Hodeau, P. Martinetto, M. Anne, Synchrotron Radiation in Art and Archaeology (SR2A-2005), ESRF-CNRS joint workshop, Grenoble, France, 9-11 Fév. 2005
- Identification of paints pots by Synchrotron microanalysis- The example of Ancient cosmetics, E. Welcomme, J. Salomon, E. Van Eslande, Ph. Walter, M. Cotte, J. Susini, A. Simioniovici, P. Martinetto, E. Dooryhee, Synchrotron Radiation in Art and Archaeology (SR2A-2005), ESRF CNRS joint workshop, Grenoble, France, 9-11 Fév. 2005
- Investigation on white pigments used as makeup during the Greco-roman period, E. Welcomme, Ph. Walter, E. Van Elslande, G. Tsoucaris, E-MRS Spring meeting, juin 2005, Strasbourg (France)
- New Insights into pigment processing in Ancient Egypt, Ph. Walter - invited, E-MRS Spring meeting, juin 2005, Strasbourg (France)
- Ancient cosmetics and paintings studied by combination of micro-analytical techniques, M. Cotte, Ph. Walter, E. Welcomme, B. Fayard, J. Susini, C. Gratziu, A. Moscato, A. Bertagnini, XRM2005, Himeji, Japon, 26-30 Juill. 2005
- Powder Diffraction in Art and Archaeology – XX Congress of International Union of crystallography E. Dooryhée, P. Martinetto, M. Anne, J.-L. Hodeau, P. Walter, M. S. del Rio, juillet 2005, Florence (Italie)



(1)





	Fitting area of X-rays fluorescence signal after PyMCA treatment	
	Sb-Grain	**Pb-matrix**
S K	**590**	6
Pb M	650	**2067**
Sb L	**4529**	180
Ca K	770	689

(2)

X-ray fluorescence imaging, Example of 2 green layers in a cross-section from Issenheim altar piece. (1) Observation of the distribution of copper chrorides; (2) identification of 5µm long stibnite grains by XRF and µXANES.

Table of the analysed samples :

Sample	ID21 XRF	ID21 XANES	ID21 FTIR	ID22 XRF	ID22 XANES	ID22 XRD	ID22 tomo	ID18F
Grunewald G1	X	X					X	
Grunewald G4	X	X		X	X	X	X	
Grunewald G5	X	X					X	
Grunewald MGN1	X	X					X	
Grunewald MGN2	X	X		X	X	X	X	
Grunewald MGN3	X	X					X	
Grunewald MGN4							X	
Grunewald MGN5							X	
Grunewald MGN6							X	
Grunewald MGN7	X	X		X	X	X	X	
Grunewald MGN8	X	X		X	X	X	X	
Grunewald MGN10	X	X						
Grunewald MGN12	X	X					X	
Grunewald MGN13							X	
Grunewald MGN14							X	
F12208	X	X		X	X	X		
F12097	X	X						
162/8	X	X						
Paestum 1	X	X		X		X		X
Eleusis 1	X	X		X		X	X	X
Eleusis 2	X	X		X		X	X	X
Keramikos 1	X	X		X		X		
Keramikos 3	X	X		X		X		
Volos 1	X	X		X		X		X
Volos 2	X	X		X		X		X
Volos 439	X	X		X		X		X
Volos BE 16158				X		X		
Volos BE16683				X		X		
ThebesA11				X		X		
Pompei 06	X	X	X					X
E32A	X	X		X		X	X	X

In the second part of the LTP, we aim at compelting this table and studying more painting samples.