

# Discrimination of blue copper phthalocyanine polymorphs by chemometric analysis of micro-Raman results from paint layer samples of 'real fakes'

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INTRODUCTION



*Female act lying with cat*, oil on canvas - No. 112  
Supposedly Hermann Max Pechstein, 1909 (54,4 cm x 60,2 cm)  
peculiarities: **phthalocyanine**  
Results of the Samples **P1**, **P2** and **P10** are presented

The Rathgen Research Laboratory of the National Museums Berlin studied a group of paintings, supposedly from **1905-1927**, made by the **forger Wolfgang Beltracchi**.

By micro-Raman spectroscopy ( $\mu$ RS) **blue copper phthalocyanine** (CuPc or PB 15), a synthetic organic pigment commercialised from **1935**, was found.

Two of the analysed paintings are:  
No. 112 – *Female act lying with cat*  
No. 115 – *Cubistic still life*



*Cubistic still life*, oil on canvas - No. 115  
supposedly Fernand Léger, 1913 (55,4 cm x 38,0 cm)  
peculiarities: **rutile and phthalocyanine**  
Results of the Sample **P13** are presented

METHODE

Colour Index generic name	Crystal modification	Comment	Patent date
PB15:0	$\alpha$	not stabilized	1935
PB15:1	$\alpha$	stabilized against re-crystallization e.g. by chlorine substitution	1962
PB15:2	$\alpha$	resists flocculation	
PB15:3	$\beta$	fine dispersed $\beta$ -form	1950
PB15:4	$\beta$	resists flocculation	
PB15:5	$\gamma$	less commercial significance	
PB15:6	$\epsilon$	stabilized, un-substituted	1962

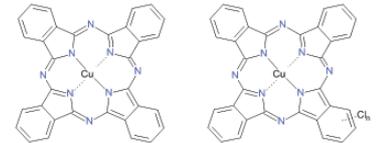
## Blue copper Phthalocyanine (CuPc):

- occurs in several **crystal modifications**
- chemically modifications** may be introduced
- may contain **additives**

The  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\epsilon$ -forms were used as **pigments**

**Patents** give information on date of commercialisation

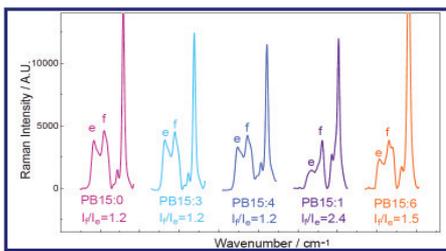
**Discrimination** of CuPc polymorphs  $\rightarrow$  help **DATING**



CuPc (left) and a chlorinated form (right) to prevent re-crystallisation

**Raman:** peak intensity ratios

$\rightarrow$  identification of crystal modification



Raman spectra (1250-1115  $\text{cm}^{-1}$ ) from dry reference pigments

The discrimination was made by a linear discriminant analysis (**LDA**)<sup>[1]</sup>; a supervised classification method, which means that the dataset has to be split into a training set – used to develop the classification model and a validation set, to evaluate the outcome from the analysis. Twelve discriminant intensity ratios have been used as variables of the LDA. The LDA classification of paint samples based on data from dry pigments as training set was found to be better than 90 % (expressed as % of correct classified unknown samples).

Twelve discriminant intensity ratios from dry pigments

Intensity ratios	Wavenumber ranges for the selection of the local maximum ( $\text{cm}^{-1}$ )
$I_{745}/I_{678}$	(740–755)/(670–680)
$I_{1189}/I_{1214}$	(1175–1195)/(1205–1220)
$I_{480}/I_{593}$	(475–485)/(585–595)
$I_{950}/I_{1005}$	(945–955)/(1000–1010)
$I_{1521}/I_{678}$	(1515–1525)/(670–680)
$I_{1141}/I_{950}$	(1135–1145)/(945–955)
$I_{480}/I_{255}$	(475–485)/(250–260)
$I_{480}/I_{172}$	(475–485)/(165–180)
$I_{950}/I_{829}$	(945–955)/(820–835)
$I_{950}/I_{1446}$	(945–955)/(1440–1455)
$I_{1141}/I_{1105}$	(1135–1145)/(1095–1110)
$I_{775}/I_{715}$	(765–780)/(705–720)

RESULTS

**Four samples** analysed:

**CuPc-blue** was found in **blue and green** paint

The **peak intensity ratios** of the Raman spectra from these samples were used to **identify the crystal modification** by chemometric analysis.

Colour	Sample name	Highest Group		Second Highest Group	
		predicted group	P(G=g   D=d)	predicted group	P(G=g   D=d)
blue	112_P1_c	alfa	1,000	epsilon	,000
	112_P1_d	alfa	,977	epsilon	,022
	112_P1_dbis	alfa	,999	epsilon	,001
	112_P1_e	epsilon	,999	alfa	,001
	112_P1_f	alfa	,817	epsilon	,183
green	112_P2_b	beta	,923	alfa	,077
	112_P2_d	beta	1,000	alfa	,000
	112_P2_e	alfa	,994	beta	,004
greenish blue	112_P10_b	alfa	,579	epsilon	,420
	112_P10_c	beta	,621	alfa	,378
	112_P10_d	beta	,991	alfa	,008
	112_P10_e	alfa	,999	beta	,001
	112_P10_f	alfa	,976	beta	,023
green	115_P13_b	beta	,999	alfa	,001
	115_P13_c	beta	1,000	alfa	,000
	115_P13_d	beta	1,000	alfa	,000

Painting	Sample code	Sampling area	Pigments detected by $\mu$ -RS
<i>Female act lying with cat</i> No. 112	<b>P1 (112)</b>	<b>Blue</b>	<b>PB15, PB29</b>
	<b>P2 (112)</b>	<b>Green</b>	<b>PB15, PY34</b>
	<b>P10 (112)</b>	<b>Turquoise</b>	<b>PB15</b>
<i>Cubistic Still Live</i> No. 115	<b>P13 (115)</b>	<b>Green</b>	<b>PB15, PY34</b>

## CONCLUSIONS

Paintings contain  **$\beta$ -CuPc**



Production date **after 1950**

[1] Defeyt et al. (2013)

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