Historical and scientific identification of an early XXth century artist pigments' collection

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The availability of chemically and colorimetrically exact references on painters' pigments is very important in order to distinguish the artistic employment of the various materials from their use during conservation treatments. For this purpose it is started a systematic campaign of scientific analyses on an early XXth century pigments collection belonged to famous florentine restorers, in order to obtain chemical, physical and historical classification of each material. The aim of research is to characterise all pigments in a database periodically uploaded and integrated with new analytical data, by supplying references on the products commercialised between 1850 and 1950 that were largely used for conservation treatments.

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Introduction

Chemical composition of artistis' pigments is known from recipes contained in documentary sources and scientific analyses executed on paintings, where the pigments are variously mixed and always bound in vehicle which the aging and alterations can modify their perception. The identification of original hue of ancient pigments can be questionable, while chromatically better turns out the situation of modern pigments synthetised in laboratory, largely employed since early XIXth century. In this case, their industrial production has sometimes returned the chemical composition difficult for the lacked correspondence with what declared by producers in their labels.

Thus the study of an early XXth century pigments' collection belonged two famous florentine restorers represents an opportunity to closely relate the scientific identification and the history of pigments' industrial production.

The collection (Figure 1) is composed by 190 glass vessels containing pigments in powder, divided in two main set: in the first series, vessels with variable but medium great dimensions are gathered (those greater are high 4.5 cm and 9.5 cm in diameter of vessel's bottom, while the smaller are high 3 cm and wide 3 cm in diameter). The second series is formed by original glass phials of 1.5 cm in diameter, and closed with screw caps tin in two sizes: high standard in 8.7 cm and the other smaller of the half (4.8 cm) for more expensive pigments.

Figure 1: Pigments in the collection.

In order to avoid any dispersion, the vessels have been photographed and numbered, also to project the systematic classification and to prepare diagnostic campaign for scientific pigments' identification.

Preliminary research put attention to vessels' first series without producers label, because the identification of second series will be easier by consulting historical catalogue of manufacturers that are sometimes very famous and still active on artistic materials market, such as Winsor & Newton, Reeves & Sons, Scheveningen Holland, Lechertier Barbe, Kreul.

On the basis of the preliminary results of the research, still in progress, the agreement between the composition declared on the label and the material actually contained in the vessels was verified relating to Emerald green, Oxide of Chromium and Viridian by Winsor & Newton.

Such data testifies as much very rarely today it is found a total coincidence. Since XIX-century the discussion (but also the controversy) on the best quality of industrial products commercialised by chemistry was particularly lively [20,25].

Informations reported from florentine restorer Alessandro Gori, current owner of collection that has received it in inheritance from the father Paolo, also restorer, date the pigments to the end of XIX century and early XX century. The labels applied on some vessels and glass tubes seem confirm this datation. These are written in German (typewritten and handwritten), english and italian language (typewritten), setting the provenance of some pigments from Cesare Pegna, owner since 1860 of a florentine apothecary selling also pigments in powder.

The typewritten label of a vessel containing «Bianco di Piombo. Eligio Di Volo» returns to another florentine pigments' manufacturer, active since 1915.

It seems reasonably correct to affirm the florentine birth of the collection. In the second half of the XIX century Florence became the meeting point for several German artists (i.e. Arnold Böcklin) and restorers trained in the cultural environment of Munich Academy [20]. The well known Otto and Augusto Vermehren, protagonists of the most important florentine painting restorations, were the early owners of the pigments today included in this collection.

Otto Vermehren born in Güstrow in 1861, started his activity as a painter at the Kunstschule in Weimar and then at the Munich Academy (1880-1884), where was influenced by Anselm Feuerbach (1829-1880), follower of Arnold Böcklin, which was in advance painting professor at the Weimar Academy (1860-62), before moving to Munich (1871 and 1876).

Vermehren lived in Florence for the first time between 1887 and 1890. Here he married Margherita Papini. His son Augusto was born in the town in 1888, but two years later the family came back to Munich, to work as a restorer close to Alois Hauser, at the Königlich-Bayerischen Zentralgemälde-Galerie. In 1891 Otto became the chief restorer at the Kunstmuseum in Basel.

In 1900 he went again in Florence, where he started an activity as painter and copyst (after Titian, Rubens, Rembrandt), but mostly as restorer in florentine Galleries (Uffizi and Pitti). In 1916 he went back to Güstrow, where he died in 1917.

During his stay in Florence he spent a lot of time with Arnold Böcklin, who had bought a cottage in San Donato di Fiesole, where he died in 1901, bequeathing to Otto his pigments [19].

Thanks to his deep knowledge about the ancient painting techniques, learned during his academic training, Otto Vermehren was instructed to lead some difficult restorations on paintings in the Uffizi Gallery. A severe debate involved these treatments, regarding particularly the cleaning and varnishing phases [9,10].

Otto's son, Augusto Vermehren (Florence 14.01.1888 – 15.12.1978), after an artistic training at the Stuttgard Academy and an apprenticeship with Max Klinger, became a restorer working with his father in the Uffizi Gallery. Keen on chemistry and physics, he carried out scientific analyses to identify ancient pigments and binders. He addressed his work also to the photography as scientific documentation of painting restoration, by using, since 1914, a stereoscopic device Voigtländer.

In 1934 he set up the Restoration Laboratory in the Uffizi Gallery, under the direction of Ugo Procacci. In 1935 he designed a stereo-radiography equipment able to investigate panel and canvas painting. The prototype of this instrument was assembled in Florence by Berardi company, then manufactured (since 1950) and retailed by Rich. Seifert & Co.

From 1949 he methodically used to provide a documentation about his restorations by means macro-, IR-, stereo- and UV-photography. Due to his technical and scientific knowledge, in 1949 he was appointed in the Technical committee (Consiglio tecnico) of the Istituto Centrale del Restauro in Rome, directed by Cesare Brandi. He taught and cooperated in the scientific laboratories arrangement at the same Institute until 1957, spending the experience acquired during the restorations on the *Annunciazione* by Antonello da Messina, *Sant'Anna Metterza* by Masaccio and Masolino, the *Four philosophers* by Rubens and *Portinari's triptych* by Hugo van der Goes [4,9,19,23].

Materials and Instruments

The items of the collection were described according to the *Pigments Compendium* [8] and to previous researches leaded on pigments' collection [7,12,14], by using a report form structured as showed in Figure 2.

Researches on the catalogue of the pigment manufacturer were started in order to obtain some information about the chronology of the pigments included in the collection [3,6,13,21,24].

Pigments' samples have been examined under reflected, transmitted polarised light and epi- UV fluorescence microscope (OM) for the study and documentation of optical characteristics, XRF spectrometry for elemental characterisation (XRF), XRD analyses to identify mineral compound (XRD) and FT-IR spectrometry to investigate organic compound (FT-IR).

Identification • Reference number (item) • Producer • Denomination • Macroscopic description • Colour • Appearance
Description in O.M. – reflected light • Overall colour • Colour distribution • Saturation • Particle grain size • Grain size distribution • Grain shape • Geometry • Roundness • Sphercity • Relief of the edges • Facrtures • Aspect of the surfaces • Notes
Description in O.M. – transmitted light • Transparency • Pleochroysm • Briefringence Notes
Analyses • XRF spectrum • XRD spectrum • FT-IR spectrum
Chemical composition

Figure 2: Illustration of report form in database.

Results and Discussion

Tables 1 – 4 summarise the pigments manufactured by industrial producers.

Alizarin Crimson	Indian red
Alizarin Orange	Italian Pink
Alizarin Yellow	Lacca Monaco
Antwerp blue	Light red
Brown Madder	Magenta
Brown Madder n. 46	Mars Yellow
Burnt Carmine	Naples Yellow
Burnt Sienna	Oxide of Chromium
Cadmium deep	Pale Vermilion
Cadmium yellow extra pale	Raw Sienna
Carmine Fine	Raw Umber
Cerulean Blue	Rose dorée
Cobalt Blue	Rose Madder
Cobalt green	Scarlet vermilion
Cobalt violet	Sepia
Cremnitz white	Sky blue
Crimson Lake	Vandyke Brown
Crimson Madder	Vermilion
Elfenbeinschwarz	Viridian
Emerald green	
Flake white	
French ultramarine	

Table 1: Winsor & Newton pigments in the collection.

Blanc de Titane-oxide de titane	Ocre jaune de la haye-extraclaire
Bleu caeruleum-stannate de cobalt	Raw Umbra-A3
Bleu d'Outremer-sulf de sod. et silic. d'al.	Rouge de Venise-oxide de fer
Bleu d'Outremer Guimet-sulf. de sod. et silic. d'al.	Terre d'ombre brulée-terre d'origine calcinée
Belu de cobalt	Terre d'ombre naturelle-terre d'origine lavée calcinée
Bleu de cobalt-aluminate de cobalt	Terre de Sienne brulée
Vleu de Paris-cyanure de fer	Terre de Sienne claire
Bleu mineral-cyanure de fer	Terre de Sienne foncée
Cerulean Blue	Terre d'Ombre brulée
Noir d'ivorire-ivoire calciné	Terre Verte
Ocre brune	Vert Emeraude Foncé-oxide de chrome hydraté
Ocre d'or-terre d'origine	

Table 2: Scheveningen, Holland pigments in the collection.

Van Dyck Brown	Burnt Siena
Vermilion	Blue cobalt
Raw Siena	Terre Verte

Table 3: C.C. Macroo M&C, Stockton.

Reeves and Sons	Crimson Lake Yellow Ochre
Lechertier Barbe Ltd. London	Terre Verte
W. Nicolson, London	Cobalt Blue
C. Kreul Kunstler, Stuttgart	Dunkler Oker n. 16

Table 4: Other producers.

This study, still in progress, on the history of manufacturers and suppliers have currently stated that the labels by Scheveningen, Holland belong to most ancient manufacturer of pigments active in Low Countries since XVII century and today named Old Holland Scheveningen.

Reeves & Sons, manufacturer of two pigments in our collection, is the earliest industrial producer of artist materials, founded in London by William Reeves (1739-1803) in 1766. In 1780, joining to his brother Thomas (1736-1799), commercialised watercolour cakes awarded by the Society of Arts and the earliest colour boxes.

In 1891 the company changed his name in «Reeves & Sons Ltd», that is cited on the labels applied on the vessels of the collection, such as *Yellow ochre* e *Crimson Lake*, certainly produced after this date [6].

Lechertier Barbe Limited in London, 95 Jermyn Street, was established in 1827 by Charles Barbe, a french musical instruments producer, who in 1849 formed a partnership with Louis Lechertier, french brushstroke supplier and registered trade-mark Lechertier Barbe Ltd from 1898 to 1970 [5,6,25,26].

Winsor & Newton, founded in 1832 by William Winsor (1804-1865, chemist and artist) and Charles Newton (1805-1882, artist) in 38 Rathbone Place, kept there its original head-office until 1938. The pigments of the collection should be produced between 1881, when the company became «Winsor & Newton Ltd» as indicated of the label, and 1938, when the company moved away from Rathbon Place [3,13,21,24].

The examination of Winsor & Newton Catalogue supplies other information on chronology of pigments: the “Italian Pink” is cited only in Nineteenth-Century catalogue [24], because after a controversial debate on pigment quality the manufacturer stated to make chemical composition known [1] and declared also publicly permanence and stability of their products [2,21].

We cannot be able to recover any information on London manufacturer W. Nicolson and also on «C. C. Macroo, M. & C. Stockton», not currently active with this denomination or perhaps identifiable with a supplier selling artist’s materials by different producers. This is the case of *Alizarin Crimson* by Giuseppe Gianni of Florence which provenance arises from Winsor & Newton.

Historical provenance of 94 vessels with typewritten and handwritten labels has been particularly difficult, for the lack of any other indication. These labels were applied by the original owners of collection, i.e. Otto and Augusto Vermehren that wrote presumably the handwritten labels and those typewritten respectively. In effect it is conjecturable that handwritten labels are assignable to Otto as it is showed on *Goldocker London* containing initials “OV” (Otto Vermehren).

Same writing appears on the label of *Braun Pink* together with a red dot and the number 25, denoting a past inventory which today is totally lost. For understanding the principles of inventory, it is observed the presence of dots in two series (red and green) with independent numeration indicating the clean separation between the two series red and green.

In the red series they remain 37 vessels today, with fragmentary numeration from n. 2 and n. 82, while the green series appears more incomplete with the actual 8 vessels numerated from n. 1 to n. 32.

Also stating a serious loss of materials, it is observed that the majority of labels in red series is typewritten, while only the two labelled vessels in green series bring the pigments’ denomination

handwritten. It could therefore be supposed that the green series is the most ancient and perhaps it was pertaining to the pigments' nucleus of Otto Vermehren left him in inheritance by Arnold Böcklin.

Researches on pigments used by swiss painter were carried out in order to verify this hypothesis. The scientific examinations executed for the first time between 1969 e 1974 by Richter and Härlin [17,22] cover a particular importance to this classification, because those investigations involved chemical analysis of 70 pigments' samples supplied by Augusto Vermehren in 1972. Pigments' denomination with corresponding numeration is found in two existing vessels, but they show a too much recent appearance for being able to assign them to the inheritance received from the father. It is mainly possible that original vessels were delivered to the german researchers for their analyses, replacing them with modern jars of baby food.

The pigments in these jars are labelled with the same name and number adopted in Böcklin's collection: *Krapplack, rosa n. 50* and *Dunkler Ocker n. 16*, with annotated provenance of pigment manufactured by Carl Johann Dietrich Kreùl, in 1838 founder of a fine pigments factory well known in the end of XIX century and still appreciated today (C. Kreul Kunstler, Farben Fabrik, Stoccarda). Scientific analyses carried out in that circumstance can be usefully compared with present research, still in progress, relating currently to the pigments and dyestuff listed in Table 5.

Code	Colour	Manufacturer	Label Denomination	Analyses	Composition
1	Yellow	Reeves & Sons	Yellow ochre	OM – XRF	Yellow Ochre
2	Yellow	Winsor & Newton	Italian pink	OM – XRF	Organic Dye, Zinc Oxide
3	Brown		Böcklin: Morellen Salz	OM – XRF	Morellone
4	Yellow	Winsor & Newton	Brown Pink	OM - XRF - FT-IR	Quercitron
5	Red	Reeves & Sons	Crimson Lake	OM - XRF - XRD	Cinnnabar, Tin sulphur
6	Red		Krapplack rosa (Böcklin)	OM - XRF - XRD	Red Lake, amorphous substrate
7	Green			OM – XRF	Cadmium Yellow, Viridian
8	Green	Pegna	Verde di cobalto	OM – XRF	Rinmann Green
9	Green			OM – XRF	Malachite
10	Green		Zinobergrün Kl.	OM – XRF	Scheele Green
11	Red		Rosso a calza Kl.	OM – XRF	Red Earth
12	Blue		Indaco Kl.	OM - XRF - XRD	Ultramarin
13	Orange			OM – XRF	Mine
14	Yellow		Chromgelb hell Kl.	OM – XRF	Chrome Yellow
15	Red		Rosso indiano Kl.	OM – XRF	Indian red
16	Red			OM – XRF	Vermilion
17	Yellow		Goldocker. London OV.	OM – XRF	Yellow Ochre
18	Blue		Kobaltblau Kl.	OM – XRF	Ultramarin
19	Blue		Ultramarin Kl.	OM – XRF	Ultramarin
20	Blue	Pegna	Blu verde solfuro Sod Silic Alluminio	OM – XRF	Ultramarin
21	Yellow		Kässler Erde mittel Kl.	OM – XRF – XRD	Yellow Ochre (Goethite)
22	Red		Fresco lack Kl.	OM – XRF – XRD	Red Lake, Baryte
23	Red		Lacca garanza Kl.	OM - XRF – XRD	Red Lake, Baryte, Celestine, Cesanite
24	Red	Winsor & Newton		OM – XRF	Red Lake
25	Blue			OM - XRF	Prussian Blue
26	Green		Verde stabile Kl.	OM - XRF	Lake
27	Blue			OM - XRF	Cobalt Blue
28	Green			OM - XRF	Emerald Green
29	Blue		Ultramarin violett Kl.	OM - XRF	Ultramarin

30	Black			OM - XRF	
31	Blue			OM - XRF – XRD	Baryte, Zinc Oxyde
32	Green		Terra verde Bucarest Kl.	OM - XRF	Green Earth
33	Green		Grüne Erde	OM - XRF	Rinmann Green
34	Black		Sepi(a) Kl	OM - XRF	Sepia
35	White	Eligio di Volo	Bianco di piombo	OM - XRF	Lead White
36	Green		Verde Vagone	OM – XRF	Lake
37	White			OM – XRF	Lead White
38	Black		Nero vite	OM - XRF	
39	Green		Veroneser grüne Erde Kl.	OM - XRF	Emerald Green
40	Orange			OM - XRF	Mine
41	Red		Lacca carminata Kl.	OM - XRF	Red Lake
42	Yellow			OM - XRF	Yellow Ochre
43	Brown		Terra di Siena bruciata	OM - XRF	Raw Siena
44	Brown		Terra ombra Kl.	OM - XRF	Burned Siena
45	Yellow		Gebrannte grüne Erd Kl.	OM - XRF	Earth
46	Green			OM - XRF	Viridian
47	Yellow		Kassler : Erde Kl.	OM - XRF	Yellow Ochre
48	Orange			OM - XRF	Lake
49	Brown			OM - XRF	Earth
50	Brown	Pegna	Terra	OM - XRF	Earth
51	Green	Winsor & Newton	Emerald green	OM – XRF	Emerald Green
52	Green	Winsor & Newton	Oxide of chromium	OM – XRF	Vert emeraude
53	Green	Winsor & Newton	Viridian	OM – XRF	Viridian
54	Yellow	Winsor & Newton	Naples yellow	OM – XRF	White lead, Yellow ochre
55	Yellow	Winsor & Newton	Alizarin yellow	OM – XRF	Alizarin yellow
56	Red	Winsor & Newton	Pale vermillion	OM – XRF	Vermillion
57	Red	Winsor & Newton	Scarlet vermillion	OM – XRF	Vermillion
58	Red	Winsor & Newton	Light red	OM – XRF	Red earth
59	Orange	Winsor & Newton	Alizarin orange	OM – XRF	Alizarin orange
60	Red	Winsor & Newton	Alizarin Crimson	OM – XRF	Alizarin Crimson
61	Red	Winsor & Newton	Crimson lake	OM – XRF	Crimson lake
62	Red	Winsor & Newton	Magenta	OM – XRF	Realgar
63	Red	Winsor & Newton	Indian red	OM – XRF	Indian red
64	Brown	Winsor & Newton	Brown madder	OM – XRF	Alizarin + Copper compound
65	Black	Winsor & Newton	Sepia	OM – XRF	Sepia
66	Brown	Winsor & Newton	Raw umber	OM – XRF	Raw umber
67	Blue	Winsor & Newton	Cerulean blue	OM – XRF	Cerulean blue
68	Blue	Winsor & Newton	Antwerp blue	OM – XRF	Antwerp blue
69	Blue	Winsor & Newton	Sky blue	OM – XRF	Zinc oxide, Chrome blue

Table 5: List of materials analysed.

Often the denomination cited in the label does not correspond the chemical composition of pigment contained in the vessel, so also the labels omit to declare some not secondary components. For example, the pigment named “Italian pink” by Winsor & Newton contains an organic compound compatible with Quercitron dye cited in 1896 Winsor & Newton Catalogue [24], but it is coupled together with plentiful quantity of zinc oxide not mentioned by manufacturers. Thus the red lake by Reeves & Sons is forged with vermilion and tin sulphur, or artificial ultramarin takes often the place of cobalt blue or indigo.

Scientific analyses were carried out also for the characterisation of lakes and other dyestuff substrates, generally made out of aluminium or calcium compound [15,16]. On the contrary, in the samples examined, the substrates seem to be constituted by amorphous compounds (probably glass) or baryte.

Baryte appears often associated with strontium and calcium, generally as sulphates, and then its presumably origin is a natural mineral where barium sulphate and celestine are both present (Figure 3). In synthetic barium sulphate, the strontium is in fact absent [11,18], such as in sample 22 where also its fine grain substrate suggests an artificial origin (Figure 4).

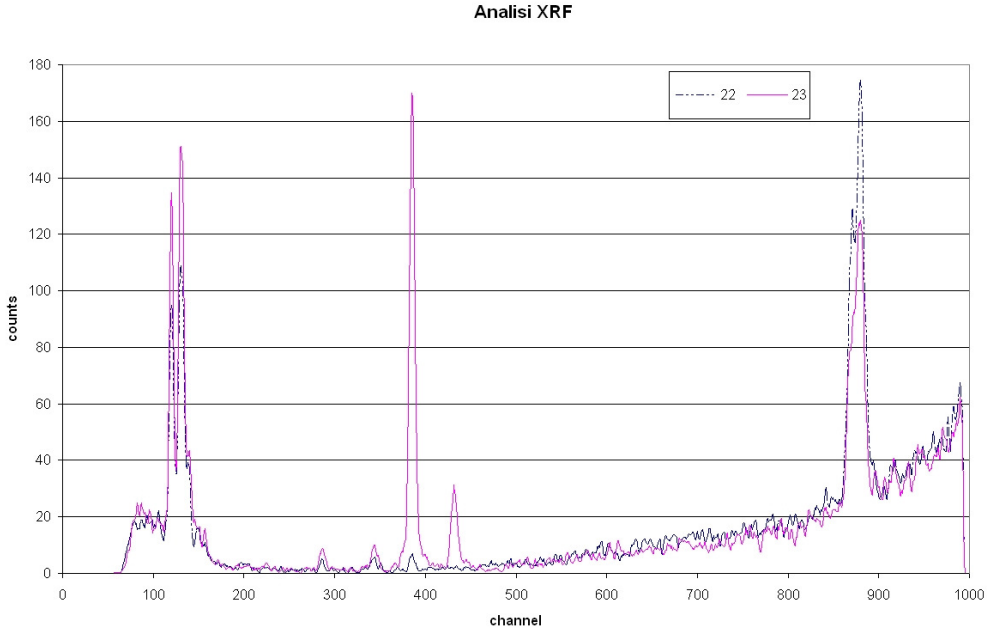

Figure 3: Item # 22 and 23. XRF spectra.

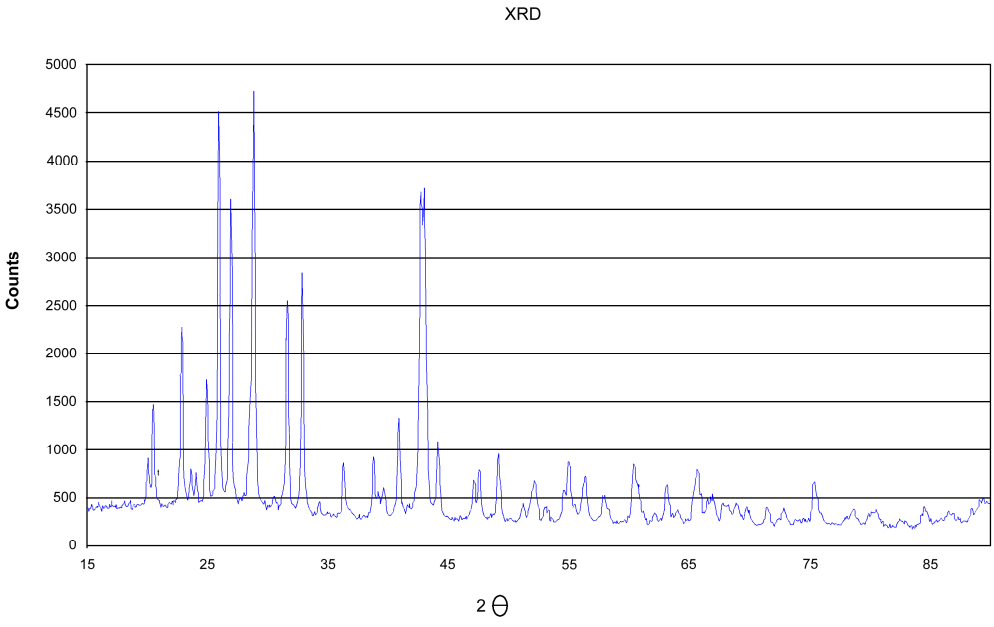

Figure 4: Item # 22. XRD spectrum.

The analysis of Winsor & Newton Brown madder has shown the presence of an organic dyestuff, Alizarin, mixed to a copper compound, detected by XRF, maybe used to precipitate the Alizarin. This practice was generally described for Indian purple [8], where copper sulphate is employed to precipitate cochineal dyestuff. Since the organic compound here identified isn't cochineal but Alizarin, the practice could be extended also to precipitate this dyestuff, maybe also in ancient time, as can be suggested by copper detection in XRF analyses of many lake pigments of XVII century.

Conclusions

Pigments' collection examined testifies like for all 19th and early 20th century the artistic experimentations and pigments' production found in German academic and in particular in Munich Academy a reference point especially rich and vibrant. A specific attention was devoted to the quality and the permanence of painting materials, including also the pigments used by the restorers. The attention paid to this aspect by the German researchers was higher than the one showed by the coeval industrial production in France (Lefranc) or English-speaking countries, but this knowledge was completely lost in the second world war.

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