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POWDERY PIGMENTS FROM THE ORIGINAL MATERIALS COLLECTION OF MUNCH: CONSERVATION TREATMENT AND ANALYTICAL CHARACTERIZATION

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Abstract

This contribution focuses on the study and preservation of 14 out of 35 powdery pigments in original paper bags. These are part of the artist materials reference collection at the Munch Museum in Oslo. The challenge of this study consists in the lack of information about the year of purchase of the pigments and its content. Some information is provided by the manufacturer's handwritten notes, some of them are, however, unreadable and a few bags have no information, nor on manufacturer or on its content. Munch has used at least four known Oslo based manufactures and some of the information from these paper bags could help giving at least some dating. Some relate to the name change of the city, from Kristiania to Oslo in 1925. Other information relates to the manufacturer's history, writing style, logos, addresses and telephone numbers. So far, the dating is the following: 1900-1925, 1922-1925 or after 1922. Some of the original paper bags, were in a very poor state and some containing highly hazardous pigments. The damages were significant and some relates to previous handling; such as tears, others had large, corroded holes on bottom or sides. All these required conservations to enable further storage of the pigments and to prevent additional damage from handling. Several bags were also stained with its powdery pigment which compromised the conservation by choosing a non-aqueous treatment. Heat activated adhesive with BEVA® 371 film lined with hand-colored Japanese tissues was applied for bridging of tears and infills of holes. 14 different pigments (of white, yellow, red, blue and green colours) were analyzed using ATR-FTIR, pXRF, SEM-EDS, XRD, Raman spectroscopy and synchrotron-based far-infrared spectroscopy for understanding their chemical composition. The analytical characterization shows a palette of pigments and lakes as one could expect from the first half of 20th century. Apart from common pigments and extenders such as chrome yellow, cadmium yellow, Prussian blue, barium sulfate and others, an amorphous silicate was found which is assumed to create texture effects or is the raw material for production of waterglass. One of the cadmium yellow samples has a remarkable content of cadmium carbonate which may be related to the production method and/or the degradation of cadmium yellow. In one sample a hydrated calcium carbonate occurs. This study opens future research regarding this artist's collection, adding new knowledge about Munch's own use of art materials but also in general on modern paint materials.

Keywords: *Powdery pigments, Art reference materials, Manufactures, Edvard Munch*

Introduction

This contribution focuses on the study and preservation of 14 out ot 35 different powdery pigments in original paper bags, part of the artist materials reference collection at the

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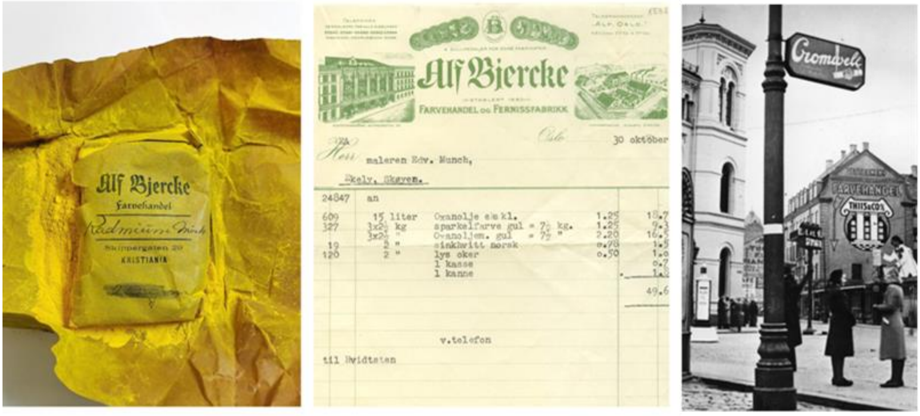
Munch Museum (MUNCH) in Oslo [1]. The challenge of this study consists in the lack of information about the year of purchase of the pigments and its content provided by the manufacturer on those without any handwritten notes.

Munch has used at least four known Oslo based manufactures and some of the information from these paper bags could help with giving at least some approximate dating (Fig. 1). Some could relate to the name change of the city, from Kristiania to Oslo in 1925.



Alf Bjercke
FARVEHANDEL OG FERNISSFABRIKK
Oslo 30 oktober
Herr maleren Edv. Munch,
Ekely, Skøyen.
24847 an
609 15 liter Ovanolje e/s kl. 1.25 18.7
327 3x2½ kg sparkelfarve gul = 7½ kg. 1.25 9.3
3x2½ " Ovanoljem. gul = 7½ " 2.20 16.5
19 5 " sinkhvitt norsk 0.98 1.5
120 2 " lys oker 0.50 1.0
1 kasse 0.7
1 kanne 1.2
49.6
v.telefon
til Hvidtsten

Fig. 1. Paper bag with cadmium yellow pigment bought from Alf Bjercke; original receipt for 2 kg of Norwegian Zinc White from Alf Bjercke, dated 1933; image from Oslo with one of the manufacturers (Farvehandel) for paint materials

Other information relates to the manufacturer's history, writing style, logoes, addresses and telephone numbers. So far, the dating is suggested as following: 1900-1925, 1922-1925 or after 1922. This suggests that most of the pigments have been purchased after Munch moved home to Norway in 1909. After several years living abroad, particularly in Germany, he first setteled in the southern town of Kragerø. His friend, Christian Gerløf, writes that in Kragerø Munch bought quantities of powdery pigments in large glass jars and made his own paints, glue paints are mentioned [2]. Later in 1916 Munch bought Ekely, at that time situated in the close outskirts of Oslo, where he lived and painted until his death in 1944. As several of the pigment bags are from Oslo-based manufacturerers, except for a few bags purchased earlier, it is rather likely that Munch bought most of them after 1916.

Some of the original paper bags were in a very poor state having significant damages from previous handling such as tears, others had large, corroded holes on bottom or sides, some containing highly hazardous pigments. They were conserved to enable further storage and to prevent additional damage from handling.

This study opens future research regarding this part of the reference collection from Edvard Munch, adding new knowledge about his own use of art materials but also in general on modern paint materials. The relevance of these materials also covers the process of ageing of the commercial pigments, preserved in original paper bags, as they were purchased by Munch. Considering that more than 100 years already passed since these bags (and the pigments they contain) have been produced, the preservation state was not very good and proper conservation procedures were required for assuring a better storage condition for the powders.

Experimental part

Conservation treatment

Severeal of the bags were stained with its powdery pigment which compromised the conservation by choosing a non-aqueous treatment. Heat activated adhesive with BEVA® 371 film lined with hand-colored Japanese tissues was applied for bridging of tears and infills of holes (Fig. 2).

Fig. 2. Paper conservator Emma Chan treating a paper bag; paper before treatment; image of several bags in a better storage condition

Analytical protocol

Among the 35 pigments, a selection of 14 different pigments (of white, yellow, red, blue and green colours, Table 1) was analyzed using analytical techniques from the scientific laboratories of MUNCH and from the Museum of Cultural History in Oslo: ATR-FTIR, pXRF, SEM-EDS, XRD, Raman spectroscopy and synchrotron-based far-infrared (SR-FIR) spectroscopy from Bessy II light source in Berlin. This analytical protocol allowed a better understanding of their chemical composition.

pXRF

A Thermo Scientific Niton XL3t GOLDD+ portable XRF analyzer was used, with the head mounted on a tripod for measuring on spots on horizontally positioned cardboard. The measurements were performed in Mining method Cu/Zn, with an Ag anode X-ray tube operating at 50kV, 200uA and geometrically Optimized large Drift Detector (GOLDD), 1 measurement/reading, 120s scanning time, 3mm small spot collimator. For the interpretation of results an Niton Data transfer (NDT) software was used and the data downloaded into an Excel xls sheets.

FTIR - ATR

A Thermo Fisher Scientific Nicolet iS50 FTIR-ATR module with a monolithic diamond crystal and DLaTGS detector was used to acquire spectra from the samples (powders). The system operated at different values of scans (16-32 scans), at a resolution of 4cm^{-1}, operating in MID and FAR IR ranges covering the interval of 4000-200cm^{-1}. The spectra acquired were compared to the reference spectra from the library of the instrument using an OMNIC software. Additional measurements were carried out using a similar instrument in mid- and far-infrared region (4000-425cm^{-1} and 1800-125cm^{-1}); here pigments produced by Kremer Pigmente, Aichstetten, Germany were used as references as well as reference data from literature.

SEM-EDS

Scanning electron microscopy images were taken and EDX analyses conducted by using a FEI Quanta 450 instrument, equipped with an Oxford Instrument X-Max^{N} EDS detector and Aztec software package. Measurements were carried out in point and area as well as in mapping mode.

XRD

Measurements were carried out at a Panalytical Empyrean X-ray diffractometer, using copper K_{α} radiation.

Raman spectroscopy

Measurements were performed by means of a Renishaw inVia Raman Microscope, using an excitation wavelength of 514 nm.

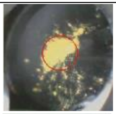
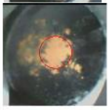
Synchrotron-based far-infrared spectroscopy

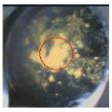
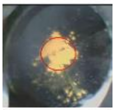
Synchrotron-based far infrared spectroscopy experiments were carried out at the IRIS beamline at the BESSY II electron storage ring [3]. Measurements were carried out in transmission mode using a Bruker V70v spectrometer equiped with a FIR detector (Liquid He Silicon Bolometer or Cryogen-free THz Bolometer) and synchrotron radiation as an external FIR source. Synchrotron light provides higher flux (intensity) in the FIR region than achieved from spectrometer internal sources resulting in higher signal to noise ratio measured from a smaller sample spot. The spectra were collected with 128-256 sample and background scans and 4cm^{-1} spectral resolution. For the sample measurements a small amount of dry pigment was pressed between two diamonds windows (~2mm diameter) of a Spectra-Tech Micro-Compression cell. The use of SR-FIR in studying pigments from artists' possession was demonstrated earlier [4, 5].

Results and discussion

The analytical characterization of 14 powedery pigments shows a palette of pigments and lakes as one could expect from the first half of 20th century. The summary of results of investigation of these 14 powdery pigments together with the type of analysis performed on each sample and identified compounds are given in Table 1.

Table 1. Selection of 14 pigments and the type of analyses performed. Main and secondary elements traced through pXRF analysis and possible attribution of compounds are listed

Sample Image (XRF camera)	Sample ID	Colour	Type of analyses	Main Elements (pXRF)	Secondary Elements (pXRF)	Compounds identified (multi-analytical approach)
	MMI1367y	yellow	XRF, MIR and FIR, SEM-EDS, XRD	Pb/S, Ba	Ca, Cr, Fe	Chrome yellow, barium sulfate (barite), gypsum
	MMI1368r	red	XRF, MIR and FIR, SEM-EDS, XRD	Ca, P, Fe	S, Al, Si, Cl	Madder/Alizarine, Al silicates
	MMI1414w	white	XRF, MIR and FIR, SEM-EDS, XRD	Fe, K, Si	Ca, Cl, Al, Ti?	Glassy grey material
	MMI1416y	yellow	XRF, MIR and FIR, SEM-EDS, XRD	Fe	Si, Ca, K, Ti?	Yellow ochre
	MMI1417y	yellow	XRF, MIR and FIR, SEM-EDS, XRD, Raman	Cd	S	Cadmium yellow
	MMI1422y	yellow	XRF, MIR and FIR, SEM-EDS, XRD, Raman	Fe, Si	Ca, K	Yellow ochre

	MMI1425g	green	XRF, MIR and FIR, SEM-EDS, XRD, SR-FIR	Fe	Ca, Ti, K, S, Cl	Green earth
	MMI1426y	yellow	XRF, MIR and FIR, SEM-EDS, XRD, Raman	Cd, Zn	Cu, Fe, S	Cadmium yellow, probably some zinc white and silicate
	MMI1427g	green	XRF, MIR and FIR, SEM-EDS, XRD	Ca, Fe	K, S, Sr	Ca-carbonate hydrate, Ca-carbonate. Minor components: potassium sulfate, iron, silicate
	MMI1428y	yellow	XRF, MIR and FIR, SEM-EDS, XRD	Pb/S, Cr	Fe, Ca	Chrome yellow
	MMI1430b	blue	XRF, MIR and FIR, SEM-EDS, XRD, SR-FIR	Fe	Ca, K, S, Cl, Al	Prussian blue aluminum hydroxide, clay mineral
	MMI1431y	yellow	XRF, MIR and FIR, SEM-EDS, XRD, Raman	Pb/S, Cr	Ca, Ba, Fe, Sr	Chrome yellow, Calcium sulfate Minor silicate content
	MMI1434g	green	XRF, MIR and FIR, SEM-EDS, XRD	Ba, Pb/S	Ca, Sr, Fe, Al, Si	Chrome yellow, barite, Prussian blue, minor amount of silicates
	MMI1435r	red	XRF, MIR and FIR, SEM-EDS, XRD	Pb/S	Ba, Cu, Fe, Ca	Minium, barite, very small amount of silicates

XRF analysis showed the presence of major and minor elements pointing out to certain pigments (Cr/Pb yellow, Cd yellow, yellow ochre, Prussian blue, green earth etc.) and additives or extenders (gypsum, chalk, barite, clay minerals/silicates). Further analyses using multiple methods gave a more detailed picture, allowed characterization of complex mixtures and identification of some unusual materials. Some of the investigated pigment samples allowed conclusions regarding the manufacturing process as discussed below.

In sample 1430b SEM/EDS measurements revealed, apart from iron, potassium and a small amount of silicates, a significant amount of aluminum being present. X-ray diffractogram and IR-spectrum show the presence of aluminum hydroxide compounds (Fig. 3). Prussian blue, easily distinguished by IR absorbance band due to C≡N vibration band in the 2100-2200 cm^{-1} range and very intense colour, was often adulterated with different materials, ranging from ochres to alum. Products produced in different ways were sold under different trade names, such as Antwerp Blue, Chinese Blue etc. [6-11].

To link reports on manufacturing processes to the analytical results, one has to be aware that the term ‘alumina’ was used for aluminum oxide as well as for aluminum hydroxyl compounds which was used extensively as carrier or substrate for lakes. Processes using ‘alumina’ as adulteration Prussian blue are described by several authors [7; 6-11].

The use of synchrotron radiation allows to extend the range of measurement to below $50cm^{-1}$. The spectrum of sample MM.I.1430b (Fig. 4) clearly shows the characteristic bands of Prussian blue at 498, 263, $236cm^{-1}$, compared to literature 496, 257 and $243cm^{-1}$ [12]. Exact positions of bands may change due slight differences in the crystalline structure of Prussian blue samples from different sources.

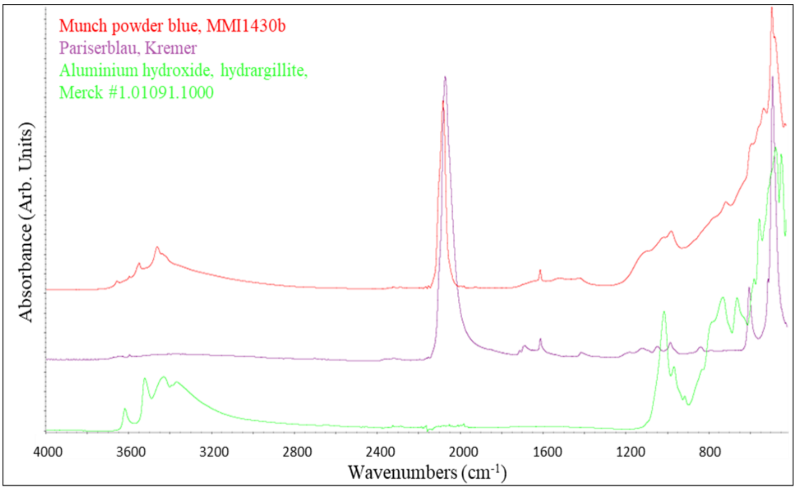


Fig. 3. ATR-FTIR spectrum of sample MMI1430b and reference spectra of Prussian blue and gibbsite ($Al(OH)_3$)

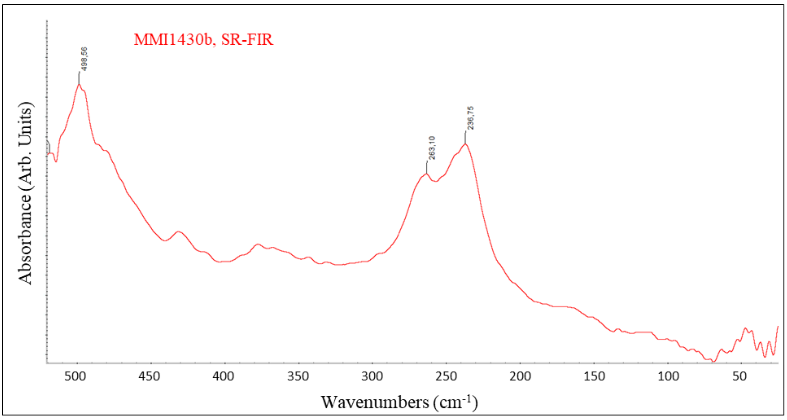


Fig. 4. SR-based FIR spectrum of sample MM.I.1430b showing clearly the characteristic bands of Prussian blue

In sample MMI1414w an amorphous silicate was found (Fig. 5). Its purpose is not clear. The IR spectrum shows presence of a glassy material. It may be a material used to create a texture effect, or as the raw material to produce waterglass, or it could simply be used as a grey pigment.

One of the cadmium yellow samples (MMI1417y) has a remarkable content of cadmium carbonate which may be related to the production method and/or the degradation of cadmium yellow.

In sample MM.I.1427g the FTIR spectrum pointed out to a presence of a small amount of a hydrated calcium carbonate, and a following XRD measurement revealed presence of calcium carbonate hexahydrate, also known as mineral ikaite, beside calcium carbonate PDF 01-084-6874 and 01-080-2775, resp. It is an open question whether the calcium carbonate hydrate has been produced intentionally or was formed by accident. For a deeper discussion on formation and structure of calcium carbonate hydrates see [13]. It should be mentioned that calcium carbonate was produced by various precipitation processes [6], in which, due to concentration conditions and nucleation, calcium carbonate hydrate compounds may have been formed.

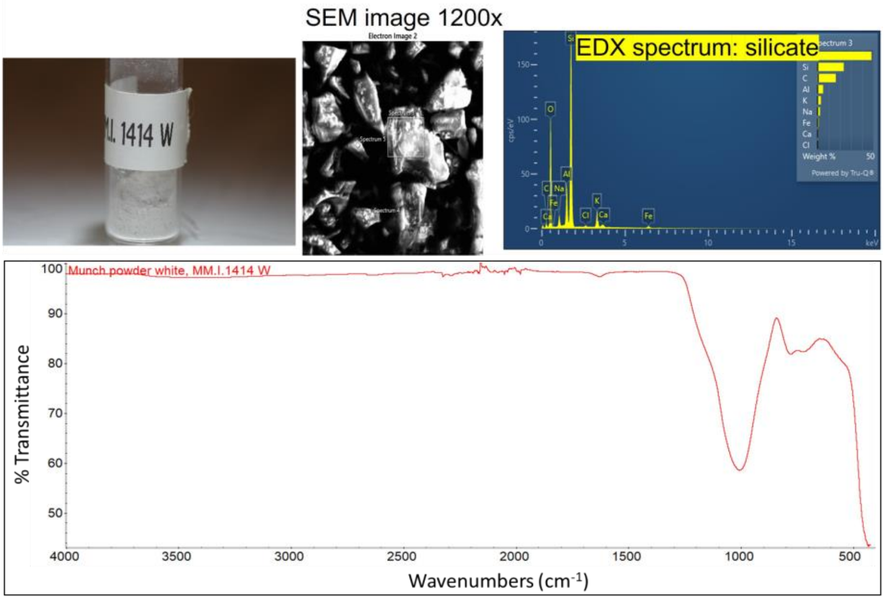


Fig. 5. FTIR and SEM-EDX spectra of white powder (MMI1414w)

Another yellow pigment (MMI1431y) was identified to be a mixture of chrome yellow (lead chromate) and gypsum, as shown by results ploted in figure 6. The Raman spectrum of a yellow grain in the sample shows typical marker bands of lead chromate at 359 and 840cm^{-1} [8], whereas the X-ray diffraction shows presence of both lead chromate and gypsum.

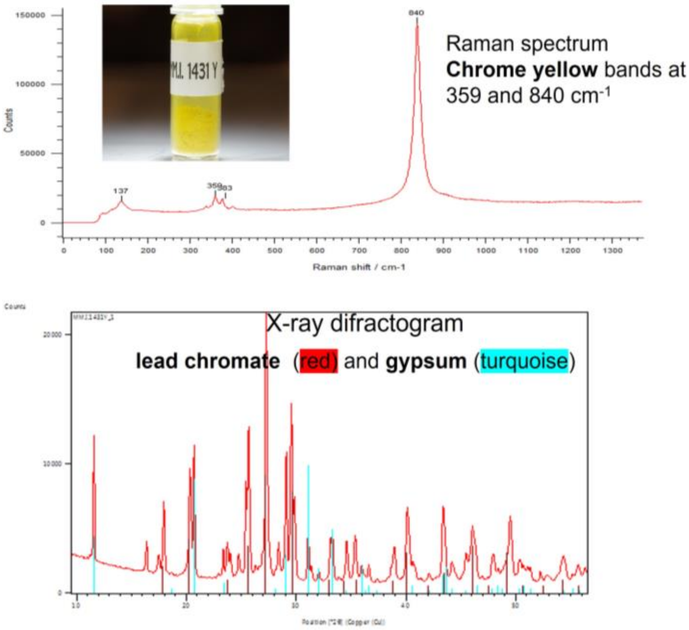


Fig. 6. Raman and Xray diffraction identification of a chrome yellow (MMI1431y) pigment

A green pigment (MMI1434g) has also been identified to consist of a mixture of Chromium yellow (lead chromate) and Prussian blue, barite and some silicates (Fig. 7). Zerr et al. reported in 1908 a manufacturing process that fits very well these analytical results:

«The pigment is known as Chrome Green, Green Vermillion, or Satin Green. The so-called chrome greens… are exclusively obtained by mixing chromes of different shades with Prussian Blue, and finely ground barytes which is taken up in almost unlimited quantities by the pure mixture. Great variety of shades by selection of different types of chromes (chromates) *and Prussian Blues. It was used for (oil) paintings but also for printing wall papers and litho and letterpress work».* [9]

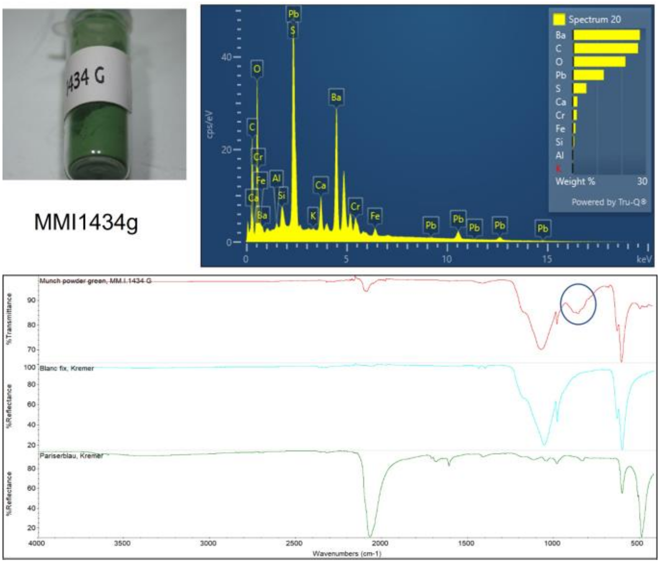


Fig. 7. Identification of a green pigment (MMI1434g) using SEM-EDX and FTIR spectroscopy

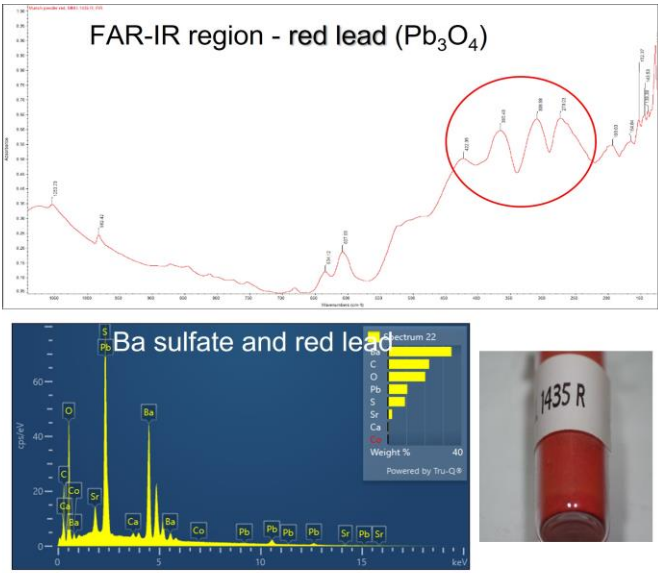
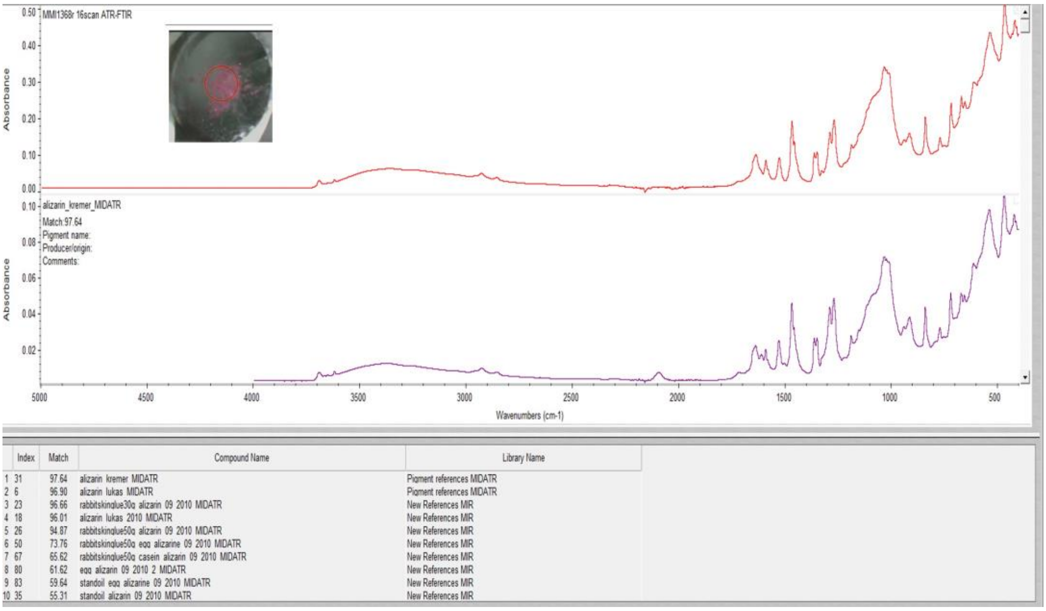


Fig. 8. Red pigment (MMI1435r) identified using SEM-EDX and FAR-IR spectroscopy

The present study gave us the occasion to compare different analytical methods. Sample MM.I.1435r (Fig. 8), an orange-red pigment was first investigated by SEM/EDS. Lead, barium and sulfur were identified as the main elements.

To identify whether the red pigment massicot or the pigment red lead is present, the sample was measured in the FIR region since both lead oxides don't show significant signals in the mid-infrared region (or only at the edge). Characteristic bands, observed at 422, 365, 308, and 273cm^{-1} (Fig 8 top) when compared with literature refences, point out to red lead matching well with reported values at 426, 363, 308 and 426cm^{-1} [14]. The results were further confirmed by XRD. This underpins the usefulness of using FIR spectroscopy in cases where few or no signatures are observable in the mid-infrared region.

For another red pigment (MMI1368r), characteristic absorption bands in the FTIR spectrum (Fig. 9) pointed out to a red lake.



	Index	Match	Compound Name	Library Name
1	31	97.64	alizarin kremer MIDATR	Pigment references MIDATR
2	6	96.90	alizarin lukas MIDATR	Pigment references MIDATR
3	23	96.66	rabbitskinglue30g alizarin 09 2010 MIDATR	New References MIR
4	18	96.01	alizarin lukas 2010 MIDATR	New References MIR
5	26	94.87	rabbitskinglue50g alizarin 09 2010 MIDATR	New References MIR
6	50	73.76	rabbitskinglue50g egg alizarine 09 2010 MIDATR	New References MIR
7	67	65.62	rabbitskinglue50g casein alizarin 09 2010 MIDATR	New References MIR
8	80	61.62	egg alizarin 09 2010 2 MIDATR	New References MIR
9	83	59.64	standoil egg alizarine 09 2010 MIDATR	New References MIR
10	35	55.31	standoil alizarin 09 2010 MIDATR	New References MIR

Fig. 9. Red pigment MMI1368r identified as Red lake using FTIR-ATR spectroscopy

The spectrum exhibits a good match with that of Alizarine/madder lake produced by Kremer. SEM/EDX revealed a high content of aluminum, and other analyses by XRD showed the presence of kaolin (PDF 00-058-2006) and aluminum oxide hydrate (01.070-0384), leaving, however, a number of reflections not assigned.

Conclusions

This study on powdery pigment samples opens future research regarding the original artist materials collection at MUNCH, adding new knowledge about his own use of art materials but also in general on modern paint materials.

The raw pigments analyzed here are already aged for more than 100 years and this is an interesting topic to explore in terms of relationship to the historical formulations of these modern materials for paintings. Further studies can include the comparison between these pigmetns and the paint tubes formulation in relationship to the real artworks for better understanding of the way Munch used these materials.

Acknowledgments

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