

## EDVARD MUNCH'S COLLECTION OF DRAWING MATERIALS: CRAYON CHARACTERIZATION

Ana Margarida CARDOSO<sup>1,2,\*</sup>, Irina Crina Anca SANDU<sup>1,3</sup>, Erika SANDBAKKEN<sup>3</sup>,  
Ana MANHITA<sup>1</sup>, Sara VALADAS<sup>1,2</sup>, Cristina DIAS<sup>1</sup>, António CANDEIAS<sup>1,2</sup>

<sup>1</sup> HERCULES Laboratory, IN2PAST Associate Laboratory and ERIHS.pt – Institute for Advanced Studies and Research, Évora University, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal

<sup>2</sup> City University Macau Chair on Sustainable Heritage – Institute for Advanced Studies and Research, Évora University, Rua Dom Augusto Eduardo Nunes 7, 7000-651 Évora, Portugal

<sup>3</sup> MUNCH Museum, Edvard Munchs plass 1, 0194 Oslo, Norway

### Abstract:

*This paper contains an interpretation of the results obtained from Fourier Transform Infrared micro-spectroscopy ( $\mu$ -FTIR) and Pyrolysis - Gas Chromatography coupled with Mass Spectrometry (Py-GC-MS) techniques applied on the crayons used by Edvard Munch (1863-1944) and now stored at the Munch Museum (MUNCH). Around 100 of different brands from Edvard Munch's collection of reference materials available at the Munch Museum were analyzed. Micro-destructive methods as  $\mu$ -FTIR and Py-GC-MS were used to characterize the constituent materials of crayon samples, with a special focus on organic binding medium, to allow the classification of different brands of crayons. Two natural waxes (beeswax and carnauba wax) were identified by  $\mu$ -FTIR, but the most specific chemical information on wax mixtures was attained by Py-GC-MS. The present study adds more analytical data on Edvard Munch's legacy and was developed under the framework of the collaborative research project "THE SCREAM-Touchstone for Heritage Endangered by Salt Crystallization: a Research Enterprise on the Art of Munch" between the HERCULES Laboratory and the Munch Museum in Oslo.*

**Keywords:** Edvard Munch; Crayon; Brand;  $\mu$ -FTIR; Py-GC-MS; Wax

### Introduction

In 1909 Edvard Munch returned forever to Norway, after passing a few years outside his native country, mainly in Germany. He started by living in his property near Kragerø, located at the coastal area south of the capital, and there he created the first sketches for the huge decorative project of the Aula at the University of Oslo [1].

Munch Museum in Oslo (MUNCH) has around 150 canvas sketches ideated by Edvard Munch, most of them large-format canvas paintings for decorative projects. Part of these sketches, executed in the period 1909-1916, were preliminary studies for his decorative project for the Aula [2]. The sketches created by Munch mainly consist of paint layers and crayons or crayons mixed with some paint strokes [3]. Crayons would be more useful to add motifs or casual details without using paint and brush [2].

The MUNCH also owns a large collection of original painting materials - paint tubes, dry pigments, palettes, easels, bottles with binders, chalk, pastels, crayons, and brushes [4]. The

\* Author for correspondence: amcardoso@uevora.pt

crayons/pastels used by Edvard Munch from the MUNCH collection, include different brands namely Dr. Fr. Schoenfeld, Crayola, Günther Wagner, AW Faber pastels, drawing crayons Conté à Paris and Feinste Ölkreide. Among the represented brands, only for Crayola, the original labels point out some dates (1903, 1904 and 1914) indicating probably the date of production. However, there is little information on the timeframe when these crayons were produced and used by Munch. Thus, it is not possible to assess whether the analyzed crayons were used by the artist to create the sketches on canvas for Aula's paintings, although there is an overlap with some of the years that the Crayola brand has on labels, and the period when the sketches were created.

One hundred crayons/pastels samples with a brand identity taken from this collection were sent for analysis at the HERCULES Laboratory, grouped by colors: white, red/pink/brown, yellow/orange, green, blue/violet, and grey/black, but the color and number of these items are uneven. The main objective of this study is to verify if there are differences in the composition of the crayons from different brands, and if the organic materials identified allow them to be categorized. This approach will provide useful information on the composition in terms of organic and inorganic materials.

The novelty of this paper consists mainly in the attempt to classify the crayon-type materials in the MUNCH's collection based on the findings from the analytical approach involving two types of micro-destructive techniques:  $\mu$ -FTIR and Py-GC-MS. The focus is on binding media characterization, as the literature review below showed that is the organic components that gives special properties and uses to these drawing materials.

## Experimental part

### *State of the art of crayons for drawing purposes*

Little is known about the early formulations of oil pastels and crayons, due to imprecise and confusing terminology around wax-like materials, and literature often reports them as being wax crayons or sometimes pastels [5, 6]. Since Antiquity, waxes have been applied for different artistic goals, but the wax-based drawing medium increased at the late 18<sup>th</sup> century along with the lithographic method [6]. With industrial development throughout the 19<sup>th</sup> century, synthetic waxes and oil-soluble dyes provided a wide range of drawing materials [6].

Crayons are any stick-shaped drawing materials produced in a continuous range of dry medium, such as chalks, conte crayons, oil pastels and wax crayons, independently of the type of their binder [7, 8]. Conte crayons are made from pigments compressed with chalk paste. It is the trade name given to the French brand's crayons, in honor of Nicholas Conté, who developed and patented the modern manufacture of graphite pencils, in 1790 [8]. The pastel term is used to designate the artistic material and pastel work [8]. This technique is used without a fluid medium and the color is applied directly on the support selected. Pastel painting originated in prehistoric times, but pastel as it is now known began between the 16<sup>th</sup> and 18<sup>th</sup> centuries, becoming vogue in Paris in the 1720s by Rosalba Carriera and in the early 20<sup>th</sup> century by Edgar Degas [8]. In dry pastels water-based gums are generally used, such as gum arabic or gum tragacanth or a water-based binder [8]. In oil pastels a non-drying oil is used as a binder [7, 8].

Holben Ellis and Brigitte Yeh, in the article *The history, use and characteristics of wax-based drawing media* classify wax-based drawing material into six sets according to its composition and appearance: "colored pencil, grease pencil, lithographic crayon, wax crayon, oil pastel, and paint stick" [6]. These classes are described below.

Colored pencil or colored crayon pencil was first produced by J.S. Staedtler, in 1833. Its components are: kaolin, talc or chalk for extender, pigment or dye, cellulose ethers and

vegetable gums as binding material, and beeswax or carnauba wax [6].

Lithographic crayon or lithographic pencil was produced by Alois Senefelder, in the late 18th century. It's a kind of lampblack grease stick used to draw on lithographic stone. Lithographic crayon contains: carnauba wax and beeswax, copal or shellac resins and other components such as tallow, soap, lampblack, olive oil, graphite, saltpeter and lye [6, 7].

Grease pencil, also called marking pencil or China marker, was used commonly from the mid-20<sup>th</sup> century in art [6]. In the mid-19th century it was produced by several companies, such as the Binney & Smith Company and the American Crayon Company [6]. Grease pencil has a limited palette and a similar consistency to soft lithographic crayon, and contains: talc or kaolin for extender, pigment or dye, paraffin, beeswax, ceresin, carnauba or spermaceti and may include chrome or lead, tallow and potassium carbonate [6].

Wax crayon, crayon or drawing crayon was first produced by Binney & Smith Company (Crayola), in 1903 [6]. Later, Louis Prang created his line of watercolor crayons in the American Crayon Company. Wax crayons have in their composition: kaolin or talc for extender, paraffin, microcrystalline, polyethylene, beeswax, ozokerite, Japan wax or carnauba, pigment or dye and tallow [6, 7].

Oil pastel contain finely ground pigments or dyes and fillers mixed with a small portion of binder [7]. Oil pastels or pastel pencils were introduced in Japan by the Sakura Cray-Pas Company, in 1925 [6]. They differ from crayons because they have oil in their composition, which includes: calcium carbonate as extender, pigment or dye, paraffin or microcrystalline wax, tallow and mineral or coconut oil [6, 7].

Paint stick has been commercially available since 1966. Its composition is similar to oil pastel but contains a higher concentration of oils than oil pastel [6]. It is made with paraffin wax, pigment or dye and a drying oil such as linseed or poppy [6, 7].

#### **Application of FTIR and Py-GC-MS for characterization of waxes in Munch's crayons**

Waxes have been used since ancient times for artistic purposes but in the 19th century the wax mixtures (natural and artificial) were marketed as drawing medium [9]. Natural waxes can come from both animals such as beeswax and spermaceti, and plants such as carnauba, candelilla and Japan wax. Natural waxes are a complex molecular mixture whose main components are some long-chain alkanes, primary and secondary alcohols, fatty acids, and esters formed from fatty acids [10]. Some waxy materials are fossil waxes such as paraffin (that consists of a series of hydrocarbons, without the alcohols or esters found in plant waxes and beeswax) [10, 11].

In IR spectra, the waxes are identified by the pattern of spectral bands: strong and narrow bands close to 2918 and 2850 $\text{cm}^{-1}$  due to the stretching vibrations of  $\text{CH}_2$  (methylene groups) and a small band at 2956 $\text{cm}^{-1}$  of  $\text{CH}_3$  (methyl groups) [12]; C-H bending vibrations in the region 1475-1377 $\text{cm}^{-1}$  due of an aliphatic compound and sharp doublets at 1473 and 1463 $\text{cm}^{-1}$  due  $\text{CH}_2$  bending vibrations [12]; at 730/720 $\text{cm}^{-1}$  appear the rocking vibrations of  $\text{CH}_2$  groups (a doublet near 730  $\text{cm}^{-1}$  indicates the presence of at least four methylene groups in the chain) [11, 12]. Table 1 shows the main assignments of the IR bands to vibrational modes of some waxes.

Analytical pyrolysis has become a suitable technique for the analysis of waxes, mainly because they are not easily solvable in organic solvents and the high molecular weights of their major components yield them too involatile to pass through the column, even at high temperatures [20]. Due to the complex composition of natural waxes, their detailed analysis is not an easy task, but different waxes can be mainly distinguished by the distribution of fatty acids, fatty alcohols, hydrocarbons, and wax esters on their chromatographic profiles, along with the presence of biomarkers, which are specific for each species and remain stable with

aging or are stable aging products of materials [10, 21]. The main biomarkers of some waxes are summarized in Table 2.

**Table 1.** Assignment of the main vibrational modes to the FTIR spectra of some waxes given in the literature [9, 12-19]

Beeswax	Carnauba	Japan (Wavenumber/cm <sup>-1</sup> )	Candelilla	Paraffin	Approximate assignment of vibrational mode
2918 (s)	2926 (s)	2916 (s)	2916 (s)	2915 (s)	$\nu_{as}(\text{CH}_2)$ (methylene)
2849 (s)	2853 (s)	2850 (s)	2848 (s)	2848 (s)	$\nu_s(\text{CH}_2)$
1737 (s)	1736 (s)	1741 (s)	1736 (s)		$\nu(\text{C}=\text{O})$ esters
1710 (vw sh)		1729 (s)	1714 (s)		$\nu(\text{C}=\text{O})$ COOH carboxylic acid
	1633 (w)				$\nu(\text{aromatic ring})$
	1606 (m)		1606 (w)		$\nu(\text{aromatic ring})$
	1515 (m)				$\nu(\text{aromatic ring})$
1473, 1464 (s)	1470 (s)	1464 (m)	1463 (s)	1471, 1464 (s)	$\delta(\text{CH}_2, \text{CH}_3)$
	1415 (w)	1413 (w)			$\nu(\text{C}-\text{O})$ or $\delta(\text{O}-\text{H})$ carboxylic acid
1376 (w)	1376 (w)	1393 (w)	1379 (s)	1375 (s)	$\delta(\text{CH}_3)$
1246 (w)		1266-1196 (w)	1241(w)		$\nu(\text{C}-\text{O})$ esters
1176 (s)	1170 (s)	1174 (s)	1168 (s)		$\nu(\text{C}-\text{O})$ alcohols, esters $\nu(\text{C}-\text{O})$
		1105,			$\nu(\text{C}-\text{O})$ esters
		1100 (s, doublet)			
	920 (w)	922 (vw)	900 (vw)		$\gamma(\text{O}-\text{H})$ carboxylic acid
	888 (w)	889, 878 (vw)	882 (w)		$\gamma(\text{C}-\text{H})$ aromatic ring
	833 (m)	836, 781 (vw)			$\gamma(\text{C}-\text{H})$ aromatic ring
729, 719 (s)	724 (s)	720 (s)	724	720 (s)	$\rho(\text{CH}_2)$ long chain hydrocarbon with four or more methylene units

s: strong, m: medium, w: weak, v: very, sh: shoulder,  $\nu$ : stretching vibration,  $\delta$ : in-plane deformation vibration,  $\gamma$ : out-of-plane deformation vibration,  $\rho$ : rocking vibration, s<sup>(as subscript)</sup>: symmetric, as<sup>(as subscript)</sup>: antisymmetric.

**Table 2.** Main biomarkers of some waxes [10, 22, 23]

Name	Main biomarkers
Beeswax	Even-numbered fatty acids, C22 to C34, with tetracosanoic acid (C24) being the main compound. Odd-numbered <i>n</i> -alkanes, C21 to C33, peaking at C27 ( <i>n</i> -heptacosane). Palmitic esters with even-numbers, C40 to C52.
Carnauba wax	Even-numbered <i>n</i> -alcohols, C28 to C34, of which C34 is the main compound. Even-numbered esters, C48 to C62, with C56 being the main compound.
Japan wax	Triacylglycerols, with tripalmitin as the main component.
Candelilla wax	C20 and C22 dicarboxylic fatty acids can be used as biomarkers for the presence of this wax. Odd-numbered <i>n</i> -alkanes, C29 to C33, showing C31 <i>n</i> -alkane and C30 fatty alcohol as the major compounds in their classes.
Paraffin	Series of odd and even-numbered <i>n</i> -alkanes, C21 to C35, peaking at C27.

The characterization of the crayons of Munch's atelier, currently kept at MUNCH, was carried out using FTIR and Py-GC-MS analyses.

### Selected samples

The FTIR analysis of 100 samples from Munch's studio, of unknown composition, allowed the identification of some waxes. To corroborate and complement the FTIR results, 15 samples were selected to be investigated by Py-GC-MS in order to confirm and identify the waxes and ascertain the organic constituents of samples from different brands: Faber Pastel (2), Conté à Paris (2), Crayola (3), Dr. Fr. Schoenfeld (2), Feinste Ölkreide (3) and Günther Wagner (3).

Figure 1 presents a selection of the analyzed items from 6 different brands belonging to the MUNCH collection.

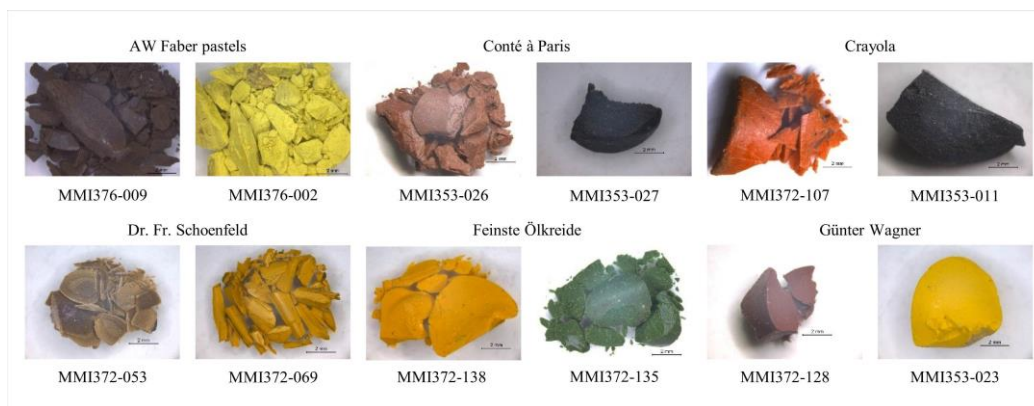


Fig. 1. Some images of the crayons acquired with a stereomicroscope

### Sample preparation

In the  $\mu$ -FTIR characterization, diamond cell is generally used for very small samples. Each sample is placed and then compressed outside between the two diamond windows [11]. Cell pressure allows the sample to spread over the diamond, increasing its surface area while decreasing its thickness [11]. In this way, the IR radiation can pass through the thin section of the sample and its IR spectrum can be obtained in transmission mode [11].

Pyrolysis-GC-MS allows direct identification of micro-samples compounds without requiring prior preparation [24]. The pyrolysis temperature must be adequate to allow complete pyrolysis and do not induce excessive fragmentation which can destroy specific pyrolysis products [25]. A few  $\mu\text{g}$  of sample is placed in a stainless-steel Eco-cup capsule and treated with the derivatizing reagent tetramethyl-ammonium hydroxide (TMAH) in methanol and the specimens are introduced directly into the Frontier Lab pyrolyzer. The volatile products formed during pyrolysis are analyzed and identified by GC-MS [10, 26]. To avoid cross-contamination, blanks were run between each sample.

### Instruments and parameters

Binders and pigments were identified by  $\mu$ -FTIR using a BRUKER Tensor 27 Mid-IR (MIR) spectrometer. The spectrometer coupled to the HYPERION 3000 microscope is controlled by the OPUS 7.2 software (Copyright© 2012 BRUKER Optics and Microanalysis GmbH, Berlin, Germany) and has a Mercury Cadmium Telluride (MCT) detector, cooled with liquid nitrogen, that allows the spectra acquisition in different points of the sample [27]. The samples were analyzed in transmission mode using a 15x objective and a diamond compression microcell EX'Press with a large clear aperture of 1.6mm, STJ-0169. The IR spectra were plotted in the region of  $4000\text{-}600\text{cm}^{-1}$  collecting 64 scans at a resolution of  $4\text{cm}^{-1}$  [27].

Experimental conditions used during Py-GC-MS analysis are presented in Table 3. Compound and material identification were performed using AMDIS software integrated with the NIST-Wiley database (match factor  $>700$ ) and the Expert System for Characterization with AMDIS Plus Excel (ESCAPE) [28].

Table 3. Py-GC-MS experimental conditions

Instrumentation	Frontier Lab PY-3030D double-shot pyrolyser Shimadzu GC2010 gas chromatographer Shimadzu GCMS-QP2010 Plus mass spectrometer		
Capillary column	Phenomenex Zebtron-ZB-5HT (30-m length, 0.25-mm internal diameter, 0.50- $\mu\text{m}$ film thickness)		
Carrier gas	Helium /1.5 mL $\text{min}^{-1}$ flow rate		
Split ratio	15:1		
Injection temperature	250 °C		
Temperature program	Rate ( $^{\circ}\text{C min}^{-1}$ )	Temperature ( $^{\circ}\text{C}$ )	Hold time (min)

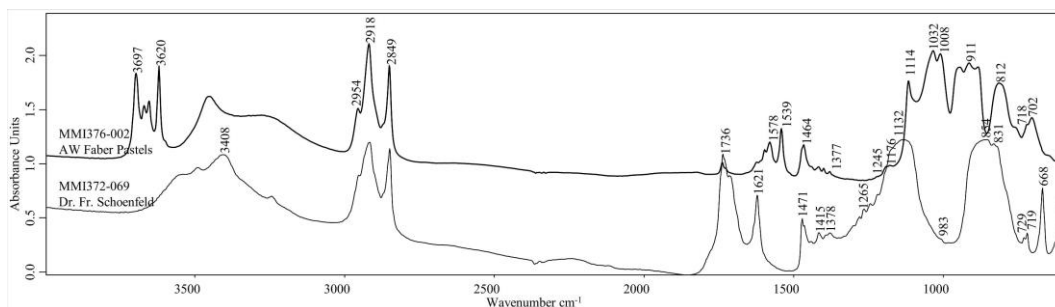
	-	35	1
	60	110	-
	4	240	-
	6	280	-
	30	320	6
Ion source temperature	240 °C		
Interface temperature	280 °C		
Scan range		40-1090 m/z	
Sample derivatization	300 µg of sample weighed in a 50-µL Eco-cup capsule and derivatized with 3 µL of tetramethylammonium hydroxide (TMAH) (2.5% in methanol, v/v)		
Pyrolysis temperature	500 °C		
Pyrolysis interface	280 °C		

## Results and Discussion

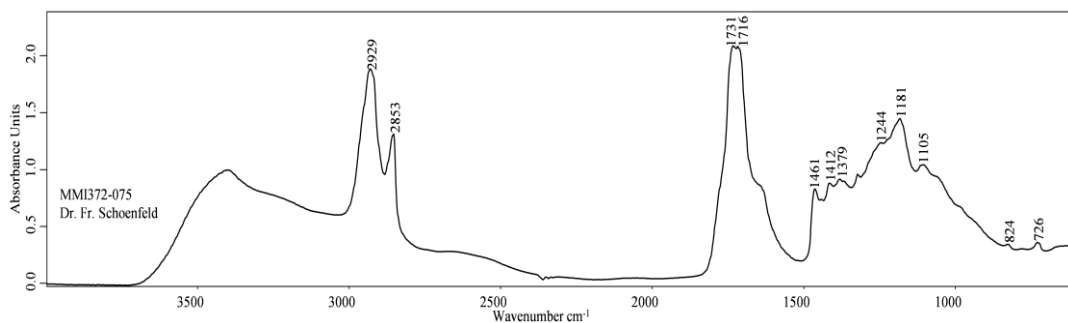
### *µ-FTIR results*

The composition of each sample was carried out by the interpretation of characteristic absorption bands of the compounds or functional groups revealed in FTIR spectrum based on the standard values wavenumbers using OMNIC software library and FTIR spectra databases.

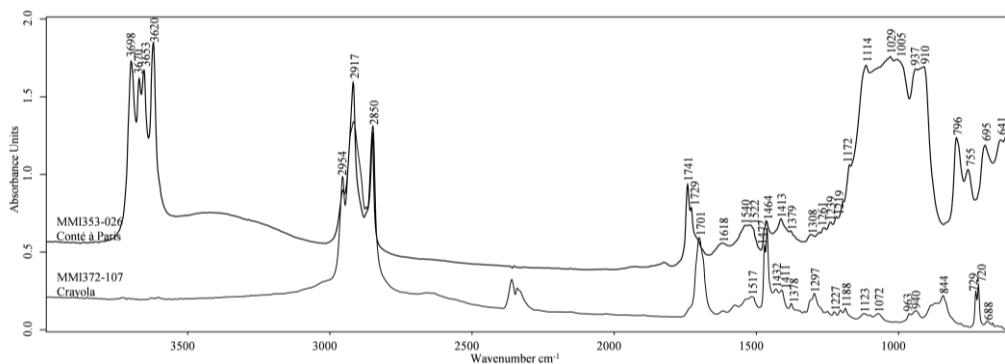
Figures 2, 3, 4 and 5 show FTIR absorbance spectra of four samples showing typical features and wavenumbers that identify each component.



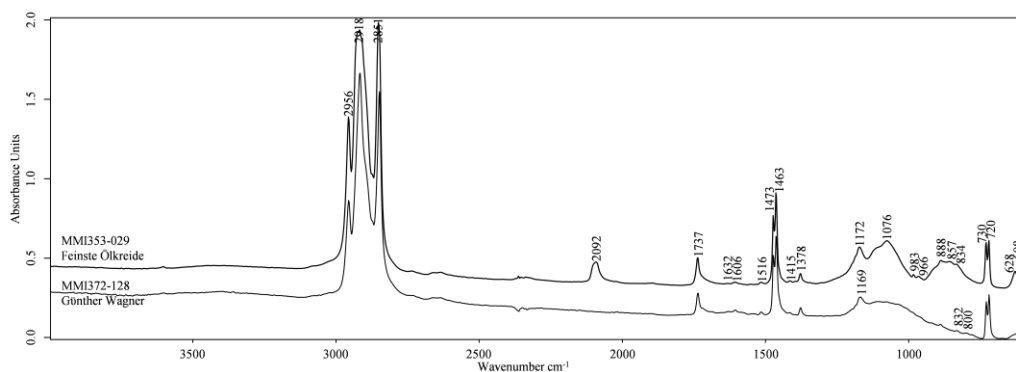
**Fig. 2.** MMI376-002 (yellow) AW Faber Pastels. FTIR spectrum of beeswax (2954, 2918, 2849, 1736, 1464, 1377, 1245, 1176, 718 $\text{cm}^{-1}$ ) and kaolinite (3697, 3620, 1114, 1032, 1008, 911 $\text{cm}^{-1}$ ); MMI372-069 (yellow) Dr. Fr. Schoenfeld. IR peaks of wax (2953, 2917, 2850, 1736, 1713, 1471, 1464, 1415, 1378, 1299, 1280, 1265, 1244, 1219, 729, 719 $\text{cm}^{-1}$ ), baryte (983  $\text{cm}^{-1}$ ), chrome yellow (854, 831 $\text{cm}^{-1}$ ) and gypsum (3408, 1621, 668 $\text{cm}^{-1}$ )



**Fig. 3.** MMI372-075 (yellow) Dr. Fr. Schoenfeld. FTIR spectrum of oil (2929, 2853, 1731, 1716, 1461, 1412, 1379, 1244, 1181, 1105, 726 $\text{cm}^{-1}$ )



**Fig. 4.** MMI353-026 (red) Conté à Paris. FTIR spectrum of wax (2954, 2917, 2850, 1741, 1729, 1464, 1379, 1308, 1261, 1239, 1219 $\text{cm}^{-1}$ ) and kaolinite (3698, 3670, 3653, 3620, 1114, 1029, 1005, 937, 910, 796, 755, 695 $\text{cm}^{-1}$ ); MMI372-107 (orange) Crayola. FTIR bands of wax (2954, 2917, 2850, 1472, 1464, 1378, 729, 720 $\text{cm}^{-1}$ )



**Fig. 5.** MMI353-029 (green) Feinste Ölkreide. FTIR bands of carnauba wax (2956, 2918, 2851, 1737, 1632, 1606, 1516, 1473, 1463, 1378, 888, 730, 720 $\text{cm}^{-1}$ ), Prussian blue (2092 $\text{cm}^{-1}$ ), chrome yellow (857, 834, 628 $\text{cm}^{-1}$ ) and baryte (1172, 983 $\text{cm}^{-1}$ ); MMI372-128 (red) Günther Wagner. FTIR bands of carnauba wax (2956, 2917, 2849, 1737, 1634, 1606, 1515, 1473, 1463, 1378, 832, 729, 720 $\text{cm}^{-1}$ )

Table 4 shows the results obtained with  $\mu$ -FTIR spectroscopy for the samples of different brands.

Trough FTIR analysis, wax was found in all samples. Some Faber Pastels samples contain beeswax in their composition. Spectra from Dr. Fr. Schoenfeld's samples show a mixture of waxes, probably with beeswax or Japan wax. An oil was identified in a sample. In the samples from Feinste Ölkreide and Günther Wagner carnauba wax was identified in their composition. In Conté à Paris samples it is difficult to identify the type of wax due to the overlapping absorption bands, although the bands in the region 1330-1000 $\text{cm}^{-1}$  point to Japan wax. In the spectra of Crayola samples, bands in the region 1740 to 1710 $\text{cm}^{-1}$  and the peak around 1170 $\text{cm}^{-1}$  are absent. This fact suggests the presence of mineral wax.

FTIR provides a general characterization of waxes, but in wax mixtures, a complex spectrum can result, in which the overlapping bands of each component make it difficult to observe the material individually [11, 17]. The greatest difficulty in identifying paraffin wax occurs when it is mixed with other waxes, which mask its presence in the resulting spectrum and, therefore, the possibility of mixing other waxes with paraffin cannot be excluded [15]. Most specific chemical information on waxes and wax mixtures can be obtained by performing additional analysis by other analytical techniques to corroborate and complement the FTIR results such as Py-GC-MS.

**Table 4.** Materials identified by  $\mu$ -FTIR

Colors (No. items analysed)	AW Faber	Conté à Paris	Crayola	Dr. Fr. Schoenfeld	Feinste Ölkreide	Günther Wagner
<b>White</b> (9)	Beeswax Gypsum Kaolinite	Wax Kaolinite, Hydro cerussite	Wax Baryte	Wax Baryte Kaolinite	-	Carnauba wax Baryte
<b>Red/Pink/ Brown</b> (36)	Beeswax Gypsum Kaolinite	Wax Kaolinite	Wax Baryte Kaolinite	Wax Baryte Kaolinite Quartz	-	Carnauba wax Baryte Hydro cerussite Kaolinite Quartz
<b>Yellow/ Orange</b> (17)	Beeswax Gypsum Kaolinite	-	Wax Kaolinite Quartz	Wax Chrome yellow Gypsum	Carnauba wax Chrome yellow	Carnauba wax Chrome yellow Baryte
<b>Green</b> (20)	Beeswax Emerald green Kaolinite	-	Wax Baryte Chrome yellow Kaolinite Prussian blue	-	Carnauba wax Baryte Chrome yellow Kaolinite Prussian blue	Carnauba wax Baryte Chrome yellow Kaolinite Prussian blue Quartz
<b>Blue/ Violet</b> (14)	Beeswax Kaolinite	-	Wax Baryte Kaolinite Prussian blue Ultramarine blue	-	-	Carnauba wax Baryte Hydro cerussite Kaolinite Prussian blue
<b>Grey/ Black</b> (5)	Beeswax Kaolinite Gypsum	Wax	Wax	-	-	Carnauba wax

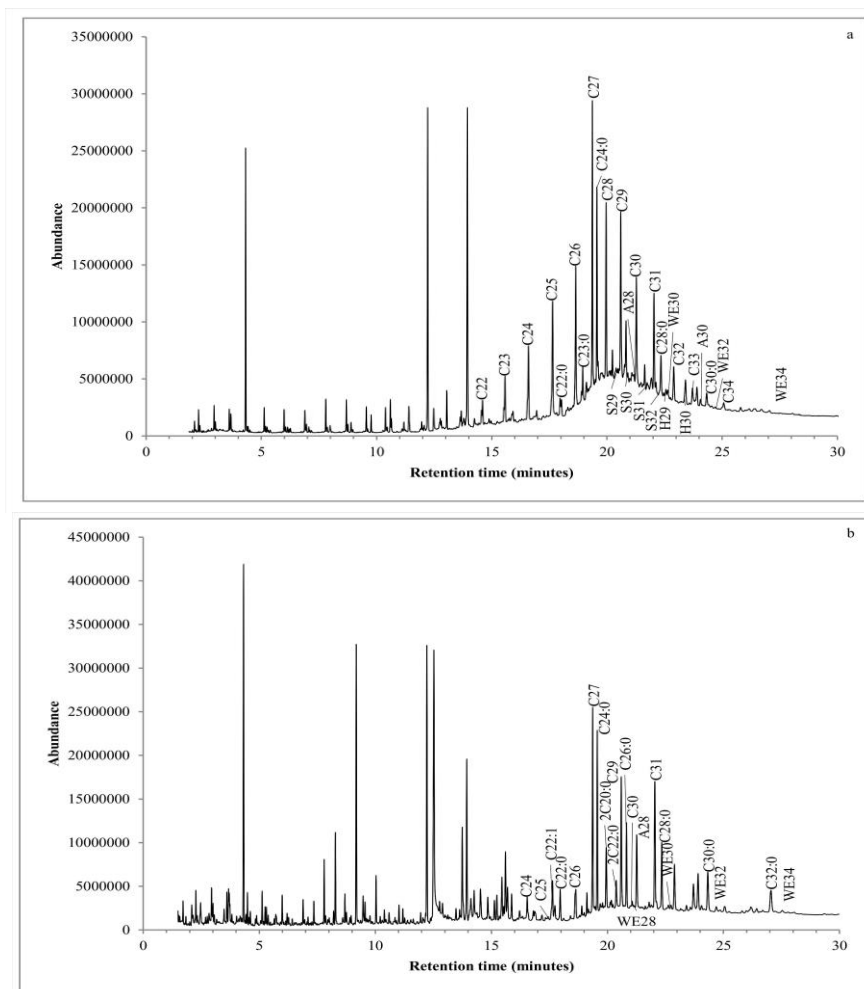
### *Py-GC-MS results*

The selected samples were pyrolyzed at 500 °C, in an inert atmosphere with the control of temperature and heating time, to identify their composition. The thermal fragmentation reduces larger molecules into smaller molecules that form a pattern of distinct fractions that contain information related to the primitive molecule [25]. For each wax one or more groups of pyrolysis products serve as discernment markers [25]. Figures 6a and 6b show two examples of chromatograms of samples, from Faber Pastels and Dr. Fr. Schoenfeld, pyrolyzed at 500 °C in the presence of TMAH, each peak corresponding to a single pyrolysis product with its mass spectrum. For retention data and peak identification, see Table A.1. (Appendix A) where the identified compounds of 6 representative samples are listed.

#### *Faber Pastels*

376-002 (yellow) - Possibly paraffin. A series of odd and even-numbered *n*-alkanes with a simple distribution, peaking at C27, is related to the presence of paraffin [10, 22]. Lignoceric acid (C24:0) as major compound in the class of fatty acids and some long-chain palmitic acid esters (tetradecyl, hexadecyl and octadecyl) were detected, which could be related with beeswax. However, long-chain alcohols are practically absent but no palmitic acid esters in the range C40-C50 were detected [10, 22, 29, 30]. Additionally, some hopene and steranes were detected. These compounds are usually related to the presence of bituminous materials, but no pristane or phytane were detected [10].





**Fig. 6.** Pyrolysis-GC-MS chromatograms:

a) MMI376-002 (yellow) Faber Pastels; b) MMI376-069 (yellow) Dr. Fr. Schoenfeld

Cx n-alkane with x carbon atoms; Ax linear alcohol with x carbon atoms; Cx:y fatty acid with x carbon atoms and y double bonds; 2Cx:y dicarboxylic acid with x carbon atoms and y double bonds; Hx hopane with x carbon atoms;

Sx - sterane with x carbon atoms; WEx - wax ester with x carbon atoms

The organic compounds of the samples analyzed by Py-GC/MS are described below:

376-009 (brown) - profile similar to 376-002.

*Conté à Paris*

353-026 (red) - The presence of dicarboxylic fatty acids C20 and C22 may be related to Japan wax, which is constituted by lipid biomarkers [10, 23]. Alkanes and long-chain fatty alcohols are practically absent.

353-027 (black) - Possibly paraffin.

*Crayola*

372-107 (orange) - Paraffin (series of odd and even-numbered *n*-alkanes with a simple distribution) and some long-chain fatty alcohols.

372-120 (blue) - Profile similar to 372-107.

353-011 (black) - Profile similar to 372-107.

*Dr. Fr. Schoenfeld*

372-053 (pink) - Oil-based crayon containing a mixture of waxes. Linear alkanes and long-chain fatty alcohols in reduced number. The presence of dicarboxylic fatty acids C20 and C22 may be related to Japan wax [23]. C31 alkane and C30 fatty alcohol as major compounds in their classes can be related to the presence of candelilla wax [10, 22, 30]. Several mono- and di-carboxylic fatty acids and their distribution point to the presence of a slightly heat-bodied oil [28].

372-069 (yellow) - Oil-based crayon containing a mixture of Japan wax and paraffin. Several mono- and dicarboxylic fatty acids with a distribution pointing to the presence of oil [28]. Erucic acid (Docosenoic acid, C22:1), a biomarker for the presence of Brassicaceae oils was also detected (not a major compound) [10]. Lignoceric acid (C24:0) detected as major compound in the class of fatty acids and some long-chain palmitic acid esters (dodecyl, tetradecyl, hexadecyl and octadecyl) were detected, which could be related with beeswax, but no other evidence for the presence of beeswax was detected [10].

*Feinste Ölkreide*

372-138 (yellow) - Mixture of carnauba wax and paraffin. C32 fatty alcohol as a major compound in its series, and the presence of p-methoxy-cinnamic acid are characteristic of carnauba wax [10, 22, 29].

353-029 (green) - Mixture of carnauba wax and paraffin. Some biomarkers for the presence of Pinaceae resin were also detected (Methyl dehydroabietate, 7-Oxodehydroabietic acid methyl ester and 15-Hydroxy-7-oxodehydroabietic acid methyl ester) [10, 22, 28].

372-135 (green) - Paraffin and triterpenoids lupeol and ursonic acid were detected [10].

*Günther Wagner*

372-128 (red) - Mixture of carnauba wax and paraffin.

353-023 (yellow) - Mixture of carnauba wax and paraffin.

372-133 (grey) - Mixture of carnauba wax and paraffin.

Saturated and unsaturated monocarboxylic fatty acids were detected in all samples, not always related to the presence of oil. The results for the samples from Faber pastels, Conté à Paris, Dr. Fr. Schoenfeld, Feinste Ölkreide, and Günther Wagner reveal a mixture of waxes in their composition. In the Crayola samples, paraffin wax was identified. In some cases, samples of the same brand show different wax patterns. Identified materials are summarized in Table 5.

**Table 5.** Materials identified by Py-GC-MS

Colors (No. items analyzed)	AW Faber	Conté à Paris	Crayola	Dr. Fr. Schoenfeld	Feinste Ölkreide	Günther Wagner
<b>Red/Pink/ Brown</b> (4)	Paraffin	Japan wax	-	Oil-based crayons Japan wax Candelilla wax	-	Carnauba wax Paraffin
<b>Yellow/ Orange</b> (5)	Paraffin	-	Paraffin	Oil-based crayons Japan wax Paraffin	Carnauba wax Paraffin	Carnauba wax Paraffin
<b>Green</b> (2)	-	-	-	-	Carnauba wax Paraffin	-
<b>Blue</b> (1)	-	-	Paraffin	-	-	-
<b>Grey/ Black</b> (3)	-	Paraffin	Paraffin	-	-	Carnauba wax Paraffin

According to the results obtained and the classification given by Holbein Ellis and Yeh

for crayons as a wax-based drawing medium, it is considered that the samples of Faber pastels, Conté à Paris, Crayola, Feinste Ölkreide and Günther Wagner can be categorized as wax crayons. The absence of cellulose ethers or vegetable gums as binding materials also excludes their classification as colored pencils. The classification as grease pencil is also excluded, since these crayons have a limited palette and were only used for artistic purposes from the mid-20th century onward. They cannot belong to the class of lithographic crayon because several pigments were identified and lamp-black was not present. The absence of oil excludes their classification as oil pastel or paint stick. This last one was not commercially available until 1966. However, Dr. Fr. Schoenfeld's samples contain an oil in their composition and several waxes were identified. The presence of oil suggests their classification as oil pastel, although some waxes and other identified organic materials do not match the components mentioned in the classification given by Holbein Ellis.

In 2021, *Jacopo la Nasa et al.* [31] published a multi-analytical study of several pastel crayons of only two brands (LeFranc and Dr. Fr. Schoenfeld), not analysed previously, from the MUNCH collection of original artist materials. This study found that all 44 crayons analysed are oil-based, the identified binders being a mixture of drying oil (safflower or linseed oil), palm oil or Japan wax, and beeswax [31]. In addition, several pigments such as ultramarine, chrome yellow, Prussian blue, manganese violet and viridian, were identified [31].

In the present paper, inorganic pigments and fillers/extenders, were identified by FTIR in the crayon samples of 6 different brands of the MUNCH collection, such as baryte, chrome yellow, gypsum, kaolinite, lead white, Prussian blue and ultramarine blue. Py-GC-MS has detected in two samples from Dr. Fr. Schoenfeld an oil and a mixture of wax with Japan wax, among other materials. In general, these results are in agreement with those presented by *Jacopo la Nasa et al.* [31] concerning organic components found in samples of the two brands.

## Conclusions

This study based on the  $\mu$ -FTIR and Py-GC-MS techniques allowed to find differences in the composition of the crayons of different brands used by Edvard Munch, mainly in the mixture of waxes used. FTIR has previously evaluated organic materials and identified beeswax, carnauba wax and oil, but more specific chemical information on wax mixtures was obtained by Py-GC/MS which identified several waxes as well as other organic compounds. The analyzes carried out make it possible to group the crayons into specific classes, according to the organic materials that make up the samples. However, other complementary analytical techniques will be performed to aggregate more information about the composition of these crayons in order to increase knowledge about the wax-based drawing materials of the invaluable MUNCH collection.

## Acknowledgments

The study was performed under the framework of THE SCREAM Project - "Touchstone for Heritage Endangered by Salt Crystallization, a Research Enterprise on the Art of Munch" (ref. FCT-ALT20-03-0145-FEDER-031577) financed by the Portuguese Foundation for Science and Technology (FCT) through National and European Funds. The authors wish also to thank the City University of Macau for support and the MUNCH for giving access to the samples for this study.

A. Manhita acknowledges FCT for the Individual Scientific Employment Contract nr. CEECIND/00791/2017.

The authors would like to acknowledge to HERCULES Laboratory of Evora University and the Portuguese platform of the European Research Infrastructure for Heritage Science (ERIHS.pt) for the availability of the equipment to carry out the analyses.

## References

- [1] E.G. Sandbakken, E.S. Tveit, *Preserving a Master: Edvard Munch and His Painted Sketches*, **Journal of Urban Culture Research**, **5**, 2012, pp. 86-104.
- [2] E.G. Sandbakken, *A close up: some degradation phenomena in Edvard Munch's Aula sketches* **Munch's Laboratory: The Path to the Aula** (editors: P. G. Berman, P. Pettersen, I. Ydstie), Munch Museum, Oslo, 2011, pp. 320-332.
- [3] E.G. Sandbakken, E.S. Tveit, *Edvard Munch's Monumental Sketches (1909-1916) for the Aula of the Oslo, Norway: conservation issues and treatments*, **Studies in Conservation**, **57**(1), 2012, pp. S258-S267. <https://doi.org/10.1179/2047058412Y.0000000030>.
- [4] J.S. Ferrer, A. Hull, T. Syversen, *Investigating surface phenomena in paints and paintings by Edvard Munch (1863–1944) in the context of the artist's painting materials in: Colour Change in Paintings* (editors: A. Gent, H. Dowding), Archetype Books, London, 2016, pp. 126-130.
- [5] A. Lluveras Tenorio, J. La Nasa, B. Ferriani, M.P. Colombini, F. Modugno, *The chemistry of pastels: Investigation of the organic materials in a drawing by Umberto Boccioni*, **Journal of Cultural Heritage**, **35**, 2018, pp. 235-241. <https://doi.org/10.1016/j.culher.2018.12.009>.
- [6] M. Holben Ellis, M. Brigitte Yeh, *The history, use and characteristics of wax-based drawing media*, **The Paper Conservator**, **22**, 1998, pp. 48-55.
- [7] N. Ash, S. Homolka, S. Lussier, **Descriptive Terminology for Works of Art on Paper**, (editor: R. Wolcott), Philadelphia Museum of Art, 2014.
- [8] <https://www.askart.com › art › glossary/> (accessed on 16/12/2021)
- [9] D. Gramtorp, K. Botfeldt, J. Glastrup, K.P. Simonsen, *Investigation and conservation of Anne Marie Carl-Nielsen's wax models*, **Studies in Conservation**, **60**(2), 2015, pp. 97-106.
- [10] M.P. Colombini, F. Modugno, **Organic Mass Spectrometry in Art and Archaeology**, (editors: Jonh Wiley & Sons, Ltd), Pisa, Italy, 2009.
- [11] M.R. Derrick, J.M. Landry, **Scientific Tools for Conservation Infrared Spectroscopy in Conservation Science**, The Getty Conservation Institute, Los Angeles, 1999.
- [12] V. Beltran, N. Salvadó, S. Butí, G. Cinque, *Micro infrared spectroscopy discrimination capability of compounds in complex matrices of thin layers in real sample coatings from artworks*, **Microchemical Journal**, **118**, 2014, pp. 1-25.
- [13] M. Baglioni, G. Poggi, G. Ciolli, E. Fratini, R. Giorgi, P. Baglioni, *A Triton X-100-based microemulsion for the removal of hydrophobic materials from works of art: SAXS characterization and application*, **Materials**, **11**(7), 2018, pp. 1-15. <https://doi.org/10.3390/ma11071144>.
- [14] H. Kühn, *Detection and Identification of Waxes, including Punic Wax, by Infra-Red Spectrography*, **Studies in Conservation**, **5**(2), 1960, pp. 71-81.
- [15] G.L. Shearer, *An Evaluation of Fourier Transform Infrared Spectroscopy for the Characterization of Organic Compounds in Art and Archaeology*, **PhD Thesis**, University of London, 1989, p. 399.
- [16] V. Vyshniak, O. Dimitriev, S. Litvynchuk, V. Dombrovskiy, *Identification of beeswax and its falsification by the method of infrared spectroscopy*, **Ukrainian Food Journal**, **7**(3), 2018, pp. 421-433.
- [17] U. Knuutinen, A. Norrman, *Wax Analysis in conservation objects by solubility studies, FTIR and DSC*, **15<sup>th</sup> World Conference on Nondestructive Testing**, 15-21 October 2000, Roma, Italy.
- [18] M. Masae, P. Pitsuwan, L. Sikong, K. Kooptarnond, P. Kongsong, P. Phoempoon, *Thermo-physical characterization of paraffin and beeswax on cotton fabric*, **Thammasat International Journal of Science & Technology**, **19**(4), (2014), pp. 69-77.

- [19] L. Svečnjak, M. Vinceković, S. Prđun, D. Bubalo, I.T. Gajger, *An approach for routine analytical detection of beeswax adulteration using ftir-atr spectroscopy*, **Journal of Apicultural Science**, **59**(2), 2015, pp. 37-49.
- [20] A.M. Shedrinsky, T.P. Wampler, N.S. Baer, *Pyrolysis gas chromatography (PyGC) applied to the study of natural waxes in art and archaeology*, **Science, Technology and European Cultural Heritage** (Editors: N.S. Baer, C. Sabbioni, A.L. Sors), Butterworth-Heinemann, Oxford, 1991, pp. 553–558.
- [21] M.P. Colombini, A. Andreotti, I. Bonaduce, F. Modugno, E. Ribechini, *Analytical strategies for characterizing organic paint media using gas chromatography/mass spectrometry*, **Accounts of Chemical Research**, **43**(6), 2010, pp. 715-727. DOI: 10.1021/ar900185f.
- [22] M. Regert, J. Langlois, S. Colinart, *Characterisation of wax works of art by gas chromatographic procedures*, **Journal of Chromatography A.**, **1091**, 2005, pp. 124-136.
- [23] J. Lamberton, *The Dibasic Acids of Japan Wax*, **Australian Journal of Chemistry**, **14**(2), 1961, pp. 323-324.
- [24] Analytical Methods Committee Technical Briefs (AMCTB), *Analytical pyrolysis in cultural heritage*, **The Royal Society of Chemistry**, **10**, 2018, pp. 5463-5467.
- [25] Scientific Working Group for Materials Analysis (SWGMA), *Standard Guide for Using Pyrolysis Gas Chromatography and Pyrolysis Gas Chromatography/Mass Spectrometry in Forensic Tape Examinations*, **Journal of the American Society of Trace Evidence Examiners**, **5**(1), 2014, pp. 42–50.
- [26] I. Bonaduce, M.P. Colombini, *Characterisation of beeswax in works of art by gas chromatography-mass spectrometry and pyrolysis-gas chromatography-mass spectrometry procedures*, **Journal Chromatography**, **1028**(2), 2004, pp. 297-306.
- [27] <https://www.ru.nl/bruker-tensor-ftir-instructions/> (accessed on 10/01/2022)
- [28] H. van Keulen, M. Schilling, *AMDIS & EXCEL: A Powerful Combination for Evaluating THM-Py-GC/MS Results from European Lacquers*, **Studies in Conservation**, **64**(1), 2019, pp. S74-S80. <https://doi.org/10.1080/00393630.2019.1594580>.
- [29] A. Asperger, W. Engewald, G. Fabian, *Analytical characterization of natural waxes employing pyrolysis-gas chromatography-mass spectrometry*, **Journal of Analytical and Applied Pyrolysis**, **50**(2), 1999, pp. 103-115.
- [30] A. Asperger, W. Engewald, G. Fabian, *Thermally assisted hydrolysis and methylation - A simple and rapid online derivatization method for the gas chromatographic analysis of natural waxes*, **Journal of Analytical and Applied Pyrolysis**, **61**(1-2), 2001, pp. 91-109.
- [31] J. La Nasa, F. Sabatini, C. Braccini, I. Degano, F. Modugno, C. Miliani, B. Doherty, F. Rosi, F.T.H. Broers, J. Moles Matinero, I.C.A. Sandu, L. Cartechini, *Integrated analytical study of crayons from the original art materials collection at the MUNCH museum in Oslo*, **Scientific Reports**, **11**, 2021, Article Number: 7152, [doi.org/10.1038/s41598-021-86031-6](https://doi.org/10.1038/s41598-021-86031-6).

---

Received: August 16, 2022

Accepted: December 21, 2022

## Appendix A

Table A.1. List of identified compounds in the pyrograms of six samples at 500°C.

RT (min)	Compound name	AW Faber	Conté à Paris	Crayola	D. Fr. Schoenf	Feinste Ölkreid	Günther Wagner
2.988	Pentenoic acid, methyl ester (C5:1)				+		
3.158	Pentanoic acid, methyl ester (C5:0)				+		
3.730	Hexenoic acid, methyl ester (C6:1)	+		+	+		
3.823	Hexanoic acid, methyl ester (C6:0)	+			+		
4.485	Heptenoic acid, methyl ester (C7:1)	+		+	+	+	
4.563	Heptanoic acid, methyl ester (C7:0)	+			+		
4.612	Butanedioic acid, dimethyl ester (2C4:0)				+		
5.299	Octenoic acid, methyl ester (C8:1)			+			
5.384	Octanoic acid, methyl ester (C8:0)	+			+		
5.476	Pentanedioic acid, dimethyl ester (2C5:0)				+		
6.182	Nonenoic acid, methyl ester (C9:1)	+		+	+		
6.263	Nonanoic acid, methyl ester (C9:0)	+			+		
6.423	Hexanedioic acid, dimethyl ester (2C6:0)				+		
7.172	Decanoic acid, methyl ester (C10:0)	+			+		
7.353	Heptanedioic acid, dimethyl ester (2C7:0)				+		
8.002	Undecenoic acid, methyl ester (C11:1)			+	+		
8.265	Octanedioic acid, dimethyl ester (2C8:0)		+		+		
8.967	Dodecanoic acid, methyl ester (C12:0)	+					
9.174	Nonanedioic acid, dimethyl ester (2C9:0)	+	+	+	+		
10.024	Decanedioic acid, dimethyl ester (2C10:0)			+	+		
10.421	p-methoxycinnamic acid, methyl ester					+	+
10.649	Tetradecanoic acid, methyl ester (C14:0)	+	+	+	+	+	
10.849	Undecanedioic acid, dimethyl ester (2C11:0)				+		
11.433	Pentadecanoic acid, methyl ester (C15:0)	+	+	+	+	+	
11.632	Dodecanedioic acid, dimethyl ester (2C12:0)				+		
12.086	Hexadecenoic acid, methyl ester (C16:1)	+		+	+		
12.218	Hexadecanoic acid, methyl ester (C16:0)	+	+	+	+	+	
12.434	Tridecanedioic acid, dimethyl ester (2C13:0)				+		
13.044	Heptadecanoic acid, methyl ester (C17:0)	+		+	+		
13.674	Heneicosane (C21)			+		+	+
13.787	Octadecenoic acid, methyl ester (C18:1)	+		+	+		
13.941	Octadecanoic acid, methyl ester (C18:0)	+	+	+	+	+	+
14.602	Docosane (C22)	+		+		+	
14.872	Nonadecanoic acid, methyl ester (C19:0)			+		+	
15.576	Tricosane (C23)	+		+		+	+
15.874	Eicosanoic acid, methyl ester (C20:0)	+	+	+	+	+	+
16.485	Methyl dehydroabietate					+	
16.591	Tetracosane (C24)	+	+	+	+	+	+
16.908	Heneicosanoic acid, methyl ester (C21:0)	+				+	
17.638	Pentacosane (C25)	+	+	+	+	+	+
17.743	Docosenoic acid, methyl ester (C22:1)				+		
17.967	Docosanoic acid, methyl ester (C22:0)	+	+	+	+	+	+
18.643	Hexacosane (C26)	+		+	+	+	+
18.897	Tricosanoic acid, methyl ester (C23:0)	+		+	+		
18.905	7-Oxodehydroabietic acid, methyl ester					+	

**Table A.1. List of identified compounds in the pyrograms of six samples at 500°C.**

RT (min)	Compound name	AW Faber	Conté à Paris	Crayola	D. Fr. Schoenf	Feinste Ölkreid	Günther Wagner
		376-002 yellow	353-026 red	372-107 orange	372-069 yellow	353-029 green	372-128 red
19.097	Eicosanedioic acid, dimethyl ester (2C20:0)		+		+		
19.366	Heptacosane (C27)	+		+	+	+	+
19.561	Tetracosanoic acid, methyl ester (C24:0)	+		+	+	+	+
19.966	Octacosane (C28)	+		+		+	+
20.122	15-Hydroxy-7-oxodehydroabietic acid,					+	
20.353	Docosanedioic acid, dimethyl ester (2C22:0)		+		+		
20.469	C29 Sterane (S29)	+					
20.597	Nonacosane (C29)	+		+	+	+	+
20.769	C30 Sterane (S30)	+					
20.825	Hexacosanoic acid, methyl ester (C26:0)	+		+	+	+	+
21.067	Hexadecanoic acid, dodecyl ester (WE28)				+		
21.257	Octacosanol, methyl ether (A28)	+		+	+	+	+
21.279	Triacontane (C30)	+		+	+	+	+
21.772	C31 Sterane (S31)	+					
22.040	Hentriacontane (C31)	+		+	+	+	+
22.312	C32 Sterane (S32)	+					
22.344	Octacosanoic acid, methyl ester (C28:0)	+		+	+	+	+
22.560	C29 Hopane (H29)	+					
22.627	Hexadecanoic acid, tetradecyl ester (WE30)	+			+		
22.900	Dotriacontane (C32)	+				+	
23.366	C30 Hopane (H30)	+					
23.904	Tritriacontane (C33)	+		+		+	
24.057	Triacantanol, methyl ether (A30)	+				+	+
24.328	Triacantanolic acid, methyl ester (C30:0)	+			+	+	+
24.696	Hexadecanoic acid, hexadecyl ester (WE32)	+			+	+	+
25.068	Tetracontane (C34)	+		+		+	+
26.723	Dotriacontanol, methyl ether (A32)						+
27.055	Dotriacontanoic acid, methyl ester (C32:0)	+			+	+	+
27.532	Hexadecanoic acid, octadecyl ester (WE34)	+			+		
27.606	Hexatriacontane (C36)			+			+
28.357	Tetracosanol, methyl ether (A34)					+	+
19.366	Heptacosane (C27)	+		+	+	+	+
19.561	Tetracosanoic acid, methyl ester (C24:0)	+		+	+	+	+
19.966	Octacosane (C28)	+		+		+	+
20.122	15-Hydroxy-7-oxodehydroabietic acid,					+	
20.353	Docosanedioic acid, dimethyl ester (2C22:0)		+		+		
20.469	C29 Sterane (S29)	+					
20.597	Nonacosane (C29)	+		+	+	+	+
20.769	C30 Sterane (S30)	+					
20.825	Hexacosanoic acid, methyl ester (C26:0)	+		+	+	+	+
21.067	Hexadecanoic acid, dodecyl ester (WE28)				+		
21.257	Octacosanol, methyl ether (A28)	+		+	+	+	+
21.279	Triacontane (C30)	+		+	+	+	+
21.772	C31 Sterane (S31)	+					
22.040	Hentriacontane (C31)	+		+	+	+	+
22.312	C32 Sterane (S32)	+					

**Table A.1. List of identified compounds in the pyrograms of six samples at 500°C.**

RT (min)	Compound name	AW Faber	Conté à Paris	Crayola	D. Fr. Schoenf	Feinste Ölkreid	Günther Wagner
		376-002 yellow	353-026 red	372-107 orange	372-069 yellow	353-029 green	372-128 red
22.344	Octacosanoic acid, methyl ester (C28:0)	+		+	+	+	+
22.560	C29 Hopane (H29)	+					
22.627	Hexadecanoic acid, tetradecyl ester (WE30)	+			+		
22.900	Dotriacontane (C32)	+				+	
23.366	C30 Hopane (H30)	+					
23.904	Trtriacontane (C33)	+		+		+	
24.057	Triacntanol, methyl ether (A30)	+				+	+
24.328	Triacntanoic acid, methyl ester (C30:0)	+			+	+	+
24.696	Hexadecanoic acid, hexadecyl ester (WE32)	+			+	+	+
25.068	Tetratriacontane (C34)	+		+		+	+
26.723	Dotriacontanol, methyl ether (A32)						+
27.055	Dotriacontanoic acid, methyl ester (C32:0)	+			+	+	+
27.532	Hexadecanoic acid, octadecyl ester (WE34)	+			+		
27.606	Hexatriacontane (C36)			+			+
28.357	Tetracosanol, methyl ether (A34)					+	+

RT - Retention time; C<sub>x</sub> - *n*-alkane with x carbon atoms; A<sub>x</sub> - linear alcohol with x carbon atoms; C<sub>x</sub>:y - fatty acid with x carbon atoms and y double bonds; 2C<sub>x</sub>:y - dicarboxylic acid with x carbon atoms and y double bonds; H<sub>x</sub> - hopane with x carbon atoms; S<sub>x</sub> - sterane with x carbon atoms; WEx - wax ester with x carbon atoms