

Analysis of Wilhelm Ostwald's "Colour Organ" with Raman microspectroscopy

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Abstract The "Scientific Colour Organ" is a collection of 680 pigment powders, created by the chemist Wilhelm Ostwald in 1925 as a means to represent his colour system. Today, it remains a leading part of colour theory. Analysis of these materials was undertaken to understand how the colour system was realised and to gain indications for preservation of the collection to which it belongs. Dispersive Raman microspectroscopy was applied directly to the powders, as well as using alternative techniques to suppress fluorescence. Barium sulphate was detected in all of the samples with one exception. Portable X-ray fluorescence revealed that this compound was a constituent of lithopone pigment. Raman spectroscopy furthermore revealed synthetic ultramarine (C.I. PB 29) as well as six different synthetic organic pigments and dyes (C.I. PY3; C.I. PO5; C.I. PR81:1; C.I. PV2 and two different triarylmethane dyes). Thin-layer chromatography was applied to determine the exact combination of dyes causing the gradual change in colour of each powder compared to the adjacent samples. With the exception of triarylmethane, the synthetic organic dyes could be identified with Raman spectroscopy directly on the chromatographic plate. The efficiency of thin-layer chromatography combined with Raman spectroscopy for identification of organic pigments could thus be shown. X-ray fluorescence indicated the

presence of tungsten–molybdenum lakes in some samples. Comparison of the analytical results to information published by Ostwald in 1917 showed that he switched to more light-stable synthetic organic pigments used for his "Scientific Colour Organ".

1 Introduction

Wilhelm Ostwald (1853–1932) was one of the pioneers of physical chemistry and catalysis, for which he earned the Nobel Prize in 1909. After retirement from Leipzig University, he focused on colour theory [1]. From the year 1914, Ostwald developed a specific colour system based on the "grey-scale" and the "colour circle". The grey-scale is a mixing sequence from black to white. The colour circle is formed by "full colours" which theoretically contain no black or white. Here, complementary colours are situated opposite to each other. Furthermore, the hues in the colour circle have equal distance to perception by the human eye. All other hues can be achieved by addition of white and/or black to the full colours, forming a triangle with the greyscale as vertical edge. Combining all triangles leads to a "double cone" ("Farbkörper") with white and black at the tips and the full colours at the outer diameter. Here, the full colours are designated with numbers (1–24) and the letter combination "pa". Pure white is designated as "aa" and pure black as "pp" [2]. Various models of the colour system were produced, such as the "Colour Book", or the "Colour Organs". A huge number of publications as well as different systematic material collections are still kept at Ostwald's former estate "Villa Energie" at Grossbothen near Leipzig, Germany, forming an important part of the tangible heritage of science. Although the theoretical background of the colour system is well understood, little is known about the chemical composition of

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the materials representing it. A few details were given by Ostwald himself [3, 4], but no analysis has been published in the literature so far. In order to achieve the clearest hues possible, Ostwald preferred synthetic dyes over traditional inorganic pigments. It is known from his own records that the dyes were used either for staining paper strips or, as in the case presented here, to impregnate white pigment. As a contribution to the deeper knowledge of Ostwald's historic materials, 24 powder samples from the so-called Scientific Colour Organ, produced in 1925, were investigated in this study (Fig. 1). In reality, the pigments representing the full colours may be mixtures of a restricted number of full colours, but without any addition of black or white pigment. Additionally, a white powder "aa" used for preparing powders with lighter hues was investigated.

Already Wilhelm Ostwald was aware that the synthetic organic dyes he used were not sufficiently light fast, especially in the green and blue section of the colour circle. Knowledge of the composition of the powders therefore is not only interesting to understand how the colour system was realised, but also essential to estimate their light fastness and to derive recommendations for the further storage of the historic items.

2 Experimental

2.1 Material and samples

According to his own publication from 1917 [3], Ostwald produced pigment powders by precipitation of soluble

Fig. 1 Pigment samples from Ostwald's "Scientific Colour Organ" from 1925, Wilhelm Ostwald Park, Grossbothen, Germany. The 24 powders represent the "full colour" circle. (photograph: Thomas Prestel)



synthetic organic dyes on white lithopone powder making use of tannin or "tartar emetic" (potassium antimonyl tartrate) for basic dyes and barium chloride or lead nitrate for acid dyes. Furthermore, it is well known that cationic (basic) dyes usually are transformed to insoluble pigments using a complex acid, such as phosphotungstomolybdic acid (PTMA). This may be the case for the phenylxanthen dyes as well as for the triarylmethane (TAM) dyes.

Synthetic organic pigments are based on synthetic organic dyes. In contrary to a dye, a pigment generally is insoluble in its vehicle (binder or solvent). Synthetic organic pigments usually are classified according to their chemical constitution [5]:

- Azo pigments: mono azo yellow and orange, disazo, β -naphthol, naphthol AS, azo pigment lakes, benzimidazolone, disazo condensation, metal complex, isoindolinone and isoindoline pigments;
- Polycyclic pigments: phthalocyanine, quinacridone, perylene and perinone pigments, thioindigo, dioxazine, TAM, quinophthalone, diketopyrrolopyrrole;
- Anthraquinone pigments: anthrapyrimidine, flavanthrone, pyranthrone, anthanthrone.

Almost all current synthetic organic pigments are members of the two main pigment families, the azo and the polycyclic pigments. The samples investigated in this study origin from a "Scientific Colour Organ" ("Wissenschaftliche Farborgel") kept by the "Wilhelm Ostwald Park" at Grossbothen (Germany). They are designated "pa", defining the colour circle of the most saturated "full colours". They are coloured dry powders and one of the first pigment preparations made by Ostwald in order to

establish his colour theory. However, the distribution of colour distances between neighbouring colours is not as homogeneous as Ostwald has intended. Colour measurements at the powders revealed a large variation in colour distances in the range of $8.2 \leq dE76 \leq -41.8$ (Thomas Prestel, personal communication, pre-publication).

According to the type of the containers, the powders have been stocked for approximately 40 years in closed plastic cups in the dark in a cupboard. The storage conditions before that period are unknown. For investigation, small portions from each container were sampled.

2.2 Optical microscopy

Samples were either directly investigated under incident light with 100× magnification (Leica DM2500) or distributed in immersion oil and viewed under transmitted polarised light (PLM) with 200× magnification (Carl Zeiss Jena Jenavert).

2.3 Raman spectroscopy

Raman experiments were performed using a dispersive Horiba Jobin–Yvon XPlora Raman microscope equipped with objectives 10×, 50× and 100× and a charge-coupled device (CCD) detector. A diode-pumped solid-state laser and a continuous wave diode laser, emitting light at 532 and 785 nm, respectively, were used as excitation sources. A holographic grating of 1200 rulings mm^{-1} provided a dispersion of $14.2 \text{ cm}^{-1}\text{mm}^{-1}$ (532 nm) or $6.5 \text{ cm}^{-1} - \text{mm}^{-1}$ (785 nm). Output laser powers were $P \leq 50 \text{ mW}$ for 532 nm and $P \leq 12 \text{ mW}$ for 785 nm, adjusted to the Raman response of the different samples. The spectra were collected over a wavenumber range from 100 to 1800 cm^{-1} which corresponds to the relevant range to identify synthetic organic pigments [6–8].

Fluorescence is a common feature in Raman spectroscopy. For various samples of the analysed set, a strong and fluorescent background could be observed for the two laser wavelengths available. To quench the intensity of the fluorescent background which overwhelmed the pigments' signal, powder samples were photo-bleached prior to acquiring the spectra, using the same wavelength as for the measurement [9, 10]. Photo-bleaching was applied until no decrease in fluorescence could be observed for times that varied between 1 and 10 min depending on the sample. Another solution used to reduce the fluorescent background is to include samples in potassium bromide pellets [8]. Around $100 \mu\text{g}$ of sample was mixed with 200 mg of KBr powder, previously air-dried at $130 \text{ }^\circ\text{C}$. Pellets of 13 mm diameter were prepared using a hydraulic press.

The spectra of samples 01–12 pa were measured using the 785-nm laser. Photo-bleaching was applied on samples 04–08 pa (5 min) and 09–12 pa (10 min). Spectra of the same samples measured at 532 nm showed a strong fluorescent background rendering the spectra inoperable. Spectra of the samples 13–23 pa were measured using the laser at 532 nm. These spectra obtained high signal/noise ratios. With the exception of sample 23 pa, the spectra of these samples measured at 785 nm were not operable because of high fluorescence background. Raman spectroscopy on reference samples of green and blue TAM dyes turned out to be most effective when prepared as potassium bromide pellets and using a 532-nm laser.

TLC investigations have provided more accurate information on the composition of the Ostwald samples mixtures than that could be determined by Raman spectroscopy alone. It seemed desirable to identify the different components by Raman spectroscopy directly on the different spots visible on the TLC plate. The Raman spectrum of the silica gel substrate (measured using the identical parameters) is characterised by a plateau below 500 cm^{-1} and thus does not interfere with the region of interest in the spectrum of synthetic organic dyes.

The resulting Raman spectra were interpreted using automated searches in different databases of pigments, especially synthetic organic pigments, containing their own data as well as data obtained from the literature [11]. The identified synthetic organic dyes and pigments are designated according to the Colour Index (C.I.) [12].

2.4 Thin-layer chromatography (TLC)

TLC was carried out to separate the components of the powder samples. A preliminary study of the solvent and eluent was carried out based on the work of Strauß [13] and Billmeyer [14]. The solubility of the 24 pigments' mixtures was first investigated for four different solvents: trichloromethane, methylbenzene, methanol/hydrochloric acid (1 %) and dimethylsulphoxide. From the results, trichloromethane solubilises all of the samples except 13 pa and therefore was chosen as the solvent for this study. From the eluents tested, three groups of samples were identified from amongst the set of powders which require the use of three different eluents to insure the optimal separation of the powder components. The eluents are reported in Table 1 along with the samples they are the most appropriated for.

For the TCL analysis, $500 \mu\text{g}$ of powder sample was extracted with 5 drops of solvent. One microlitre solution was placed for each spot on a silica gel plate (Macherey–Nagel, Polygram Sil G/UV), allowed to dry and developed using the

Table 1 Solvents used for thin-layer chromatography

Sample	Eluent
06–12, 14–19 pa	A = dichloromethane + methanol + water (75/15/10)
14–21 pa	B = dichloromethane + ethanol + water (50/40/10)
01–06, 23, 24 pa	C = pyridine + methylbenzene + n-hexane (15/20/65)

appropriate eluent (Table 1). The plates were evaluated under visible and UV light (254 nm). The separation rate R_f characteristic for each spot was calculated according to:

$$R_f = \frac{\text{(Distance travelled by the compound)}}{\text{(Distance travelled by the eluent)}}$$

2.5 X-ray fluorescence (XRF)

For the elemental analysis on selected powder samples, a portable XRF-spectrometer was used (Thermo Niton, XL3 Air). A tube equipped with a silver anode was run with 50 kV at 200 μ A, providing excitation radiation with a power of 2 W. Measurements were taken directly on the powder samples covered with a Mylar film with a spot size of 8 mm. The SDD-“GOLDD”-detector recorded the fluorescence radiation through three different filters with the following measuring times: Main 40 s, Low 10 s, Light 30 s. The signals were calculated using the internal software applying a “Plastics” routine.

3 Results

3.1 General

Light microscopy revealed that the powders of the “Colour Organ” are generally composed of differently coloured particles. With the exception of sample 13 pa identified as a pure pigment powder, all the samples seem to be mixtures of two or three pigments.

The Raman spectra from all “pa” samples except sample 13 pa from Ostwald’s “Scientific Colour Organ” generally display a similar set of bands around 988, 613 and 463 cm^{-1} which can be attributed to barium sulphate. As already mentioned by Ostwald [3], lithopone, a mixture of barium sulphate and zinc sulphide (C.I. Pigment White 5), was used for mixing white and grey powders as well as for the preparation of coloured pigment powders. However, the band at 345 cm^{-1} characteristic for ZnS was measured only on a white pigment sample from the Colour Organ. In the Raman spectra of the “pa” samples, this signal was not detectable due to a high and overlaying fluorescent background. For confirmation, elemental analysis was applied using the portable XRF. Strong signals for Zn, Ba and S proved the presence of lithopone in the analysed samples (01, 05, 07, 11, 15, 19, 21 pa).

In the region of the violet to blue–green samples (11–15 pa), the inorganic synthetic ultramarine pigment (C.I. Pigment Blue 29) was detected with both excitation wavelengths. As only pure pigment sample without the admixture of lithopone, 13 pa has to be taken as an exception amongst the “pa” samples the “Colour Organ” (Fig. 2).

In the following, it seems reasonable to discuss the composition of the pigment powders concerning synthetic organic dyes in two parts, found on both sides of the pure blue hue of powder 13 pa.

3.2 Yellow (01 pa) to violet (12 pa)

Generally, Raman spectra measured on the first part could be easily recorded using the 785-nm laser. The Raman spectral analyses indicate that one or two synthetic organic pigments have been used in addition to lithopone to create the different coloured powders. The colour of each powder results from a gradual change in pigments combination between adjacent samples. Four synthetic organic pigments or dyes could be identified (Table 2) as well as one synthetic inorganic compound in 11 and 12 pa identified as the synthetic ultramarine blue also known as French Ultramarine. The gradually varying concentration of the synthetic organic pigments is reflected in different intensities of the characteristic Raman bands in the spectra of consecutive samples. However, the relative concentrations of the individual pigments could not be estimated based on the intensity of the different Raman peaks because a non-linear correlation with concentration was found for reference pigment mixtures. Moreover, four samples of the first series seemed to consist only of one pigment mixed with lithopone: 01, 02, 06 and 09 pa.

TLC separation of samples 01–06 pa using eluent C (Table 1) showed the presence of a yellow component with $0.65 \leq R_f \leq 0.69$ in the samples 01–05 pa as well as an orange component with $0.20 \leq R_f \leq 0.23$ in the samples 02–06 pa. Although these substances were already identified as C.I. Pigment Yellow 3 and C.I. Pigment Orange 5 by Raman spectroscopy, the presence of the yellow pigment in sample 02 pa could only be shown by TLC (Table 2). In order to verify the results from Raman spectroscopy, the samples 06–12 pa were separated together with a C.I. Pigment Violet 2 and C.I. Pigment Red 81 reference using TLC (eluent A, Table 1). After separation,

Fig. 2 Raman spectra.
a Sample 13 pa (excitation 785 nm). **b** C.I. Pigment Blue 29 reference

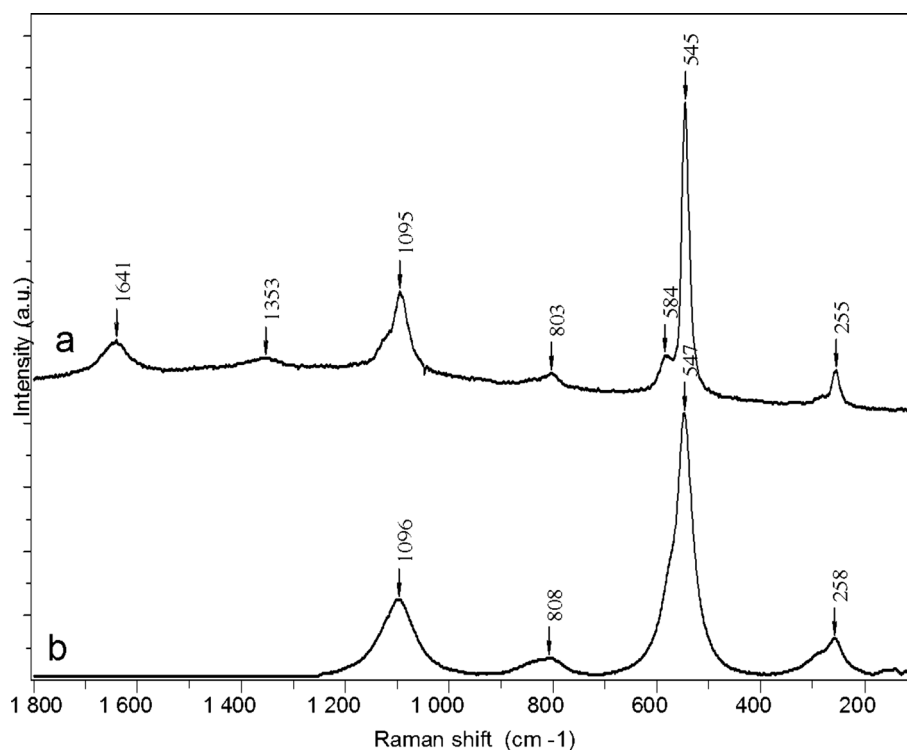


Table 2 Synthetic pigments identified with Raman spectroscopy in the first part of the "pa" series from the "Scientific Colour Organ", indicated by the techniques that were helpful in this identification

C.I. generic name	Pigment Yellow 3	Pigment Orange 5	Pigment Red 81	Pigment Violet 2	Pigment Blue 29
C.I. constitution number	11,710	12,075	45,160	45,175	77,007
Class	Mono azo/acetoacetanilide	Mono azo/ β -naphthol	Phenylxanthene	Phenylxanthene	Inorganic
Year of first occurrence in the literature [13]	1911	1907	1892	1922	
Sample ↓					
01 pa	RS, TLC				
02 pa	RS, TLC	TLC			
03 pa	RS, TLC	RS, TLC			
04 pa	RS, TLC	RS, TLC			
05 pa	RS, TLC	RS, TLC			
06 pa		RS, TLC	TLC		
07 pa		RS, TLC	RS, TLC		
08 pa		RS, TLC	RS, TLC		
09 pa			RS, TLC	TLC	
10 pa			RS, TLC	RS, TLC	
11 pa			RS	RS, TLC	RS
12 pa				RS, TLC	RS, TLC

RS Raman spectroscopy, TLC thin-layer chromatography, TLC + RS Raman spectroscopy on the TLC plate

each sample appeared as several coloured spots (Fig. 3). This observation is particularly relevant for the samples for which only one synthetic organic pigment could be identified by Raman spectroscopy. Samples 06–08 pa share an orange component ($R_f = 1.0$, non-fluorescent) which

correlates with C.I. Pigment Orange 5. One red spot ($R_f = 0.71$, green fluorescence) is shared by samples 06–10 pa and may be assigned to C.I. Pigment Red 81 since this pigment had been previously identified by Raman spectroscopy in these samples. The samples

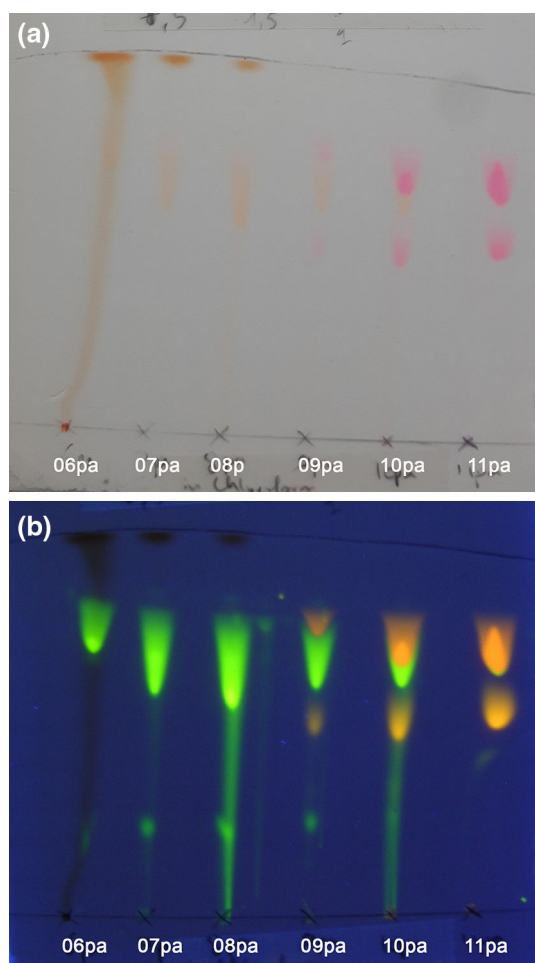


Fig. 3 Thin-layer chromatograph of samples of the samples 6 pa–11 pa (eluent A, Table 1). **a** Visible light. **b** UV (254 nm)

09–12 pa share two pink spots at ($R_f = 0.52$ and 0.72 – 0.77 resp.) which may be attributed to PV2, as confirmed by Raman spectroscopy (see below). In contrary to Raman spectroscopy, the TLC measurements revealed additional pigments: C.I. Pigment Red 81 in sample 06 pa and C.I. Pigment Violet 2 in sample 09 pa. Due to their small particle sizes, these components could not be detected under the Raman microscope and hence measured separately. In the Raman spectra obtained from those samples, the characteristic bands of these additional components were not visible due to their low intensity. Sample 13 pa has been previously identified as insoluble, inorganic ultramarine blue pigment, which consequently remained immobile in each TLC experiment ($R_f = 0$). Samples 12 and 14 pa also appear to contain ultramarine, as well as 11 and 15 pa, although for these last samples the spots remained less clear.

The spots on the TLC plates obtained for samples 06–11 pa (Fig. 3) were investigated by Raman spectroscopy using the 785-nm laser. The orange spot

($R_f = 1.0$) in samples 06–08 pa was confirmed as PO5. The two pink spots from samples 09–11 pa revealed similar Raman spectra despite different R_f values. This indicates the presence of two components with very similar molecular structures in the dye originally used. The spectrum of the upper pink spot ($R_f = 0.76$) shows characteristic peaks of C.I. Pigment Violet 2 (1649 , 1525 , 1504 , 1380 , 1358 , and 1279 cm^{-1}) (Fig. 4), confirming the result obtained by Raman spectroscopy on the powder samples 10–12 pa. From the red spot ($R_f = 0.57$ – 0.71 , green fluorescence under UV), no workable spectra could be obtained because of the paucity of material on the plate.

3.3 Blue (13 pa) to yellow (24 pa)

The Raman spectra on the second part of the powders were measured using the 532-nm laser. The results again indicate that the colour of each powder results from the combination of one or two pigments with lithopone. Generally, the Raman spectra of samples 14–24 pa indicate the presence of dyes of the TAM type (Table 3). In a first group of powders (14–19 pa), the Raman spectra resembles that of C.I. Pigment Green 1/Basic Green 1 (C.I. 42040), characterised by a triplet in the range of 1230 – 1160 cm^{-1} (Fig. 5) (TAM type 1). A second group of powders (20–24 pa) shows Raman spectra resembling that of C.I. Pigment Blue 24 (C.I. 42090) characterised by a doublet in the range of 1230 – 1160 cm^{-1} (Fig. 6) (TAM type 2). Furthermore, C.I. Pigment Yellow 3 was identified in the yellowish-green powders 22–24 pa.

However, the apparently overlapping occurrence of at least two different TAM dyes in the powder samples from the “Scientific Colour Organ” according to Raman spectroscopy is far from a reliable identification. Moreover, the colour of the suggested TAM dyes does not match the hues of the powders from the “Colour Organ” to which they show similar Raman spectra. Literature mentions [15] that it is difficult to differentiate TAM dyes only on the base of Raman spectra because of the similarity of the spectra (Figs. 5, 6).

TLC separation using eluent B (Table 1) was applied to the blue and green samples for further identification of the TAM pigments detected by means of Raman spectroscopy. The TLC plates revealed that two TAM pigments were involved in the production of the samples series 14–24 pa besides ultramarine (in 11–15 pa, $R_f = 0$) and C.I. Pigment Yellow 3 (20 and 21 pa, $R_f = 1.0$). One blue component ($0.86 \leq R_f \leq 0.91$) appears in samples 15–19 pa. A second blue–green component ($R_f = 0.20$) appears in 19–20 pa (Fig. 7). Hence, except of sample 19 pa, only one TAM dye is present in each sample. Additional TLC separations together with pigment

Fig. 4 Raman analysis of a pink spot on the TLC plate of samples 09–11 pa (Fig. 3). (excitation 785 nm) **a** Pink spot 10 pa ($R_f = 0.76$). **b** C.I. Pigment Violet 2 reference. **c** TLC silica substrate (*blank*)

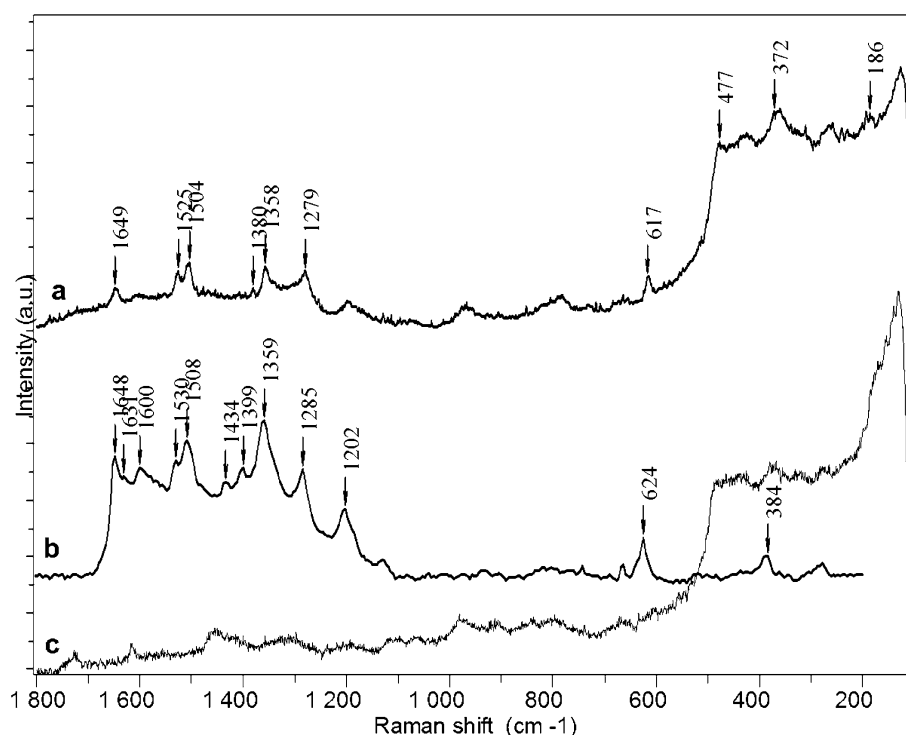


Table 3 Synthetic pigments identified with Raman spectroscopy in the second part of the "pa" series from the "Scientific Colour Organ", indicated by the techniques that were helpful in this identification

C.I. generic name	Pigment Yellow 3	TAM type 1 (blue)	TAM type 2 (blue-green)	Pigment Blue 29
C.I. constitution number	11,710			77,007
Class	Mono azo/acetoacetanilide	Triarylmethane	Triarylmethane	Inorganic
Year of first occurrence in the literature [13]	1911			
Sample ↓				
13 pa				RS, TLC
14 pa		RS		RS, TLC
15 pa		RS, TLC		RS
16 pa		RS, TLC		
17 pa		RS, TLC		
18 pa		RS, TLC		
19 pa		RS, TLC		
20 pa	TLC		RS, TLC	
21 pa	TLC		RS, TLC	
22 pa	RS, TLC		RS, TLC	
23 pa	RS, TLC		RS, TLC	
24 pa	RS, TLC		RS	

RS Raman spectroscopy, TLC thin-layer chromatography, TLC + RS Raman spectroscopy on the TLC plate

reference samples revealed that C.I. Pigment Green 1 is not present in any of the powders from the "Colour Organ" which is contradictory to the Raman spectroscopic results (see above). Additional TLC experiments using eluent C (Table 1) showed the presence of C.I. Pigment Yellow 3 in the yellowish-green samples 23 and 24 pa with $0.65 \leq R_f \leq 0.69$ as well as in sample 01 pa.

In sample 22 pa, PY3 was detected by TLC using a different eluent (ethanol).

The application of Raman spectroscopy on TLC plates appears to be useful as well as for the identification of the two TAM pigments previously only detectable by Raman spectroscopy. However, no workable Raman spectra from the spots corresponding to the two TAM pigments could be

Fig. 5 Raman spectra. **a** Sample 16 pa (excitation 532 nm). **b** C.I. Pigment Green 1 reference in KBr (excitation 532 nm)

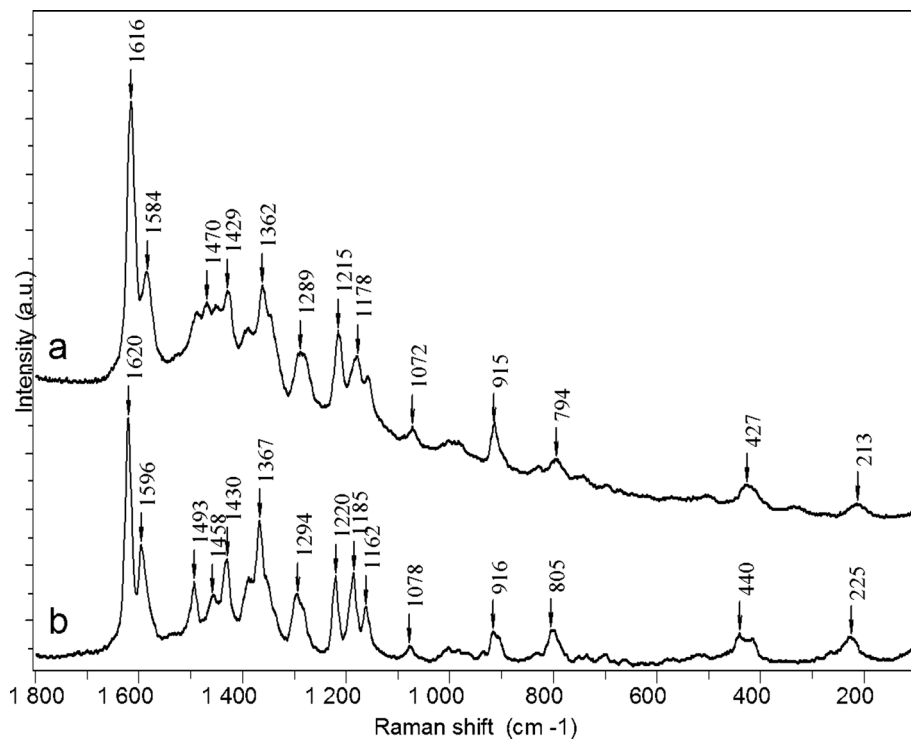
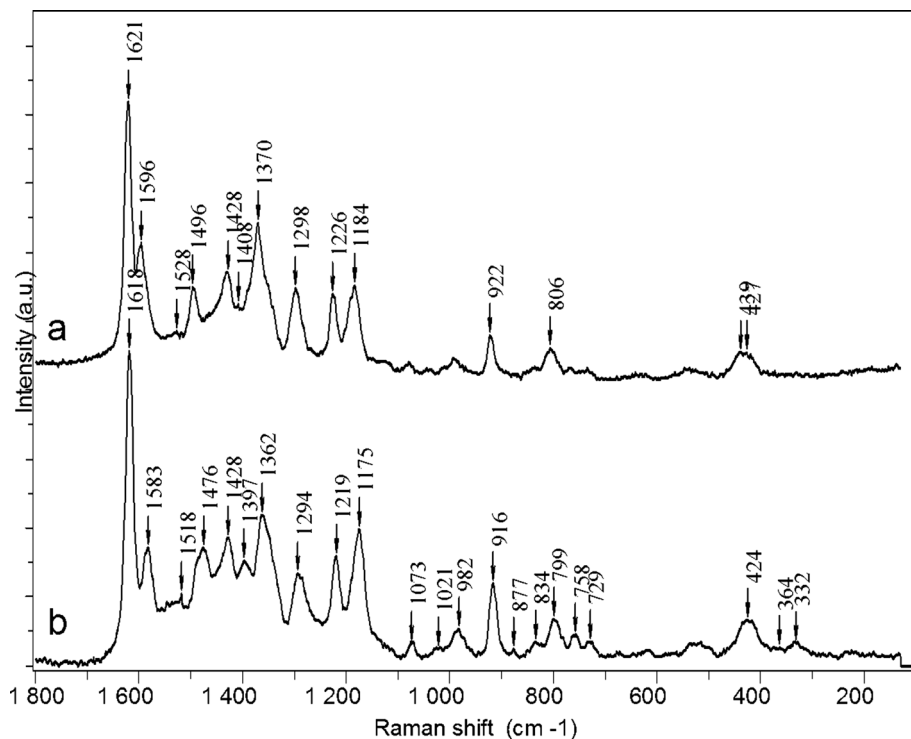


Fig. 6 Raman spectra **a** sample 20 pa (excitation 532 nm). **b** C.I. Pigment Blue 24 reference in KBr (excitation 532 nm)



measured. Both spectra showed a strong overlaying fluorescent background when using both the 532-nm and 785-nm lasers.

3.4 Elemental analysis

Elemental analysis of the samples 07, 11, 15, and 21 pa revealed weak signals for molybdenum (Mo-K α , K β) and

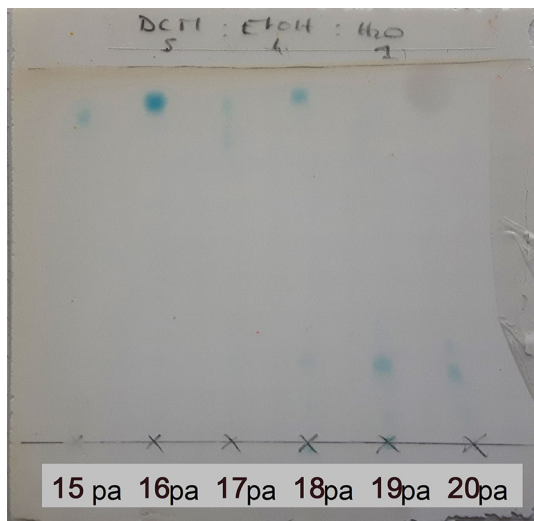


Fig. 7 Thin-layer chromatograph of samples of the samples 14–24 pa (eluent B, Table 1)

tungsten (W-L-series) besides the main components zinc, barium and sulphur already mentioned above (Fig. 8). This indicates that C.I. Pigment Red 81 (PTMA salt of C.I. Basic Red 1/45175) in sample 07 pa, C.I. Pigment Violet 2 (PTMA salt of C.I. Basic Violet 11/45160) in sample 11 pa as well as PTMA salts of the TAM dyes in samples 15 and 21 pa are present. Phosphorous was not detected, probably due to its low X-ray cross section. On the other hand, tartar emetic can be excluded due to the absence of antimony.

4 Conclusions

Using Raman spectroscopic analysis, it has been shown that for the production of his "Scientific Colour Organ" from 1925, Wilhelm Ostwald has used two monoazo pigments, two xanthene-PTMA lakes, synthetic ultramarine and at least two TAM dyes as PTMA lakes. However, these results do not match the list of organic dyes mentioned by

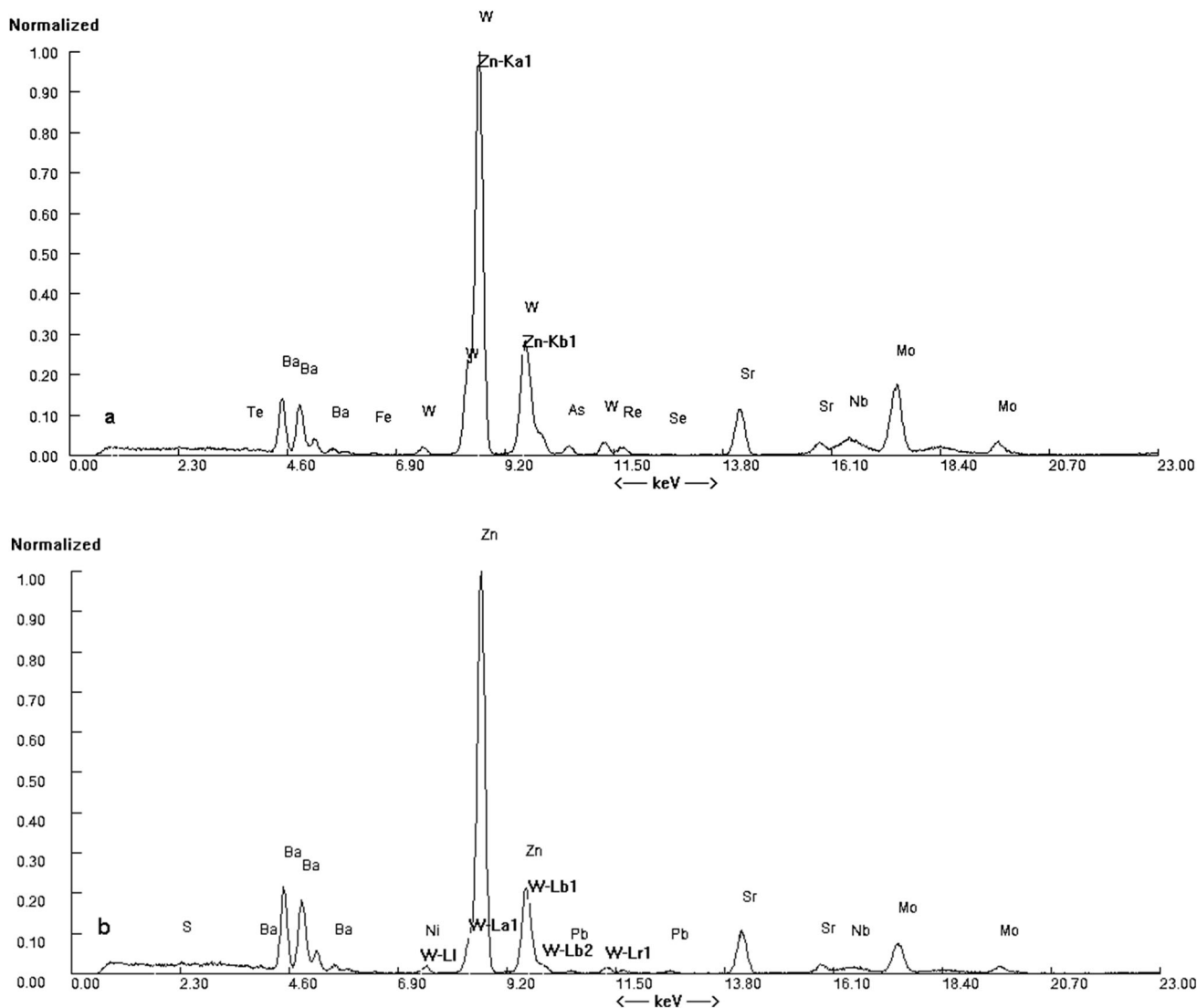


Fig. 8 X-ray fluorescence analysis. **a** Sample 07 pa. **b** Sample 21 pa

Ostwald in 1917 [3] for the production of yellow, red and purple pigment powders (yellow: C.I. 59000, dark yellow: C.I. 41000, orange: C.I. 15510, bright red: C.I. 45380, purple: C.I. 45170). Only the TAM dyes mentioned by Ostwald for blue and green hues (C.I. 42735, C.I. 42095, probably C.I. 42090) may be similar or identical to the dyes detected in this study. It can be assumed that Wilhelm Ostwald switched to more light-stable synthetic organic pigments for his “Scientific Colour Organ” in 1925. He has explicitly changed to the most light fast pigments available for the production of the new “Powder Colour Organ” in 1922, whereas he did not care about the technical properties of the dyes in the years before ([4], p. 313).

Thin-layer chromatography allowed for a more reliable analysis of the coloured powder samples from the Colour Organ, allowing parallel comparison. Some of the preliminary results from Raman spectroscopy could be corrected. All samples contain two or three coloured components, except 01 and 13 pa which showed only one synthetic pigment. Furthermore, besides pigments identified by Raman spectroscopy, TLC in the case of samples 09–12 pa revealed the presence of additional compounds with very similar composition in the dye originally used. Identification of the TAM dyes was not satisfactory, even when applying thin-layer chromatography. For this class, an improved Raman spectroscopic technique such as surface enhanced Raman spectroscopy (SERS) or mass spectrometric techniques should be tested.

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