

Article

The Manufacture of Lake Pigments from Artificial Colours: Investigating Chemistry and Recipes in the First Book on Synthetic Dyes-Based Lakes

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Abstract

In 1900, Francis Herbert Jennison's book *The Manufacture of Lake Pigments from Artificial Colours* was published in London. In the early 20th century, the technical literature focussing on synthetic dyes mainly dealt with their use for dyeing. Conversely, the literature on lake pigment manufacture is less comprehensive, and Jennison's publication was the first monograph on this topic. His book comprises descriptions of the dyes, substrates, and various methods for lake making. Practical examples complete the work: sixteen colour plates with original samples of lake pigments showcase the practical effect on colour of the different dyes and preparation methods. Herein, we present an overview of the context of Jennison's research and delve into a selection of formulations. Green lake pigment plates were sampled and analysed by liquid chromatography coupled with spectroscopic and spectrometric detectors and by X-ray fluorescence spectroscopy to correlate the chemical composition with the recipes reported in the book. Seldom or no longer used and unexplored historical dyes were detected, along with polyphenolic compounds possibly used as precipitating agents in lake pigment formulations. Moreover, the examination of two different editions of the Jennison manuscript (i.e., the English and German books) revealed different chemical profiles corresponding to the same lake pigment formulation. This emphasizes the significance of Jennison's book, confirming how understanding of early formulations is needed to elucidate the later ones.

Keywords: lake pigments; synthetic dyes; tannins; historical sources; Jennison; LC-DAD-MS/MS



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1. Introduction

There is only little information about Francis Herbert Jennison. He was a Fellow of the Institute of Chemistry of Great Britain and Ireland, and he studied at Yorkshire College in Leeds. An obituary published by the institute remains the only source of biographical information up to the present. It reveals that in 1892, Jennison started his career as a colour chemist, working for the First Moscow Cop-Dyeing Company. Jennison returned

to England in 1895 and worked first at the Craighall Colour Manufacturing Company in Glasgow and afterwards for the West of England Ochre and Oxide Company nearby Bristol. Between 1911 and 1915 he was employed by the Crown Chemical Company in London. After the war, he worked for Holmes & Sons in Newcastle upon Tyne and later for Alexander Ferguson & Company, again in Glasgow. Jennison died on 11th September 1939 at the age of 71 [1].

Jennison's book *The Manufacture of Lake Pigments from Artificial Colours* was published in 1900 [2]. This was the first monograph focussed on lake pigment manufacture. Besides detailed descriptions of the dyes, substrates, and procedures for lake making, the book contains sixteen colour plates with original swatches. The book was translated into German by Dr. Robert Rübenkamp just one year after its initial publication. A second revised edition was published in London in 1920 [3,4]. In fact, while historical recipes document that paint manufacturers used the new synthetic dyes quite early on [5–7], the methods used for making lake pigments from these new products are rarely mentioned in the literature before Jennison's book.

The fact that Jennison's publication also contains colour plates with original lake pigments makes his work even more interesting for art technological studies since these paint samples could provide a reference along with the recipes reported in the book. Notably, no information is available on the actual production of the colour plates, making their characterisation fundamental. Moreover, the identification of colourants by-products in reference materials of lake pigments can provide valuable insights into the technologies used in the early days of synthetic dyes and lake manufacturing industry. This information not only could enhance our understanding of historical painting techniques but also may help revealing specific degradation patterns or synthetic strategies useful for authentication and provenance studies while supporting conservation and restoration efforts.

For these reasons, the study of archival paint materials and reproductions of lake pigments prepared from synthetic dyes has come into the focus of scientific research in recent years [8–10]. Raman and UV–VIS/NIR reflectance spectroscopy proved to be effective in identifying the main colourant of green historical colour charts [8], enabling the colour characterisation in a non-destructive way. However, micro-destructive techniques such as liquid chromatography coupled to diode array detector or tandem mass spectrometry are nowadays the approaches par excellence for obtaining an in-depth profiling of dyes, ensuring to reveal novel by-products or side-products in historical dyestuff collection [11,12], textile swatches catalogue [13], or colour charts [14].

The aim of this study is to provide an overview of the literature on the topic of lake manufacturing, focussing on the development of lake-making methods until Jennison's book was published, and to reveal the chemical profiles of green lake pigments he produced, for supporting art technological studies.

Thus, ten samples collected from two different plates of the first edition books (i.e., English and German editions) of *The Manufacture of Lake Pigments from Artificial Colours* were analysed to thoroughly elucidate the chemical composition of these lake pigments in terms of organic and inorganic components. This involved the application of X-ray fluorescence and Raman spectroscopies and liquid chromatography coupled to diode array and tandem mass spectrometric detectors (HPLC-DAD and HPLC-ESI-Q-ToF). The outcome of our chemical investigation revealed both matched and mismatched formulations, thus highlighting the importance of studying these early formulations by determining and comparing materials used in their preparation. Moreover, the high sensitivity and selectivity of the HPLC-ESI-Q-ToF system enabled us to access for the first time in the literature the molecular profile associated with tannins used as precipitating agents in lake pigment formulations. Our chemical analyses were supported by an in-depth comparison

with the literature and historical recipes, aiming at understanding paint manufacture in the late 19th century.

1.1. Contents of Jennison's Book

Jennison's book comprises 13 chapters. In the beginning, the didactic intention of the book is stated: *"To manufacture lakes from artificial dyestuffs, in order to produce the best and most economical results, to adapt the lake to the purpose for which it is required, it is necessary to understand the chemistry, constitution, and properties of the colours used"* [2] (p. 2). The book was intended for pigment manufacturers. Jennison considers it imperative to understand the chemical nature of a dye to precipitate it correctly. In the first chapters, he gives an overview of the various compounds and their formulas and divides the synthetic dyes into groups. The next chapters deal with the practical application of the dyes. Jennison describes the available commercial sources of materials and their quality, providing practical information and including recommendations on where to purchase specific dyes. Then, he proceeds to describe suitable precipitating agents for acid and basic dyes. He mentions salts of barium, lead, zinc, aluminium, tin, antimony, and calcium as precipitants for acid dyes. According to Jennison, tannic acid was the most common precipitant for basic dyes. Furthermore, phosphoric, arsenious, antimonious, stannic, and resinous acids were used.

Next, Jennison continues by describing the "lake bases" used in the production of lake pigments. The term "base" was commonly used in the contemporary literature for what is nowadays labelled as substrate or filler. It was considered legitimate to add fillers to increase hiding power and general workability of the material, influence the shade, and reduce the cost of a lake.

According to Jennison, various types of substrates *"are introduced into the pigment either by suspending them in water and precipitating the lake on them, or by producing them and the lake at the same time, or by combination of the two methods"* [2] (p. 60). After listing the most common substrates (i.e., barium sulphate, aluminium hydrate, red lead, and others), Jennison debates the properties, advantages, and disadvantages of each material.

In the beginning of his book, Jennison defines a lake as a pigment *"made from dyestuffs and colouring matters, by precipitating the colouring matter as an insoluble compound"*. But in the chapter "The Principles of Lake Formation", it becomes clear that the formation of lake pigments was more complex and still a matter of discussion at that time. Here, Jennison describes the precipitation of lakes as a formation of salts, in which the dye either *"plays the part of the acid or the base"* [2] (pp. 1, 72). Furthermore, he discusses the matter of adsorption of a dye onto a substrate such as starch, clay, or green earth, and although he does not consider such "pigments" as proper lakes, he admits that adsorption phenomena may also occur in a true lake. In addition, during lake production, some dyes were not precipitated but *"merely carried down by the pigment formed."* [2] (p. 89). He discusses the permanence in accordance with the amount of precipitant and shows examples of lakes made with the minimum quantity of precipitant as well as the theoretically required quantity in Plate IV. Then, he deals with the various "lake-forming groups" (namely, the chemical functional groups) of the dyes and their precipitants. In the following chapters, Jennison goes into the details of lake production. A whole chapter is dedicated to the production of red lakes, while a second one deals with other colours. A third, shorter chapter focusses on the production of insoluble azo colours in the form of pigments.

The sixteen colour plates document what Jennison describes in these chapters; examples demonstrate how the concentration of the dye influences the intensity of a lake. Other samples show how dissolving the dyes together or separately or when hot or cold affects the resulting shade, while others show how different precipitants or substrates (lake bases) influence the colour of a lake pigment.

The last part of Jennison's book contains practical information for paint manufacturers. One chapter discusses the stability or instability of lake pigments and the influence of the binding medium on the fastness properties. Jennison describes how hiding power and tinting strength are influenced by the "base" (substrate) and the dye and deals with the issue of bleeding. In the chapter "Washing, Filtering, and Finishing", Jennison explains why the washing process is the most important working step and how to further process the prepared pigments. The final chapter deals with the examination of samples. Here, Jennison describes various methods that are supposed to help the colour chemist to identify the dyes used in a sample provided by the customer to reproduce the lake.

1.2. Earlier Literature on Lake Pigments

The first synthetic dyes provided new bright colours that had not been seen before and created a demand for more of these colours. The development of the early synthetic dyes and their application in textile dyeing was promoted by chemical education [15] (pp. 231–233) and the advancements in synthetic organic chemistry. With the growth of the chemical industry, industrial laboratories changed the approach to research and development. By 1880, the search for new compounds had become more systematic [15] (pp. 237–239). Likewise, the amount of literature about synthetic dyes grew in the late 19th century. But, while most publications deal with the manufacture of the dyes, their chemical composition, their properties, or their use in dyeing, there is relatively little literature on making lake pigments with synthetic dyes. For instance, Josef Bersch (1840–1907), an oenologist who worked as schoolteacher, did not mention them in his book *The Manufacture of Mineral and Lake Pigments*, which was published in 1878 [16]. Bersch also published on the use of synthetic dyes for textile dyeing in the same year, but he emphasized that whilst they were already used in watercolours, for inks or wallpaper printing, no method had yet been found to make them suitable for oil painting [17] (pp. 401–402, 485–488, 507–510). In the following, a summary of German and English sources including chapters on the production of lakes is provided with the intention to give an overview over the knowledge on the topic at the time, specifically until Jennison published his monograph.

Johann Georg Gentele (Württemberg 1813–Sweden 1895), a renowned colour chemist who worked in paint factories, added a chapter about lake pigments from coal tar dyes to the second edition of his manual on paint manufacture in 1880 [18] (pp. 477–541). He stated that only after the dyes found widespread use in textile dyeing did they become cheaper and were then exploited for producing lake pigments. Whereas he admits that some of them yield nice colours, in his opinion, these dyes are more suited for textile dyeing than for producing lakes since they were more difficult to fix onto the traditional substrates. Gentele recommended precipitating basic dyes with tannins on a substrate of alum and starch. Fuchsin (Basic Violet 14, C. I. 42510) lakes could also be obtained by first mixing the dye solution with starch, then adding alum and precipitating with soda [18] (pp. 481, 484–485, 518, 522). In contrast, acid dyes were dissolved with sodium hydroxide and precipitated onto a filler using alum [18] (pp. 494–495). Furthermore, Gentele described how to make vermilion imitations by dissolving eosin (Acid Red 87, C. I. 45380 or Acid Red 91, C. I. 45400) with sodium hydroxide and precipitating the dye onto a chrome red substrate with lead acetate. While eosin was used for that purpose until the early 20th century, Gentele's description differs from historic recipes and the later literature, which used red lead as a base. However, while the author stated that eosin was not commonly used for lake making because of its high price, he had the foresight to predict that this dye would find wider use soon [18] (p 503).

In 1892, George Hurst published a book that included a chapter on "Aniline-Lakes". Hurst divides the dyes into basic, acid, and adjective dyes [19] (p. 262 ff.). Mordant dyes

like alizarin (Mordant Red 11, C. I. 58000) were referred to as “adjective dyes” because their colour depended on the mordant used to fix them onto a substrate [19] (pp. 266–268). Like Gentile, Hurst described the precipitation of basic dyes with tannic acid. He recommended using tartar emetic (antimony potassium tartrate) in combination with tannins to complete the precipitation and improve the fastness of the lake. He explains that antimony ions react with tannic acid and form an insoluble antimony tannate. Some dyes could be precipitated with picric acid, although its yellow colour would influence the resulting lake. Furthermore, the dyes could also be precipitated with “resinates of alumina or magnesia”, formed by dissolving rosin in caustic soda in the presence of aluminium or magnesium sulphates [19] (pp. 263–264, 267, 271). Acid dyes were precipitated either with lead acetate, barium chloride, or aluminium sulphate. Hurst considered barium chloride as the best precipitant because the colours were less affected by sulphur than the ones made with lead acetate [19] (pp. 264–266).

Around the same time, Carl Otto Weber, possibly a professional chemist, published an extensive article on the analysis of the formation of lakes, which appeared in four parts in 1892 and 1893 in the *Dingler’s Polytechnisches Journal*. Weber discussed the use of tannins as precipitant for basic dyes and the problem of determining their correct amount. Like Hurst, he suggested adding tartar emetic to complete the precipitation. According to Weber, the use of lead and zinc salts was obsolete, but tin chloride was still used, although fastness of the corresponding lakes was poor. Furthermore, he mentions the use of the acids of antimony or arsenic, phosphoric acid, or soap as precipitants for basic dyes. Although he stated that the latter offered good fixation of the dye, he considered the obtained lakes toxic and not lightfast [20] (pp. 160–162, pp. 183–187). According to Weber, the formation of lakes with acid dyes was more complex because different and several lake-forming chemical functional groups were present. He divided the dyes by these lake-forming groups and discussed the hydroxyl group, the sulfonic group, and the carboxyl group separately [20] (p. 160). Weber listed the dyes with lake-forming hydroxyl groups and stated that dyes with two or more hydroxyl groups have better lake-forming properties, provided that these hydroxyl groups are in an ortho position [20] (pp. 162–164). He then discussed the lake formation with dyes that contain a carboxyl group and mentioned that chrome lakes with excellent fastness properties were formed with these dyes [20] (p. 186–187). According to Weber, the presence of sulfonic acid functional groups ($-\text{SO}_3\text{H}$) turned the dye into a strong acid, which reduced its lake-forming abilities. If the molecule contained too many sulfonic acid groups, the lake formation was decreased accordingly [20] (p. 187). The best results in lake formation with these dyes were achieved with barium salts [20] (p. 188). However, Weber recommended adding tannins to improve the colour and fully fix the dye [20] (pp. 188–189). This aspect is resumed by Jennison when discussing how to prepare lakes with these dyes [2] (pp. 75, 81–82, 97–99).

In 1898, Stanislaus Mierzinski, possibly a professional author, published another manual on paint manufacture, which includes a chapter on lakes made with synthetic dyes [21]. Like Hurst, he divided the dyes into acid and basic dyes as well as adjective dyes [21] (p. 924). He considered basic dyes especially suitable for making lakes. In addition to the precipitants mentioned in earlier publications, he included sodium phosphate, waterglass, Turkish red oil, albumin, and casein [21] (pp. 921, 924, 926–927), [22]. Regarding acid dyes, Mierzinski suggested the use of strontium chloride as an alternative to barium chloride [21] (pp. 921, 928). Apart from that, the publications by Hurst and Mierzinski are similar, and both include practical information on the suitability or stability of the lakes in paints and varnishes, which is not mentioned by the other authors.

Figure 1 shows a timeline summarizing the development of precipitation methods reported in the literature between 1880 and 1900. The early literature reflects the little

knowledge available at the time about the new dyes, and much of the authors' information came from their own experience. The experiments described by Gentele and the systematic approach by Weber reflect the development of research in the dye industry, which had become less empiric and more systematic [15] (p. 238).

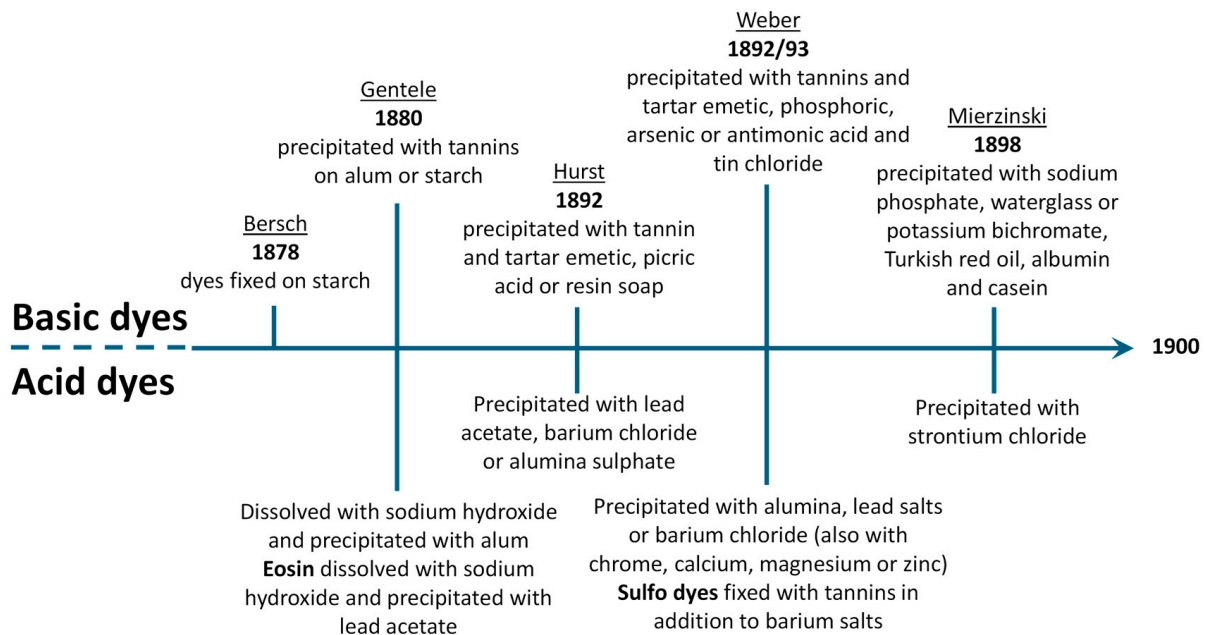


Figure 1. Timeline showing the development of precipitation methods as described in the literature between 1880 and 1900.

Due to new developments, documented, for example, by Friedländer in *Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige*, the literature was quickly outdated. Considering that each publication added some new information, the progress within 20 years was enormous. The publications by Mierzinsky and Hurst contain methods of which Gentele obviously did not know. Weber's text is more complex and deals with the chemistry of lake formation in an analytical rather than practical way. There is no information on whether Jennison knew these publications, but the precipitation methods described by Weber and Jennison are remarkably similar. When comparing Jennison's chapter on the principles of lake formation with Weber's article, it seems as if Jennison was indeed aware of Weber's publication [2] (pp. 72–83). While research on historic literature and recipes has shown that the methods described by Jennison were not entirely new, his work was better structured and was by far the most comprehensive work on lake pigments made from synthetic dyes with respect to any previous publication.

2. Materials and Methods

2.1. Provenance of the Books

The English book used in this study was previously owned by Louis Atwell Olney (1875–1949), a former professor at Lowell Textile School and the founder of the American Association of Textile Chemists and Colourists [23]. The book was part of the Olney collection at the Lowell Technological Institute until it was put up for sale by an antiquarian book trader and purchased by one of the authors. Olney carried out a "10 days light test" on the original colour charts. He cut out parts of the samples, exposed them to light, and glued them back after the fading test (Figure 2). The light-aged samples were not analysed since the evaluation of the possible ageing mechanisms were not the aims of the present study. The German edition used in this study was also purchased from an antiquarian.

The previous owner was G. Siegle & Co. (Stuttgart), as documented by a stamp of the company. This well-known German pigment producer was founded in Stuttgart in 1848 by Heinrich Siegle as a factory for lake pigments made from natural dyes. His son Gustav Siegle expanded the business significantly. G. Siegle & Co. produced mineral pigments and lake pigments at multiple locations and became a distributor for aniline dyes of the BASF from 1873 to 1889. Gustav Siegle died in 1905, so he might have read this book personally [24]. This version is in better condition than the English edition used in this study. The colour charts are quite well preserved and have not been cut or exposed to light. The previous owner only used pencils to mark passages or correct the chemical formulas in Jennison's introduction. In Figure 2, a comparison of an exemplative page, Plate XIII, from the English and German versions is provided to outline differences.

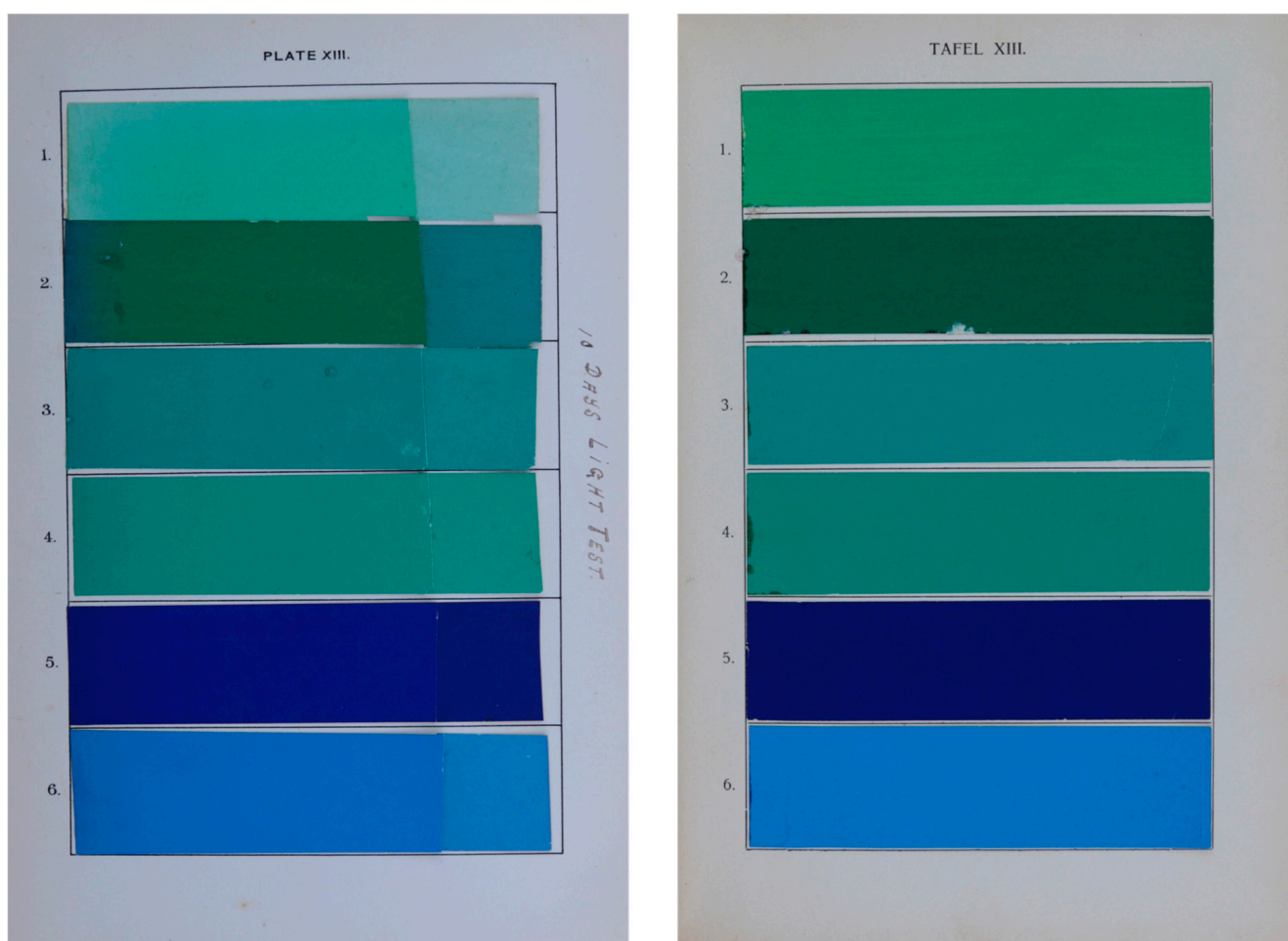












Figure 2. Plate XIII from the first English edition (on the left) and the German translation (on the right).

2.2. Lake Pigments Investigated

Samples of Jennison's lakes collected from two original versions, the first edition of the English publication and its German translation, were analysed in the present work. Among the lake pigments described in the book, several representative formulations considering dyes and/or precipitating agent combinations were chosen (see Table 1). Jennison's and (previously) Weber's comments on the precipitation of dyes with sulfonic acid groups with barium and tannic acid drew attention to the green lakes selected for this study [2] (pp. 80–82, 97–99) [25] (pp. 188–189). Jennison does not disclose the binder used for the paintouts, and it was not analysed in this investigation. The list of samples analysed with X-ray fluorescence, Raman spectroscopy, and liquid chromatography–diode array detector

and tandem mass spectrometry, along with their description according to Jennison's book, is reported in Table 1.

Table 1. Overview of the samples selected for analysis, Jennison's description, and results of the chemical investigation (* as detected by Raman). All the dyes are indicated by the common name (bold), the generic C.I. name and number, and Schultz number [25].

Sample	Photo (English Book)	Photo (German Book)	Description	Results of Chemical Investigation	
				English Book	German Book
Plate XII, sample 3			Lake pigment made of Acid green D tinted with Naphthol yellow S	Light green SF yellowish (Acid Green 5, C.I. 42095, No. 765), Pb , tannins	Light green SF yellowish (Acid Green 5, C.I. 42095, No. 765), Naphthol Yellow S (Acid Yellow 1, C.I. 13016, No. 19), Ba , S
Plate XII, sample 4			Lake pigment made of Acid green D and Quinoline yellow	Diamond green (Basic Green 1, C.I. 42040, No. 760) Auramine O (Basic Yellow 2, C.I. 41000, No. 752), Pb , tannins	Light green SF yellowish (Acid Green 5, C.I. 42095, No. 765), Naphthol Yellow S (Acid Yellow 1, C.I. 13016, No. 19), Ba , S , barium sulphate *
Plate XII, sample 5			Lake pigment of Acid green D and Metanil yellow, precipitated with barium and tannic acid	Light green SF yellowish (Acid Green 5, C.I. 42095, No. 765), Diamond green (Basic Green 1, C.I. 42040, No. 760) Auramine O (Basic Yellow 2, C.I. 41000, No. 752), Metanil yellow (Acid Yellow 36, C.I. 13065, No. 169), tannins	Light green SF yellowish (Acid Green 5, C.I. 42095, No. 765), Diamond green (Basic Green 1, C.I. 42040, No. 760), Naphthol Yellow S (Acid Yellow 1, C.I. 13016, No. 19), Orange II (Acid Orange 7, C.I. 15510, No. 189), Ba , S , Pb
Plate XIII, sample 3			Barium lake of Acid Green D and Naphthol yellow S	Light green SF yellowish (Acid Green 5, C.I. 42095, No. 765), Ba , S , Pb , barium sulphate *, tannins	Light green SF yellowish (Acid Green 5, C.I. 42095, No. 765), Naphthol Yellow S (Acid Yellow 1, C.I. 13016, No. 19), Ba (traces)
Plate XIII, sample 4			Barium lake of Acid green D and Naphthol yellow, but tannin and tartar were added to complete precipitation	Light green SF yellowish (Acid Green 5, C.I. 42095, No. 765), Ba , S , Pb , barium sulphate *, tannins	Light green SF yellowish (Acid Green 5, C.I. 42095, No. 765), Naphthol Yellow S (Acid Yellow 1, C.I. 13016, No. 19), Ba , S

2.3. Chemicals

The solvents used for HPLC-DAD and HPLC-ESI-Q-ToF analysis and sample pre-treatment were water (LC-MS grade, Sigma Aldrich, St. Louis, MO, USA), acetonitrile (LC-MS grade, Sigma Aldrich, St. Louis, MO, USA), formic acid (98–100%, Sigma

Aldrich, USA), ethylenediaminetetraacetic acid (EDTA, Sigma Aldrich, USA), and *N,N*-dimethylformamide (Sigma Aldrich, USA).

2.4. Apparatus

2.4.1. HPLC-DAD and HPLC-ESI-Q-ToF

The HPLC-DAD system consists of a PU-2089 quaternary pump equipped with a degasser, an AS-950 autosampler, and an MD-2010 spectrophotometric diode array detector (DAD) (all modules Jasco International Co., Hachioji, Japan). The DAD detection parameters were wavelength range 200–650 nm, resolution 4 nm, and acquisition rate 0.2 s. The HPLC-ESI-Q-ToF consists of an HPLC 1200 Infinity, coupled to a Jet Stream ESI-Q-ToF 6530 Infinity detector and equipped with an Agilent Infinity autosampler (Agilent Technologies, Palo Alto, CA, USA). High-resolution MS and MS/MS spectra were obtained in positive ionisation mode in the acquisition range of 100–1700 m/z , with a scan rate of 1.04 spectra/sec (CID voltage 30 V, collision gas N_2 , purity 99.999%). Chromatographic separation was performed in both instrumentation on an analytical reversed-phase column Poroshell 120 EC-C18 (3.0 × 75 mm, particle size 2.7 μm), equipped with a Poroshell 120 EC-C18 (3.0 × 5 mm, particle size 2.7 μm) guard-column. The eluents used as mobile phase were A = water with 1% (*v/v*) formic acid (FA); B = acetonitrile with 0.3% (*v/v*) formic acid (FA). The flow rate was 0.6 mL/min, and the program was 5% B for 2.6 min, then to 50% B in 13.0 min, to 70% B in 5.2 min, to 100% B in 6.2 min, and then held for 3.0 min; re-equilibration took 11 min. Further details on instrumentation and chromatographic method can be found in [26].

Prior to HPLC analysis, 100–400 μg of lake pigment samples were treated with 150 μL of 0.1% EDTA aqueous solution–DMF (EDTA-DMF method, further details on sample pre-treatment protocol are reported in [27]). Injection volumes were 1–2 and 10 μL for HPLC-ESI-Q-ToF and HPLC-DAD analysis, respectively.

2.4.2. XRF

XRF experiments were performed using the Elio portable XRF Analyzer (Bruker, GmbH, Billerica, MA, USA), equipped with a 10–40 keV/200 μA X-ray tube (Rh electrode, 1 mm collimated beam on the sample) and a large-area Energy Dispersive Si-Drift detector (130 eV FWHM at Mn $K\alpha$). All the XRF spectra were acquired for 90 s with 40 kV of voltage and 80 μA of current. The lake pigment samples were analysed as-is, without any further pre-treatment.

2.4.3. Raman

Raman measurements were made on a Renishaw InVia instrument coupled with an optical Leica DLML microscope, equipped with a NPLAN objective 50×. The laser source was a laser at 785 nm, and laser power output was set at 2 mW. The spectrometer consists of a single grating monochromator (1200 lines mm^{-1}) coupled with a CCD detector, a RenCam 578 × 400 pixels (22 μm × 22 μm), cooled by a Peltier element. The spectral calibration of the instrument was performed on the 520.7 cm^{-1} band of a pure silicon crystal. All SERS spectra were recorded between 350 and 2000 cm^{-1} , where the main Raman and SERS signals of dyes are located, with 10 accumulations and exposure times of 10 s.

2.4.4. Colourimetry

To provide an evaluation of colour differences between the twelve paintouts, visual and digital comparisons were performed. Three areas were selected from each of the twelve samples by using photos collected from the two manuscripts using a colour calibration chart. L^* , a^* , and b^* values of the CIE $L^*a^*b^*$ colour space of the recto were determined using

Photoshop 8.0 software (Adobe, San Jose, CA, USA). The results represent the average of three determinations with an average relative standard deviation of 2%.

3. Results

This section focuses on the identification and characterisation of chemical components (i.e., synthetic organic pigments and inorganic fillers) used in the early days of lake manufacturing. Exemplificative samples, specifically green lakes collected from Plate XII and XIII of *The Manufacture of Lake Pigments from Artificial Colours* [2] were analysed with liquid chromatography-based techniques (HPLC-DAD and HPLC-ESI-Q-ToF), Raman, and X-ray fluorescence (XRF) spectroscopies. The analytical approach applied for investigating samples collected from Jennison's book makes it possible to highlight both concordances (matched formulations) and discrepancies (mismatched formulations) in lake formulations when compared to Francis H. Jennison's description or to the different editions (i.e., English and German book). In the first case, the dyes profile corresponds to the indications reported for each lake plate. In the second case, different or additional components with respect to those reported by Jennison were identified by revealing some secrets behind the lake pigment manufacture in the early 20th century. The results achieved are summarised in Table 1.

3.1. Inorganic Fillers, Precipitating Agents, or Inorganic Pigments

XRF measurements were used to investigate the elemental composition of Jennison lakes, enabling the detection of inorganic species potentially linked to inorganic pigments, lake fillers, or the counter ions used in precipitating synthetic dyes. The results primarily indicated the presence of barium (Ba) and sulphur (S) in samples collected from Plate XIII in the English book and in almost all samples from the German book. To rationalise the XRF findings, Raman spectroscopy was performed. Analyses were carried out on both the front (recto) and back (verso) of a selection of the lake paper mock-ups to assess whether the detected Ba and S originated from the paper support or the lake itself. Specifically, Raman analysis on the verso identified scatterings associated with calcite (CaCO_3) only, while on the recto, barium sulphate (BaSO_4) was detected. Lead was also identified in several samples, but Raman spectroscopy did not provide useful information on possible Pb-containing inorganic pigments.

3.2. Synthetic Colourants

Jennison describes all the lake pigments investigated in the present work as "Acid Green D-based", with a different yellow component (Naphthol Yellow S in Plate XII sample 3, Plate XIII sample 3 and Plate XIII sample 4, Quinoline Yellow in sample 4, and Metanil Yellow in Plate XII sample 5) to achieve different green hues. While Raman spectroscopy revealed very similar spectra, characterised by unsatisfying S/N ratio and featuring peaks related to Diamond Green only, HPLC-DAD and HPLC-ESI-Q-ToF enabled us to rationalize this evidence by pointing out more differences than those reported by the scholar for their production.

HPLC-based techniques (HPLC-DAD chromatograms are reported in Figure 3 for lake pigments collected from the German book) identified the green component as Light Green SF yellowish (C.I. 42095, Acid Green 5, AG5) in most of the lake pigments investigated. While this dye was identified in all the samples collected from the German book, in the English version, Light Green SF yellowish was determined only in Plate XII sample 3 and 5 and in Plate XIII sample 3 and 4. However, Diamond Green (C.I. 42040, Basic Green 1, BG1) was also detected in some lake pigments: as the only green component in Plate XII sample 4 of the English book and in combination with Light green SF yellowish in

Plate XII sample 5 of both English and German versions. Both green dyes were identified along with N-dealkylated products (namely, BG1-Me, AG5-Et, and AG5-C₇H₇SO₃) and benzophenone derivatives (AG5 and BG1 degradation products [13]), consistent with previous findings in the literature [13,28,29], which originates either by ageing processes or by the procedure steps applied for obtaining the lake pigments. The analytical results suggest that triarylmethane dyes such as Light Green SF yellowish and Diamond Green were used in the samples indicated by Jennison as prepared with “Acid Green D”.

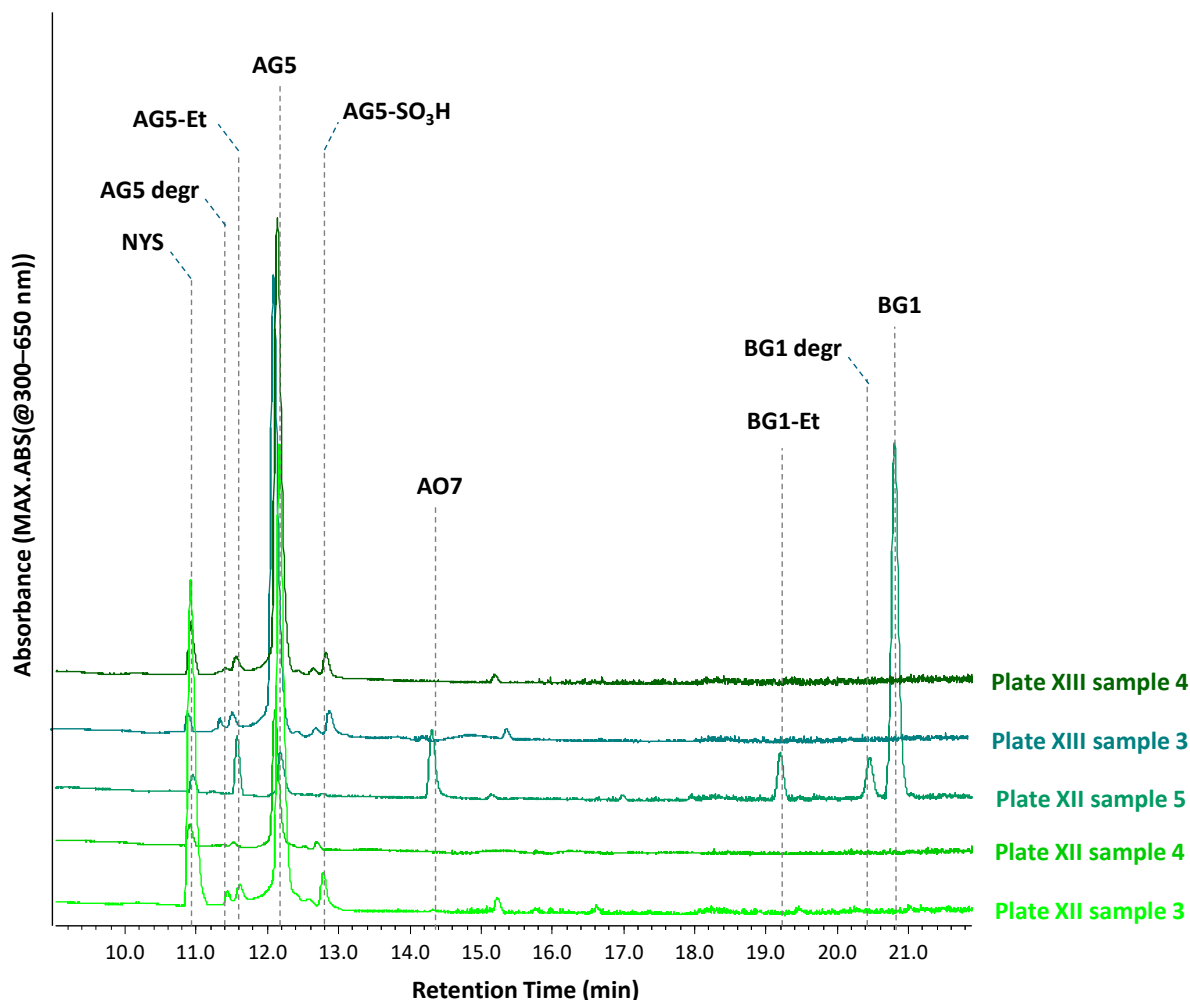


Figure 3. HPLC-DAD chromatograms (350–650 nm) of Jennison’s lake pigments collected from Plates XII and XIII of the German book. Diamond green (BG1) and its de-ethylated (BG1-Et) and degradation products (BG1 degr), Orange II (AO7), Naphthol Yellow S (NYS), and Light Green SF yellowish (AG5) and its degradation products (AG5-SO₃H, AG5-Et, and AG5 degr). All chromatograms are presented in the same scale and are stacked for purpose of clarity.

More differences were outlined by examining the chemical profiles associated with yellow dyes. A match with Jennison’s description was rarely determined. Indeed, the composition declared by Jennison was confirmed only in the lake pigments collected from Plate XII sample 3, Plate XIII sample 3, and Plate XIII sample 4 of the German edition, with HPLC-DAD and HPLC-ESI-Q-ToF results confirming the presence of Naphthol Yellow S (C.I. 13016, Acid Yellow 1, NYS) in the formulations. In the corresponding samples of the English version, no yellow organic pigment was identified by chromatographic methods and no inorganic pigment by Raman spectroscopy, although XRF analysis highlights the possible presence of a lead-based yellow inorganic pigment (see Section 3.1). Additionally, Naphthol Yellow S was detected in Plate XII samples 4 and 5 in the German edition. Sample

5 additionally contains Orange II (C.I. 15510, Acid Orange 7, AO7) to adjust the yellow hue towards a more reddish hue. Conversely, in the English edition, Auramine O (C.I. 41000, Basic Yellow 2, Au) was found in both samples, and sample 5 also contained the declared Metanil Yellow (C.I. 13065, Acid Yellow 36, AY36).

3.3. Natural Tannins

Despite Jennison's description, which reports tannins only in Plate XII sample 5 and Plate XIII sample 4, polyphenolic compounds were detected in all the lake pigments analysed in the English version of the manuscript. The profiles (Figure 4) include molecular markers identified in previous studies in iron gall inks (e.g., gallic acid, ellagic acid, digallic acids, mono- galloyl glucoses, tri- galloyl glucoses, tetra- galloyl glucoses, and m_5 and m_{10} gallic acid degradation products [30]) but also additional compounds. Ethyl gallate (8.3 min, $[M - H]^- = 197.043$), already described in the literature in reference textiles dyed with tannins extracted from walnut [31], was identified along with dimers formed by its condensation reaction with gallic acid (gallic acid-ethyl gallate dimers, eluting at 10.5 and 11.3 min, $[M - H]^- = 349.053$). To the best of our knowledge, this is the first report of these dimers in the literature (tandem mass spectra presented in Figure 5). Furthermore, an unknown compound (12.9 min, $[M - H]^- = 299.090$) with a similar tandem mass spectrum to that of hematein, a marker of logwood dye (8.3 min, $[M - H]^- = 299.058$, as acquired for an analytical standard in the same experimental conditions), was also detected and labelled as pseudo-hematein. Its molecular structure has been proposed to be derived from hematein, with the absence of a hydroxyl group and the presence of a methoxy substituent. This structural hypothesis (Figure 6) is supported by the lack of fragments corresponding to water loss and the presence of fragments indicating the loss of both methyl and methoxy groups in the MS/MS spectrum.

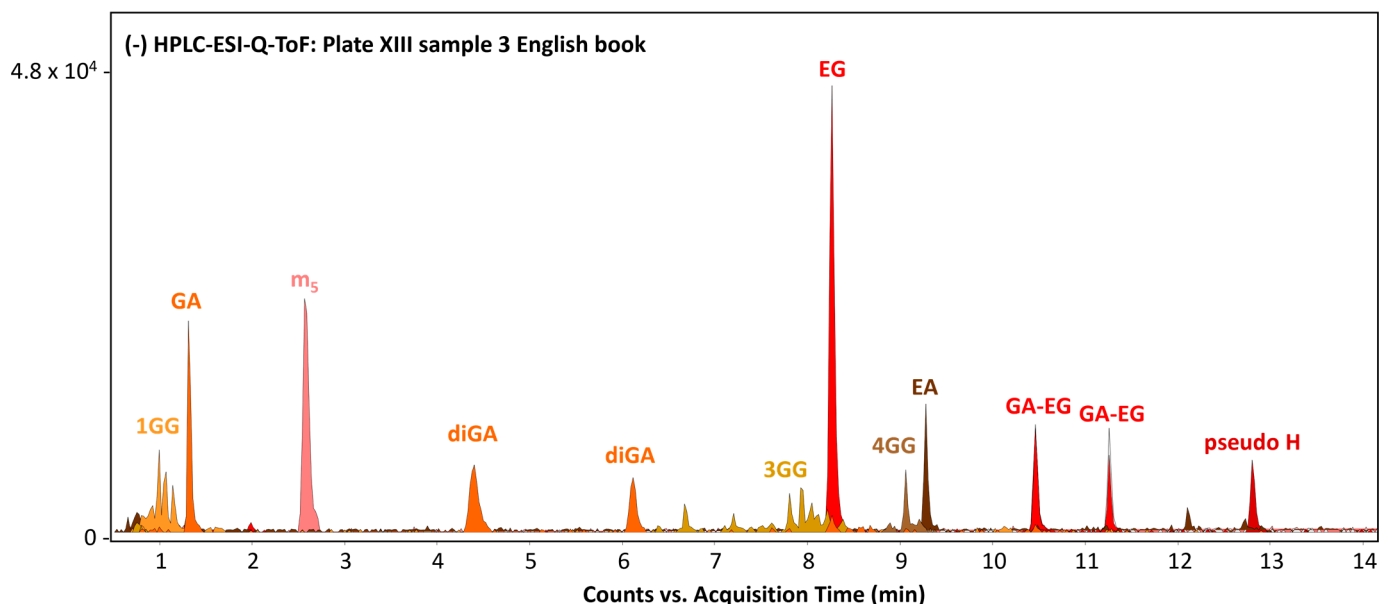


Figure 4. HPLC-ESI-Q-ToF Extract Ion Chromatograms (EICs) of compounds detected in the EDTA-DMF extract of Plate XIII sample 5. Negative acquisition mode. Extract Ion Chromatograms (EICs) of the components identified: $C_7H_6O_5$ (gallic acid, GA), $C_8H_6O_5$ (gallic acid degradation product, m_5), $C_{14}H_6O_8$ (ellagic acid, EA), $C_{14}H_{10}O_9$ (digallic acid, diGA), $C_{13}H_{16}O_{10}$ (mono galloyl-glucose, 1GG), $C_{27}H_{24}O_{18}$ (tri galloyl-glucose, 3GG), $C_{34}H_{28}O_{22}$ (tetra galloyl-glucose, 4GG), $C_9H_{10}O_5$ (ethyl gallate, EG), $C_{16}H_{14}O_9$ (gallic acid-ethyl gallate dimer, GA-EG), and $C_{17}H_{16}O_5$ (pseudo-hematein, pseudo H).

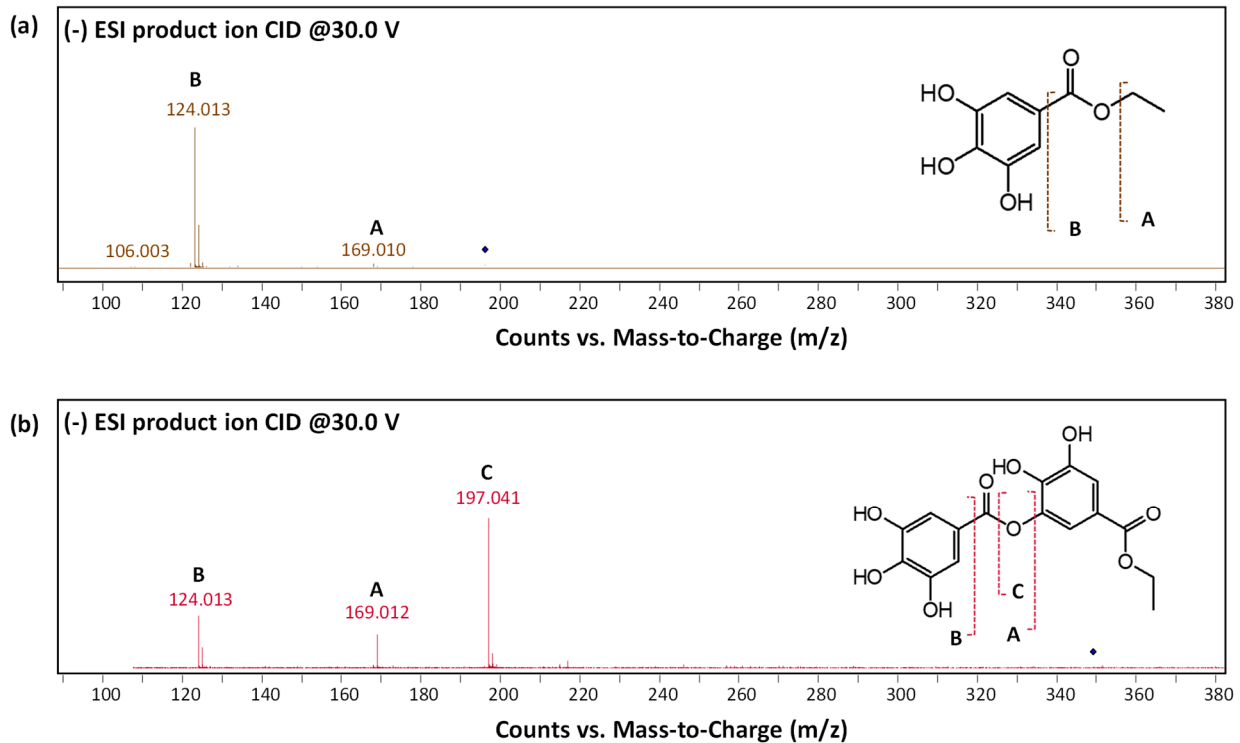


Figure 5. Tandem mass spectra of (a) ethyl gallate ($t_R = 8.3$ min, $C_9H_{10}O_5$); (b) gallic acid-ethyl gallate dimers ($t_R = 10.5$ min and 11.3, $C_{16}H_{14}O_9$).

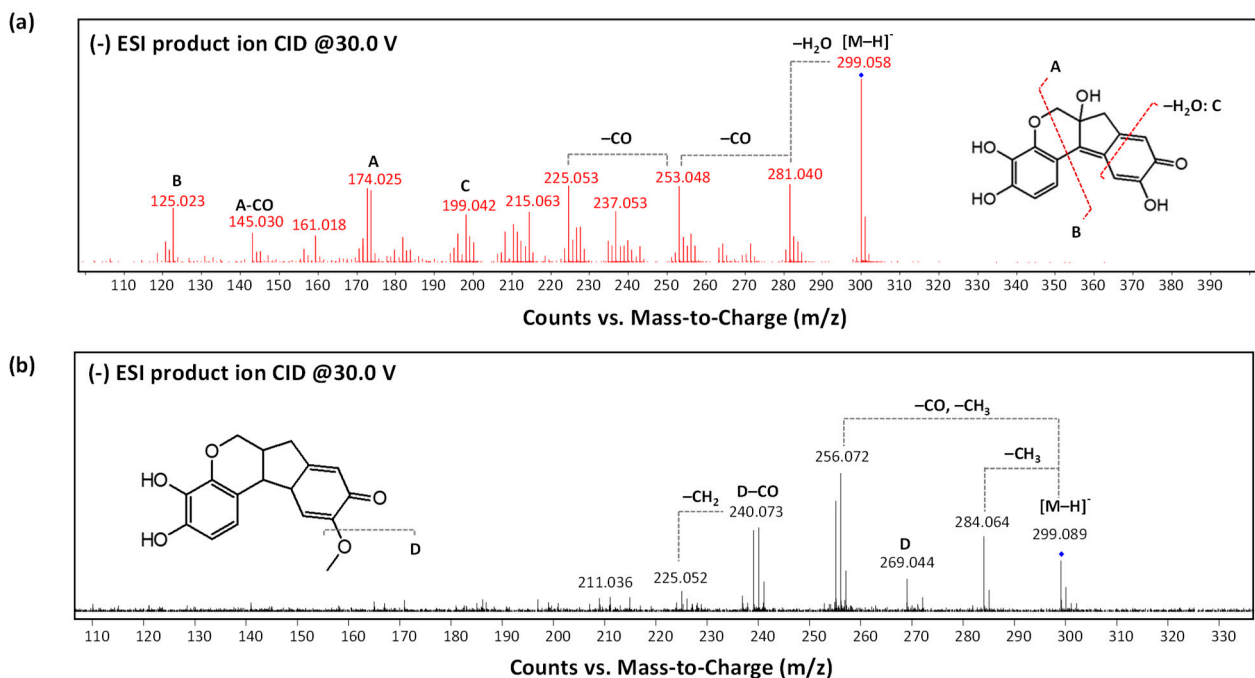


Figure 6. Tandem mass spectra of (a) hematein (analytical standard, $t_R = 10.0$ min, $C_{16}H_{12}O_6$). The ring expansion that results in fragment A has been hypothesised accordingly to [32]; (b) pseudo-hematein ($t_R = 12.9$ min, $C_{17}H_{16}O_5$).

4. Discussion

The results obtained for both the organic and inorganic components of the analysed samples provide interesting insights and pose some questions. With regard to the synthetic dyes used to produce the pigment lakes, the green lakes produced by Francis H. Jennison were all based on *Light Green SF Yellowish* (Schultz N° 765, also sold as Säuregrün or

Acid Green, discovered by Köhler in 1879), with the only exception of Plate XII sample 4 from the English book, which featured *Diamond Green* (Schultz N° 760, also sold as Brillantgrün or Brilliant green, discovered by Bindschedler and Busch in 1879). Instead, the greenish hue was modulated by the addition of yellow/orange organic pigments, allowing us to detect *Auramine O* (Schultz N° 752, first synthesized by Gruüwald in 1883), *Naphthol Yellow S* (Schultz N° 19, also sold as Säuregelb or Acid Yellow, patented by Caro in 1879), *Orange II* (Schultz N° 189, also sold as Säureorange A or Acid Orange II, discovered by Roussin in 1876), and *Metanil Yellow* (Schultz N° 169, also sold as Victoriageleb I or Tropaeolin G, discovered by Bayer & Co (Leverkusen) in 1879). These dyes were discovered between 1876 and 1883 and found widespread use in the late 19th century, as documented in previous studies on German and English textile swatch catalogues [13,25,33]. Unexpectedly, the observed differences in final colour of the green hues were not obtained only by exploiting different yellow organic pigments or precipitating agents, as declared by Francis H. Jennison, but by adding additional and undisclosed synthetic colourants in some formulations.

The colourimetric evaluation allowed us to evidence the colour differences among the five samples belonging to the same book and among the respective two versions, while HPLC techniques enabled us to outline different molecular profiles for supposedly corresponding swatches from the English and German editions. The mismatching composition among the respective samples of the two book versions is clearly evidenced by the resulting total colour difference (ΔE), which ranges from 35 for Plate XIII sample 3 to 5 for Plate XII sample 4. As expected, all the samples exhibit rather negative a^* value, all of them being green, with Plate XII sample 5 from the German edition showing the highest a^* value among the set due to the detection with HPLC-ESI-Q-ToF of Orange II in this lake formulation. In addition, for the samples described by Jennison as Naphthol Yellow-based (i.e., Plate XII sample 3, Plate XIII sample 3 and 4) we detected the colourant in the German edition, while no yellow pigment was found in the corresponding samples from the English book. These findings align with the lower b^* values observed in the lake pigments of English manuscripts. However, not only the qualitative profile but also the different ratio between the components present in the formulations can contribute to such differences.

With respect to the fillers and precipitating agents necessary to produce lake pigments starting from organic dyes, the identification of barium as barium sulphate (BaSO_4) on the recto of the samples does not allow a straightforward explanation. As barium salts were commonly used as precipitants for lakes based on acid dyes, barium sulphate may have formed along with the lake or might have been added before (or, less likely, after) precipitation in the lakes collected from Plates XII and XIII. Similarly, the detection of lead could be associated both with the presence of a yellow inorganic pigment (not detected by Raman spectroscopy) or the counter-ion used to precipitate the detected yellow organic pigment (see Section 3.2).

On the other hand, tannic acid was mentioned in recipes for preparing lake pigments starting from water-soluble basic dyes. Indeed, the chromatographic analyses identified polyphenolic compounds in all the lake pigments analysed from the English edition of the manuscript, and this marks the first instance in the literature where tannins used as precipitating agents for basic dyes have been detected analytically.

According to Francis H. Jennison, tannic acid was the first choice for precipitating basic dyestuffs, as it produces more permanent lake pigments compared to arsenous and oleic acids, although the latter could result in more brilliant colours. Jennison reported that the most common method for producing lakes of basic dyes involved combining tannic acid with tartar emetic (potassium antimonyl tartrate), which acted as a fixative for the basic colours precipitated by tannic acid. Tannins also were used to complete the precipitation of

acid dyes containing sulfonic acid groups with barium chloride. However, the description provided by Jennison is somewhat ambiguous in light of contemporary knowledge about tannic acid and polyphenolic compounds. On page 54 of the first edition, Jennison refers to “Tannic acid, digallic acid- Tannin”, suggesting some confusion in the understanding of the composition of polyphenolic extracts in the early 20th century. While “tannins” is a general term for the polyphenolic compounds extracted from natural sources, digallic acid ($C_{14}H_{10}O_9$) and tannic acid ($C_{76}H_{52}O_{46}$) are specific poly-galloyl gallates and poly-galloyl glucoses [34,35], respectively. In the second edition of the manuscript (Francis H. Jennison, 1920) [4] (pp. 46–47), Jennison further clarifies that the tannic acid used for precipitation was sourced from different suppliers, who extracted the compound from materials like gall nuts or sumach using water or alcohol. This is consistent with our results, highlighting a peculiar chemical profile for the tannin fraction of the lake pigments, which probably is linked to the use of a specific natural source of tannins, a mixture of raw sources, or even a treatment with specific chemicals. As far as we know, in the literature, there is no evidence of such profile, and thus, further investigation is required for highlighting its vegetable origin. Nonetheless, given the current knowledge, the detection of ethyl gallate, gallic acid–ethyl gallate dimers, and pseudo-hematein could help in discriminating when tannins applied on paper are used as colourants (as in iron gall inks) or as precipitating agents of synthetic dyes (as in lake pigments manufacture).

5. Conclusions

This paper presents the first technical and analytical study of Jennison’s book on the manufacture of lake pigments based on synthetic dyes. By an analytical point of view, we report for the first time the identification by means of chemical analysis of tannins being used as precipitating agents both for basic and acid dyes. Additionally, previously undescribed polyphenols were detected in these formulations, revealing a chemical profile that does not correspond to any of the commonly known natural sources of tannins.

By a technical and historical point of view, the differences in the chemical profiles acquired for the English and German books, already clearly visible by naked eye from the variances in hues (Figure 1), raise several questions. These include concerns about the reliability of these materials as reference for historical formulations due to the mismatch between the declared and the detected composition as well as questions regarding the identity of the lake pigment’s producer since it is unknown whether Jennison produced the lakes for the colour plates himself. Considering that he was a colour chemist, it is possible that he just provided a single specimen and somebody else was assigned to produce larger quantities of the lakes for the books. It was common practice in paint manufacture that a customer provided a sample, and then, the company had to produce a matching colour [36,37]. If the production of the lakes for the book plates was outsourced, and the company could not match the sample provided by Jennison, they might have adjusted it by adding other ingredients. This might explain the mismatch of Jennison’s descriptions and the analysed samples, but at the same time, it questions the reliability of Jennison’s historic lakes as references, further highlighting the importance of conducting thorough chemical investigation through sensitive and selective analytical methods in parallel with the study of the technical literature.

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