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ORIGINAL RESEARCH OR TREATMENT PAPER

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Breaking Bad Pigments: Unmasking the False Origins of Cadmium Yellow

Leonardo Pantoja

Department of Natural Sciences, Faculty of Science and Technology, Middlesex University, London, UK

ABSTRACT
This study investigates the earliest documented occurrences of cadmium pigments through chemical analysis of nine historical pigment samples dated 1836, 1838, and 1851. Cadmium sulphide (CdS), though proposed as a pigment shortly after cadmium's discovery in 1817, is not materially verified in any surviving samples prior to the mid-nineteenth century. SEM-EDX, Raman spectroscopy, FTIR, and UV–NIR reflectance were used to analyse pigment specimens from Friedlieb Ferdinand Runge's *Einleitung in die technische Chemie für Jedermann* (1836) and *Technische Chemie der nützlichsten Metalle für Jedermann* (1838), alongside a documented Reeves & Sons watercolour set dated 3rd February 1851. Contrary to Runge's textual descriptions claiming cadmium oxide and cadmium sulphide preparations, none of the 1836–1838 swatches contained detectable cadmium. Instead, the samples were found to contain lead chromate ($PbCrO_4$), basic zinc carbonates ($Zn_5(CO_3)_2(OH)_6$), and copper-chromate phases. In contrast, the Reeves & Sons 1851 samples contain barium chromate ($BaCrO_4$) and unequivocal cadmium sulphide representing the earliest currently verified material evidence of cadmium pigment production (earlier documentary references predate the earliest analytically confirmed sample of 8 March 1851). These results clarify the historical timeline of cadmium yellow, demonstrate that early printed references do not correspond to actual cadmium-based materials, and provide the first analytical verification of pigment substitutions in Runge's colour plates.

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Material analysis; Raman; FTIR; SEM-EDS; Pigment substitution; Historical materials

Introduction

Cadmium: discovery, early history, and pigment development

Cadmium, a soft, bluish-white metal, was first isolated in 1817 by Friedrich Stromeyer, a German chemist, during his research on zinc ores (Stromeyer 1819). Stromeyer discovered cadmium as an impurity in zinc carbonate, later recognising it as a distinct element. The name 'cadmium' derives from the Greek word 'kadmeia', referring to calamine, the mineral from which it was extracted. Despite its initial discovery, cadmium did not see immediate widespread use, primarily due to its difficulties in extraction and hence high cost during the early nineteenth century.

Claims that the natural cadmium sulphide minerals greenockite and hawleyite were historically used by artists over two millennia still have no material evidence to support them (Fiedler and Bayard 1986). Instead, practical pigment production emerged only in the mid-nineteenth century, when cadmium sulphide (CdS) began to be manufactured as a synthetic pigment (Fiedler and Bayard 1986). Despite its high price, cadmium yellow offered properties unmatched by contemporary yellow pigments such as chrome yellow (lead chromate-based pigments), gamboge, Indian yellow, or orpiment (Gettens and Stout 1966). CdS provided exceptional lightfastness, chromatic purity, chemical stability, and inertness in mixtures (Fiedler and Bayard 1986), offering a reliable alternative to the fugitive organic yellows and the instability of lead chromate (Kühn and Curran 1986). Manufacturers anticipated that expanding zinc refining would increase cadmium availability and reduce prices; these expectations helped justify the early introduction of CdS despite its cost.

By the end of the nineteenth century, cadmium yellows and oranges were highly valued for their brightness and range of hues, from pale lemon to deep orange, controlled not only through particle size and crystallinity of cadmium sulphide (CdS), but also through compositional modification, including zinc incorporation to form Cd–Zn sulphide solid solutions ($Cd_{1-x}Zn_xS$) for lighter, greener yellows and selenium substitution to produce cadmium sulfoselenides ($CdS_{1-x}Se_x$) for deeper orange to red tones (Fiedler and Bayard 1986; Mayer 1991).

Nevertheless, cadmium remained scarce. Global production in 1871 was estimated at only 115 kg/year (Fiedler and Bayard 1986). Its price reflected this

CONTACT Leonardo Pantoja l.pantojamunoz@mdx.ac.uk Department of Natural Sciences, Faculty of Science and Technology, Middlesex University, The Burroughs, London, NW4 4BT, UK
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limitation: in 1878 cadmium yellow was roughly twenty times more expensive than chrome yellow, a synthetic lead chromate pigment manufactured from more readily available lead and chromium based raw materials (Ghirardello et al. 2021). These factors made cadmium pigments luxury materials and delayed their mainstream adoption until increasing industrial refinement after the 1860s lowered costs and improved supply.

Early documentation of cadmium pigments and unresolved historical claims

Although cadmium was proposed as a pigment soon after its discovery in 1817 (specifically in 1818), no confirmed material examples pre-dating the 1850s are known (Stromeyer 1819). The oldest scientifically verified cadmium pigment is a sample held at the Courtauld Institute, prepared on 8 March 1851 and likely associated with the Great Exhibition in London; analysis confirmed it as cadmium sulphide (Ghirardello et al. 2018).

Earlier textual mentions exist but lack material corroboration. A frequently repeated claim states that cadmium was introduced into oil painting in 1829 by a painter named Melandri (Eibner 1909), but no primary documentation has been identified. In 1830, Jean-François-Léonor Mérimée described cadmium sulphide in chemical terms, commenting on its scarcity, cost, and incompatibility with lead-based pigments, but explicitly stated he had not seen it used in painting nor provided any recipe or preparation method (Mérimée 1830). Thus, his reference represents theoretical awareness rather than evidence of practical use.

Commercial documentation predates surviving physical samples. Winsor & Newton listed cadmium yellow in their 1846 catalogue (Carlyle 2001), and the Roberson firm recorded a purchase from the Paris supplier Victor Fayoux in 1849 (Carlyle 2001). Lefranc Frères catalogues issued between 1840 and 1851 appear to list cadmium yellow (Lefranc-Bourgeois 2025), although the currently accessible online reproduction is low resolution and limits precise verification of the entry (Lefranc-Bourgeois 2025) and no analysed samples confirm this production. Winsor & Newton archival records note that cadmium metal was imported from Antwerp for pigment manufacture in the 1850s, aligning with known continental European cadmium sources including Silesia, Saxony, and the Harz region (Fiedler and Bayard 1986; Ghirardello et al. 2021). These references indicate awareness, experimentation, and early distribution, but do not constitute proof of material production before 1851. A detailed chronology of such claims is summarised in Table 1.

Chromatic documentation and naturalist publications in the early nineteenth century

During the late eighteenth and early nineteenth centuries, scientific interest in natural history, botany, and mineralogy expanded dramatically. Naturalist and chemical treatises and books combined empirical observation with meticulous visual documentation. These volumes often included detailed colour illustrations and chromatic tables intended to systematise natural descriptions of colour and serve as accurate reference tools for artists, scientists, and explorers. Such works exemplify the tight integration of empirical science and visual communication in this period (Ford 2003; Paclt 1983). For example, Charles Darwin relied on Syme's *Nomenclature of Colours* to record biological observations, highlighting the centrality of precise colour standards in scientific practice (Simonini 2018).

Within this context, Friedlieb Ferdinand Runge (1794–1867), best known for discovering aniline and caffeine, emerged as an influential figure whose work bridged analytical chemistry, dye chemistry, and public education Maar (2025). Runge's publications, such as his books *Einleitung in die technische Chemie für Jedermann*[1] (1836) and *Technische Chemie der nützlichsten Metalle für Jedermann*[2] (1838), reflect the era's merging of colour science and chemical instruction. These works included coloured plates showing the products of reactions and prepared chemical substances, presented as *chemische Verbindungen in natura*, that is, as actual material samples rather than printed illustrations. The colour samples were not printed directly onto the page but were applied as discrete swatches affixed to the paper support. Microscopic examination (Supplementary Material Figures

Table 1. History of cadmium yellow from its first mention in scientific literature.

Year	Claim/event	Party involved	Evidence type	Reference
1829	Melandri used cadmium in oil painting	Unknown/Melandri	Anecdotal claim (no citation)	(Eibner 1909)
1830	Cadmium is described chemically	Mérimée	Technical text only, no pigment use	(Carlyle 2001)
1836	'Cadmium yellow' swatch printed	F.F. Runge	Printed book, unverified material	(Runge 1836)
1838	'Cadmium oxide' and 'cadmium yellow' printed	F.F. Runge	Printed book, unverified material	(Runge 1838)
1841	Pigment description (no sample)	George Field	Textual mention, no sample	(Carlyle 2001)
1846	Listed in the W&N catalogue	Winsor & Newton	Commercial listing, no sample	(Carlyle 2001)
1849	The purchase was recorded from Fayoux	Roberson	Purchase ledger (No.1, *p.* 291–2)	(Carlyle 2001)
1851	Cadmium yellow sample dated March 8th	W&N (Courtauld Institute)	Scientifically confirmed material	(Ghirardello et al. 2018)
1852	First catalogue listing at Reeves	Reeves & Sons	Printed listing, no sample	(Carlyle 2001)

S10–S13) shows that the material is deposited onto a fibrous woven support (cellulosic substrate) and that the colour layer consists of particulate matter consistent with paint application rather than dye penetration. The morphology suggests manual application of prepared material to the support, rather than printing ink or textile dyeing.

Although these substances were frequently designated by contemporary pigment names, thereby linking them to the pigment and dye trades, they were framed primarily as chemical compounds and technical products within a broader program of practical chemistry. Importantly, these books contain some of the earliest references to 'cadmium yellow' and 'cadmium oxide' pigments. However, the actual material identity of these swatches has remained unverified.

This historical placement of Runge's books within the naturalist-scientific publishing tradition is essential: these volumes used colour both didactically and scientifically, and their claims form part of the broader narrative regarding early awareness of cadmium pigments before industrial production took hold. Given the unresolved chronology of cadmium pigment availability and the lack of verified material evidence before the 1851 Courtauld sample, scientific investigation of these swatches is crucial.

Aim

This work investigates the chemical composition and historical context of pigment samples dated 1836, 1838, and 1851 to assess undocumented or uncertain early uses of cadmium-based pigments. The study aims to determine the authenticity and material nature of early 'cadmium' references, clarify the presence or absence of cadmium within these historical sources, and evaluate the implications for the chronology of cadmium pigment availability, production, and adoption in nineteenth century artistic practice.

Materials and methods

Description of the samples used

Watercolour blocks found in a Reeves & Sons, (150 Cheapside, London) box were tested. Each block has an impressed stamp with the date 3rd February 1851 and also features a registered design number: 76407 (Archives 2025)

- Cadmium, Figure 1(A)
- Neutral orange, Figure 1(B)
- Lemon Yellow, Figure 1(C)

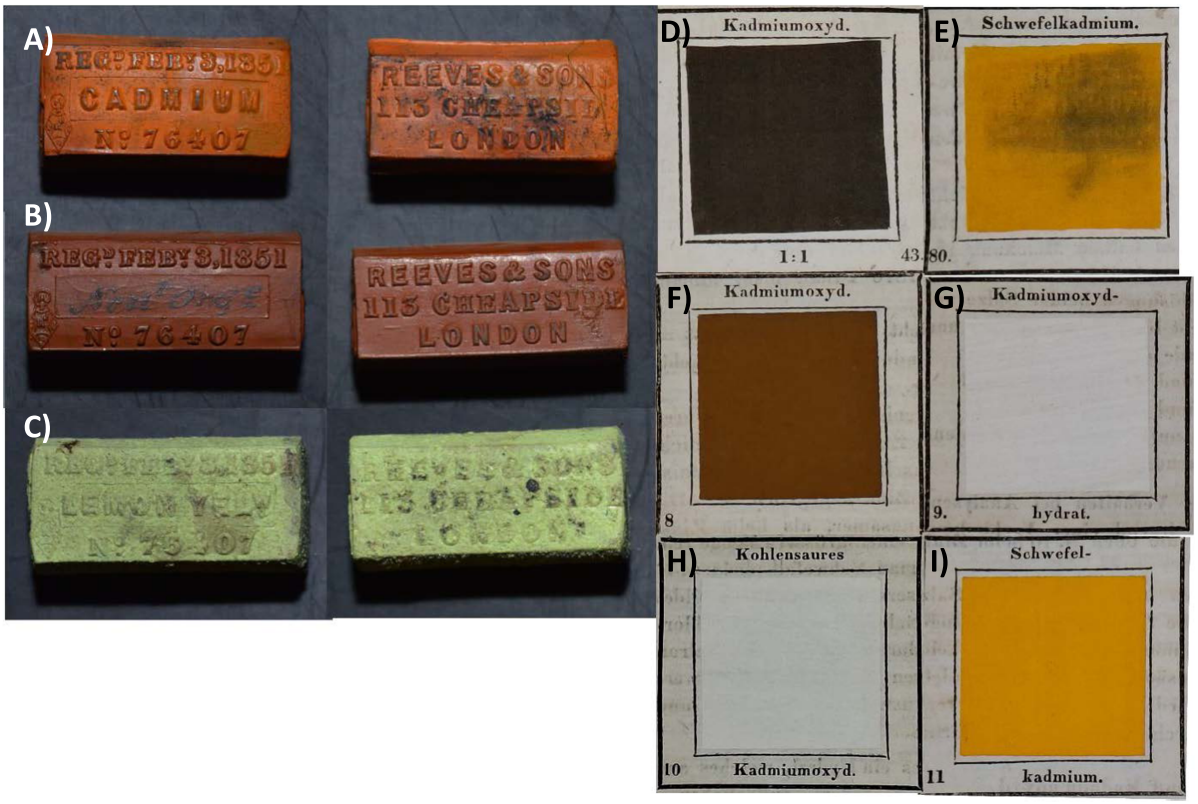

Figure 1, Historical samples used in the present study, Reeves & Sons, dated 3rd Feb 1851, (A) Cadmium, (B) Neutral orange and (C) Lemon yellow, Runge (1836). *Einleitung in die technische Chemie für Jedermann*, (D) Page 68, plate 43 Kadmiumoxyd and (E) Page 154, plate 80 SchwefelKadmium. Runge (1838) *Technische Chemie der nützlichsten Metalle für Jedermann*, Band 1, (F) Page 50, plate 8 Kadmiumoxyd, (G) Page 51, plate 9 Kadmiumoxyd hydrat, (H) Page 52, plate 10 Kohlensaures Kadmiumoxyd, (I) Page 54, plate 11 SchwefelKadmium.

The book Runge (1836), *Einleitung in die technische Chemie für Jedermann*, Berlin: Verlag der Sanderschen Buchhandlung, was tested:

- Page 68, plate 42 Kadmiumoxyd, Figure 1(D)
- Page 154, plate 80 SchwefelKadmium, Figure 1(E)

Runge (1838). *Technische Chemie der nützlichsten Metalle für Jedermann*, Band 1. Erster Teil: Zink, Kadmium, Mangan, Chrom, Wismuth, Antimon und Arsenik, mit 142 Abbildungen im Text. Berlin: Verlag von Ferdinand Dümmler.

- Page 50, plate 8 Kadmiumoxyd, Figure 1(F)
- Page 51, plate 9 Kadmiumoxyd hydrat, Figure 1(G)
- Page 52, plate 10 Kohlensaures Kadmiumoxyd, Figure 1(H)
- Page 54, plate 11 SchwefelKadmium, Figure 1(I)

The samples were sourced from a private collection in the UK and permission was given to take microsamples.

Synthesis of copper chromate ($CuCrO_4$)

Copper chromate was prepared by aqueous precipitation under controlled pH conditions. A 0.1 M potassium chromate solution (100 mL) was adjusted to either pH 8.5 or pH 7.0 using dilute H_2SO_4. For the pH 8.5 synthesis, the chromate solution was added dropwise to 50 mL of a 0.1 M $CuSO_4{\cdot}5H_2O$ solution under continuous stirring. For the pH 7.0 synthesis, the order of addition was reversed to minimise local acidification: the $CuSO_4{\cdot}5H_2O$ solution was added dropwise into the pH-adjusted chromate solution. In both cases, the resulting precipitate was collected by vacuum filtration, washed briefly with deionised water, and dried in an oven at 40 °C.

Fourier transformed infrared spectroscopy (FTIR)

FTIR analysis was done using an Agilent Cary 630 (Agilent Technologies). The instrument has a deuterated tryglycine sulphate (DGTS) detector and a ZnSe beam splitter; the range used was 650–4000 and 4 cm^{-1} resolution. Data acquisition was done using the ATR accessory, collecting the average of 40 backgrounds as well as sample spectra. All FTIR spectra show absorbance units in the y-axis. Software used for collection was MicrolabPC. In order to allow direct comparison and for consistency, the x-axis in all spectra shows increasing wavenumbers from left to right.

Raman spectroscopy

Confocal Raman microscopy was performed using a Labram Aramis (Horiba Scientific) with a 532 nm laser (10% power) and a 633 nm (HeNe laser, 1% power), a 50X objective, a 600 l/mm grating, a 50 µm pinhole, a 1–30 s integration time, and an average of 30 spectra accumulations, with the spectra baseline corrected. The instrument was calibrated using a silicon wafer and automatic software correction (Labspec 6). All reference spectra were taken from the RRUFF and UCL (Clark and Gibbs 2011; Lafuente et al. 2015). All Raman spectra show intensity in arbitrary units on the y-axis.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX)

Samples were analysed with a Phenom Pharos (Thermo Scientific) field emission gun scanning electron microscope (SEM) at high vacuum of 0.1 Pa and 15 kV acceleration voltage. Samples were mounted in aluminium studs using double-sided carbon adhesive tabs (Ted Pella); no coating was performed. Elemental composition was investigated through EDX with a silicon drift detector (SDD), 60 s analysis time per sample. Quantification was performed using the instrument's built-in fundamental parameters (FP) method, applying standard ZAF/φ(ρz) matrix corrections (ZAF = Atomic number, Absorption, Fluorescence).

Ultraviolet-near infrared (UV-NIR) reflectance

UV-NIR reflectance measurements were performed using a QualitySpec Trek spectroradiometer (Analytical Spectral Devices Inc.). The instrument covers 350–2500 nm, with spectral resolutions of 3, 9.8 and 8.1 nm at 700, 1400 and 2100 nm, respectively. Calibration was carried out using the manufacturer-supplied Spectralon® white reference. Illumination was provided by the instrument's internal quartz–tungsten–halogen lamp. Light is delivered through a fibre-optic probe aligned with a quartz sampling window; the illumination geometry is fixed at 55° relative to the window and the collection angle at 78°, minimising specular reflection. The fibre-optic cable has a 25° field of view, corresponding to a sampling spot of approximately 0.82 cm at the window surface. Data acquisition was performed using the instrument's integrated software.

Results

All samples were analysed for both elemental composition and molecular structure using a combination of SEM-EDX, Raman spectroscopy, UV-NIR and FTIR. A summary of the elemental and molecular data is presented in Table 2. SEM–EDX results are presented here as complementary evidence to the molecular and vibrational assignments. Because the analysed paints are complex heterogeneous systems containing

Table 2. Elemental and molecular analysis results of the samples tested in the present study.

ID	Sample	Description	Date	Elemental analysis	FTIR	Raman
A	Cadmium	Reeves & Sons	3rd Feb 1851	Cd (69.3), S (14.1), O (13.5), Ca (2.2), C (0.5)	ND	CdS
B	Neutral orange	Reeves & Sons	3rd Feb 1851	Cd (40.1), O (35.1), S (10.6), Fe (6.3), Br (2.8), Si (2.7), Ca (1.5), C (0.85)	ND	CdS
C	Lemon yellow	Reeves & Sons	3rd Feb 1851	Ba (46.5), O (35.5), Cr (15.2), In (1.7), Si (0.8)	ND	$BaCrO_4$
D	Page 68, plate 43 Kadmiumoxyd	Runge, F.F. Einleitung in die technische Chemie für Jedermann	1836	O (57.7), Cu (23.7), Cr (13.0), K (5.7)	ND	CrO_4^{2-} likely $CuCrO_4$
E	Page 154, plate 80 SchwefelKadmium	Runge, F.F. Einleitung in die technische Chemie für Jedermann	1836	Pb (47.3), O (40.9), Cr (8.3), C (3.5)	ND	$PbCrO_4$
F	Page 50, plate 8 Kadmiumoxyd	Runge, F.F. Technische Chemie der nützlichsten Metalle für Jedermann, Band 1	1838	O (73.1), Cu (15.1), Cr (5.4), C (6.5)	ND	CrO_4^{2-} likely $CuCrO_4$
G	Page 51, plate 9 Kadmiumoxyd hydrat	Runge, F.F. Technische Chemie der nützlichsten Metalle für Jedermann, Band 1	1838	Zn (51.9), O (41.5), C (4.5), S (1.2), Cl (1.0)	$Zn_5(CO_3)_2(OH)_6$	ND
H	Page 52, plate 10 Kohlensaures Kadmiumoxyd	Runge, F.F. Technische Chemie der nützlichsten Metalle für Jedermann, Band 1	1838	O (56.8), Zn (39.2), C (2.8), S (1.3)	$Zn_5(CO_3)_2(OH)_6$	ND
I	Page 54, plate 11 SchwefelKadmium	Runge, F.F. Technische Chemie der nützlichsten Metalle für Jedermann, Band 1	1838	Pb (64.8), O (23.0), Cr (12.0)	ND	$PbCrO_4$

ND: Data was generated, but no species were detected in the spectra. For elemental analysis parenthesis denotes mass concentration (%).

binders, substrates, reaction by-products, contaminants, and possible alteration products, the measured elemental mass percentages are not expected to reproduce ideal pigment stoichiometries. Instead, the EDX data are used primarily to assess the presence or absence of diagnostically relevant elements and to constrain the range of plausible pigment identifications in combination with vibrational data.

Elemental analysis revealed that only the samples from the Reeves & Sons watercolour box contained cadmium (Table 2 and supplementary material Figures S1-9). Raman spectra acquired at 532 and 633 nm excitation confirmed that cadmium sulphide (CdS) is the principal chromophore in both the cadmium and neutral orange watercolours (Figure 2(A, B)). In such samples, the spectra are dominated by the characteristic CdS longitudinal optical phonon and its overtone, observed at ~302–305 cm^{-1} (A_1(LO)) and ~600–602 cm^{-1} (2LO), respectively. At 532 nm excitation (Figure 2(A, B)), these modes appear with high intensity and narrow line shape due to the proximity of the laser wavelength to the CdS band-gap energy. As demonstrated by Rosi et al. (2016), the band gaps of historic CdS and $Cd_{1-x}Zn_xS$ pigments lie in the range of 2.63–2.32 eV (472–534 nm), meaning that 532 nm illumination places CdS under near-resonance or weakly resonant conditions, strongly enhancing the LO and 2LO modes and suppressing weaker TO or multiphonon features (Rosi et al. 2016).

At 633 nm, which lies well outside the resonance window for CdS (Rosi et al. 2016), the same LO and 2LO bands are observed (Figure 2(A, B)), albeit with reduced intensity and modest broadening. Under these off-resonance conditions, pure CdS phases may exhibit additional TO and E_2 modes that allow differentiation between cubic (hawleyite) and hexagonal (greenockite) polymorphs. However, in the present cadmium sample no such modes are detected, and only the LO and 2LO phonons are visible. The absence of phase-diagnostic TO/E_2 bands in this sample therefore reflects either their intrinsically weak intensity or their suppression by particle-size and defect broadening, and the CdS crystal structure cannot be unambiguously determined from Raman data alone.

The neutral orange watercolour (Figure 2(B)) exhibits the characteristic CdS A_1(LO) and 2LO modes at ~302 and ~602 cm^{-1} in the 532 nm spectrum, confirming the presence of cadmium sulphide. Under 633 nm excitation (Figure 2(B)), the Raman spectrum becomes markedly more complex due to additional pigmentary components. Prominent Raman bands at ~224 and ~408–409 cm^{-1} are consistent with hematite contributions, while the feature near ~667 cm^{-1} suggests additional Fe-oxyhydroxide (e.g. goethite) contribution. Overall, the spectra are best interpreted as containing a mixed iron-oxide/oxyhydroxide mixture rather than a single-phase assignment (De Faria and Lopes 2007). These iron-oxide bands dominate the 200–700 cm^{-1} region and partially obscure weaker CdS lattice modes that would otherwise be detectable under non-resonant excitation. The enhanced iron-oxide response explains the pronounced spectral differences between the neutral orange and the cadmium sample, indicating that the shift toward an orange hue results from deliberate addition of goethite/hematite rather than variations in CdS crystal structure.

The sample labelled Lemon Yellow was included in the analysis because historical sources indicate that some manufacturers occasionally marketed pale yellow colours under this name using a variety of formulations, including cadmium-containing compositions in the early nineteenth century (Eastaugh et al. 2008; Fiedler and Bayard 1986). In the present

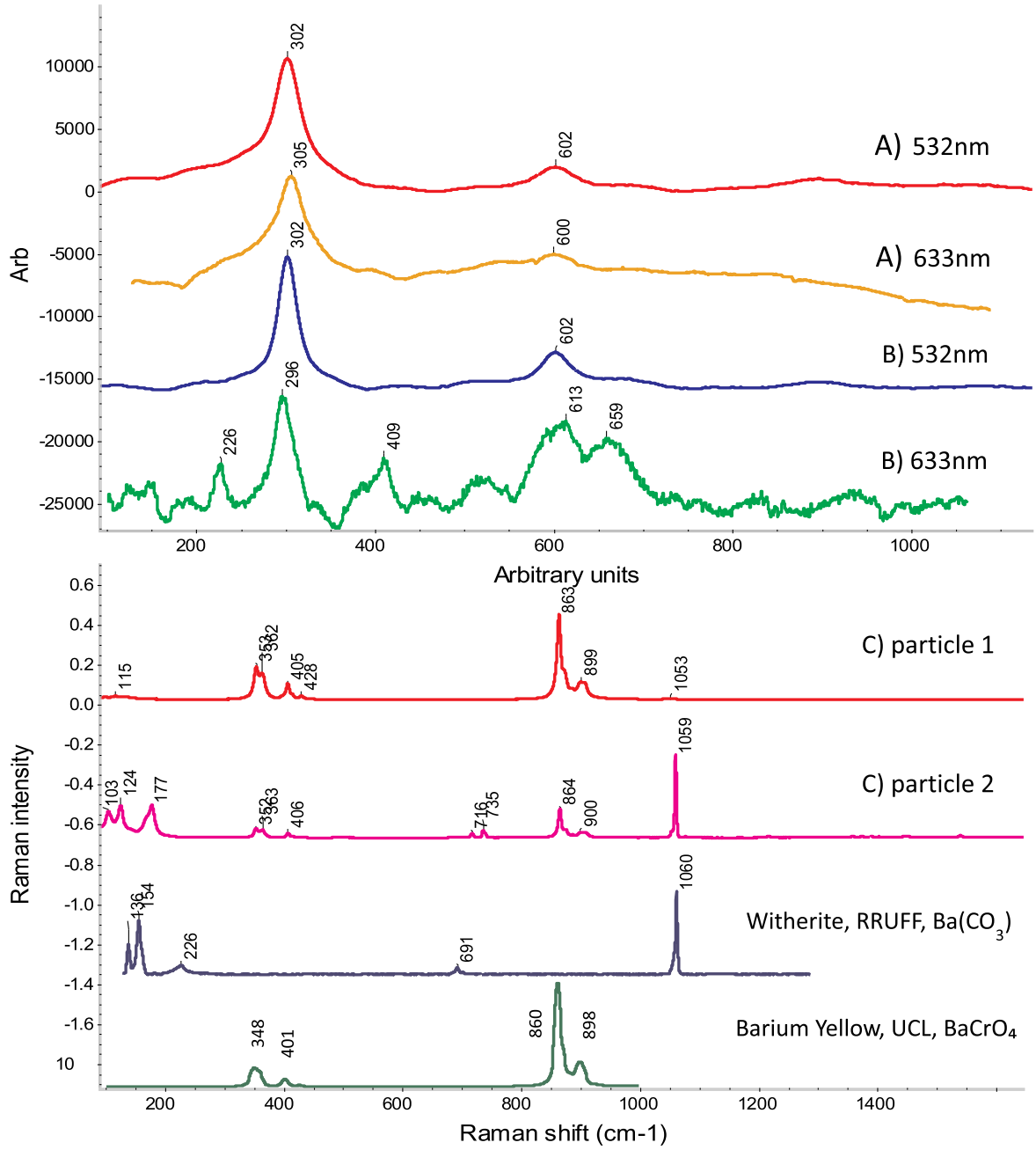

Figure 2. Raman analysis of Reeves & Sons watercolour blocks, Cadmium sample (A) 532 and 633 nm laser, Neutral orange sample (B) 532 and 633 nm laser and Lemon Yellow sample (C) particles 1 and 2 (633 nm laser) compared to different analytical standards.

case, however, no cadmium was detected in this sample (Table 2, sample C). Raman spectra collected from particle 1 (Figure 2(C)) display the characteristic vibrational modes of barium chromate ($BaCrO_4$), with an intense chromate symmetric stretch at ~873–906 cm^{-1} and bending modes at ~352–362, 406 and 429 cm^{-1}, in agreement with published reference spectra for $BaCrO_4$ (Bell, Clark, and Gibbs 1997). EDX analysis supports this assignment, showing Ba (46.5%), O (35.5%) and Cr (15.2%) as the principal elements; minor In and Si likely reflect trace impurities or other minor constituents. Taken together, the spectral and compositional data identify the pigment as the pale 'lemon' variety of chrome yellow based on barium chromate, which is historically documented for nineteenth-century paint and watercolour manufacture (Fiedler and Bayard 1986).

A second particle from the same Lemon Yellow sample was also examined (Figure 2(C) particle 2). Its Raman spectrum again shows the $BaCrO_4$ chromate modes, but additionally exhibits a strong band at ~1060 cm^{-1}, which corresponds to the ν_1 symmetric stretching vibration of witherite ($BaCO_3$) (Kaabar, Bott, and Devonshire 2011). The presence of $BaCO_3$ in barium-chromate pigments is well documented: it may occur as an unreacted precursor from the precipitation process, as a deliberate extender or diluent used to obtain the characteristic pale 'lemon' shade, or as a secondary carbonate formed during ageing via slow carbonation in the presence of CO_2 and moisture

(Fiedler and Bayard 1986; Gettens and Stout 1966). Its detection in this sample is therefore consistent with the known production history and ageing behaviour of barium-chromate-based lemon yellows.

In contrast to the nineteenth century labels, the two 'Schwefelkadmium' swatches from Runge's 1836 and 1838 books (samples E and I) contain no detectable cadmium (Table 2). SEM–EDX shows that both are dominated by Pb, Cr and O, with minor C, and their elemental ratios are compatible with $PbCrO_4$. The Raman spectra of E and I (Figure 3(E and I)) are essentially identical to a modern chrome yellow reference, with an intense $\nu_1(CrO_4^{2-})$ symmetric stretching band at ~845 cm^{-1}, accompanied by the expected lower-wavenumber chromate bending and lattice modes. The VIS–NIR reflectance curves for both samples show a steep absorption edge in the violet–blue region (< ~480 nm) and high reflectance at longer wavelengths, characteristic of a bright yellow chromate pigment. Taken together, the elemental composition, Raman chromate signature, and chrome-yellow-type reflectance behaviour demonstrate that samples E and I are conventional lead chromate rather than cadmium sulphide, indicating that Runge's 'Schwefelkadmium' designation is contradictory.

The two 'Kadmiumoxyd' swatches (samples D and F) likewise contain no cadmium. Instead, SEM–EDX reveals that both are Cu–Cr–O rich, with D additionally containing K, and no Pb or Zn (Table 2). Their Raman spectra (Figure 3(D and F)) differ fundamentally from those of the $PbCrO_4^-$ based swatches.

Sample F shows an intense chromate ν_1 band at ~866 cm^{-1} with a shoulder or second component near ~914 cm^{-1}, together with low-wavenumber modes at ~88 and 369 cm^{-1} attributable to Cu–O lattice vibrations. Sample D exhibits a broader ν_1 band centred at ~845 cm^{-1} and additional bands near 338 cm^{-1} on a higher fluorescent background.

These Cu–Cr Raman signatures closely match those obtained from copper–chromate precipitates synthesised in the laboratory at pH 7.0 and 8.5, both of which produce light- to dark-brown, amorphous Cu–chromate materials whose Raman spectra are indistinguishable from those of samples D and F. The agreement with these amorphous synthetic standards contrasts sharply with the crystalline $CuCrO_4$ produced by hydrothermal methods: Baran (1994) reports a well-resolved Raman spectrum for crystalline copper(II) chromate that does not resemble the spectra observed here (Baran 1994).

Importantly, Runge's own books contain, in separate sections, both a recipe and colour swatch for chromsaures Kupferoxyd prepared by simple double decomposition of $CuSO_4$ and K_2CrO_4, the same chemistry used in the present study to generate amorphous Cu–chromate material. The analytical signatures of the material produced in the historical synthesis correspond with the analytical signatures of the materials in D and F. This correspondence indicates that D and F are copper–chromate pigments rather than lead chromate or zinc compounds; within the limits of the present data, they are best described generically as

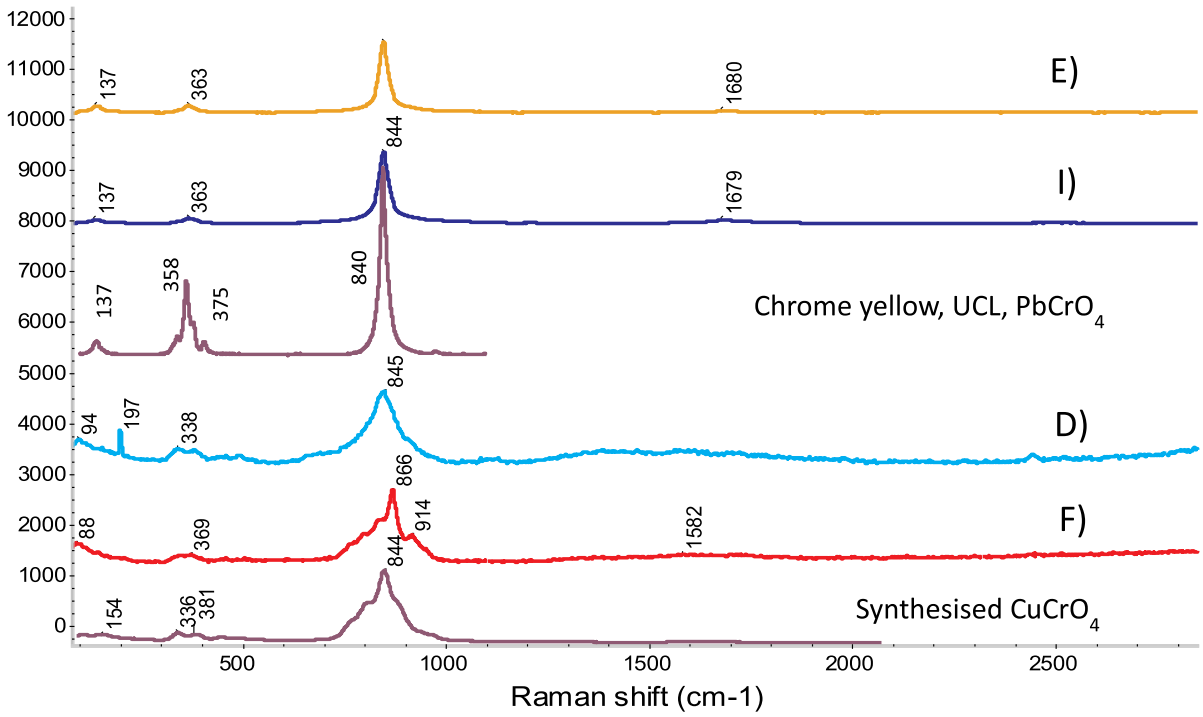

Figure 3. Raman analysis of the pigment swatches from Runge's 1836 and 1838 publications (*Einleitung in die technische Chemie für Jedermann* and *Technische Chemie der nützlichsten Metalle für Jedermann*, Band 1) samples (E) Plate 80 (P80) SchwefelKadmium, (I) Plate 11 (P54) SchwefelKadmium, (D) Plate 43 (P68) Kadmiumoxyd and (F) Plate 8 (P50) Kadmiumoxyd, compared to the Chrome Yellow analytical standard and lab-synthesised $CuCrO_4$.

Cu–Cr chromate phases ($CuCrO_4$ / basic copper chromate) rather than cadmium-bearing materials.

The reflectance spectra of D and F, as displayed in Figure 4(D and F), are consistent with this assignment. Both display a strong absorption in the blue–violet region but, unlike the bright chrome yellow samples, their overall reflectance is lower in the visible range and more gradually increasing toward the NIR, producing brownish hues. Superimposed on this continuum are short wave infrared absorption features attributable to chromate and hydroxide combination and overtone bands, again indicating a chromate-based Cu pigment. The agreement between Cu–Cr–O elemental composition, Cu–chromate-type Raman spectra, and brown chromate-like reflectance behaviour confirms that Runge's 'Kadmiumoxyd' plates are in fact based on copper chromate pigments and contain no cadmium.

The FTIR spectra of samples G and H (Figure 5(G and H)), which contain zinc as the dominant inorganic element according to SEM–EDX, exhibit the characteristic carbonate and hydroxyl features associated with basic zinc carbonate (Sanna 2013), specifically hydrozincite ($Zn_5(CO_3)_2(OH)_6$). Both samples display a strong, broadened absorption between 1500 and 1400 cm^{-1}, corresponding to the ν_3 asymmetric

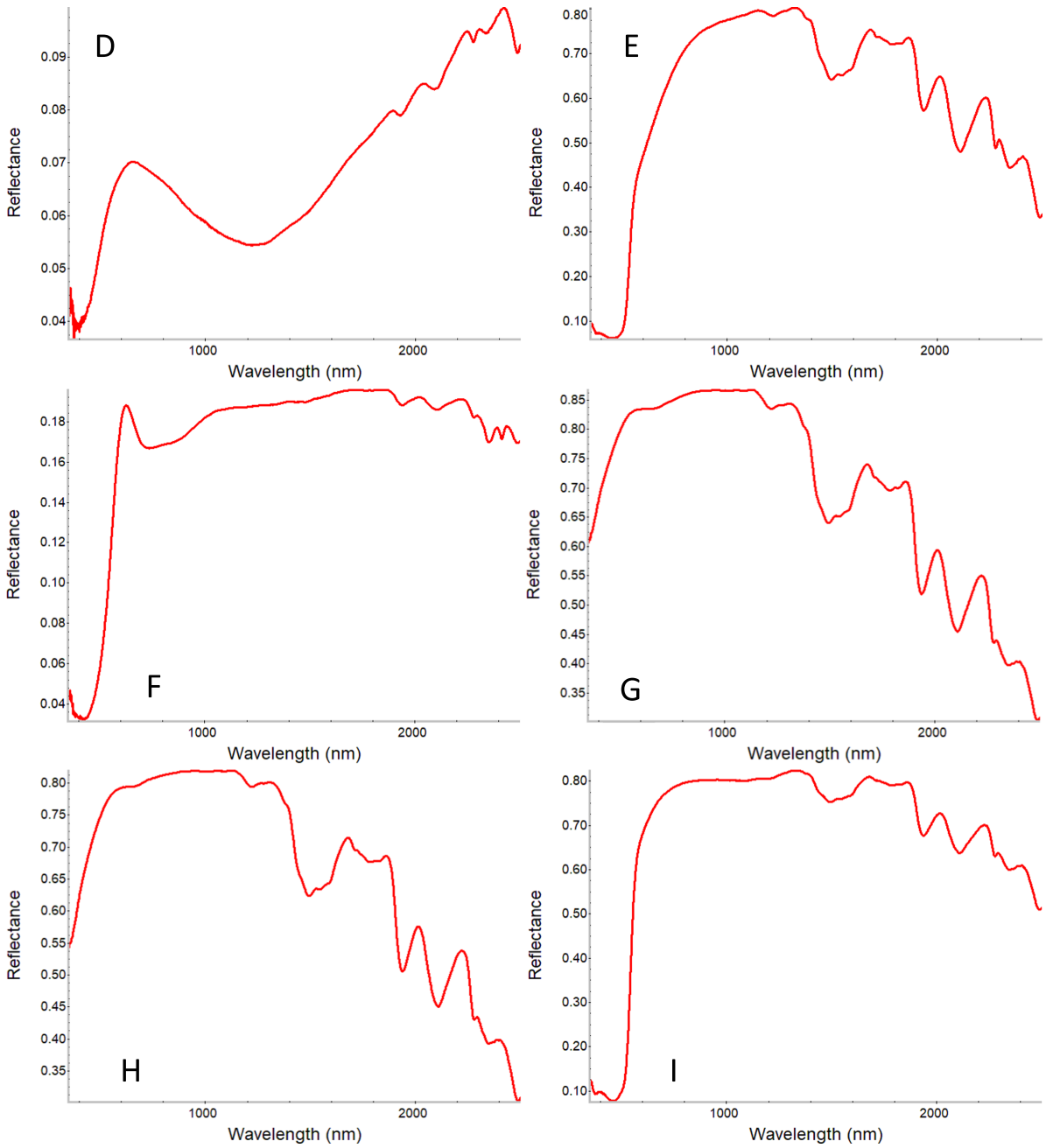

Figure 4, VIS–NIR reflectance spectra (350–2500 nm) of the six pigment swatches from Runge's 1836 and 1838 publications (*Einleitung in die technische Chemie für Jedermann* and *Technische Chemie der nützlichsten Metalle für Jedermann*, Band 1). D) Plate 43 (P68) Kadmiumoxyd, (E) Plate 80 (P80) SchwefelKadmium, (F) Plate 8 (P50) Kadmiumoxyd, (G) Plate 9 (p51) Kadmiumoxyd hydrat, (H) Plate 10 (p52) Kohlensaures Kadmiumoxyd and (I) Plate 11 (P54) SchwefelKadmium.

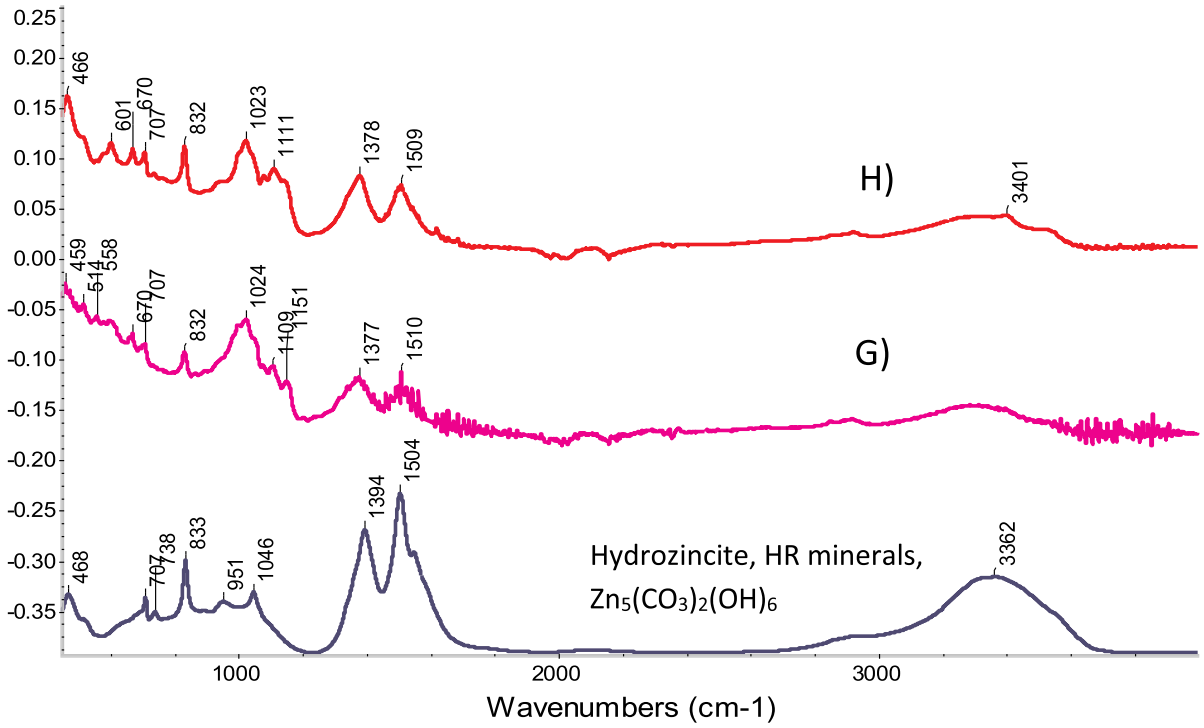

Figure 5. FTIR analysis of the pigment swatches from Runge's 1838 publication (*Technische Chemie der nützlichsten Metalle für Jedermann*) samples (H) plate 10 (p52) Kohlensaures Kadmiumoxyd and (G) plate 9 (p51) Kadmiumoxyd hydrat, compared to Hydrozincite analytical standard (HR minerals).

stretching modes of CO_3^{2-}. This multiplet structure, although partially obscured, is consistent with the split ν_3 pattern reported for hydrozincite in the literature (Sanna 2013). A broad band centred near 1030–1050 cm^{-1} corresponds to the ν_1 symmetric CO_3^{2-} stretch, though its profile is heavily modified by cellulose contributions in the 1200–1000 cm^{-1} region. The O–H stretching region shows a broad band at 3300–3400 cm^{-1}, consistent with combined contributions from hydrozincite structural hydroxyls and the cellulose support. Typical cellulose features also show for C–H stretching near 2900 cm^{-1}. A distinct band at ~832–833 cm^{-1}, representing the ν_2 out-of-plane carbonate bending mode, is clearly present and matches the reference hydrozincite spectra. Additional carbonate bending contributions (ν_4) are observed in the ~700–760 cm^{-1} region.

In the UV–NIR reflectance spectra (Figure 4(H and G)), both samples exhibit the optical behaviour expected of white carbonate–hydroxide: high visible reflectance with a steep UV absorption edge and well-defined carbonate/hydroxyl overtone and combination bands in the 1400–1500 nm, 1900–2000nm, and 2200–2350 nm regions. These NIR signatures are diagnostic of CO_3^{2-} and OH^- containing zinc minerals and correspond closely to reported hydrozincite overtone patterns (McConachy et al. 2007).

Together, the FTIR carbonate and hydroxyl modes, the strong ν_2 band at ~833 cm^{-1}, the CO_3 and OH overtone structure in the reflectance and derivative spectra, and the Zn–O–C elemental composition provide mutually reinforcing evidence that the material present in samples G and H is hydrozincite, with minor spectral distortion arising solely from the cellulose substrate.

Discussion

Contradiction between Runge's text and the material evidence

In both *Einleitung in die technische Chemie für Jedermann* (1836) and *Technische Chemie der nützlichsten Metalle für Jedermann* (1838), Friedlieb Ferdinand Runge provides detailed descriptions of cadmium pigments, including preparation methods, chemical behaviour, and their suitability for artistic use. His accounts describe cadmium sulphide's formation via precipitation and its resilience in mixtures with other pigments, explicitly promoting its use as an alternative to chrome yellow.

However, scientific analysis of the colour swatches in extant copies of these books reveals that the samples labelled as 'cadmium yellow' and 'cadmium oxide' contain no cadmium at all, but are instead composed of lead chromate, copper chromate, and hydrozincite. This stark contradiction raises questions about the integrity or practicality of pigment presentation in these volumes. Whether due to economic constraints, material substitution, or a deliberate visual proxy, the swatches do not support Runge's written claims and should not be considered verified cadmium samples.

Evaluation of the 'Dual edition' hypothesis

In order to interpret the absence of cadmium in both analysed 'Kadmiumoxyd' swatches, two explanations can be considered: (i) Runge's label reflects contemporary nomenclature/marketing rather than verified chemical composition; or (ii) materially different editions existed (e.g. a higher-quality cadmium-containing version and a lower-cost substitute version). It is noteworthy that there is no documented evidence of such a practice in Runge's books, and this is therefore treated as a hypothetical scenario only.

While (ii) cannot be excluded *a priori*, the sampling context constrains its plausibility. The two copies (1836 and 1838) were obtained independently via general online markets in 2025, without targeting provenance, institution, country, or edition. After 189 years of ownership turnover and geographic dispersal, such acquisitions are reasonably treated as approximately independent draws from the surviving population rather than from a single provenance stream (e.g. the same library collection or local book trade). Under a two-edition scenario in which cadmium-bearing copies occur at non-trivial frequency, the likelihood of obtaining two independently sourced copies in which the 'Kadmiumoxyd' swatches both lack cadmium is reduced unless the non-cadmium (substitute) variant is the dominant form among surviving copies.

Accordingly, the most parsimonious interpretation is that the 'Kadmiumoxyd' designation does not guarantee cadmium content in these plates. If edition-dependent material differences did exist, then the results presented here imply that the non-cadmium formulation was at least common (and possibly predominant) among extant copies, and that cadmium-free 'Kadmiumoxyd' swatches should be expected to occur frequently, an inference that can be tested by analysing additional copies.

Reliability of early technical literature on cadmium

The discrepancy between Runge's detailed descriptions and the absence of cadmium in the swatches reflects a broader issue in evaluating early technical and artists' literature. Similar instances appear in the writings of Mérimée and George Field (Carlyle 2001; Mérimée 1830), both of whom discussed cadmium pigments in the 1830s and 1840s. However, it remains unclear whether these references were based on first-hand observation of actual pigment material or derived from secondary sources and theoretical expectations.

In Field's case, the lack of explicit sourcing, and the absence of corroborating physical samples, casts doubt on whether he ever handled real cadmium sulphide. As such, early textual accounts, while valuable, must be treated cautiously unless supported by material evidence.

Practical and economic explanations for substitution

The absence of cadmium in the swatches from Runge's 1836 and 1838 books may have been due to several practical or economic factors. One possibility is cost: cadmium compounds were expensive and difficult to isolate in sufficient quantities before the 1850s, and their inclusion in print runs may have been financially unfeasible.

Additionally, technical limitations in the printing or binding process may have led publishers to use chromatically similar substitutes, such as lead chromate, to visually represent cadmium yellow. It is also plausible that the intention was not to provide chemically exact samples, but rather to illustrate colour appearance, even if the actual substance differed from what was described. A fuller examination of these production constraints and editorial decisions would require dedicated archival and technical study and falls beyond the scope of the present analysis, but represents a valuable direction for future research.

Notably, there is no disclaimer in the text indicating that the swatches were illustrative rather than materially accurate, nor any indication that they might differ in composition from the pigments described. This absence further complicates interpretation, as readers would reasonably expect the labelled samples to correspond materially with the written descriptions.

Purpose and expectations of pigment swatches in early publications

The case of Runge's books prompts a broader consideration of the function of pigment swatches in early scientific and technical publications. Such samples may have served a didactic purpose, offering readers a visual reference for colour and appearance rather than a chemically exact replication of the substances described in the text. In this context, the absence of cadmium in the analysed swatches, despite the specificity of the accompanying chemical descriptions and their presentation as in natural specimens, raises the possibility that illustrative fidelity sometimes took precedence over strict material accuracy in nineteenth century practice. Recognising this distinction is important for historians and conservators, as it cautions against assuming that labelled specimens in historical technical works necessarily correspond to modern expectations of compositional precision.

Material substitution in colour samples, printed catalogues, and commercial pigment preparations is well documented in the 18th and 19th centuries. Studies of the historical pigment trade and artists' suppliers show that adulteration, replacement with cheaper analogues, and the use of extenders were widespread and often went unrecorded (Arie, Hermens, and Peek 1995; Dootson 2019). Archival evidence from colourmen demonstrates that pigments supplied under prestigious labels could vary substantially from their nominal compositions, making it difficult to identify where, or by whom, adulteration or substitution occurred within the production chain (Dootson 2019).

Against this broader context, the Runge swatches stand out: Runge was an accomplished analytical chemist who not only described the synthesis of the pigments he claimed to include, but also showed the ability to distinguish fine chromatic and chemical differences in inorganic colourants. Given his level of expertise and the simplicity of the reactions involved, it is unlikely that the complete substitution of cadmium-based pigments with visually similar chromate or zinc compounds could have happened without his knowledge.

The material evidence therefore points not to accidental error, but to a deliberate substitution of a visually similar pigment under the 'cadmium' label. The close visual correspondence of the analysed material to the yellow hue expected of cadmium sulphide suggests intentional colour matching rather than incidental material variation. In the nineteenth century, however, the elemental composition of such specimens would have been effectively impossible to verify analytically. As a result, substitution based on visual equivalence would have been unlikely ever to be detected and may not have been regarded as problematic if the didactic objective, accurate colour representation, was achieved. While such practice would be unacceptable under modern standards of material specification and labelling, it appears consistent with contemporary technical publishing conventions in which visual fidelity could outweigh compositional precision.

The importance of combined analytical and textual approaches

This case exemplifies the importance of coupling textual scholarship with scientific investigation. Only through SEM-EDX, Raman spectroscopy, UV-VIS reflectance, and FTIR analysis could the true composition of the Runge swatches be determined, overturning assumptions that had persisted based solely on textual evidence.

Historical claims, particularly those involving materials, should therefore be treated as hypotheses subject to material verification. This integrative approach strengthens the evidentiary foundation of pigment histories and prevents the perpetuation of inaccurate or anecdotal accounts.

Implications for the chronology of cadmium pigments

These findings carry important implications for efforts to date the introduction and spread of cadmium pigments. The presence of a pigment name or description in a book or catalogue does not in itself constitute proof of its availability or use. In the absence of authenticated physical samples, such claims remain provisional. For heritage science and conservation, this highlights the need to anchor pigment chronologies in scientifically verified materials, not merely printed references.

Earliest confirmed cadmium pigments: the Reeves & Sons samples

The presence of cadmium exclusively in the Reeves & Sons watercolour box samples, with confirmed CdS composition and a dated label of 3rd February 1851, establishes these materials as the earliest securely dated and analytically verified examples of cadmium pigment in an artist-ready format presently known. While cadmium sulphide was reported in the literature earlier in the century (Ghirardello et al. 2018), materially confirmed examples from the 1830s and 1840s have remained absent.

Crucially, the compositional analysis of the 1836 and 1838 Runge swatches demonstrates that earlier, frequently cited specimens do not in fact contain cadmium. This provides direct material evidence of absence where presence might otherwise have been assumed. Together, the confirmed absence in the 1830s and the verified presence in 1851 bracket the material record and clarify the evidentiary timeline of cadmium pigment use in artist materials.

In this sense, the study clarifies the chronology of cadmium pigment availability at the material level. While textual references to cadmium compounds appear earlier in the nineteenth century, physically verified examples in artist-use form have not been documented before 1851. The combined evidence of confirmed absence in the 1830s and confirmed presence in 1851 therefore establishes a materially supported boundary for cadmium pigment adoption in artists' materials, rather than merely refining an already documented date by a few weeks.

The absence of cadmium in the Lemon Yellow sample further reinforces that during this period, pigment nomenclature remained inconsistent, with some names not directly reflecting chemical content. The clear documentation and verified composition of the 1851 Reeves & Sons samples offer a rare and

valuable reference point for future studies of pigment adoption and commercialisation in artist materials.

Conclusion

The chemical and spectroscopic results presented here establish that the pigment swatches labelled as cadmium compounds in Runge's 1836 and 1838 publications do not contain cadmium and were never cadmium-based materials. Instead, they consist of lead chromate, barium chromate, copper–chromate phases, and zinc carbonates, demonstrating that the colour plates relied on readily available chromate and zinc pigments rather than the cadmium compounds described in the accompanying text. Because no plausible chemical pathway allows cadmium sulphide to transform into any of these chromate or carbonate phases, the absence of cadmium in two independent historical copies confirms that the chromatic materials originally applied were misrepresented relative to the text.

In contrast, the Reeves & Sons watercolours dated 3rd February 1851 contain authentic cadmium sulphide and represent the earliest securely dated and analytically verified examples of cadmium yellow in artist-ready form currently documented. The material evidence demonstrates that by early 1851, pigment-grade cadmium sulphide was not only known but commercially prepared and incorporated into finished artist materials.

Although laboratory preparation and purification of cadmium sulphide were reported earlier, no securely dated, physically verified artist materials, production records, or commercial specimens from the 1830s or 1840s have been documented. The compositional absence of cadmium in the 1836 and 1838 Runge swatches further reinforces this absence in the material record.

Taken together, the evidence indicates that while cadmium sulphide was chemically known prior to 1851, pigment-relevant production and documented artist availability are not materially evidenced before that date. The 1851 Reeves & Sons samples therefore provide the earliest currently verifiable anchor point for cadmium pigment manufacture at scale, rather than merely refining an already established chronology.

By distinguishing textual assertion from physical evidence, the study contributes a clearer and more accurate understanding of the early history, availability, and adoption of cadmium-based pigments.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used [ChatGPT 5] in order to support language editing and academic phrasing. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

Notes

1. *Introduction to Technical Chemistry for Everyone*.
2. *Technical Chemistry of the Most Useful Metals for Everyone*.

Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

Leonardo Pantoja http://orcid.org/0000-0001-8364-7595

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