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APPLICATION OF CATHODOLUMINESCENCE IN PAINT ANALYSIS

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Abstract

When solving cases of burglary or investigating ship collisions, the forensic scientist frequently has to examine several layers of paint of the same color, often white. As a rule, the usual microscopic and spectroscopic methods [fluorescence microscopy, FT-IR (Fourier Transform Infrared Spectroscopy), pyrolysis, GC/MS (Gas Chromatography - Mass Spectrometry), etc.] are not sufficient to prove that the paint traces found on the scene, which are often only available in the form of fragments, originated from the same source as the reference material. It is possible to achieve convincing proof of this using either an optical cathodoluminescence-microscope or a cathodoluminescence-scanning electron microscope, both of which can be coupled to a visible (VIS)-spectrometer.

Key Words: Scanning electron microscopy, cathodoluminescence (CL), paint, pigments, forensic science, optical CL microscopy.

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Introduction

Paints and their components often play a decisive role as evidence in solving crimes. The forensic scientist analyzing such material must not only determine the origin of unknown paints (identification and classification) but in addition compare traces collected from objects in the suspect's possession or found in his environment with those traces secured at the scene of the crime.

In most cases, these comparative analyses are conducted to answer the question whether the incriminating material and the comparative sample are identical or whether significant differences exist between the two. If the traces prove to be analytically and morphologically identical, the forensic scientist is also required to furnish a statement on the evidential value of his results for court interpretation purposes.

This can only be achieved through a comprehensive analysis of the paint's composition, provided sufficient data on the frequency of the paint or its components of use or occurrence is available. Paint comparisons are especially difficult if the trace specimen consists of several coats of paint of similar color - especially white and cream colors. These flakes often occur in connection with burglaries (e.g., paint flakes from doors and windows) and ship collisions. Flakes with up to 35 layers of a similar color are not unusual. The individual layers can be between 20 μm and 200 μm thick and often, thicknesses within small sections of the same coat can vary by more than 100 %. When such flakes are examined with the help of optical microscopic methods (polarization, interference contrast, fluorescence, bright-field and dark-field illumination), it is almost impossible to determine the number and thickness of the individual layers. In addition, it is often the case that layers disintegrate due to chipping and poor adhesion, so that only fragments are found. Assigning these fragments to comparative specimens with intact layer structures is often impossible under these circumstances and using the methods mentioned above.

There is only a limited number of pigments and extenders that can be used in white, grey, and cream-colored paints (Table 1). Therefore, many white paints produced by different manufacturers do not differ in pig-

ment composition. This fact must not be neglected in paint examination, especially as analysis of binders by FT-IR (Fourier transform infrared spectroscopy) microscopy is often not feasible for multilayered systems because the thickness of individual layers is not sufficient.

Nevertheless, further differentiation of paint pigment layers exhibiting identical phases is possible since individual pigment phases may differ, depending on the production process used and subsequent treatment, for instance, in grain size distribution, crystal habit, and especially in the kind, and number, of their foreign atoms and other lattice imperfections. The analysis of these latter characteristics also provides a basic approach to the problem of establishing identity in comparative examinations. The classic methods of pigment analysis (X-ray diffraction, polarization microscopy) are not capable of proving the presence of lattice imperfections. Cathodoluminescence methods, however, have that capability.

Cathodoluminescence (CL) is the emission of radiation in the region of visible light and neighboring wavelengths following excitation by electrons where these, originating from a cathode and accelerated in an electric field, strike upon an insulator or semiconductor. This paper describes CL-analysis methods which assist in solving complex paint analysis problems.

Experimental Procedure

Equipment and measurement procedures

Cathodoluminescence analysis of paints can be performed in either a scanning electron microscope (SEM) or in a relatively simple specimen chamber devised for optical microscopy.

Optical cathodoluminescence microscopy

Vacuum specimen chambers with observation windows and cold-cathode electron guns have been described by a number of authors (Sippel, 1965; Geake *et al.*, 1970; Bartz, 1973; Dudley, 1975; Barker and Wood, 1987; Marshall, 1988). We use a contrasting unit according to Bartz (1973) produced by the firm Leica (Göbel and Patzelt, 1976). Specimens with a maximum diameter of 35 mm and up to 18 mm thick can be placed in the chamber (Fig. 1). The chamber is evacuated with a rotary pump. 10-15 kV are applied across the discharge tube. The working pressure (approximately 5.5 x 10^{-2} mbar) needed in the chamber in order to obtain the optimal electron beam current density, and thus the maximum luminescence intensity, is controlled by means of a needle valve. It is advisable to use a protective gas (nitrogen or helium) as the specimens consisting of organic matter oxidize within a very short time. The beam currents and beam current densities utilized (0.3-0.8 mA = approximately 5 x 10^2 A/m^2) pose a high thermal strain on the paint specimen and the embedding agents. In order to avoid thermal damage, the polished surfaces are covered with aluminum foil (0.03 mm thick) so that only a small area (5-10 mm^2) on the flake cross-section is directly exposed to the electron beam. The organic matrix of the uncovered area is pyrolytically decomposed within a few minutes. The interaction of the electron beam with the paint produces decomposition and discoloration and the differences in decomposition of the various paint layers can be utilized for material contrast and visualization. If the paint specimen is exposed to the electron beam for only a short time (less than one minute), which is more than sufficient for a luminescence analysis in the microscope, the depth of electron beam induced damage remains below 1 μm. Light polishing with diamond paste removes all damage. In order to obtain qualitative and quantitative results using CL spectra, the Bartz cell is coupled to a microspectrophotometer (Fig. 1). The Zeiss microspectrophotometer UMSP 80 used for CL measurements is equipped with an

Table 1. CL colors of white pigments and extenders. BL: blue, GR: green, RE: red, YE: yellow, OR: orange, BR: brown, WH: white.

WHITE PIGMENTS AND EXTENDERS	BL	GR	YE	OR	RE	BR	WH	NO CL
β– ZnS SPHALERITE			⊗					
ZnS WURTZITE		⊗						
ZnO ZINC WHITE	⊗	⊗					⊗	
$CaCO_3$ CALCITE				⊗	⊗	⊗		
$CaMg(CO_3)_2$ DOLOMITE					⊗			
TiO_2 RUTILE								⊗
TiO_2 ANATASE	⊗							
$BaSO_4$								⊗
$PbCO_3$ CERRUSITE								⊗
$Pb(CO_3)_2(OH)_2$ LEAD WHITE								⊗
SiO_2 QUARTZ						⊗		⊗
CHINA CLAY	⊗							
$PbSO_4$ ANGLESITE								⊗
$CaSO_4 \cdot H_2O$ GYPSUM								⊗

List of Abbreviations

BSE: Backscattered Electrons
EDX: Energy Dispersive X-ray Spectrometry
FT-IR: Fourier Transform Infrared Spectroscopy
GC-MS: Gas Chromatography - Mass Spectrometry
PM: Photomultiplier
PMT: Photomultiplier Tube
SE: Secondary Electrons
VIS: Visible
WDX: Wavelength Dispersive X-ray Spectrometry

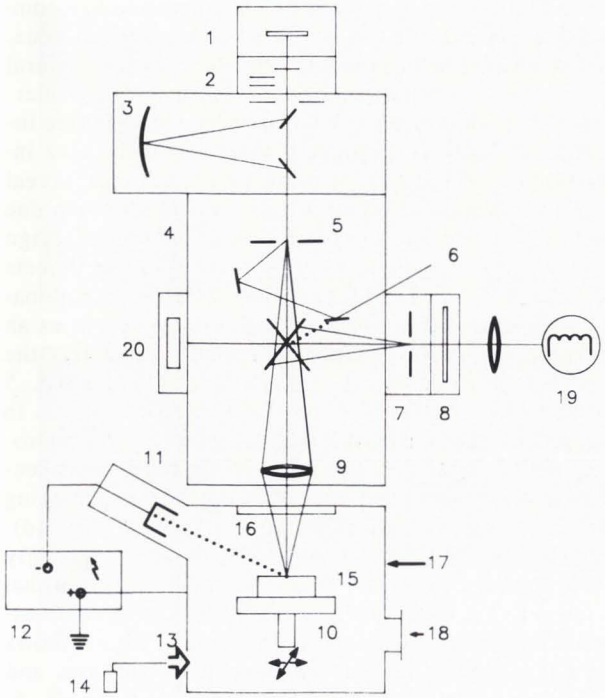

Figure 1. Schematic diagram of a CL detection system for the visible range. The basic components are a currently available stage (Leica contrasting unit; Germany) for optical CL microscopes and a microspectrophotometer (Zeiss UMSP 80; Germany). 1: Photomultiplier tube (PMT)-Detector; 2: Filter; 3: UV-VIS-Monochromator (240-850 nm); 4: Photometer head; 5: Measuring diaphragm; 6: Ocular; 7: Luminous field diaphragm; 8: Light shutter; 9: Objective with dark field illuminator; 10: Sample holder with height adjustment (turnable and movable in two dimensions); 11: Cathode discharge tube; 12: Voltage supply; 13: Needle valve; 14: Gas bottle; 15: Specimen; 16: Quartz glass window; 17: Vacuum chamber; 18: Vacuum pump fitting; 19: Halogen illuminator (12V/100W); 20: Camera.

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epi-illuminator (long working distance objective: epi 10/0.22, working distance: 7.5 mm) and an image-side grating monochromator. The CL signals (at 2 nm intervals) from 380 nm to 700 nm are stored on floppy discs and plotted when required. In most cases, paint analyses produce weak CL signals. In order to obtain results with an improved signal-to-noise ratio, a suitable measurement diaphragm must be selected. The area which is analyzed should be at least 20 μm x 100 μm. Thirty seconds is still the time span needed in order to register a spectrum. With the follow-up model (Zeiss MPM 800) scan times can be reduced to 2 seconds per spectrum.

Cathodoluminescence scanning electron microscopy

The CL analyses are performed with an CamScan model S4 SEM which is equipped with a Kevex Delta IV electron beam microanalysis system and a CL measuring

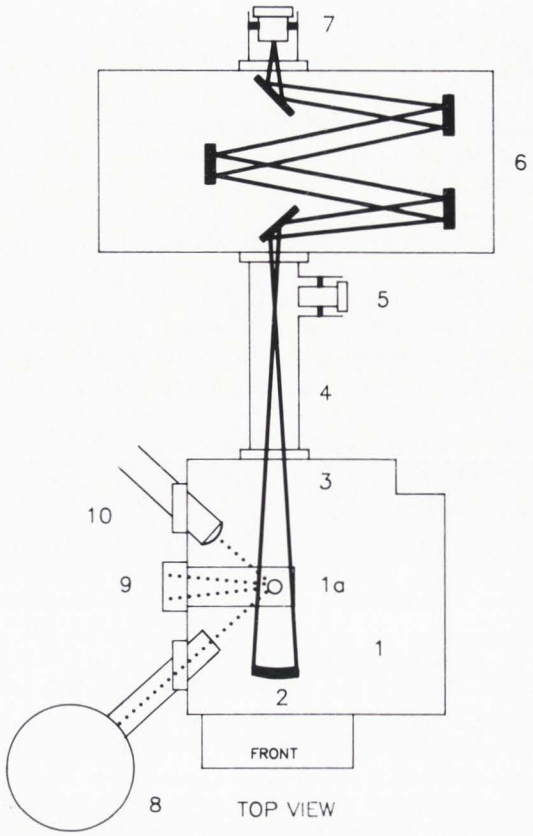

Figure 2. Schematic diagram of a SEM system for spectral analysis of X-rays and cathodoluminescence. 1: SEM specimen chamber; 1a: Specimen; 2: Ellipsoidal mirror segment; 3: Quartz glass window; 4: Light channel; 5: PM-I (side window type); 6: Monochromator with UV-VIS grating; 7: PM-II (end window type); 8: EDX Detector; 9: BSE Detector; 10: SE Detector.

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system developed by E.O. Elektronenoptik Service (Dortmund, Germany). Fig. 2 illustrates the basic set-up of the CL detection system. The system, developed by G. Koschek (1991) has the following components: **1)** a collector in the form of an ellipsoidal mirror segment which is installed at the specimen stage and can be elevated or lowered under vacuum from outside; **2)** a quartz glass window opposite the collector; **3)** a light channel with a chamber wall flange on one side, a flange for a monochromator on the other side, and a vertical tube for insertion of a photomultiplier (side window type) PM I; **4)** a video amplifier with switch (backscattered/CL), an integrated CamScan device; **5)** a digital controlled UV-VIS grating for spectral dispersion of the CL signals; **6)** an adapter for an additional photomultiplier (end window type) PM II at the monochromator exit slit; and **7)** personal computer (PC) with necessary CL software.

The ellipsoidal, vertically movable mirror focuses the light passing through the quartz window either on the monochromator entrance slit or on the photomultiplier PM I when it is inserted into the path of the beam. This

configuration allows production of panchromatic CL micrographs, monochromatic CL micrographs, or CL spectra. A large number of other CL detection systems have been discussed in scientific literature (for details see Yacobi and Holt, 1990, and references therein). The special advantage of the CL system described above lies in its capability of receiving CL signals without influencing detection of X-ray photons or secondary and backscattered electrons. In addition, the specimen stage can be moved and adjusted almost without restriction. Even a wavelength dispersive system for WDX analyses (Microspec PC 3) can be mounted without any difficulty. In all SEM experiments, the embedded paint samples were prepared by carbon coating to eliminate charging effects using a Balzers type 250 T coating system. By carbon coating there is no noticeable effect in reducing specimen damage.

Sample preparation

Layer structures can be best examined in the form of cross-sections, which we prepare in our laboratory from flakes of paint which may be under 1 mm in diameter. The flakes are embedded in a cold-hardening, colorless, polyacrylate based resin (e.g., Kulzer 4004, Kulzer GmbH, Technical Division, Philipp-Reis-Straβe 8, D-6393 Wehrheim/Ts., Germany) and ground and polished after hardening. However, particles of the polish are likely to remain on the cross-section surface. Glossy cross-section surfaces, free of polishing compound, are obtained by milling the resin with a high-speed rotary diamond blade of an ultramilling cutter Polycut-E, produced by Reichert-Jung/Cambridge Instruments (Anonymous, 1977).

Microtome section techniques are also employed (Stoecklein and Gloger, 1988). As mentioned above, it is often not possible to distinguish individual layers of paint in a cross-section using an optical microscope (Figs. 3a, 3b). The best high-contrast images are obtained by using a scanning electron microscope (Fig. 3f). However, neither secondary and backscattered electron micrographs nor optical microscopic fluorescence images allow assignments of fragments to intact layer structures on account of the monochrome results they produce. Applying reagents in order to stain the cross-sections, thus obtaining contrasts (Beattie *et al.*, 1979), does not solve the problem of assignment either.

Staining techniques are also not advisable because they irreversibly alter or even destroy the sample. Results with a high degree of information, however, can be obtained through various cathodoluminescence methods.

Results and Discussion

The various CL spectra of the pigments and extenders existing in the individual paint layers and also the quantitative variations of the CL intensities or the complete absence of CL emissions result in very characteristic luminescence patterns of high evidential value when paint cross-sections are analyzed in an optical CL microscope (Fig. 3c and Fig. 4b). These patterns very much facilitate assignment of paint fragments to a complete succession of paint layers in comparative analysis. As is the case with minerals, the CL colors of natural and synthetic pigments and extenders can vary considerably. The luminescence colors determined so far are included in Table 1. Pigments which normally have intrinsic or extrinsic luminescence bands, at times, reveal no CL intensities at all within the visible spectrum due to the presence and concentration of inherent foreign ions. These act as quenching centers. Lattice defects (dislocations, etc.) can lead to non-radiative recombination processes. Figs. 4a-f, sample 5, may serve as an example. X-ray diffraction analysis revealed that the zinc contained in the first layer of paint flake no. 5 existed solely in the form of zinc oxide (in addition to the phases rutile, anatase and dolomite). The micrographic display of zinc (X-ray mapping) in the cross-section of flake no. 5 indicates that the phase containing zinc is homogeneously distributed in layer 1 (Fig. 4d). The fact that the CL emission of zinc oxide appears only along the edge of layer 1 (Figs. 4b and 4c) is proof that a second zinc oxide phase without detectable luminescence properties must exist in this layer. Fig. 5 shows the CL spectra of the red luminescent second layer and the green-white luminescent fifth layer of flake no. 5, produced by the UMSP 80 microspectrophotometer in the visible (VIS) range (measurement aperture 20 μm x 100 μm) (Fig. 4b).

The same sections were scanned with our CL system in the SEM (measurement area 10 μm x 10 μm). The spectra obtained show much more detail (Fig. 6). As the spectra in the SEM were determined in a more extensive wavelength range (250 nm - 900 nm), it is quite evident that the green-white luminescent layer 5 of this flake contains two different emission peaks at 373 nm and at 509 nm. The different peak ratios in the green and blue regions of the spectra of layers 1 and 5 (Fig. 6) clearly show that two ZnO phases of different luminescence are present. The absolute intensity differences of the two spectra, however, are presumably due to a difference in pigment volume concentration. In this case, X-ray diffraction and WDX analyses also revealed that layer 1 does not include any other zinc containing phase (e.g., ZnS). The curve No. 2 in Fig. 6 represents the red luminescent phase (calcite) found in layer 2 of flake 5.

In order to obtain CL spectra in the SEM measuring system, beam currents up to 70 nA (approx. 3×10^5 A/m^2) were applied. These are ten times stronger than those used for panchromatic CL images. This leads to considerable pyrolytic decomposition of the paint resin. Simple polishing of the sample surface, sufficient in the case of CL microscopy, however, does not remove these pyrolytic products when scanning methods are employed (Fig. 3a and 3b). Several μm must be taken off the cross-sections through milling after this type of experiment.

The panchromatic CL images in the SEM are much less informative than the color images of paint

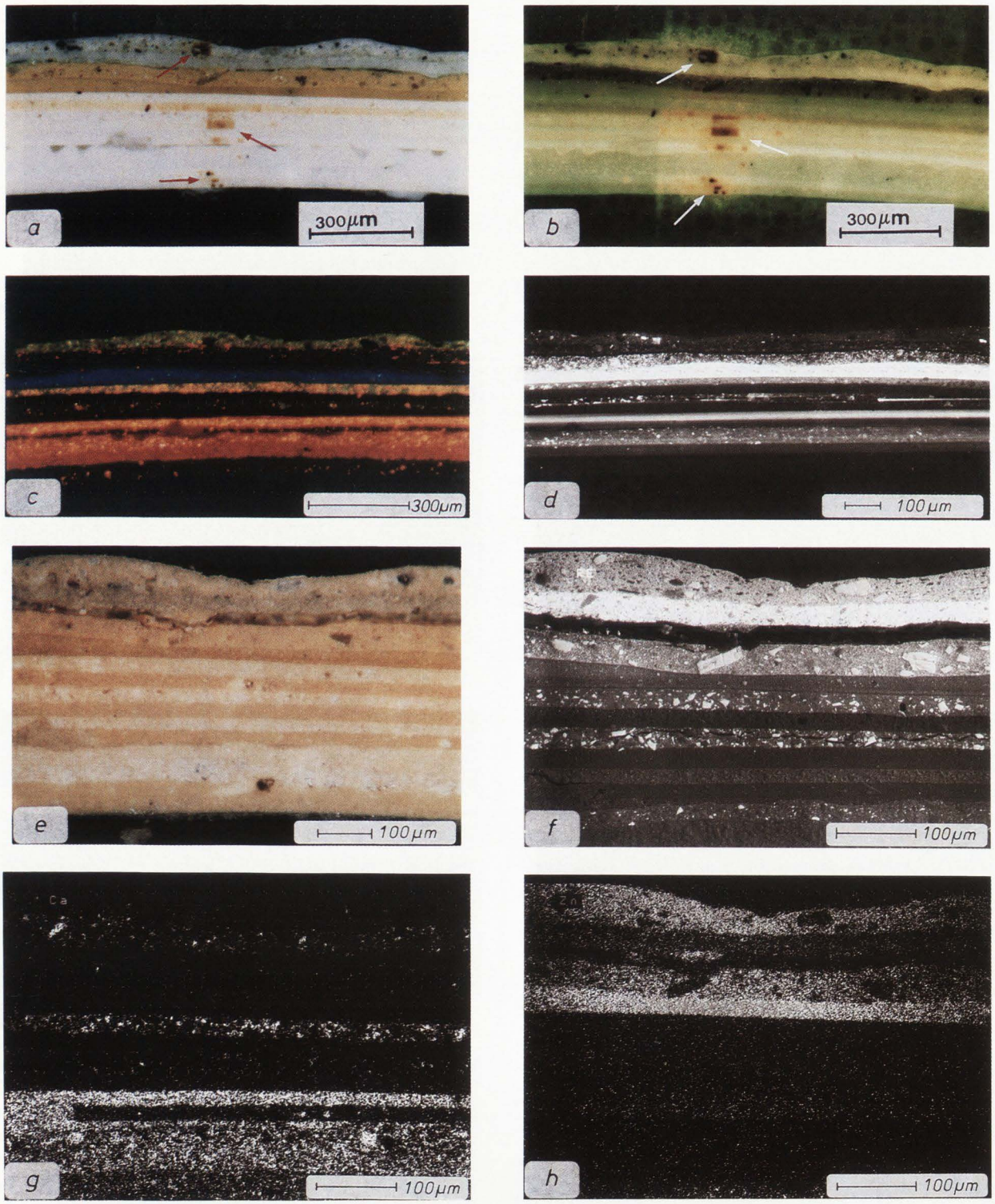
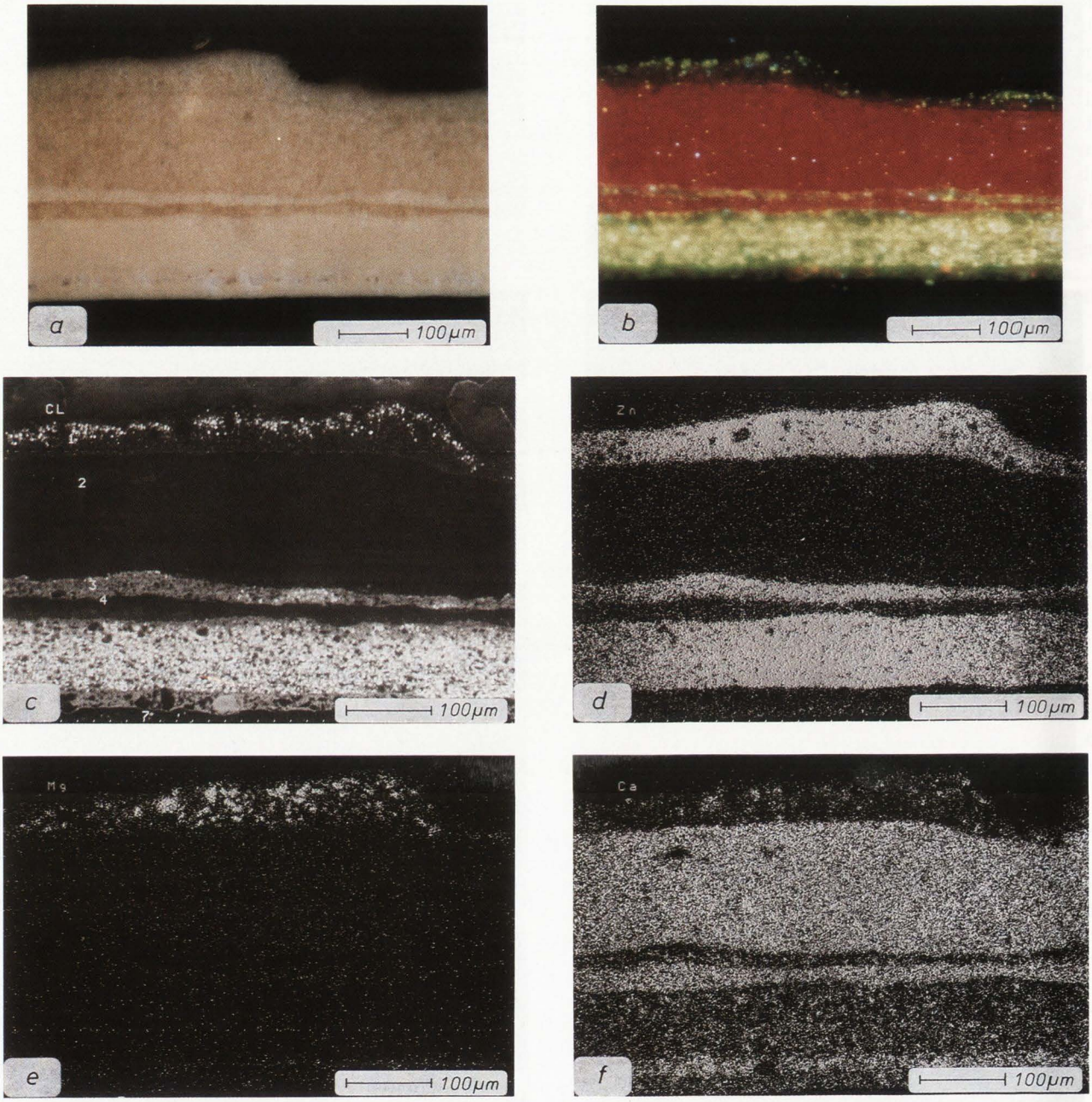


Figure 3. Cross-section of a fragment of household paint (14 layers) (3a-3c and 3e: Fujicolor HG 100). **3a**. Optical microscope image (darkfield illumination) of the polished cross-section after CL spectroscopic studies in the SEM. The beam damaged areas (indicated with arrows) are not removable with diamond paste. **3b**. Fluorescence microscope image (excitation wavelength 365 nm) of the polished section in 3a with damaged areas. **3c**. CL micrograph of the cross-section in 3a, examined using the optical CL microscope. **3d**. Panchromatic CL-SEM micrograph of the cross-section in 3a. **3e**. Optical microscope image of the cross-section in 3a after etching in the optical CL microscope. The individual layers are clearly visualized by decomposition and discoloration. **3f**. BSE image, with low share of SE (Robinson detector, 20 kV). **3g**. X-ray map calcium (WDX). **3h**. X-ray map zinc (WDX).



cross-sections seen with an optical CL microscope. This can be attributed to a number of reasons. Although the detectors used are photomultipliers with multi-alkali photocathodes with relatively high and very constant efficiencies throughout the visible range (R 928 and R 374), the differences in luminescence intensity of individual pigment phases of orders-of-magnitude results in an overload on the display CRT when strong luminescence is involved, whereas paint layers with weak red or blue luminescences hardly produce any signals in the scan and thus hardly any images. These differences cannot be compensated for with filtering techniques etc. (e.g., γ-contrast). Another reason for poor resolution is

Figure 4. Cross-section of a fragment (sample 5) of household paint (6 layers) containing different ZnO-phases (4a and 4b: Fujicolor HG 100).

4a. Optical microscope image.

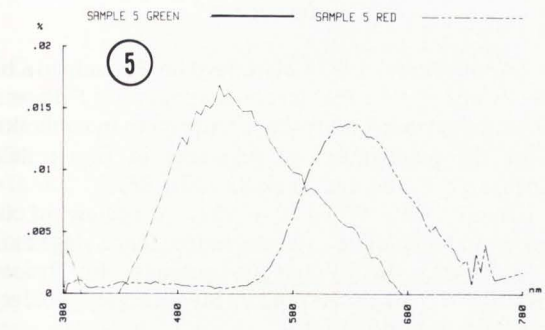
4b. Optical CL microscope micrograph.

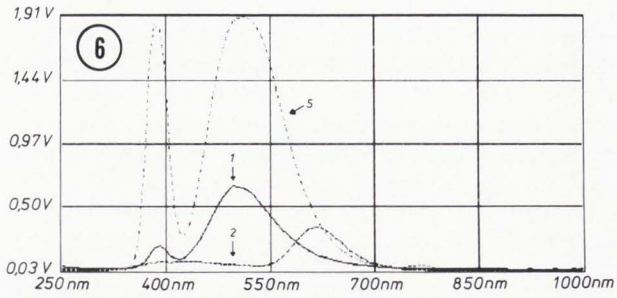
4c. Panchromatic CL SEM micrograph.

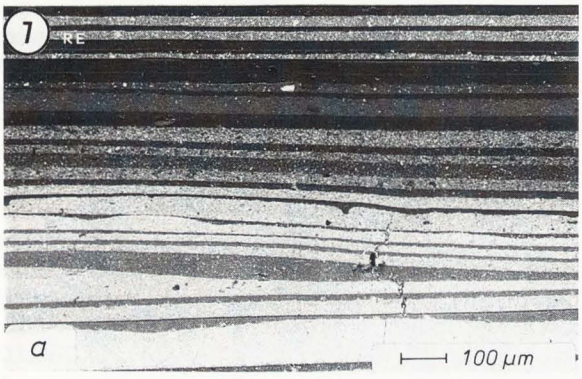
4d. X-ray map zinc (WDX).

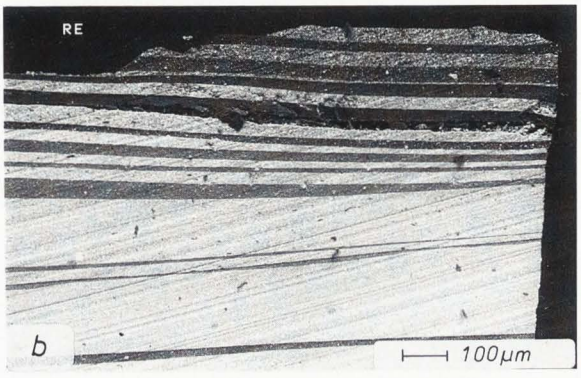
4e. X-ray map magnesium (WDX).

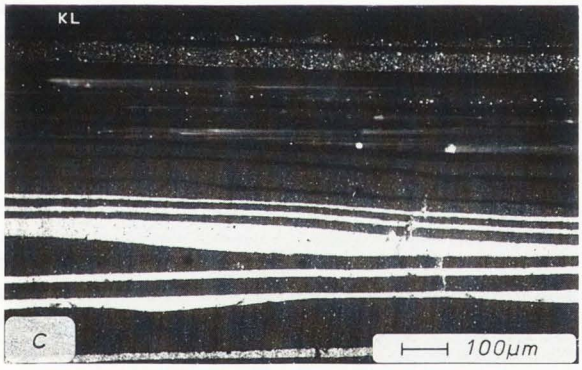
4f. X-ray map calcium HG 100.

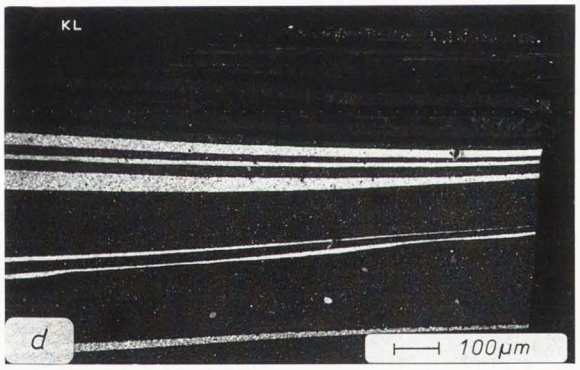












smearing effects in CL observations of pigments with long decay time luminescence (Fig. 3d). The advantage of SEM, especially in our configuration, lies in the simultaneous production of backscattered electron images and X-ray maps, or X-ray spectra of individual pigments too, in conjunction with CL signals.

It is thus generally possible to identify luminescent and non-luminescent pigments and extenders without the use of X-ray diffraction methods (Figs. 3g and 4d-f).

Case study

An example from practical case work may serve to illustrate how powerful the method is. In the Hamburg harbor, a launch had collided with a barge train in fog and two passengers of the launch drowned in the accident. The barge train moved away from the scene unidentified. A few days later, and based on the information received, the barge train "PUCH" was traced as the

Figure 5. Optical CL microscope photometry. CL spectra (T = 293 K) of layer 2 (dashed line) and layer 5 (solid line) from the multilayered white household paint sample 5 (Figs. 4a and 4b). (15 kV, 0.5 mA).

Figure 6. CL spectroscopy in SEM. CL spectra (T = 293 K) of layer 1, layer 2 and layer 5 (electron beam voltage: 15 kV, beam current: 5 nA) from the multilayered white household paint sample 5 (Figs. 4a and 4b).

Figure 7. Case Example: Cross-section of two multilayered white paint flakes taken from vessels after collision. **7a.** BSE image of sample A (launch). **7b.** BSE image of sample B (barge train). **7c.** Panchromatic CL-SEM micrograph of area in 7a. **7d.** Panchromatic CL-SEM micrograph of area in 7b.

vessel presumed to have caused the accident. Her master denied any involvement. As small amounts of foreign paint had been secured from the prow of the "PUCH", objective physical evidence was required to show if that vessel had collided with the launch or not. The reference material obtained from the launch (paint flakes in Fig. 7a, sample A) consisted of a total of 35 white layers plus a red ground coat. In the incriminating material secured from the "PUCH", no particles with a red ground coat were found (Fig. 7b, sample B with 22 layers). Positive linkage of sample A to sample B with their extreme different thicknesses of some layers was not possible with microscopic methods and instrumental analysis (polarization microscopy, fluorescence microscopy, SEM/EDX, X-ray diffraction). The samples were therefore additionally examined by means of the CL methods described above. The results are shown in Figs. 7a to 7d. Thanks to the extremely characteristic CL pattern, positive evidence was obtained proving that samples A and B originated from the same source. Faced with these findings, the master of the barge train "PUCH" confessed in court that he had caused the accident in a state of intoxication. He was eventually convicted.

Conclusions

The results obtained in this paper show that CL analysis methods can be used to identify the structure of paint flake cross-sections composed of various paint layers of the same color where other procedures fail. By using optical CL microscopy as well as CL-scanning electron microscopy, in our example preferably in combination with X-ray microanalysis, it is possible not only to determine the number and thickness of paint layers, but also to obtain individual luminescence patterns due to the different CL emissions of individual layers.

The forensic scientist thus has a method which produces results of high evidential value. Other possible applications of CL analysis in forensic science are discriminations of glass specimens and natural and synthetic gems as well as examinations of prints and copy materials and false signatures.

Acknowledgements

The authors thank Mrs. M. Franke for assistance and are grateful to Dr. Koschek for useful discussions.

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Discussion with Reviewers

W.C. McCrone: Luminescence is, in most cases, due to impurities rather than the host material. To what extent can CL identify individual paint media and pigments?
Authors: Pigment identification by means of CL is possible only in exceptional cases. This applies even more to binders. For such purposes, other methods are more suitable (e.g., X-ray diffraction and polarization microscopy, infra-red (IR) spectroscopy and pyrolysis gas chromatography mass spectrometry (GC/MS) respectively). The very strength of CL, however, is in its capability to differentiate between pigments from two different samples with the same crystallographic phase, even where grain size distribution and crystal habit are identical by means of impurities and other lattice imperfections.

D.C. Ward: The advantage of SEM CL imaging over BEI imaging for routine structure assessment is not readily apparent. Could it be that the ultimate advantage of CL analysis for white paints is for possible additional discrimination of paints when traditional methods of comparison do not reveal a difference?
Authors: The use of CL methods in routine paint comparison, as applied to automotive paint for instance, does not always make sense. In certain cases involving multilayered white, grey, or cream-colored paint systems (household paint, ship paint etc.), however, meaningful results can only be achieved via the examination of CL emissions, as illustrated by the case example presented.

D.J. Marshall: In the sample preparation procedure, do you do both polishing and milling of every sample? How high a polish do you achieve? Do you ever make actual thin sections?
Authors: For CL examinations, the embedded samples are initially only milled. A polish (Al_2O_3, grain size: 0.3 μm) is used to remove areas slightly damaged by electron beam. Where damage is pronounced, milling is used as well. The polishing depth is around 0.2 μm. In our laboratory, microtome sections are normally used for comparative examinations. Section thickness for use in the SEM (CL, BSE, EDX/WDX) is around 10 μm. For optical microscopy and spectroscopic methods (FT-IR, UV-VIS) the section thickness is 3 μm.

G. Remond: Figs. 4e and 4f show the presence of Ca and Mg bearing precipitates within the layer 1. Could these small inclusions be correlated to the presence of bright luminescent spots in layer 1 rather than with two Zn compounds?
Authors: X-ray diffraction analysis determined dolomite to be the only phase containing Ca/Mg in layer 1. Dolomite distribution is shown in Figs. 4e and 4f. It clearly does not correlate with green CL emission (cf. Fig. 4b and 4c). Further, the maximum of CL emission for dolomite was found in the red region of the spectrum. It is exactly this red emission which is also present in the areas containing dolomite in layer 1 (Fig. 4b). The green, and missing, emissions can therefore only be linked to ZnO. X-ray diffraction analysis also determined that phase to be the principal pigment component in layer 1. There was no evidence of any other phase containing zinc.

G. Remond: CL spectra in Figs. 5 and 6 for layer 2 (red) show differences in the relative intensities of the two emissions bands occurring in the blue and red parts of the spectrum. Simultaneously, the maximum position of the red band exhibits a shift between the spectra shown in the two figures. Could these differences result from instrumental factors or from the variation in the excitation mode using optical CL and SEM/CL spectroscopy?
Authors: Experience has shown that the peak ratio in a given spectrum depends, among other factors, upon the magnitude of the specimen current. Care must therefore be taken that any reference spectra are recorded under identical conditions of excitation. Due to pigment distribution being frequently inhomogeneous in white coating materials, another important aspect is that comparable sample areas should be scanned, if possible in several different locations. The shifts are probably caused by extreme temperature differences during analysis. In view of these conditions it is sometimes not possible to obtain identical spectra using the different methods (optical CL and SEM CL).

D.C. Ward: Streaking appears in Fig. 3d that could obscure thin layers. Is this a usual artifact? Are there other CL artifacts that present imaging problems?
Authors: The streaking in Fig. 3d is due to smearing caused by long-persistence CL. This effect is frequently observed in ZnS particles and cannot be avoided even by low scan rates in the SEM. In comparative work, the smearing effect can even be used as an indication of common origin if the decay times of the crime-scene sample and of the reference material are in the same order of magnitude. In optical CL, due to the nature of the process, this effect is not observed. No other artifacts are encountered in pigment examination by CL.

S. Seta: How is the degree of the intra batch variation of CL color and intensity as the reference samples for comparison?
Authors: Our experience shows that maximum grain size of the individual phase portions is around 10 μm, which means that if crime-scene, and reference sample surfaces of some hundred μm^2 are available for examination, then there is sufficient intrabatch reproducibility. Fig. 4b (layer no. 1) provides an example of the greatest inhomogeneities observed within a single layer of paint so far.

S. Seta: Does the reproducibility of color CL image affect the comparison works between crime scene and

control samples?
Authors: In optical CL, to obtain correct representation of the emissions observed in the visible region of the spectrum does in fact require some precautions. As long exposure times (3 to 5 minutes) are normally involved, it is desirable to have the crime-scene, and reference, material embedded in one sample and photographed together. Where this is not possible, recording conditions should be kept as constant as possible. Objective checking is possible by recording spectra in the SEM.

D.J. Marshall: You mention the possible faster scan rates to be realized with the Zeiss MPM 800. Isn't the scan rate limited by the signal available (signal to noise ratio)? If so, how do you expect to achieve faster scan rates with the follow-up model?
Authors: The normally weak CL emissions of paint pigments require a generous slit width setting (1.5-2.2 mm = 10-15 nm) for the monochromator of the photometer. Under these conditions, and in combination with the greater optical throughput in the MPM 800 photometer, sufficient energy reaches the PM even in fast-scan mode. Spectrum accumulation enables examiner to obtain a better signal to noise ratio with the MPM 800 than with the UMSP 80 photometer.

W.C. McCrone: In comparing two paint samples, why not use the polarized light microscope which (in trained hands) can identify individual pigments, most of them at sight?
Authors: An attempt to perform the comparative examination of paints by just one method as a rule would be grossly negligent. In order to avoid erroneous findings it is necessary to perform comprehensive state-of-the-art tests on the additives, binders, and pigments of a given paint sample using the entire arsenal of microscopic, and instrumental methods available. Besides the analytical methods, sample preparation techniques, such as embedding, microtomy etc., are a vital factor. Of course, polarization microscopy is one of the methods of pigment analysis. In our experience of twenty years' work, using that method alone, one cannot meet the requirements of completely characterizing a given material. Just as important are therefore methods such as X-ray diffraction, UV-VIS microscope photometry (especially for organic pigments), and elemental analysis (EDX-WDX in the SEM). In specific cases, optimal case work, especially in the comparative examination of multilayered white paints, is not possible without the use of CL methods.