CATHODOLUMINESCENCE IN FORENSIC SCIENCE

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ABSTRACT: The emission of photons in the UV, visible or IR-part of the electromagnetic spectrum during irradiation of solid surfaces with high energy electrons is called cathodoluminescence (CL). CL can reveal textures and variations in the chemical composition of solids like ceramics, refractory materials, glasses, biomaterials, and certain minerals which cannot be detected with other analytical methods. Therefore CL has become a standard technique for mineralogical and petrological investigations but until now has not very often been used in forensic science.

The authors have therefore examined how this non-destructive method can provide information specific in the analysis of glass and paint.

In this report the capabilities and limitations of CL-microscopy for classification and discrimination of sheet and container glass are discussed. These are the commonest types of soda-lime glass found in forensic investigations.

In addition the use of CL in examining multilayered white/beige paint chips is illustrated.

INTRODUCTION

Light emission in the UV, visible or IR-part of the electromagnetic spectrum arising from the bombardment of a solid surface by an electron beam is called cathodoluminescence (CL).

This phenomenon was discovered in the middle of the 19th century.

The creation of CL by stimulation from high-energy electrons is commonly observed under the scanning electron microscope (SEM) or the electron microprobe. CL-signal generation in the SEM takes place simultaneously with the generation of X-rays, emission of secondary, backscattered and Auger electrons, induced current in semiconducting materials, and thermal effects [13,18].

All these processes are used for materials characterisation. SEM-CL equipment provides a high spatial resolution of CL features as samples can be observed and analysed under high magnification.

CL microscopes equipped with an electron gun in the form of a "cold" or "hot" cathode can detect the optical signals of luminescence visually or by spectral measurements [7].

In such equipment CL-features on thin sections or on polished surfaces can be compared with those observed in transmitted or reflected light. The advantage of CL-microscopy compared to the SEM-CL arrangements is that real colours of CL emission can be detected and compared directly with other microscopic observations.

CL can reveal textures and variations in the chemical composition of solids like ceramics, refractory materials, glasses, biomaterials, gems and certain minerals which cannot be detected with other analytical methods (Figure 1).
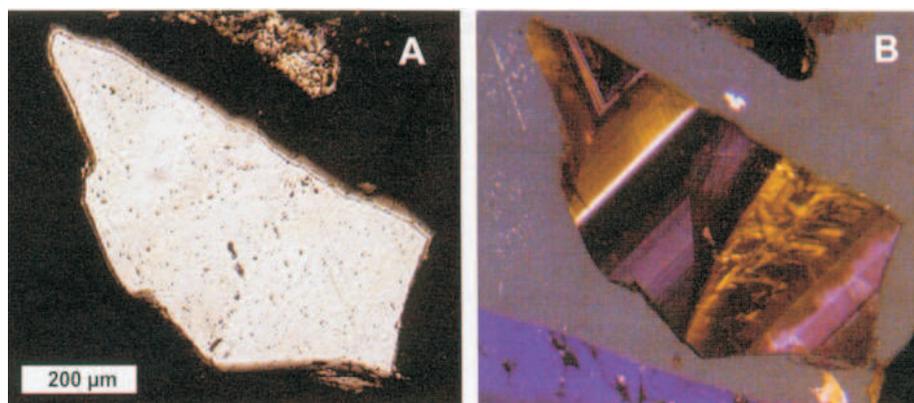
Fig. 1. CL (Figure B) reveals internal structures and growth in a hydrothermal quartz sample which are not discernible by conventional polarising microscopy (Figure A) [4].

Therefore CL has become a standard technique for mineralogical and petrological investigations [4, 11] but until now has had only very limited use in forensic science. CL methods have been described which can differentiate between natural and synthetic coloured precious stones, and to analyse coloured stones that otherwise could not been identified as fakes of expensive gemstones [9, 10]. In this report the capabilities and limitations of CL for classification and discrimination of sheet and bottle glass are discussed [16]. In addition the use of CL for paint analysis is briefly described [17].

BASIC MECHANISMS OF CL

As the result of electronic transitions in semiconductors and dielectrics the electron beam in CL-equipment generates electron-hole pairs or so called minority charge carriers [18]. Under various conditions it causes CL, induced current, induced electromotive force, or induced conductivity. Referring to the energy band diagram (Figure 2) of semiconductors and dielectrics (insulators), these effects may be explained by the fact that the electron beam energy is sufficient to transfer electrons from the filled valence band E_v into the conduction band E_c, at a level higher than $\Delta E = Eg$. Such transition is possible in case of energy absorption in the range from E_{min} to $E_{max} > \Delta E = Eg = E_c E_v$.
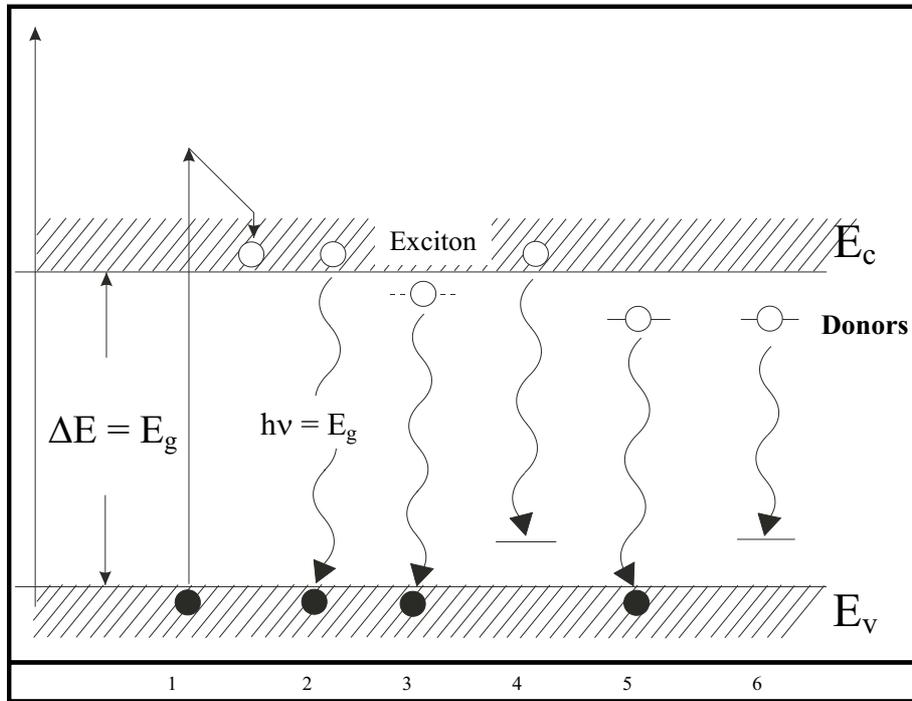
Fig. 2. 1 – An intraband transition of excited electrons reaching thermal equilibrium with lattice. Process may lead to photon emission; 2 – An interband transition. Intrinsic luminescence with the emission of a photon of energy $h\nu = Eg$; 3 – The exciton transition observable at low temperature; 4–6 – The processes arising from transitions on localised states of impurities (donors and acceptors) in the gap. Extrinsic luminescence.

As a result electrons appear in the conduction band and holes in the valence band. The transition of electrons back to the lower levels may be ac-

companied by emitting photons due to recombination, which is the basis of the CL effect.

CL-emission is the result of radiative transitions between quantum mechanical states separated by energy levels generally within the range from 1–3.5 eV (visible spectrum: 1.5–3.1 eV) in inorganic crystals, semiconductors and organic media. The emission is characterised by a delay after the excitation varying from nanoseconds up to hours for different materials. The CL-spectra from inorganic solids may be either intrinsic or edge emissions or extrinsic, activated or characteristic CL.

Intrinsic luminescence takes the form of Gaussian-shaped bands with their intensity peaks at photon energies $h\nu = E_g$ resulting from recombination of electrons and holes across an energy gap $\Delta E = E_g$. Thus changes in the gap E_g resulting from external disturbances (temperature, structural imperfection, alloying, stress, etc.) may be detected via a change of the photon energy hν. Extrinsic luminescence emission bands are activated by impurity atoms or other defects. The CL signals are formed by photons emitted as the result of electronic transitions between levels lying in the band gap of the material.

To analyse CL-information researchers usually detect such integral and local characteristics as the light emission intensity, spectral composition, kinetics of CL emission development and decay in the case of pulse excitation, and degree of polarisation of the CL.

INSTRUMENTATION

All SEM-CL analyses are performed with an Cam Scan model S4 SEM which is equipped with a Kevex Delta IV electron beam microanalysis system and CL equipment developed by E.O. Elektronenoptik Service (Dortmund Germany) [5]. Figure 3 illustrates the basic set-up of the CL detection system.

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.

In all SEM experiments the glass and paint samples were embedded in a cold-hardening resin (LC 2000) and ground and polished (Diamond, grain size 0.1 μm) after curing. The samples were prepared by carbon coating to eliminate charging effects using a Balzer type 250 T coating system.

The combination of CL and light microscopy was first performed for geoscience applications. Our instrument (contrasting unit developed by
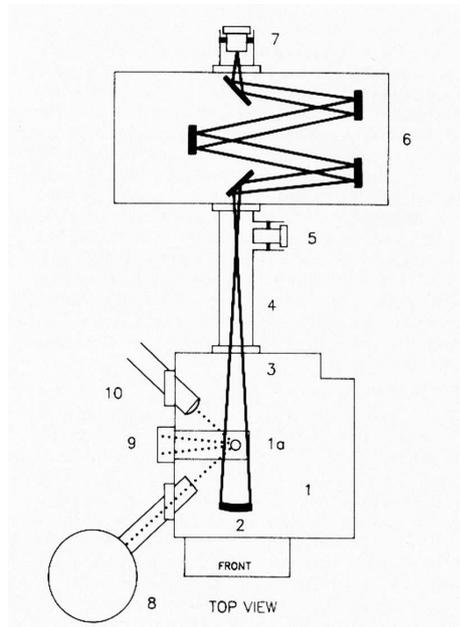
Fig. 3. Schematic diagram of a SEM system for spectral analysis of X-ray and CL. 1a – Specimen; 2 – Ellipsoidal mirror segment; 3 – Quartz glass window; 4 – Light channel; 5 – PM-I (side window type); 6 – Monochromator with UV-Vis grating; 7 – PM-I (end window type); 8 – EDX detector; 9 – BSE detector; 10 – SE detector.
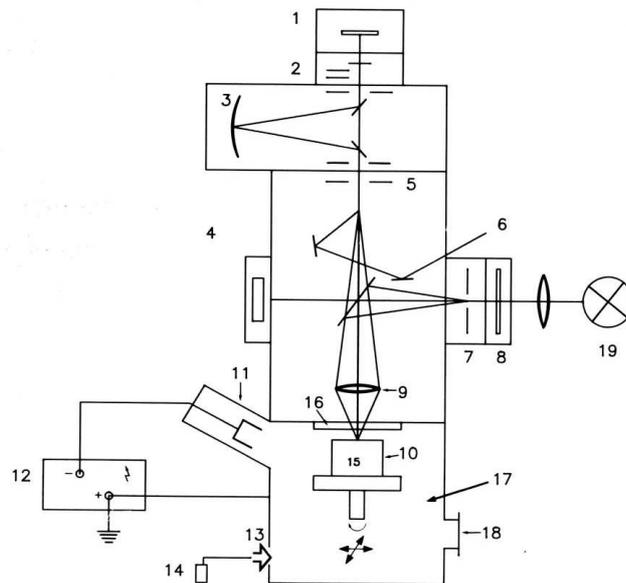
Fig. 4. CL-unit (LEICA) with microspectrophotometer. 1 – PMT detector; 2 – Filter; 3 – UV-vis monochromator; 4 – Photometer head; 5 – Measuring diaphragm; 6 – Ocular; 7 – Luminous field diaphragm; 8 – Light-shutter; 9 – Objective; 10 – Sample holder; 11 – Cathode discharge tube; 12 – Voltage supply; 13 – Needle valve; 14 – Gas bottle; 15 – Specimen; 16 – Quartz glass window; 17 – Vacuum chamber; 18 – Vacuum pump fitting; 19 – Halogen illuminator.
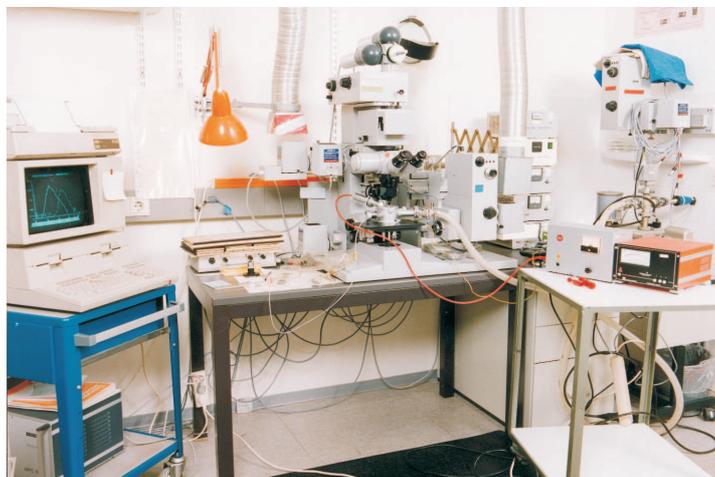
Fig. 5. The equipment for CL microscopy.

Fig. 6. CL equipment. The basic compo-
nents are a Leica contrasting unit (with
a cold-cathode electron gun) and a micro-
spectrophotometer (Zeiss UMSP 80).

Leica, Germany) is equipped with a cold-cathode electron gun (Figures
4, 5, 6) [3].

The CL microscope works in conjunction with a high-vacuum chamber
($< 10^{-6}$ bar), an acceleration voltage of 10–15 keV and a common current
density of ca. 0.5 mA/mm. For the investigation of weakly luminescing mate-
rials a hot-cathode instrument (where the electrons are emitted from
a heated filament) should be used as this technique provides a considerably
higher CL intensity than cold-cathode instruments.

CL examinations in the CL-microscope are generally carried out on embedded and polished paint cross-sections which have been coated with carbon to prevent any build-up of electrical charges during CL-operation. The objectives used had a magnification/numerical aperture of 10×/0.14 and 20×/0.40 (spatial resolution 1–2 µm).

FORENSIC APPLICATIONS

Glass

Today flat glass is almost exclusively produced by the float glass process (Figure 7). Exceptions are wired and pattern glasses which until now were produced by the continuous casting process.
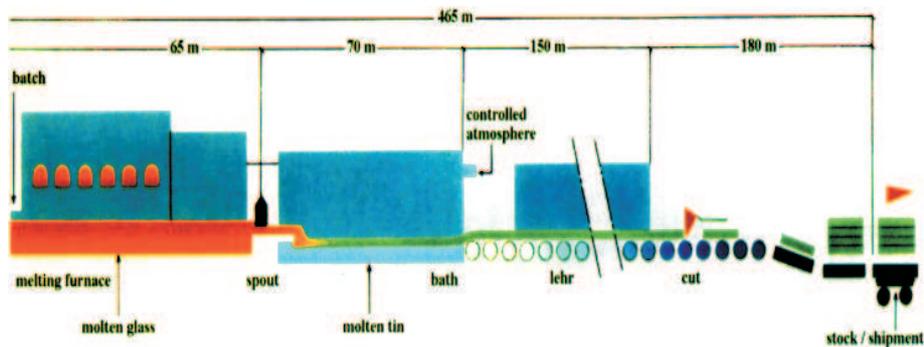
Fig. 7. The float glass process.

In the float process a continuous ribbon of glass moves out of a melting furnace and floats along the surface of an enclosed bath of molten tin [8, 14].

During the contact of the glass ribbon with the molten tin tin-ions penetrate the glass. As is already known, the tin(II)-ion concentration in the bottom surface of the ribbon can be used forensically for the classification of float glass, as it leads to an opaque fluorescence appearing at an exciting wavelength of 254 nm. However, with very small fragments this fluorescence is no longer visible. Therefore new techniques are necessary to prove that the sample is float glass. Elemental analysis using electron probe microanalysis (EMPA) in the scanning electron microscope (SEM) does not lead to conclusive results. On the outer surface modern bottle glass often has a comparable concentration of tin to float glass. This results from a hot treatment of the glass with inorganic ($SnCl_4$) and organic (n-alkyl-tin chloride) tin-compounds to upgrade the impact and tensile strength. The SnO_2 which

forms during this process fills the tiny cracks on the surface of container glass and protects from breakage [12].

The correct assignment of float glasses is possible using fluorescence spectroscopy. As Lloyd [6] already showed, pieces of float glass with bottom surfaces as small as 0.1 mm^2 (fragments of about 50 μg) can be characterised by their excitation spectra.

Any variation in tin fluorescence between different points on a window pane is small, in contrast to which comparisons of different glasses show noticeable differences in fluorescence intensity. The method can therefore be used for the discrimination of float glasses.

CL-analysis is another elegant and rapid method for identifying the tin side on a float glass sample. A wide band with a maximum at 495 nm is characteristic for tin luminescence in soda-lime glasses (Figure 8).
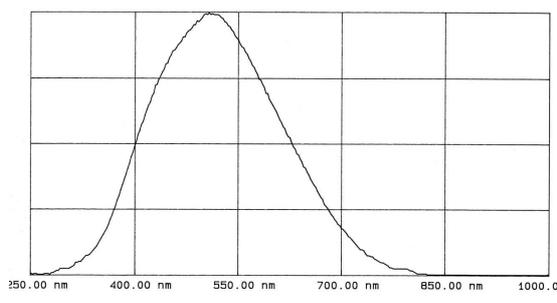
Fig. 8. CL-spectrum of the bottom surface of a float glass.

In the only float glass of the borosilicate glass type, developed by Asahi and Schott and produced since 1995, the tin signal is split into 2 bands with maxima at 525 nm and 440 nm (Figure 9).
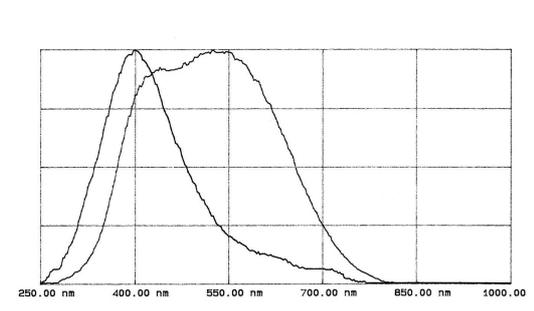
Fig. 9. CL-spectra of the bottom and top surface of the borosilicate float glass developed by Asahi/Schott.

A high tin count in soda-lime glass leads to a depression of the CL signal. Apparently with a higher tin concentration tin(II)-ions oxidise to tin(IV)-ions that don't contribute to CL (Figure 10).
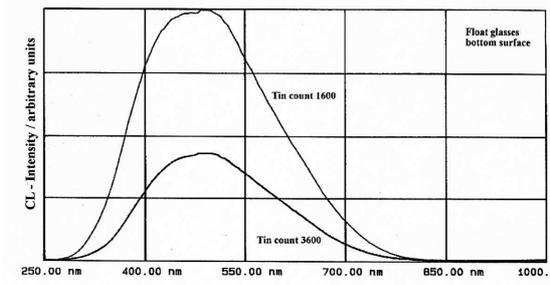
Fig. 10. CL-spectra of the bottom surfaces of float glasses with different tin count.

Because of this the tin(IV) containing outer surfaces of bottle glass and from heat protective glass can be clearly distinguished from the tin side of float glass. An example of this is the so-called K-therm glass from Pilkington, St. Helens, England. On the bottom surface this glass shows the typical tin(II)-signal and on the SnO_2 coated side only the CL signal of bulk glass (Figure 11).

Because the highest concentration of tin(II)- and tin(IV)-ions in float glass is in the upper 10–100 nm of the bottom glass surface [1, 2] and the total penetration depth of tin ions does not exceed 10–20 μm [15], not only can
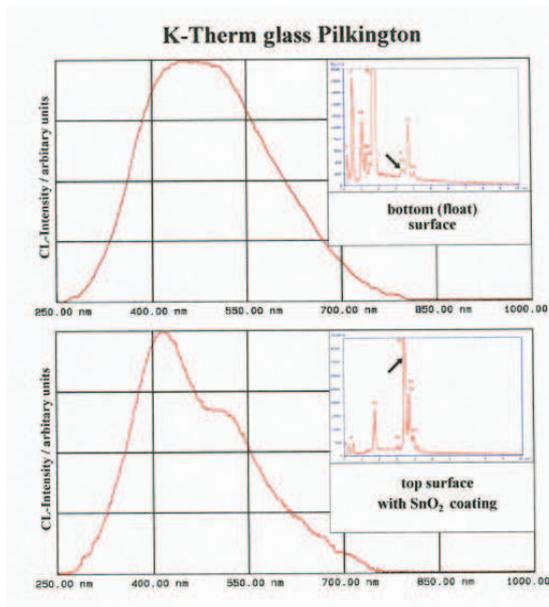
Fig. 11. CL emission spectra from the bottom and top surfaces of the K-Therm float glass from Pilkington [8].

CL analysis on the float side be carried out on the tiniest glass fragments but bulk analysis can also be performed. To do this the sample must be turned and analysed only in an area which has not been in contact with tin during the manufacturing process.

Using bulk analysis, differentiation of glass within a class is possible. Figure 12 shows the results of an examination of three colourless float glasses produced in different plants but having the same R.I.
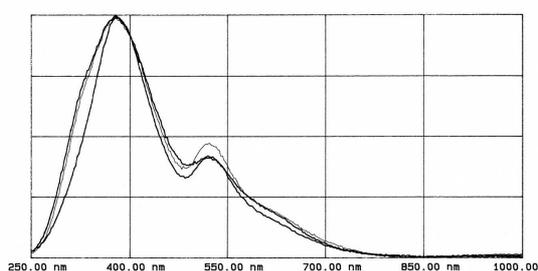
Fig. 12. CL-spectra of three float glasses from different plants: 1 – Lof (USA); 2 – PPG (UK); 3 – Flachglas AG (Germany).
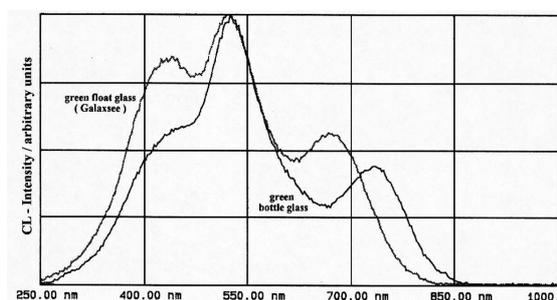
Fig. 13. CL-spectra from a tinted float glass and of a coloured bottle glass with the same refractive index.

From Figure 13 it is possible to see that the CL spectrum from tinted float glass can be clearly distinguished from the spectrum of a coloured bottle glass with the same R.I.

The colour of pale coloured glass samples that are used for example in cars as protection against strong sunlight are no longer recognisable in tiny fragments. They are not distinguishable by EDX-analysis as the glass matrix cannot be differentiated from non tinted glass from the same production line. A rapid and non-destructive identification is possible using CL-analysis, as the CL spectra from weakly coloured glasses are clearly differentiable from each other as well as from non tinted glass (Figure 14).
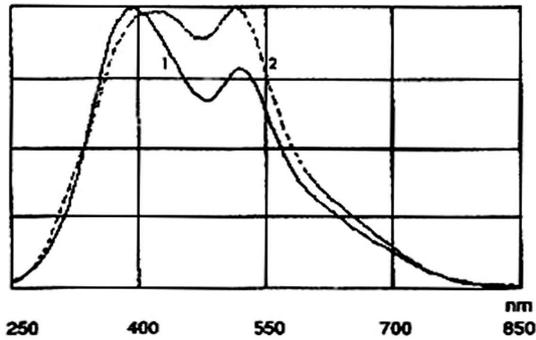
Fig. 14. CL-spectra of two samples of weakly tinted float glass (sun protection glasses), 1 – green; 2 – gray.
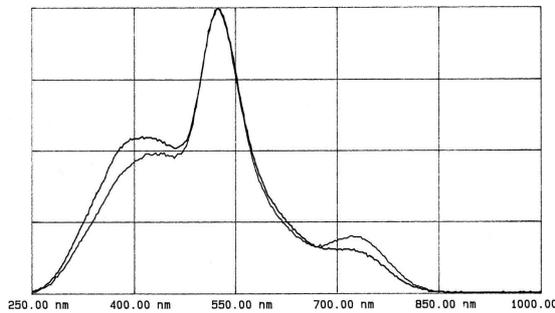
Fig. 15. CL-spectra of two samples of dark coloured bottle glass.

Fig. 16. Delay of CL emission after excitation of a glass sample with polished surface.

With more strongly coloured flat- and container glass the variety within the CL spectra makes it possible to classify them (Figure 15). After prolonged electron beam irradiation the electron beam annealing – induced enhancement of visible or infrared CL intensities (Figure 16) can also be used for the discrimination of glasses. This phenomenon can only be seen in certain types of glass.

Conditions for the analysis of glass

In order to obtain reproducible results it is necessary to adhere to certain conditions. Analysis should always be carried out on polished samples of comparable size. With non embedded and unpolished samples of varying size and surface geometry the intensity can vary dependant on the measuring field. This may be the result of scattering or because of the poor conductive properties of glass in response to different degrees of localised warming.

Because the energy levels of structural defects, lattice imperfections and band gaps are temperature dependant, this leads to shifts up to 20 nm in the position of luminescence bands or to further alterations in the character of the spectra. For spectral comparisons it is therefore advisable to use normalised spectra.

Paint

Paint comparisons are especially difficult if the trace specimen consists of several layers of similar white, grey and cream colours. The flakes often occur in connection with burglaries (e.g. paint flakes from window frames and doors) and from ship collisions. Flakes with up to 35 layers of similar colour are not unusual.

There are only a limited number of white pigments and extenders that can be used in such paints. As in the case of minerals, the CL colours of natural and synthetic white pigments can vary considerably due to the presence and concentration of inherent impurities, lattice defects etc. By using CL-microscopy it is possible not only to determine the number and thickness of paint layers, but also to obtain individual luminescence patterns.

The following examples from case work samples may serve to illustrate how powerful the method is (Figures 17, 18, 19, 20).
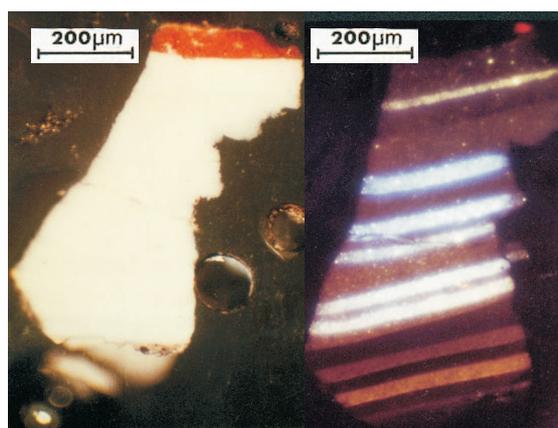
Fig. 17. Cross-section of a multilayered white paint fragment taken from an ocean liner (20 layers).
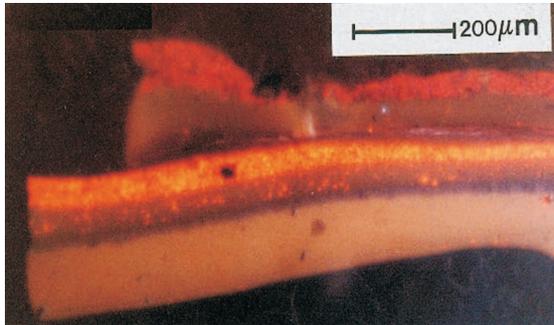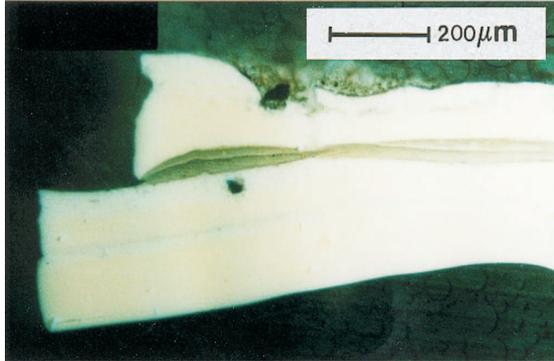
Fig. 18. Cross-section of a fragment of house-hold paint (8 layers).
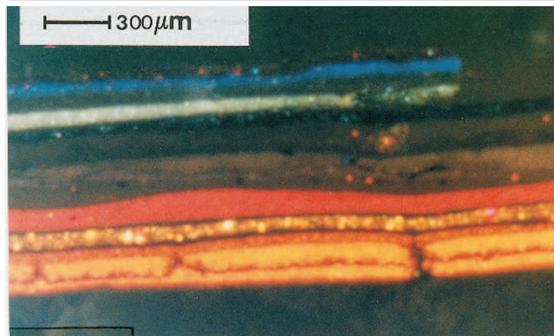
Fig. 19. Cross-section of a fragment of house-hold paint (15 layers).
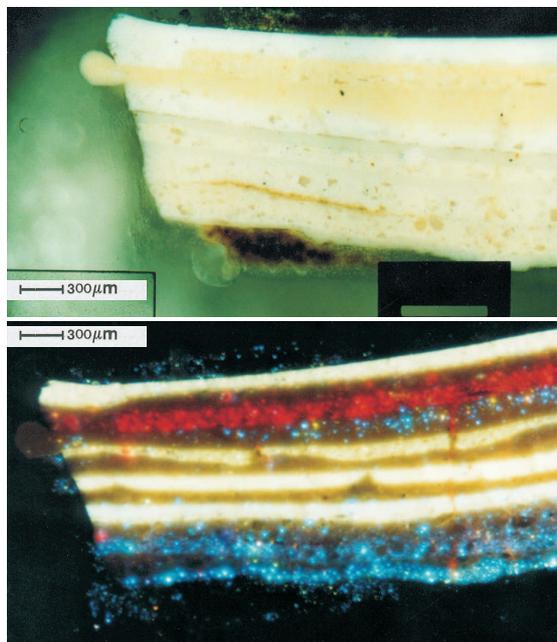
Fig. 20. Cross-section of a multilayered fragment of household paint (14 layers).

CONCLUSION

Cathodoluminescence offers a method for microcharacterisation of materials without causing substantial alteration to the sample. Using this method the comparison of recovered glass traces with a known sample to provide forensic evidence will be more informative because various glass having the same refractive index can be discriminated.

CL analyses can also be used where other methods fail to identify the structure of paint flake cross-sections composed of various layers of the same colour. Due to the different CL emission of pigments individual luminescence patterns can be obtained. The forensic scientist thus has a method which produces results of high evidential value.

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