



Distinguishing and dating carbonless copy papers by ultra-high-performance liquid chromatography and mass spectrometry



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ABSTRACT

A method to differentiate between carbonless copy papers and to date the ink entries on those papers has been developed based on ultra-high-performance liquid chromatography and mass spectrometric methods. A total of 52 paper samples were distinguished and classified according to compositional differences reflected by their chromatograms, with a discrimination power as high as 99.3%. The degradation kinetics of a common dye, crystal violet lactone, was investigated, and a quantitative determination method for the dye and its decomposition products was established. The results showed that relative peak area for both the dye and its degradation products versus aging time exhibits satisfactory linearity, which was utilized to date the ink entries on the samples. Overall, this work details an approach that can discriminate between different samples on the basis of compositional differences and describes the degradation rate of the dye, which can be used to age and authenticate ink entries.

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1. Introduction

Carbonless copy paper (CCP), which was first manufactured in 1954 by the National Cash Register Company, is a type of chemical pressure-sensitive recording paper and is an extremely common duplicating instrument [1]. It is utilized in the banking, insurance, commercial and legal industries and is ubiquitous in nearly all aspects of our daily life. Along with the increased use of convenient and efficient CCP, related criminal activities have also increased. Documents using CCP may be tampered with, altered, or recopied, which can lead to large financial losses. Thus writing or marks on CCP papers are often important subjects of forensic analysis. Accurate identification of CCP documents can help to differentiate authentic documents from forgeries and provide a scientific basis for estimating the age of any ink. Therefore, the establishment of accurate analytical approaches for authenticating CCP documents would play a key role in the field of forensic science.

CCP papers generally consist of three-parts, a coated back (CB) sheet, a coated front and back (CFB) sheet, and a coated front (CF) sheet, as illustrated in Fig. 1a. Microcapsules of dyes, buffering

agents, adhesives, etc. are coated onto the back of the CB and CFB sheets, while chromogenic agents, such as activated clay, phenolic resin, salicylic acid and other additives, are coated onto the front of the CF and CFB sheets. Generally, crystal violet lactone (3,3-bis-(p-dimethyl-aminophenyl)-6-dimethyl-aminophthalide) (CVL) is used as the main dye component (see Fig. 1b). The CVL dye is colorless, though under acidic conditions, its lactone structure is broken and forms a blue quinoid π group. The pressure of writing or printing ruptures the microcapsules, which release the dye solution to react with the chromogenic agents on the sheet to form an image [2]. The complexity of the dye components, chromogenic agents and other additives provides an opportunity to differentiate between CCP samples, while the instability of the dye components could be utilized to date ink entries on CCP.

There are many publications concerning CCP, though most are concentrated on the introduction of various functions into CCP [1–3], the development of novel types of CCP [4,5], or CCP's harm to humans [6–9]. Some publications present the synthesis or structural characteristics of the dye components [10–12] or describe the methods for determining the volatile solvents used in CCP [13–18]. However, there are very few reports relating to the forensic analysis of CCP documents. Infrared luminescence [19] has been explored to investigate the addition of suspect writing onto a questioned document. The fading of the dye component on CCP has been described, and the influence of singlet oxygen on the degradation of

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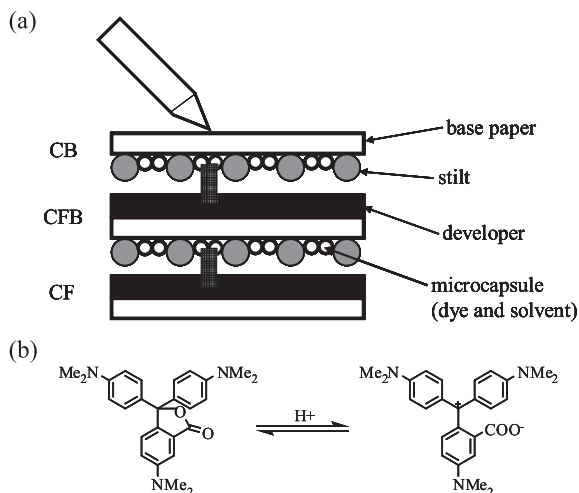


Fig. 1. Schematic diagram for the carbonless copy paper (a) (CB = coated back sheet; CFB = coated front and back sheet; CF = coated front sheet), and structures of the dye component (crystal violet lactone, CVL) in its leuco form and colored form, respectively (b).

the dye component has been investigated [20,21]. Additionally, the fading rate of the stroke was utilized to estimate the relative age of CCP documents [22].

Although a few attempts have focused on the forensic analysis of CCP documents, some important practical aspects are still limited, so systematic investigations on the identification and dating of CCP documents are urgently needed. High-performance liquid chromatography (HPLC) can be utilized to separate mixtures of compounds effectively, especially when coupled with mass spectrometry (HPLC-MS), and it is a powerful method for the identification and determination of non-volatile substances in a complex matrix. Recently, HPLC-MS and related mass spectrometric methods have been utilized in a wide range of forensic analysis applications, including the identification of ballpoint pen inks [23–28] and printing inks [29–33]. In our previous work, the differentiation and dating of various ink entries on documents, including gel pen, fountain pen and red seal inks, was investigated with chromatographic approaches coupled to mass spectrometry or other related techniques [34–39].

In this work, the differentiation of CCP samples and the dating of their ink entries were investigated by ultra-high-performance liquid chromatography (UHPLC) coupled to various mass spectrometric methods. The extracts of the CCP papers were analyzed by UHPLC with a UV–Vis detector, and the CCP samples were classified and differentiated based on the differences of their UHPLC chromatograms. The photodegradation kinetics of the common CVL dye component was explored, and the main degradation products of CVL were determined. This work demonstrates that these established methods could be utilized to differentiate and date CCP samples.

2. Experimental

2.1. Chemical and reagents

Crystal violet lactone (CVL, purity >97%) was purchased from Alfa Aesar (London, England), and HPLC grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany). Formic acid (purity >99.0%) and trifluoroacetic acid (TFA, purity >99.0%) were supplied by Acros Organics (New Jersey, USA). All other chemicals and solvents used in this study were analytical

grade and were purchased from Beijing Chemical Reagents Company (Beijing, China). Water for buffer preparation was obtained from a Millipore Milli-Q purification system (Boston, USA).

A stock solution of CVL with a concentration of 1.00 mg/mL was prepared by dissolving 10.0 mg of CVL in 10.0 mL of acetonitrile, and the solution was stored at 4 °C in a refrigerator. Subsequent solutions were obtained by dilution of the stock solution with acetonitrile.

2.2. Collection and preparation of the CCP samples

Fifty-two samples of carbonless copy paper were purchased from the markets of different Chinese cities; their brands and product numbers are listed in Table S1. The experimental samples were prepared by writing words or drawing lines on the CCP samples. For the naturally aged samples, the CCP samples were stored at room temperature and were not exposed to strong light. For the artificially aged samples, the samples were exposed to a fluorescent lamp (40 W) at a distance of approximately 10 cm, UV light with a wavelength of 254 nm, or an oven at a temperature of 80 °C.

For the differentiation of CCP samples, the samples were prepared by cutting out approximately 3 cm of the lines on the CFB papers, and then the paper was cut into small pieces, which were extracted using 1.0 mL of acetonitrile-0.1% TFA (1:1, v:v) for approximately 15 min at room temperature. The extracts were filtered through a 0.22- μ m millipore filter prior to UPLC analysis. For the aged samples, approximately 1 cm of the lines on the CF papers was cut out and extracted using 1.0 mL of acetonitrile for approximately 15 min at room temperature. The extracts were filtered through a 0.22- μ m millipore filter prior to the UPLC-MS/MS analysis.

2.3. Instruments and working conditions

2.3.1. Ultra-performance liquid chromatography (UPLC)

The separation for the extracts of the CCP samples was performed on a Waters Acquity UPLC system (Milford, MA, USA), which consisted of a quaternary solvent manager and a UV–Vis detector, with the working wavelengths set to 580 nm and 254 nm, respectively. The data were collected and processed using an Empower2 chromatography workstation. The separation column was an Acquity UPLC BEH C18 (1.7 μ m, 50 mm \times 2.1 mm), and its temperature was held at 25 °C. The mobile phase was a mixture of water containing 0.1% TFA (Eluent A) and acetonitrile (Eluent B) with a flow rate of 0.3 mL/min. The injection volume was 10 μ L. For determination of the dye components, the wavelength of the detector was set to 580 nm. The linear gradient of the mobile phase began at an initial state of 60% A, decreased to 50% A over 2 min, was held for 3 min at 50% A, decreased to 30% A over 1 min, stabilized for 3 min at 30% A, increased to the initial state (60% A) over 1 min, and was held for another 5 min to equilibrate. For differentiation of the CCP samples, the wavelength of the detector was set to 254 nm, and the program of the mobile phase began at an initial composition of 60% A, decreased to 50% A over 2 min, was held at 50% A for 3 min, decreased to 40% A in 5 min, decreased to 20% A over 2 min, stabilized for 4 min at 20% A, increased to the initial state of 60% A over 1 min and finally equilibrated for 5 min. The retention time of the components in the chromatograms have high reproducibility, and their RSD was below 1.0% ($n = 6$).

2.3.2. HPLC-micro TOF-Q II mass spectrometer

A Bruker micro TOF-Q II Mass Spectrometer (Billerica, MA, USA) equipped with an Agilent Technologies 1200 HPLC system (California, USA) was used to investigate the degradation process of CVL.

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