J1 Determination of the Age of Ink Entries From Questioned Documents With TD-GC/MS and HPLC Methods

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After attending this presentation, attendees will learn how an ink entry on a questioned document is related with entrry date.

This presentation will impact the forensic science community by demonstrating how ink age determination can be accomplished using the dynamic physicochemical properties of the ink entries on a document.

Determination of the age of an ink entry from a questioned document is a difficult and controversial issue in forensic science. Lately, the studies of ink age determination done from the dynamic properties of the ink entries have shown that the phenoxy ethanol, which is one of the solvents in ink, has different behavior against the varying thermal conditions by Thermal Desorption and Gas Chromatography/Mass Spectrometry (TD-GC/MS) during methyl losses of the pigments and presents a valuable confirmatory evidence of age using High-Performance Liquid Chromatography (HPLC).[1]

The goal of this study is the enhancement of the ink age determination methods using dynamic physicochemical properties of the ink entries on a document such as the vanishing rate of phenoxy ethanol (PE) with TD-GC/MS that is used in traditional analyses of volatile organic components and the fading rate of the pigments Crystal Violet (CV), Methyl Violet (MV), Tetramethyl Para Rosaniline (TPR), and other changes in pigment constitution.

For comparison of thermal desorption properties, the sample cut in 0.5cm in length, was placed in a completely empty and clean thermal desorber tube. The sample was analyzed in two different runs for different temperatures: 90°C and 200°C.[2] The sample was desorbed for 20 minutes at 90°C. Then the sample was trapped at -10°C. The temperature of trap was increased to 300°C. The sample was held approximately three minutes then it was given into GC. Temperature of the transfer line was 140°C. The DB-VRX column used was 60m long and had an internal diameter of 0.25mm and film thickness of 1.4 µm. The oven temperature was programmed as follows; 45°C for one min, then from 45°C to 100°C at a rate of 30°C/min and from 100°C to 190°C at a rate of 12°C/min. It was held at 190°C for four minutes then increased to 200°C at a rate of 50°C/min and held for five minutes. To ensure better quantitative accuracy, the Selected Ion Monitoring (SIM) mode was employed, due to its higher sensitivity. The chosen quantifier ion m/z is 138,10 and qualifier ion 94,0. The same sample was desorbed for five minutes at 200°C. The system conditions chosen for 200°C was the same as the one chosen for 90°C. The age of ink entry was calculated by the help of the relation between the integration values at 90°C and 200°C (M_{90}, M_{200}).

For the comparison of the time dependent methyl losses of the ink pigments on the same documents, two 1.2mm punches were extracted by methanol for 15 minutes and than 10 micro liters of extract were injected to the HPLC. The chromatograms of the questioned inks were compared to find age differences in between.

By the present methods proposed, as a result of one year work and approximately 300–350 experiments the aging curve of ink (V%) was plotted and the feasibility of ink age determination in the laboratory clear. The HPLC chromatograms have been used for prediction and/or confirmation. Two examples of the use of the proposed method in caseworks is given.[2,3]

References:

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