Analysis of the Degradation Process of Ballpoint Ink by Mass Spectrometry

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In the forensic examination of documents the legitimacy of the age of an ink entry is often an essential question. Ball-point ink contains equivalent amounts of dyes, solvents and resins. After the ink is deposited on paper, its composition begins to change qualitatively and quantitatively. The aim of this study is to develop mass spectrometric analysis of ink entries to determine their ages. First the influences of the ionisation and preparation techniques were evaluated. Then the influences of daylight, artificial light, wavelength and heat on the degradation of dye with time were studied .

The reference substances used were pure methyl violet and blue ball-point ink containing methyl violet (source BKA, Germany). BIC® ball-point (Cristal™ medium blue) was used for analysis directly from paper (main components are methyl violet and ethyl violet). Typical degradation of ball-point dyes is characterised by the loss of CH_2 groups (fig.1).

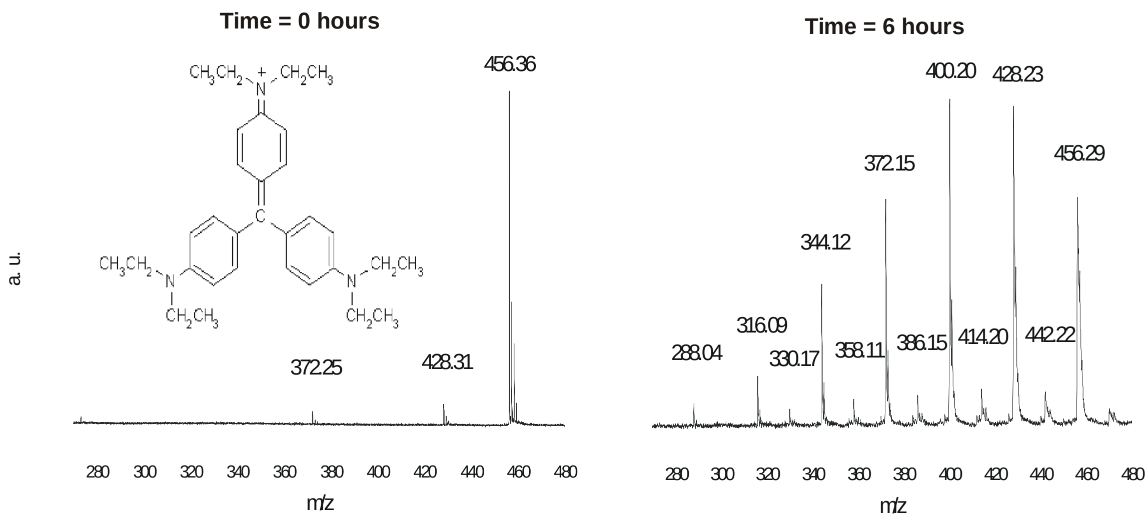

Figure 1: Degradation of ethyl violet (M^+=456.3 u) by xenon light (MALDI-MS)

Artificial aging was studied using the following treatments over different periods of time: exposure to xenon high pressure light (XBO 450W), to UV light (4W) and storage in oven at 100℃. Natural aging was studied using BIC® ball-point entries which were exposed to daylight or stored in a dark drawer over three months. Analyses were performed on a MALDI/LDI-Reflector-TOF-MS.

First the influences of the ionisation and preparation techniques on the degradation of the dye were studied. It was observed that the fragmentation of the molecular ion increases with laser irradiance. Therefore analysis of aged samples has to be performed at threshold irradiance and in comparison to non-aged samples. The influence of the irradiance on fragmentation is less pronounced for LDI than for MALDI. The use of matrix (2,5-dihydroxybenzoic acid) or hydrochloric acid for the preparation of the sample also promotes the fragmentation of the dye.

The effect of the wavelength of the degrading light was also studied. BIC® ball-point entries on paper were exposed to selected wavelengths using a xenon high pressure light and different filter glasses. The wavelengths were selected according to the absorption spectrum of methyl violet. It was observed that UV light and light at λ_{max} of methyl violet promotes the degradation of methyl violet after two hours of exposure.

Artificial aging is strong and fast under xenon light, weak and slow under UV light and very slow after oven heating.

Natural aging samples show different results for different storage conditions. Ink entries stored in the dark show no measurable change after 175 days whereas ink entries exposed to daylight show strong degradation already after 14 days(fig.2). The change of colour is also visible to the naked eye.

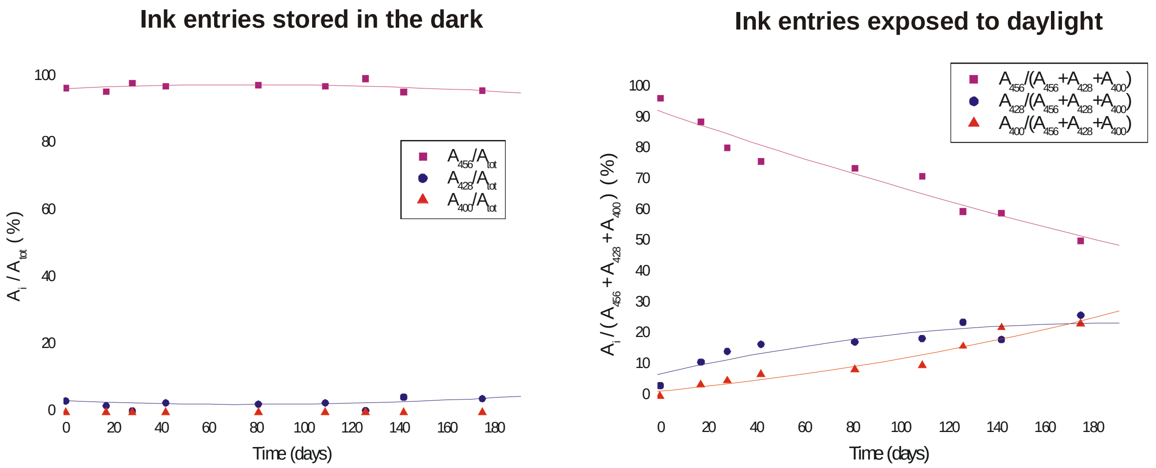

Figure 2: Natural degradation of ethyl violet (M^+=456.3 u) [A_i:Area of the signal at mass i]

The use of LDI and laser irradiances near threshold provide for useful results. The experiments show that the degradation of dye is strongly dependent on light fluence, and that the use of wavelengths close to the absorption maxima of the dye promote the degradation. The results are reproducible (relative standard deviation below 10%), but storage conditions have to be known for correct forensic interpretation. Dye analysis alone does not allow to conclude about the age of an ink entry. Therefore other ink compounds have to be analysed in addition for age determination of commercial ink entries. Degradation over longer time frames has to be monitored.