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Dating of Ink Entries by MALDI/LDI-MS and GC-MS analysis : Reality or Utopia?

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In forensic examinations of documents the legitimacy of the age of an ink entry is often an essential question. Ballpoint 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 investigation is to develop mass spectrometric methods of analysis for dyes and solvents to evaluate the aging processes of blue ballpoint ink entries with only minimal or without chemical treatment. First the influences of the ionisation step in Matrix Assisted Laser Desorption Ionisation (MALDI) and Laser Desorption Ionisation (LDI)-MS) and of the employed preparation techniques were evaluated. Then the aging processes was characterised.

The reference substances used were, on the one hand, pure dyes (methyl violet and ethyl violet) and solvents (propanediol, cresol, benzyl alcohol, hexylene glycol and phenoxyethanol) purchased from chemical companies and, on the other hand, ballpoint ink and solvent mixtures provided by the BKA (Bundeskriminalamt, Germany). BIC® ballpoint entries (Cristal™ medium blue) was used for analysis performed directly from paper.

In the first part of this work, degradation of the dyes was studied. For this, ballpoint ink entries on paper were artificially aged by exposure to light (high pressure xenon lamp) and heat (oven 100°C) over different periods of time. Afterwards small pieces of paper were cut and mounted directly on the target. These samples were analysed with an LDI mass spectrometer. The effect of the wavelength of the degrading light was also studied, by using different glass filters between the xenon light source and the sample. In addition, natural aging was studied using blue ballpoint ink entries on paper which were monitored over several months. One batch of samples was stored in the dark, while the other was fixed to a window and exposed to day light. Again a small piece of paper was cut and mounted directly on the target. LDI measurements were performed and compared.

In the second part of this work, the solvents were extracted from the paper and analysed with a GC-MS instrument with an Electron Impact (EI) source. The aging effect corresponding to evaporation of solvents from the paper was monitored over a short period of time.

First results show that LDI-MS and GC-MS are very powerful tools to analyse dyes and solvents respectively. Results are reproducible (relative standard deviation below 10%) and quantitative and qualitative information can quickly and easily be gained with minimal sample preparation.

Mass spectrometric analysis of dyes with LDI and MALDI shows 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 dyes. The dye ethyl violet was found to be more stable to light than methyl violet. The aging experiments show a strong correlation of dye degradation to the duration of light exposure, which is not observed for exposure to heat. Typical degradation of ballpoint dyes is characterised by the loss of CH_2 groups. The use of wavelengths close to the absorption maxima of the dyes promote this degradation. For natural aging, differences are observed depending on paper location, seasons and days due to the fact of different light fluencies.

Meanwhile ballpoint ink solvents vaporized rapidly at room temperature and can't be detected anymore after a relatively short period of time.

The difficulties in determination of the age of ink entries will be discussed. The state of the art of dye and solvent analysis allows to determine the approximate age of an ink entry, if both the exact storage conditions and the initial composition of the ink are known and if the aging process is still going on.