D22 Forensic Differentiation of Ink Samples Using the Pyrolysis-Gas Chromatography/Mass Spectrometry (GC/MS) Technique

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Learning Overview: After attending this presentation, attendees will: (1) learn what the pyrolysis-GC/MS technique is and how its different modes of operations (such as Evolved Gas Analysis [EGA], thermal desorption, flash pyrolysis, and heart-cutting) can be applied for material characterization of ink and dye samples; and (2) discover how pyrolysis-GC/MS can be applied to quality control, deformulation, contamination, unknown identification, and failure analyses while increasing laboratory efficiency by eliminating sample pretreatment and the "traditional" solvent-based techniques.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by introducing a relatively new and modern-day analytical technique for material characterization using pyrolysis-GC/MS. This technique allows laboratories to eliminate the time-consuming sample preparation and solvent extraction while improving precision and accuracy in analytical protocols.

In forensic investigations, the identification and differentiation of inks and dyes need to be done quickly and accurately, while the analytical method is straightforward. Most of the traditional methodologies for the determination of inks are based on solvent extraction, filtration, and concentration. These techniques are cumbersome, time-consuming, and suffer from analyst-to-analyst variability while producing data of limited value.

Today, many laboratories are integrating modern-day pyrolysis-GC/MS using the micro-furnace pyrolyzer in their analytical protocols due to the efficiency and accuracy of this technique for analyzing the organic composition of virtually any material. This technique consists of the micro-furnace pyrolyzer, which utilizes a low thermal mass ceramic furnace and a GC/MS system. The micro-furnace is directly connected to the GC injection port and enables scientists with multiple analytical techniques in addition to flash pyrolysis. This technology uses heat to thermally extract additives and light compounds from heavier and polymeric materials; any solvent extraction or sample pretreatment can be then eliminated. Due to the accuracy and precision of the micro-furnace temperature control (±0.1°C), this technology is used for quantitative analysis while producing highly reproducible data.

In this presentation, a strategic "chemical method map" approach is described using multiple modes of the micro-furnace pyrolyzer to characterize and differentiate two ink samples. The two black ink samples are analyzed and compared to identify any minor differences in their chemical composition while eliminating any solvent extraction or sample pretreatment.

The first step when developing the "method map" is the Evolved Gas Analysis (EGA) technique. EGA provides a "picture" of the sample's complexity and thermal profile. In this technique, the sample is dropped into the micro-furnace, which is at a relatively low temperature. The furnace is then programmed to a much higher temperature. Compounds "evolve" continuously from the sample as the temperature increases, then a plot of detector response versus furnace temperature is obtained. The EGA thermogram is very well correlated to Thermal Gramateric Analysis (TGA) and guides the scientist on what to do next for further separation analysis and characterization. EGA thermogram shows if thermal desorption, flash pyrolysis, or heart-cutting is needed, or if a combination of the techniques is required.

The second step is to analyze the thermal zones of interest obtained from the EGA thermogram. In this step, the selective sampler slices a thermal zone out of the sample and separates the components chromatographically using an MS. This technique is called Heart Cutting (HC).

In this report, using EGA/MS and HC modes of operations of the micro-furnace, the two ink samples, including their raw materials, are chemically characterized. From the analysis, it could be concluded that one of the ink samples contained a much higher concentration of naphthol as the unreacted raw material from the dye ingredient of the ink sample.

Pyrolysis GC/MS, Forensic Differentiation of Inks, Material Characterization