B165 Distinguishing Between Fluorinated Surface Treatments of Fibers Using Pyrolysis-Gas Chromatography Plasma-Assisted Reaction Chemical Ionization-Mass Spectrometry (py-GC-PARCI-MS)

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Learning Overview: The goal of this presentation is to demonstrate how a new ion source can be used with pyrolysis-GC/MS (py-GC/MS) to enhance the evidential value of fibers by distinguishing between identical fibers with different fluorinated surface treatments.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by informing attendees of a new tool for discrimination of single fibers based on surface chemical characteristics, currently not attainable using visual and spectroscopic techniques.

The weight of fiber evidence is directly linked to the rarity of a fiber type. Because blue and white cotton are extremely common, their value as evidence is typically extremely limited. However, if these common fibers are coated, either by the owner or by a manufacturer, their value may be significantly increased. One type of surface coating that has been probed for this purpose is fluorinated water and stain resistant coatings. Many people own blue jeans, but fewer people will have jeans that are coated with a water and stain resistant coating. The presence of these coatings can be experimentally determined by examining the contact angle of water and oil. However, there are multiple types of coatings, and distinguishing between these different types on a single fiber has not been successfully achieved except by XPS, which is expensive and often unavailable to forensic laboratories.[1]

Here, a new elemental ion source coupled to pyrolysis GC/MS is presented that has high selectivity and sensitivity for fluorine and other halogens. By using an elemental source matrix effects are significantly reduced. An additional benefit to using an elemental source is that pyrolysis products of the fluorinated coating are easily observed as peaks with m/z 19. The GC is an essential part of this instrument because it provides some structural information of the polymer that is lost by using an elemental source. It does this by separating the fluorine containing pyrolysis products prior to atomization and ionization. By comparing pyrogram relative retention times and normalized intensities the results can be stored in a library that other labs could use for comparison.

To evaluate this new approach, pre-coated cotton fibers as well as cotton fibers applied in the lab were tested. For lab applications the pad-dry-cure method or spraying was employed. For the pad-dry cure method a small swatch of cloth was soaked in the fluoropolymer solution prepared according to manufacturer specifications, then excess liquid was squeezed out and the fabric was dried and cured using a circular IR lamp. For spraying, instructions on the commercial spray bottle were followed. No heating was required for the spray applications. A thread from the treated fabric was then removed and a single fiber separated. The fiber was then cut to 10 mm and transferred to a quartz tube for pyrolysis.

With this new ion source fluorinated coatings have been successfully detected on single fibers. Furthermore, data collected thus far shows the capability of distinguishing at least three different groups of fluorinated coatings by using principal component analysis (PCA). When visually comparing raw pyrograms the differences between these groups are clear. Therefore, py-GC-PARCI-MS is capable of being used to detect and differentiate between different coatings, improving the evidentiary value of fibers that have been coated.

In this presentation a new ion source coupled to pyrolysis GC/MS will be described that has been shown to distinguish between different fluorinated surface treatments on forensically relevant single fibers. This technique could also be potentially used to detect other halogenated coatings such as some dyes, and insect repellents. Applications of this new technique are likely to expand beyond fiber analysis and may find many applications in forensic analysis.

This project was supported by Award No. 2017-R2-CX-0007, awarded by the National Institute of Justice, Office of Justice Programs, U.S. Department of Justice. The opinions, findings, and conclusions or recommendations expressed in this publication/program/exhibition are those of the author(s) and do not necessarily reflect those of the Department of Justice.

Reference(s):

1. Blackledge, Robert D. "Forensic Characterization of Surface-Modified Fibers Via X-Ray Photoelectron Spectroscopy". In *Proceedings* of the American Academy of Forensic Sciences, 2012. https://www.aafs.org/wp-content/uploads/ProceedingsAtlanta2012.pdf

Fibers, Pyrolysis, Coatings

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