

Forensic analysis of acrylic fibers by pyrolysis–gas chromatography/mass spectrometry

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Abstract

Pyrolysis/gas chromatography/mass spectrometry is proposed as a suitable technique for the differentiation of colorless polyacrylonitrile-based fibers with similar morphology. Quite frequently, a comparison between items of this type is necessary to assess the reliability of the reconstruction of a crime. Hydrocyanic acid, acetonitrile, acrylonitrile, acetic acid, methacrylonitrile, 1,3-dicyanopropene, 1,3-dicyanobutene, 2,4-dicyanobutene and 1,3,5-tricyanohexane were the degradation products deemed most useful for discrimination of the samples. Principal component analysis was employed for pattern recognition. Although fibers are industrial products very similar in structure and properties, the concentration and the distribution of head-to-head arrangements of the monomers differ slightly. These structural defects alter in a significant way the composition of the mixture of the pyrolysis products. This allows for the differentiation of fibers, which are often important traces in criminal investigations.

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1. Introduction

Textile fibers found at a crime scene can be very useful pieces of evidence in the hands of investigators [1,2]. They can provide information about contact between the victim and the suspect, or they can help in proving a connection between the crime scene and the persons implicated in the felony. Currently, forensic analysis of textile fibers is mainly of a comparative kind: a sample of unknown origin is examined in order to determine if it could share a common origin with fibers from a known source. The role of the forensic scientist, who carries out these comparisons, is very demanding because on the basis of his results the guilt or innocence of a suspect can be decided. Care must be taken to perform a complete and comprehensive analysis, so that the scientist can discriminate between apparently similar fibers. When

characterizing a sample, the aim is to rigorously assess its uniqueness and value as evidence, through a complete and specific description of the item. Polyacrylonitrile (PAN)-based fibers (acrylics) are common in the marketplace and frequently encountered in forensic casework. This kind of fibers is usually characterized by qualitatively identifying the polymer composition by Fourier Transform Infrared (FT-IR) spectroscopy [3] and by a microspectrophotometric comparison of color [4], if the items are dyed. Optical microscopy is used to complement the results of the IR and microspectrophotometric comparisons. Colorless fibers are occasionally encountered in forensic investigation, though, and another instrumental method [5] is required to replace the microspectrophotometric results. In this paper, the use of pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS) to differentiate PAN-based fibers is proposed. Thermal degradation of PAN has been investigated by many groups [6–12] and Py/GC studies of PAN have appeared in the literature [9,11–14]. Although pyrolysis can be considered a well-established

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instrumental technique at the forensic scientist's disposal [15–17], only Almer's work [14] was aimed at a qualitative forensic classification of acrylics. The purpose of this paper is to show that a quantitative analysis of the degradation products of colorless acrylic fibers can differentiate between single fibers that are indistinguishable on the basis of morphology and hue. This adds to the evidential value of these fibers frequently encountered on crime-related scenes.

2. Experimental

2.1. Samples

Fiber samples were obtained from the Reparto Investigazioni Scientifiche di Roma (RIS, Carabinieri, Italy) private collection. Thirty-six colorless PAN-based samples were chosen to span a wide range of copolymer formulations. The different items are designated with a letter, representing the manufacturer, and a number (Table 1). Fiber samples sharing the same identification letter, i.e. the four C samples, the five G samples, etc., are samples differing for production lot, manufacturing plant, additives or intended end-use. For example, samples A6, A9 and A11 were manufactured with the same process in three different industrial plants by the same company, samples D5 and D7 differ by production lot and samples C3 and C4 have a different concentration of delustrant.

2.2. IR spectroscopy

IR absorption spectra were acquired on a Nexus FTIR spectrometer (Thermo Nicolet) equipped with a Continuum

microscope (Thermo Nicolet). A mid-infrared Globar source was used and the detector was of the MCT/A type. The spectra were acquired between 4000 and 650 cm^{-1} , with a resolution of 4 cm^{-1} using 256 acquisitions. Residual CO_2 and H_2O were removed by background subtraction and baselines were normalized using the Nicolet correction routine. The spectra were acquired in the transmission mode, using fibers oriented parallel to the y-axis on the microscope stage.

2.3. Pyrolysis–gas chromatography/mass spectrometry

Py–GC/MS analyses were made using a Pyroprobe 1000 (Chemical Data Systems) coupled to a 6890N gas chromatograph (Agilent Technologies) with a 5973N mass analyzer (Agilent Technologies). Single fibers were placed in a quartz tube and pyrolyzed in a platinum coil probe at 700 °C for 5 s (10 ms rise time). The degradation products were separated on a HP-5 MS (25 m \times 0.25 mm i.d. \times 0.25 μm film thickness) (Agilent Technologies) capillary column with a (5%-phenyl)-methylpolysiloxane stationary phase. Helium was used as carrier gas. The GC interface was kept at 250 °C and the injector at 270 °C. The GC oven temperature was programmed to hold at 70 °C for 2 min, then ramped at 10 °C/min to 270 °C, and then held at 270 °C for 15 min. Mass spectrometer was used in the scanning mode ($m/z = 10\text{--}300$). Triplicates were run for each sample. The peak areas in the resulting pyrograms were integrated using the ChemStation software (Agilent Technologies). The peaks considered suitable for the differentiation of the samples were those with a mean error lower than 10%. Identification of peaks was carried out on the basis of their mass spectra.

2.4. Data analysis

Principal component analysis (PCA) [18] was used on the integrated intensity ratios of the peaks in the pyrograms. PCA is a multivariate analytical tool used to reduce a set of variables (measured ratios of intensities) and to extract a small number of latent factors (principal components, PCs). PCs are linear combinations of the original data, constructed in such a way as to represent the maximum residual variance. The usefulness of PCA can be understood considering that, when samples are characterized on the basis of k properties, they can be represented as points in a k -dimensional space. PCA, without altering the data structure, proceeds by a rotation of the k -axes of the space, to find orthogonal axes that represent the directions of maximum variance for the data. The first two or three PCs usually retain much of the information associated with the data. In the case of the present paper, fiber samples were identified by eight relevant ratios of peak intensities. PCA was useful in reducing the eight-dimensional space to a much more easily representable three-dimensional frame of reference while preserving most of the information relevant for

Table 1
Characterization of the fiber samples^a

Sample	Comonomer	Sample	Comonomer
A	VA	G2	VA
B	MA	G3	VA
C1	VA	G4	VA
C2	VA	G5	VA
C3	VA	H1	VA
C4	VA	H2	VA
D1	VA	H3	VA
D2	VA	H4	VA
D3	VA	H5	VA
D4	MA	H6	VA
E	MMA	H7	VA
F1	MA	H8	VA
F2	MA	H9	VA
F3	VA	I1	SS
F4	MA	I2	MA
F5	VA	I3	MA
F6	VA	L	/
G1	VA	M	VP

^a As determined by IR spectroscopy; MA, methyl acrylate; VA, vinyl acetate; SS, styrene sulphonate; MMA, methyl methacrylate; VP, vinylpyrrolidone.

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