

1969

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Recommended Citation

Raymond A. Janiak, Kenneth A. Damerou, Application of Pyrolysis and Programmed Temperature Gas Chromatography to the Identification of Textile Fibers, 59 J. Crim. L. Criminology & Police Sci. 434 (1968)

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THE APPLICATION OF PYROLYSIS AND PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY TO THE IDENTIFICATION OF TEXTILE FIBERS

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Forty years ago all basic clothing textiles consisted of natural fibers, principally cotton and wool. Less frequently used were the luxury fibers silk and linen. With the introduction of rayon, a new era of textile fibers began with man-made fibers taking the place of natural fibers. In a very short time, a whole new industry was born producing in addition to rayon fiber, cellulose acetate, nylons, acrylics, polyesters, elastomers, and countless blends of these fibers with each other and with cotton and wool. Because these fibers offered decided improvements over natural fibers, their popularity grew to phenomenal proportions and world-wide they now constitute more than 20% of all textile fibers used.

To identify these fibers various physical and chemical analytical procedures have been devised. Most physical methods are performed on the intact fiber, whereas the chemical methods usually involve degradations to simpler species which can be identified. Intermediate between these two methods lies the method to be discussed.

In the study of polymeric substances, pyrolytic degradation has been used extensively. As long ago as 1862, Williams (1) used pyrolysis to isolate the basic isoprene unit from natural rubber and several publications have described the use of pyrolysis as a method of obtaining information about the structures of substances. In recent years, indirect "finger-printing" methods have been used in conjunction with pyrolytic methods. Infrared and mass spectrometry, for example, have been used to "finger-print" the total products of pyrolysis from various polymers. This type of approach often involves compilation of a library of reference spectra obtained from pyrolysis of

substances of known structure, and the identity of an unknown is obtained by referring to these spectra. The approach is generally successful as the products of pyrolysis obtained under given conditions are specific for each type of substance.

As used in gas chromatography, pyrolysis may be defined as the degradation of complex materials into simpler units by heat in the absence of oxygen. Those pyrolysis products that are sufficiently volatile are separated by gas chromatographic techniques to yield a "pyrogram" which has been found to be characteristic of the material pyrolyzed.

The usefulness of pyrolytic degradation has been greatly enhanced since the advent of gas-liquid chromatography. A combination of pyrolysis with gas-liquid chromatography offers a new approach to the analysis of substances of low volatility. The important features of gas-liquid chromatography that make it an excellent analytical technique for use in conjunction with pyrolytic degradation are: (2)

1. The products of pyrolysis are rapidly separated.
2. The separations can be recorded easily and automatically.
3. Only a few milligrams of sample are required.
4. The products of pyrolysis may be identified by their retention times.
5. Further identification of the products of pyrolysis may be obtained by collecting fractions at the exit port.
6. The chromatogram of the products of pyrolysis of a substance is in itself a "finger-print" and can be used in a similar manner to IR spectra for identification.

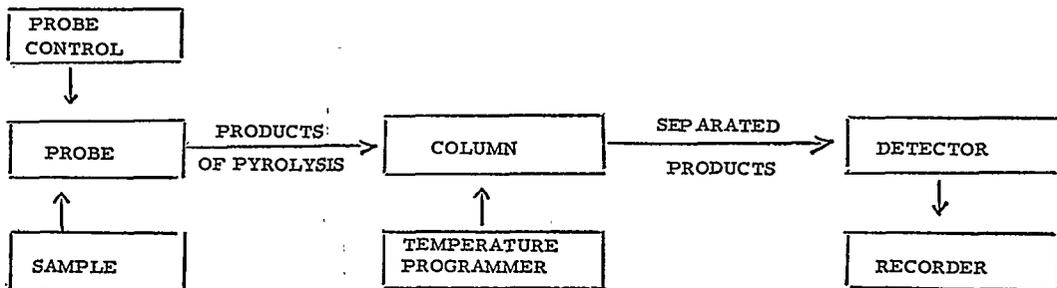


FIGURE 1

7. The pyrolysis unit can be connected directly to the injection port eliminating the chance of recombination of volatile products.

Using pyrolysis-gas chromatography in our laboratory, we have examined many fibers and fiber blends as well as other substances and were struck by the reproducibility of the pyrograms and the simplicity of technique to obtain acceptable pyrograms. Positive identifications have been made on no more than a few strands of unknown fiber. This last fact would suggest that this technique may have merit for investigative work and forensic science.

EXPERIMENTAL

The general analytical scheme employed in this work is shown in Figure 1. Instrumentation consisted of an F&M Model 700 Dual Column Gas Chromatograph equipped with dual flame ionization detectors. An F&M Model 240 Temperature Programmer was coupled to the gas chromatograph to continually increase the column temperature from 65°C to 225°C during a run. The columns were of ¼" x 6' copper tubing packed with 5% Carbowax 20M-TPA on Diatoport S. Sample and reference columns were identical.

The pyrolysis unit was an F&M Model 80 Pyrolyzer which consists of a probe filament control unit and a platinum-rhodium tipped probe. As received each probe has been calibrated so that a given filament current will produce a given filament temperature. For the purposes of this study a filament current was selected to yield a pyrolysis temperature of 1200°C. Descriptive literature of this unit is available from the manufacturer (3). Helium was used as carrier gas and its flow was maintained at 60 mls per minute through sample and reference columns. Injection

port temperature was 260°C and the detectors were operated at 290°C.

Samples consisting of a few strands of fibers were placed within the open cavity of the probe filament and by the judicious use of forceps the filament was compressed enough to hold the sample. Fiber ends extending beyond the filament were trimmed off. Probe and sample were inserted into the sample injection port and energized according to the manufacturer's instruction. Simultaneously with the firing of the probe, the recorder was started as well as the temperature programmer. The temperature of the column was raised from 65°C to 225°C at a rate of 4°C per minute and the pyrogram was ended after several minutes at 225°C.

The most characteristic features of these pyrograms are their "busy-ness". Many peaks are the general rule rather than the exception. One observes in most pyrograms locations of "skyscrapers", large prominent peaks rising above a highly populous "urban" area. These high peaks obviously represent the major constituents of the volatile portion of the pyrolysate. However, it is the overall "skyline" that is so characteristic of each material.

RESULTS

In Figure 2 are shown pyrograms of commercial nylon fibers. A distinguishing characteristic of these pyrograms is the single, high intensity peak standing quite alone at a retention time of 6 to 12 minutes. So invariant are these peaks that they can be found in pyrograms of blends of nylon with other fibers. Furthermore, the pyrograms of a given nylon type are virtually identical regardless of manufacturer.

Figure 3 compares the pyrograms of the natural fibers cotton, wool, and silk.

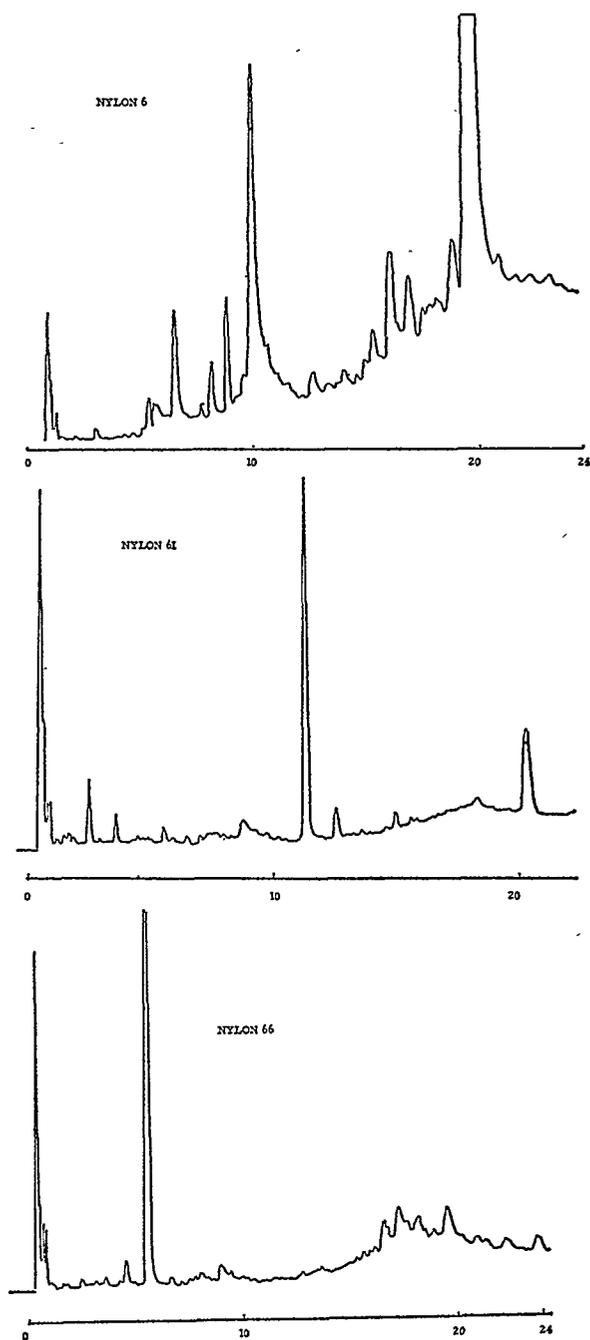


FIGURE 2

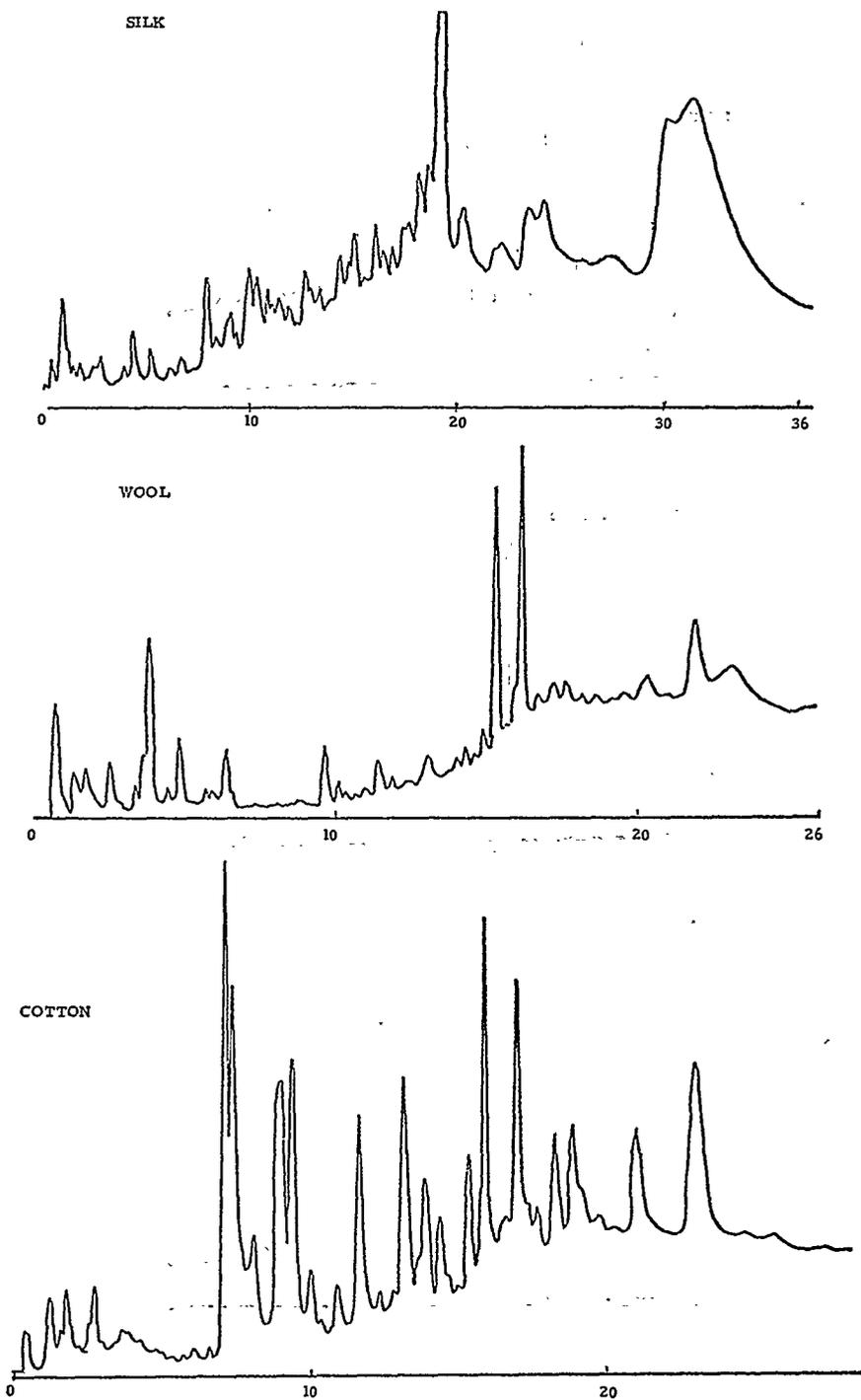


FIGURE 3

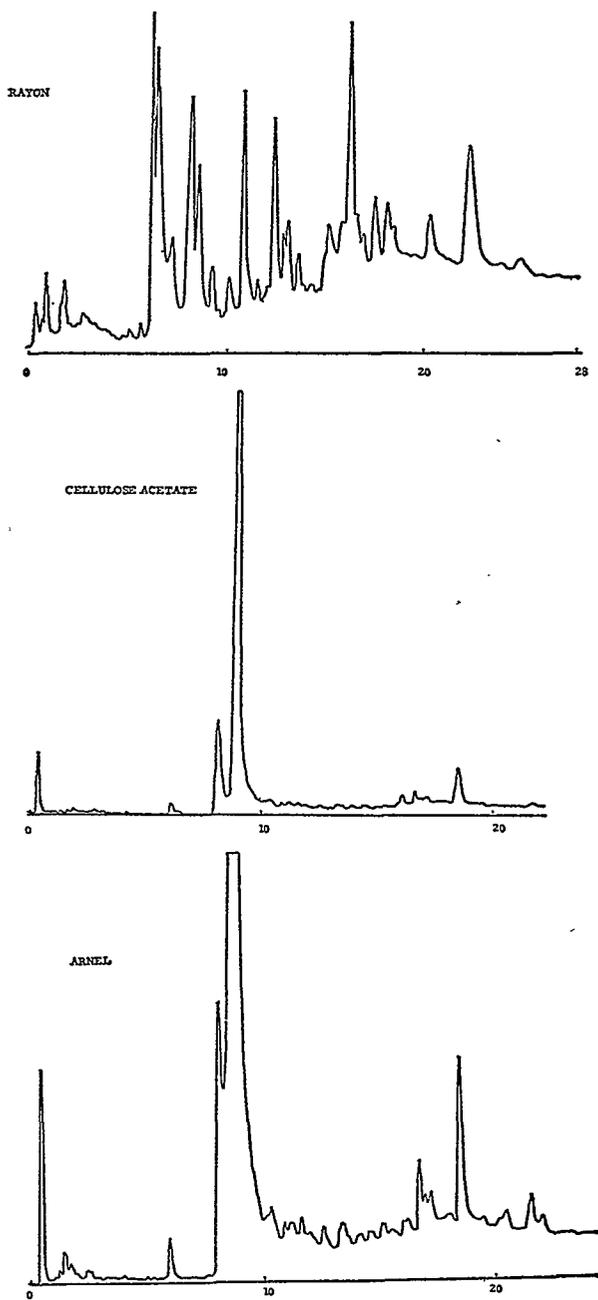


FIGURE 4

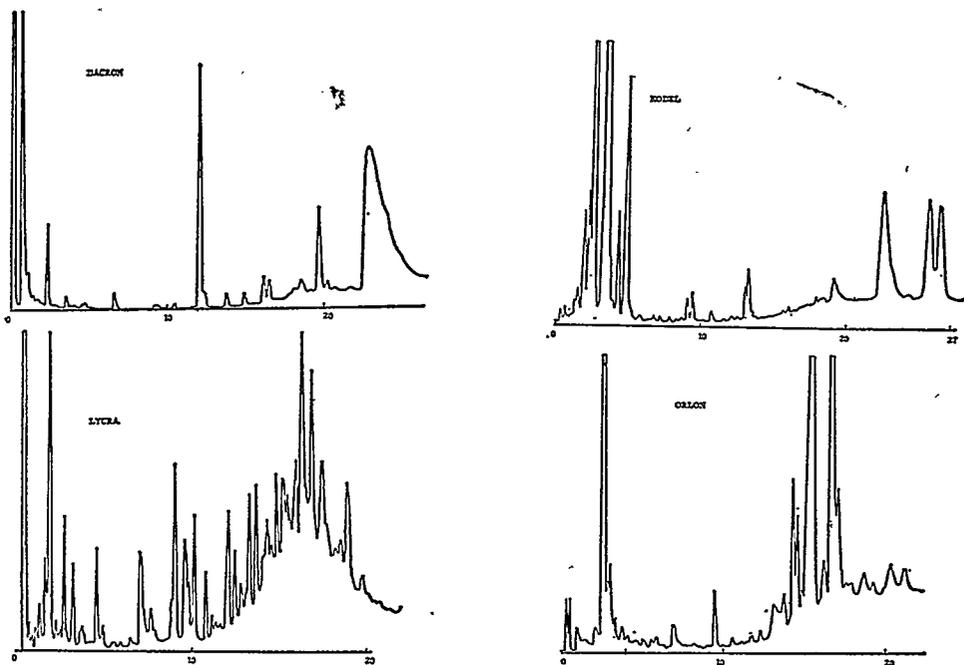


FIGURE 5

Figure 4 illustrates the pyrograms of the celulosics rayon, acetate, and Arnel® triacetate. Again, in this case, characteristic fingerprint patterns are produced. Acetate and Arnel® both give rise to a doublet with the more intense peak having the longer retention time.

Figure 5 contains a collection of proprietary fibers. Lycra® elastomer is characterized by a very "busy" pyrogram containing over 65 peaks. Fortrel® polyester fiber pyrogram at first glance resembles a nylon pyrogram. However, a pair of intense peaks in the first few minutes and a broad peak with much "tailing" after 20 minutes are distinguishing characteristics. The pyrogram of Kodel® is unique in that the first 3 most intense peaks occur within the first 5 minutes of retention time. Orlon and other acrylics are characterized by a collection of intense peaks, 4 to 6 in number, at a retention time from 13 to 18 minutes.

DISCUSSION AND REMARKS

Pyrolysis-gas chromatography combination offers a unique and welcome identification means to aid in the analysis of fibers. For retractable samples it may be the only route to an identification. An added bonus is the small sample requirement since an acceptable pyrogram can be obtained on as little as 3 to 5 milligrams of sample. Since it has been found that the pyrograms obtained are characteristic of the material being pyrolyzed, a reference library of them would serve to identify unknown materials.

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