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Note

Pyrolysis gas chromatographic analysis of some toxic compounds from nitrogen-containing fibres

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There have been few studies on the determination of hydrogen cyanide, benzene and toluene formed during thermal degradation of polymers in air, in atmospheres of inert gases or in an atmosphere containing a small amount of oxygen. For the determination of pyrolysis products, several methods have been used¹⁻⁴. When burning or similar thermal processes are carried out, the degradation of polymers and the formation of products takes place rapidly, and pyrolysis gas chromatography offers the best means for studying such degradation products.

Ingham⁵ studied the thermal degradation of untreated wool and wool treated with flame retardants using pyrolysis gas chromatography. The pyrolysis took place at 550° for 60 sec and methane, hydrogen sulphide, carbon monoxide and hydrogen cyanide were determined. Our study covered the range 625-925° and three nitrogen-containing fibres, namely wool, a polyacrylic (Acrilan) and a polyamide (Rilsan) were pyrolysed.

The problem was to determine the small amount of hydrogen cyanide formed by thermal destruction and to establish suitable conditions for the gas chromatographic separation of hydrogen cyanide, benzene and toluene.

HYDROGEN CYANIDE SEPARATION AND DETERMINATION

Previously a hot-wire detector was used for the gas chromatographic separation of hydrogen cyanide⁶, while it has been stated that under normal conditions the flame-ionization detector (FID) does not respond to hydrogen cyanide⁷. In the present time, both detectors are used⁸.

For the determination of the sensitivity of the hot-wire and FID detectors towards hydrogen cyanide a standard sample of hydrogen cyanide was synthesized according to Wöhler. Pure hydrogen cyanide was mixed with air to give a concentration of 3500-0.35 mg/m³.

A sample of size 0.1-2.0 ml was introduced into the chromatograph using a Hamilton 1001 gas syringe. The gas chromatograph used was a Perkin-Elmer Model 900 instrument with hot-wire and FID detectors connected with a Hewlett-Packard 3370 A integrator. A set of glass column was used: 2 m × 1 mm I.D. packed with 7% Carbowax 20M on Chromosorb W (80-100 mesh), plus 4 m × 4 mm I.D. packed

TABLE I
OPERATING CONDITIONS

Condition	FID	Hot-wire detector
Carrier gas (He) flow-rate (ml/min)	30	30
Hydrogen flow-rate (ml/min)	24	—
Air flow-rate (ml/min)	400	—
Oven temperature (°C)	40	40
Injector temperature (°C)	30	30
Detector temperature (°C)	150	150
Detector current (mA)	—	225

with 7% triacetin on Chromosorb W (80–100 mesh) (column I). The operating conditions used are given in Table I.

The results obtained show that the sensitivity of the hot-wire detector was 500 times lower than that of the FID; the detection limits were $0.35 \mu\text{g}$ for the hot-wire detector and $0.0007 \mu\text{g}$ for the FID.

For the determination of hydrogen cyanide, common supports such as Porapak Q, Porapak T, 1,2,3-tris(cyanoethoxy)propane, Carbowax 20M and triacetin can also be used⁹. In this study the problem of separating hydrogen cyanide from other light pyrolysis products arose, and for this purpose we used column I and a stainless-steel column (2 m \times 2 mm I.D.) packed with 5% dimethylsulpholane on Inerton AW (0.125–0.160 mm) (column II). Two pyrograms of wool obtained by using the above two columns are shown in Fig. 1.

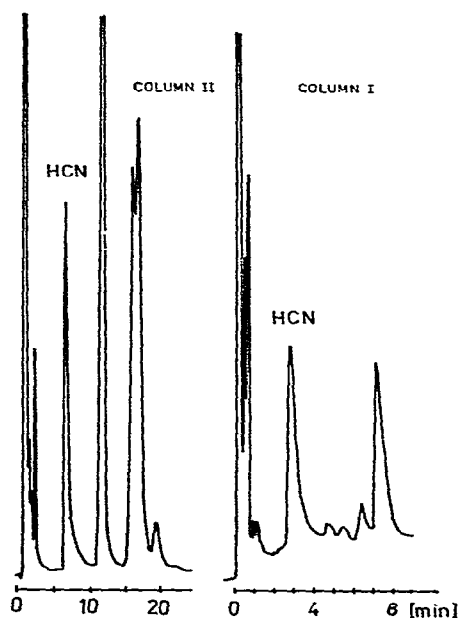


Fig. 1. Pyrograms of wool obtained with the use of columns I and II.

TABLE II
RESULTS OF ELEMENTAL ANALYSIS OF FIBRES

Fibre	N (%)	C (%)	H (%)
Polyacrylonitrile (Acrilan)	3.4	65.6	5.5
Polyamide (Rilsan)	7.6	73.3	11.2
Wool	14.7	46.0	6.2

QUANTITATIVE ANALYSIS OF PYROLYSIS PRODUCTS

For quantitative analysis a dimethylsulpholane column was used because it also separated benzene and toluene and other light compounds formed during the pyrolysis. Benzene and toluene peaks on the chromatogram were compared by using standard substances. In addition, the peaks of interest were separated and their UV spectra measured.

In order to gain some insight into the structures of the three types of fibres under study, the hydrogen, nitrogen and carbon composition was determined with a Hewlett-Packard Model 185 CHN Elemental Analyser, and the results are shown in Table II. The results are average values from triplicate determinations. Polyacrylonitrile has the highest nitrogen and the lowest hydrogen contents compared with the other polymers.

Gas chromatograms of fibre pyrolysis products at 850° are shown in Fig. 2. Although wool has a more complex structure than the other fibres, the three chromatograms of the lighter components are virtually identical, the only difference being in the peaks areas.

A furnace-type pyrolyser with a quartz tube was attached to the inlet port of the gas chromatograph with an FID detector, and the operating conditions used are given in Table III.

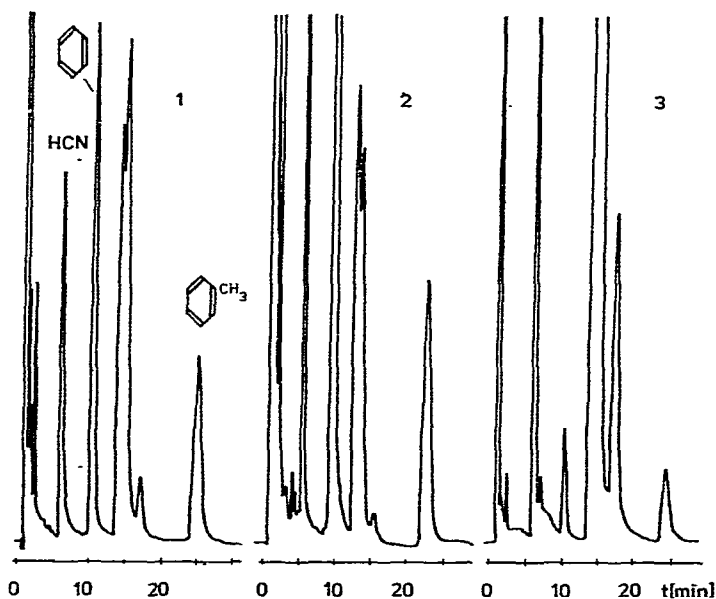


Fig. 2. Pyrograms of fibres obtained with the use of column II. 1, Wool; 2, Rilsan; 3, Acrilan.

TABLE III
OPERATING CONDITIONS WITH COLUMN II

Condition	Value
Oven temperature (°C)	20
Carrier gas (He) flow-rate (ml/min)	30
Hydrogen flow-rate (ml/min)	27
Air flow-rate (ml/min)	400
Injector temperature (°C)	150
Detector temperature (°C)	200
Pyrolysis temperature range (°C)	625-925
Time (sec)	10
Sample size (mg)	0.4-0.6

Fig. 3 shows curves for the evolution of hydrogen cyanide from the fibres studied, and it can be seen that the amount of hydrogen cyanide evolved is not proportional to the nitrogen contents of the fibres, as wool, which contains more nitrogen than Rilsan, produces less hydrogen cyanide.

The evolution of hydrogen cyanide from all three fibres is also not proportional to the temperature of pyrolysis and the curves show minima and maxima. The amounts of benzene formed are proportional to the nitrogen contents of the fibres, and not proportional to the carbon and hydrogen contents. The evolution curves also show minima and maxima (Fig. 4).

The amount of toluene formed is lower at higher temperatures, which indicates the formation of lighter products (Fig. 5).

The amounts of hydrogen cyanide, benzene and toluene evolved per gram of fibre are given in Table IV. The results indicate that the amounts evolved are high and potentially dangerous.

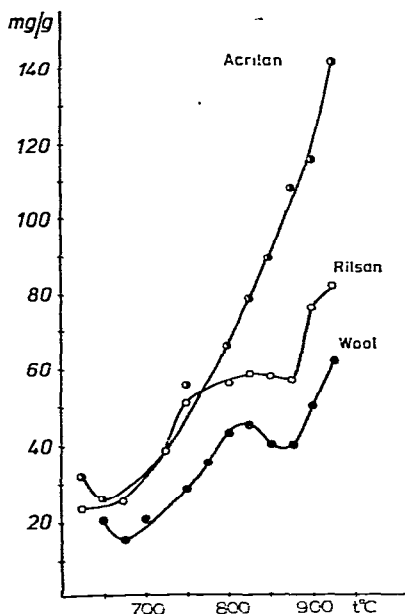


Fig. 3. HCN evolution curves for wool, Rilsan and Acrilan.

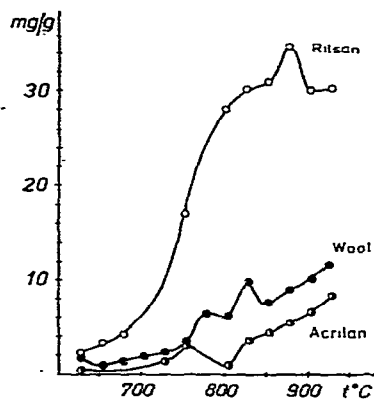


Fig. 4. Benzene evolution curves for wool, Rilsan and Acrilan.

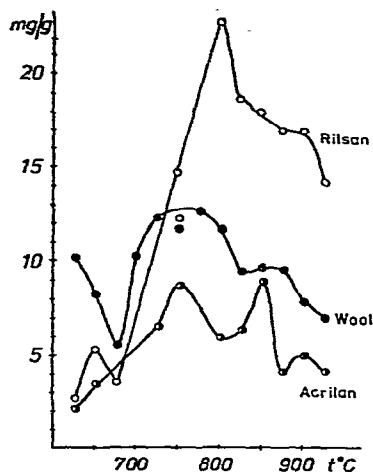


Fig. 5. Toluene evolution curves for wool, Rilsan and Acrilan.

TABLE IV

EVOLUTION OF HYDROGEN CYANIDE, BENZENE AND TOLUENE PER GRAM OF FIBRE

Pyrolysis temperature: 625–925°.

Fibre	HCN (mg/g)	Benzene (mg/g)	Toluene (mg/g)
Acrilan	32–140	0.4–8	2–8.8
Rilsan	32–82	2–35	2.6–22.8
Wool	22–62	1–11.5	5.5–12.5

The use of pyrolysis gas chromatography may introduce some errors derived from the accuracy and stability of the operating conditions, such as the stability of the pyrolysis temperature to within $\pm 10^\circ$, a small sample size and sample inhomogeneity. On the other hand, pyrolysis gas chromatography is one of the best possibilities for the selective determination of thermal degradation products using a small sample.

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