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Note

Short-time pyrolysis and spectroscopy of unstable compounds

V*. Improvement in Curie-point pyrolysis gas chromatography

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The method of Curie-point pyrolysis[2,3], in combination with gas chromatography and mass spectrometry offers a fast and reproducible way of studying pyrolysis reactions. The substance, coated on a ferromagnetic wire, is heated by a high-frequency pulse to the Curie temperature of the wire. To increase the thermal strain on the substance, spirals or thin tubes of ferromagnetic materials have been recommended[4] instead of wires.

The slight variation of this method described here has been used in our laboratory for some years[5–8]; the pyrolysis unit is shown in Fig. 1. When using materials having high Curie temperatures (up to 900°), the usual soft-glass tubes (1) are unsuitable because of the resulting thermal strain, and the use of quartz tubes (1) has the disadvantages that a metallic needle (2) cannot be fused on to the tip of the tube, and a quartz needle-tip is very fragile. To overcome these problems, we use a thin-walled quartz tube (4), resembling a melting-point capillary with an I.D. slightly larger than the ferromagnetic wire (3). This tube is heated easily by radiation from the glowing wire to a temperature only slightly lower than the Curie temperature of the wire, especially when long pyrolysis times (10 sec) are used. The molecules of substances evaporated from the wire are reflected from the hot capillary (4) back on to

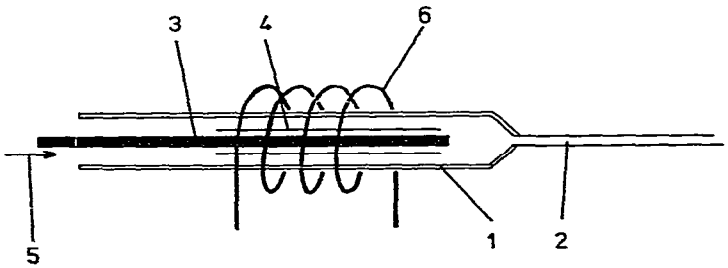

Fig. 1. Modified chamber for Curie-point pyrolysis. 1 = Glass tube; 2 = needle; 3 = ferromagnetic wire; 4 = thin-walled quartz tube; 5 = carrier-gas supply; 6 = high-frequency coil.

* For Part IV, see ref. 1.

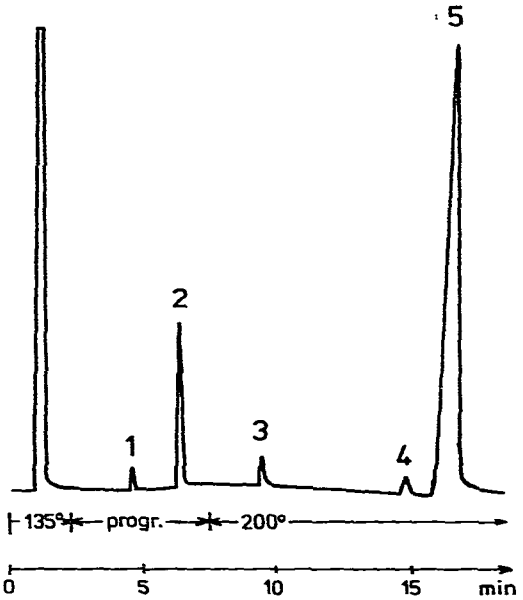

Fig. 2. Pyrolysis gas chromatogram of phenanthrenequinone: pyrolysis temperature 900°, pyrolysis time 10 sec. Column: 5 m × 0.125 in., packed with 2.5% of XE-60 on Chromosorb G AW DMCS (80–100 mesh). Peaks: 1 = naphthalene; 2 = biphenyl; 3 = fluorene; 4 = phenanthrene; 5 = fluorenone.

the wire, so that the substance receives more "impacts" on the hot surfaces and the pyrolysis rate is increased.

The advantages of this arrangement are as follows. The use of expensive and fragile quartz tubes is avoided, the period of thermal contact between the substance and the hot surfaces is increased, the ferromagnetic wire and the capillary can be cleaned easily, and ferromagnetic wires are available for more temperatures than are metallic tubes.

An example of the application of this method is the thermolysis of phenanthrenequinone (Fig. 2), which gives results similar to those of gas-phase thermolysis[9,10]; the substances formed were identified by coupled mass spectrometry.

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