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Note

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Reaction gas chromatography of microgram and sub-microgram samples using sealed glass capillaries

In the widely applicable technique of reaction gas chromatography (GC) described below, microgram, or sub-microgram quantities of material are condensed from the GC effluent in glass capillary tubing. This is then filled with a reactive gas and sealed. Reaction is effected by heating the sealed capillary, after which all the products of the reaction are re-introduced to the gas chromatograph by crushing the capillary within the injection port. Any reactive gas, such as hydrogen or ozone, may be used, and a catalyst is easily incorporated if desired. Alternatively an inert gas may be used, permitting the sample to be stored indefinitely at a low temperature or pyrolysed at a high temperature. The advantages of "off-line" operation obtained with our previous trap-reactor design[1] have been retained, with the additional advantage that there is no temperature limitation and no loss of gaseous reaction products.

Experimental

Fig. 1 depicts the collection of purified material from the outlet port of the gas chromatograph. The glass capillary, G, 1.45 mm O.D. and 115 mm long (100-μl micro cap, Drummond Scientific Co.), fire polished at both ends, is a neat fit in the PTFE connector, C. Since it is essential to confine the condensed material to the centre of the capillary tube the heated outlet line, A, is extended with an aluminium

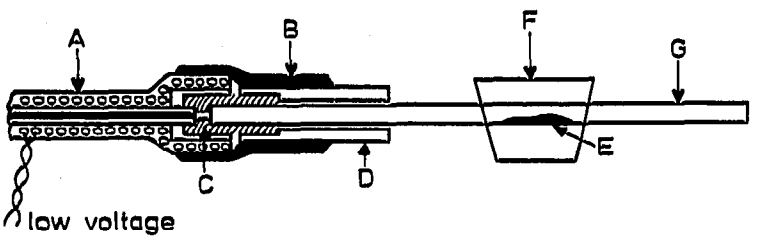

Fig. 1. Collection of the sample. A = Heated GC outlet line; B = aluminium foil and asbestos tape; C = PTFE connector; D = aluminium heat conductor; E = catalyst; F = solid carbon-dioxide cooling boat; G = glass capillary.

heat conductor, D, 10 mm diameter and 40 mm long. This conductor is a loose sliding fit on the glass capillary, and a firm push fit on the connector, C. Further mechanical support and heat transfer is obtained by wrapping aluminium foil and asbestos tape, B, over the join. If a catalyst, E, is required, it is spread over 3 or 4 mm on the wall of the capillary tube. Solid carbon dioxide contained in a plastic boat, F, assists the condensation of material from the GC effluent. When collection is completed the capillary is removed, capped with tight fitting PTFE caps and stored under solid carbon dioxide until required.

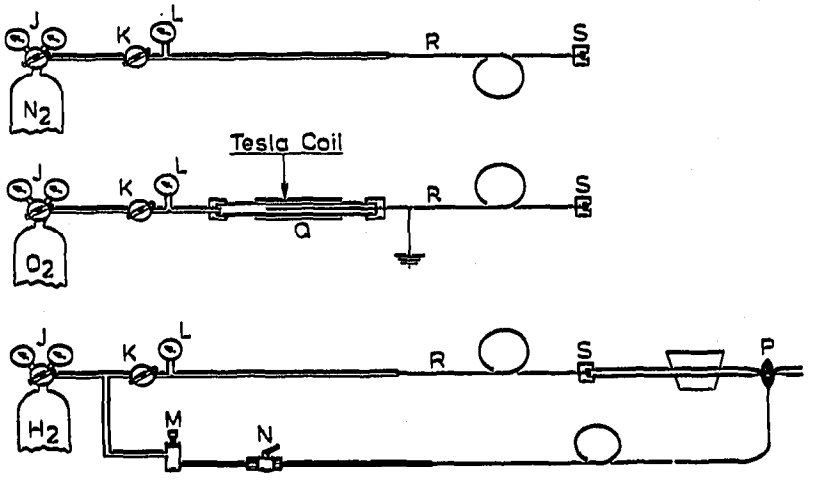

Fig. 2. Apparatus for filling the capillary with reactive gas. J = Primary pressure regulator; K = secondary pressure regulator; L = pressure gauge; M = needle valve; N = toggle valve; P = micro flame; Q = ozone generator; R = capillary line; S = PTFE outlet connector.

The apparatus used for filling the capillaries with hydrogen, ozone, or nitrogen, is represented diagramatically in Fig. 2. The gases are supplied from cylinders at reduced pressure by a two-stage-pressure reduction system composed of regulators, J and K, and a pressure gauge, L. Ozone is produced by passing a low-pressure oxygen stream through a high-voltage discharge cell, Q. This cell consists of a glass tube 6 mm bore and 25 cm long, covered by a piece of aluminium foil insulated with PTFE tape, to form the outer high-voltage electrode the inner earth electrode being the metal capillary line, R. The high-voltage is supplied by a Tesla coil.

The low-pressure gases are delivered at 7–14 kPa (1–2 p.s.i.g.) to the PTFE outlet connectors, S, by stainless-steel capillary lines, R, 25 cm long and 0.25 mm bore. The flow through these lines is controlled to 2–3 ml/min by inserting suitable lengths of 0.178-mm diameter stainless-steel wire.

A micro hydrogen flame, P, at the tip of a 0.25-mm diameter flexible capillary line 20 cm long, is adjusted to a height of approximately 1 cm by varying the flow-rate through the needle valve, N.

The glass capillary tube, open at both ends, with the solid carbon dioxide boat still in place, is attached to the outlet connector, S, and the reactive gas is allowed to fill the capillary for 1 min. The glass tubing is then softened with the micro flame, drawn down and sealed, firstly at the atmospheric end and then at the supply end. Excessive softening of the glass must be avoided, to prevent the pressurised gas from bursting through the seal.

The contents of the sealed capillary are now ready for reaction at any desired temperature and time. In this laboratory reaction conditions have ranged from 30 min at −75° for ozonolysis, to 5 min at 300° for hydrogenolysis. Many hydrogenation reactions were found to be complete in less than 1 min at 160° using platinum on charcoal as a catalyst. After reaction the external surface of the sealed capillary is washed and dried ready for re-injection of the reaction products.

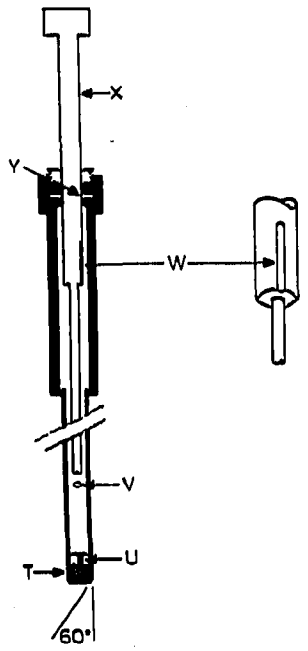

Fig. 3. Capillary crushing probe. T = Stainless-steel gauze; U = anvil; V = four axial carrier gas inlet holes (0.16-mm diameter) drilled through 3.175-mm diameter body of probe; W = vent slot; X = plunger; Y = "O" ring seal (3.175-mm I.D.)

Injection of the reaction products may be made with any device capable of breaking the capillary within the injection port. A number of these have been described[2]. The capillary crushing probe illustrated in Fig. 3 was devised for use with the ball valve type of introducer currently in use in this laboratory[1].

The sealed glass capillary is placed inside the tube against the anvil, U, and the plunger, X, is inserted through the "O" ring seal, Y, with the vent slot, W, initially positioned so that carrier gas can by-pass the "O" rings. The probe thus loaded, is inserted through the ball valve introducer until it seals against the 60° face at the bottom of the introducer. Carrier gas is allowed to escape through the vent slot for 2 or 3 sec to flush out any entrapped air, and the plunger is then pushed down just far enough to seal in the "O" rings. Pre-heated carrier gas now enters the probe through four axial holes, V, flows down over the sealed capillary, through the small hole in the centre of the anvil, U, and the stainless-steel gauze plug, T, (which retains broken glass), and into the column. When the capillary reaches oven temperature it is crushed by pushing down on the plunger, X, and the reaction products are swept rapidly into the column. The crushed glass is withdrawn, retained inside the probe.

We have successfully employed this technique for the hydrogenation and ozonolysis of a wide variety of compounds in the sample size range of 0.1–100 μg. Low-molecular-weight reaction products such as formaldehyde, acetaldehyde, glyoxal, ethane and propane were retained by this system, and were readily observed in the chromatogram of the reaction products. Acidic fragments from the thermal cleavage of the ozonides (as reported by DAVISON AND DUTTON[3]) were not observed,

probably because they were absorbed on the walls of the long stainless-steel capillary columns used in this study. The glass capillaries were found to make excellent storage containers when filled with nitrogen and sealed, and the chromatographic peaks obtained on re-injection of the stored compounds, using the glass crushing introducer, were as sharp as those obtained with conventional syringe injection.

Extension of the technique to other reactive gases such as diazomethane, the halide gases, or sulphur dioxide is anticipated.

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