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## Note

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### **Pyrolysis gas chromatography over hydrogenated graphitised carbon black**

#### **Differentiation of chewing gum bases for forensic purposes**

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Hydrogenated graphitised carbon black, introduced as a gas chromatography (GC) column packing by Di Corcia and Bruner<sup>1</sup>, enables an exceedingly wide range of compound types to be efficiently chromatographed. Although the material is uniquely suited to separations in pyrolysis GC, where mixtures of great variety and complexity are often encountered, this application has remained neglected. We wish to describe, therefore, our preparation and use of the material, together with a specific application of forensic significance in the characterisation of chewing gum bases.

#### **EXPERIMENTAL**

The hydrogenation is conducted essentially according to Di Corcia and Bruner<sup>1</sup>. Graphitised carbon black (Sterling FT), broken down and sieved to a 60-120 mesh range, is loosely packed into a stainless-steel column (2 m × 6.5 mm) to within 20 cm of each end. At the outlet end the packing is contained by a plug of asbestos wool supported on a crimp in the wall of the column. The column is coiled and inserted into a cold muffle furnace so that all of the packing will be within the subsequently heated zone, whereas the column ends project externally. To the outlet is connected a flow meter, and to the inlet, through a flow restrictor, a source of oxygen-free hydrogen, with which the packing is purged at 50 ml·min<sup>-1</sup> for 1 h before the flow-rate is finally set at 5 ml/min. The column is heated to 1000°, kept at this temperature overnight, and then, to avoid the embrittlement that occurs in some steels on slow cooling through 900-500°, removed from the still heated furnace. (Two columns repeatedly used have shown no signs of embrittlement.) When cold, the column is disconnected from the hydrogen supply, straightened and emptied, and the product sieved to give 60-80, 80-100 and 100-120 mesh fractions, which are combined with the products of other hydrogenations. Closely sieved fractions are not used in the hydrogenation because of concomitant particle breakdown. The chromatography columns referred to in the following contain 60-80 mesh material.

Because the material is fragile, columns are packed with a minimum of vibration. If on-column injection is to be used, the region contacted by syringe needles must be plugged with glass wool. Coated packings are best prepared by the in-column

technique<sup>2</sup>. As an approximate guide, the percentage of stationary phase remaining on the dried packing is similar to that of the coating solution, *e.g.* 0.5–5% OV-101 in *n*-hexane, and may be modified subsequently should an initial coating yield unsatisfactory results. Packings are purged of solvent under nitrogen (*ca.* 50 ml/min, 24 h) at room temperature, and then programmed at 1°/min to the maximum operating temperature, which is held until a stable base line is obtained. Should solvent have been inadequately removed, particle breakdown occurs when the columns are heated. This can be detected readily under a dissecting microscope if glass columns are used.

For pyrolysis GC, columns (1.8 m or 0.3 m × 2.5 mm) are installed in a temperature-programmed Pye-Unicam Model 104 chromatograph fitted with flame ionization detection and a Philip's Curie point pyrolysis unit. Samples are pyrolysed according to the technique of Coulter and Thompson<sup>3</sup> on coiled 770° wires; the timer setting is 10 sec. Quantities used are generally *ca.* 50 μg, but the high thermal stability of the columns permits this figure to be reduced to 10 μg if necessary. When each pyrogram has run to completion, the wire is energised repeatedly until no further chromatographic response occurs. Other details are given in the figure captions.

## RESULTS AND DISCUSSION

### *Choice of column conditions*

Generally, only the more volatile products of pyrolysis are eluted at temperatures up to 300° from the uncoated carbon black. In the presence of coating materials retentivity is reduced and higher-molecular-weight compounds appear. Di Corcia and Bruner<sup>4</sup> originally used Dexil 300 GC for this purpose. In our hands, although this coating yields highly efficient columns initially, decomposition occurs even in the 200° region, in contrast to the high thermal stability on acid-washed diatomaceous supports. As decomposition of Dexil is subject to basic catalysis<sup>5</sup>, we applied a variety of acid pretreatments to the hydrogenated carbon black, but none of these rectified the situation. We conclude that catalysis of the decomposition is a property inherent to the carbon black, as opposed to its stabilising effect on other coatings<sup>6</sup>.

As many important pyrolysis products are of high molecular weight, thermal stability is an essential requirement of any coating material. Obvious alternatives are the OV silicones. Of these, the OV-101 phase on hydrogenated carbon black exhibits no deterioration on prolonged exposure to 300°. With varying amounts of this coating, variation in retentivity is similar to that caused by other coatings<sup>4,6-8</sup>. Thus, separation is determined essentially by adsorption at coating levels of up to 2%, and increasingly by partition processes thereafter. This effect (in columns coated from 2 and 5% w/v solutions of OV-101 in *n*-hexane), together with those of varied flow-rate and column length, is applied to obtain the pyrograms of polyethylene shown in Fig. 1, which cover the volatility range of most pyrolysis products of significance (Kováts' indices, ≤3400). Uncoated columns yield polyethylene pyrograms similar in appearance to those from the 2%-coated column, except that retention times are substantially increased; but pyrograms of other materials sometimes exhibit significant variation in selectivity as coating levels below 2% are varied.

Pyrograms of non-polar polymers have proved identical when repeated on the same column after thirteen months' continuous use, but polar pyrolysis products sometimes yield tailed peaks after *ca.* three months. The extent to which this occurs

with samples of specific interest limits column life in practice. Coefficients of variation of retention indices, and of peak heights relative to the most prominent peak in pyrograms of the type shown are 1.8 and 8.4%, respectively.

Polyethylene pyrograms (Fig. 1) provide a useful means of assigning Kováts' indices<sup>9</sup>. The *n*-alkane peaks are readily identified by reference to the corresponding preceding *n*-alkenes, whose intensities follow a  $4n + 2$  rule, *i.e.* maximal for ethylene, *n*-hexene (particularly), *n*-decene, etc. The pattern is discernible up to C<sub>22</sub>: Presumably product formation is, to some degree, subject to orbital symmetry control.

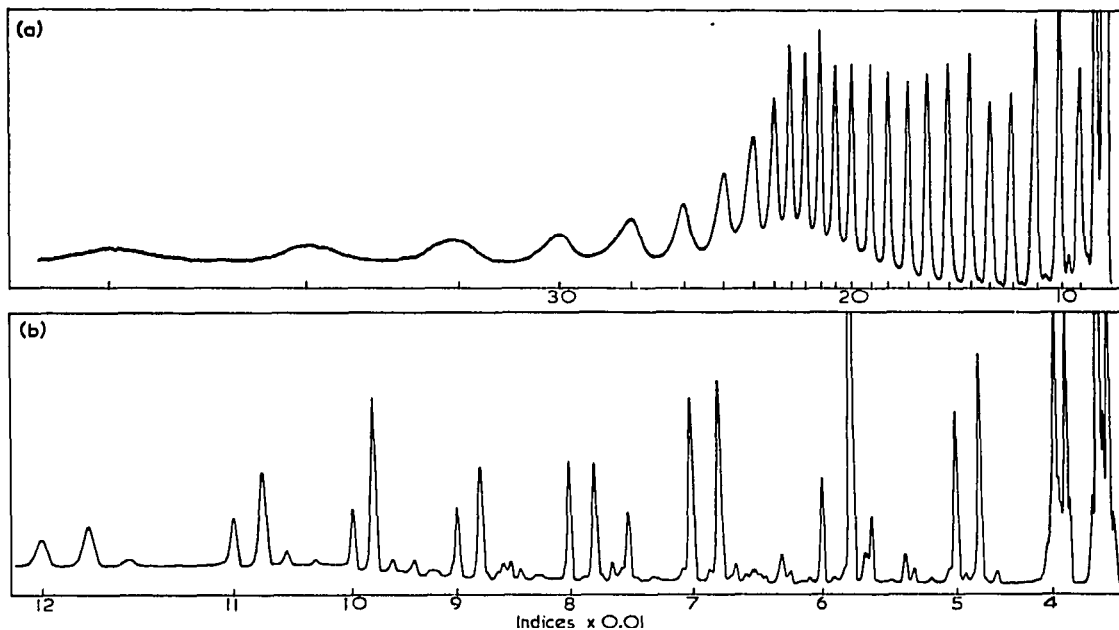


Fig. 1. Polyethylene pyrograms. (a) 0.3-m  $\times$  2.5-mm Column of hydrogenated Sterling FT coated from a solution of 5% OV-101 in *n*-hexane; carrier gas flow-rate, 50 ml/min (nitrogen); temperature, programmed from 50–300° at 12°/min. (b) 1.8-m  $\times$  2.5-mm Column of hydrogenated Sterling FT coated from a solution of 2% OV-101 in *n*-hexane; carrier gas flow-rate, 20 ml/min (nitrogen); temperature, as in (a). Retention times of dodecene are 28 min (b) and 10 min (a).

### Chewing gum bases

In order to determine the extent to which traces from scenes of crime might be correlated to various products, we recently made comparative analyses of the chewing gums obtainable in the area served by this laboratory. Samples of thirty-seven gums were examined.

Unused gums yield pyrograms dominated by carbohydrate peaks that, although a source of between-sample variation, are usually not significant in the chewed material we encounter. Our samples were treated accordingly, therefore. The products' pyrograms are uninfluenced by the identity of the consumer and by the presence of saliva, from which a relatively weak chromatographic response results. In two in-

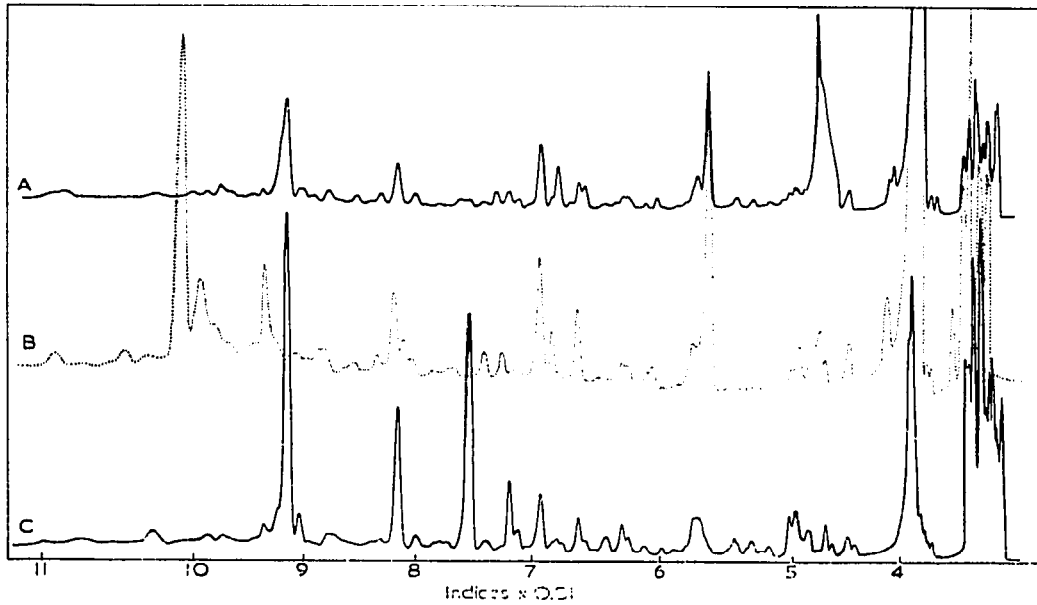


Fig. 2. Pyrograms of chewing gums of the same manufacture. 2%-Coated column as in Fig. 1.

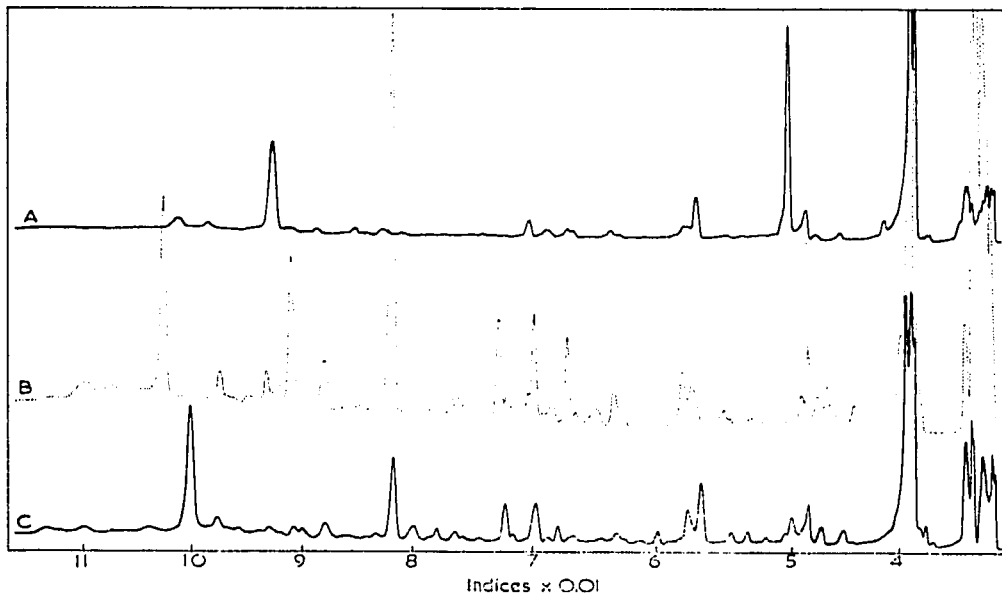


Fig. 3. Pyrograms of chewing gums varying in manufacture. 2%-Coated column as in Fig. 1.

stances, indicated below, variation in the extent to which a gum is chewed, beyond that caused simply by dissolution of carbohydrate, is detectable.

Pyrolysis products eluted from 2%-coated columns are derived mainly from elastomeric components, and to some extent from softening and flavouring ingre-

dients. Gums apparently vary widely both between and within manufacturers in these respects. Fig. 2 shows pyrograms given by products of a single manufacturer. These examples are typical of the three groups into which this set of eighteen samples may be divided. Distinctive features are: (pyrogram A) the characteristically distorted peak of acetic acid at 480 index units, presumably from polyvinyl acetate (this peak tends to decrease as chewing time increases), together with an intense off-scale series of peaks in the region of 400, attributed to polyisobutylene pyrolysis products; (B) polyisobutylene products without acetic acid but with a prominent peak at 1050; and (C) peaks at 755 and 920 prominent relative to the 400 region. Within each group a significant variation occurs, exclusive of the acetic acid variation, so that out of the eighteen samples, one set of five samples, three sets of three samples, and each of four samples are distinguishable; *i.e.* the eighteen samples may be classified under eight pyrograms.

The products of different manufacturers differ from one another widely; three examples are shown in Fig. 3. In each case strong peaks in the 400 region are present. In one case (A), however, a peak at 500, presumably due to isoprene, significantly

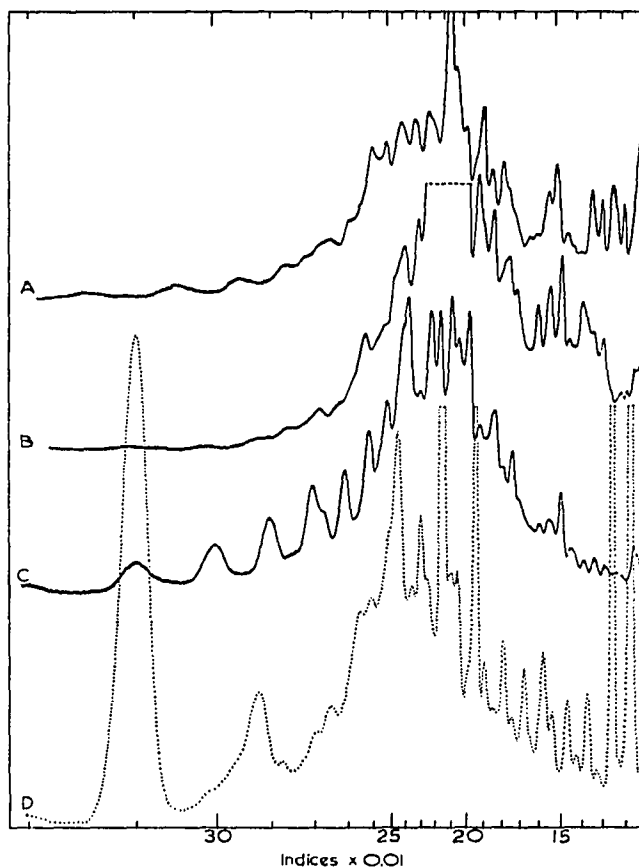


Fig. 4. Parts of pyrograms of different chewing gums of one manufacturer (A and B), and of two other manufacturers (C and D). 5%-Coated column as in Fig. 1.

varying relative to the 400 peak within this manufacturer's products, is distinctive. In **B** appear a variety of peaks absent in the other two pyrograms. Amongst the thirty-seven samples are found to be twenty-four indistinguishable pairs (the maximum number possible is 666); hence, the technique's discriminating power<sup>10</sup> within this particular collection of samples is 0.964.

The higher-molecular-weight compounds eluted from 5%-coated columns are derived mainly from wax components. Considerable variation is again apparent, as Fig. 4 shows. Pyrograms such as **A** and **B** enable this particular manufacturer's products to be classified readily into two sets of which the absence (**A**) or presence (**B**) of the triplet of peaks in the region 1450–1600 is distinctive. In **C** a homologous series of hydrocarbons, typical of paraffin wax, and in **D** a peak corresponding to hentriacontane, typical of candellila wax, are present. These products result from direct vapourisation rather than pyrolysis of the samples. On occasions, the patterns of high-molecular-weight products differentiate gums not distinguishable otherwise, but the increase in discriminating power, to 0.973, is rather small. Hence, for many evidential purposes examination of low-molecular-weight products will suffice.

Finally, some pyrograms from an actual case are shown in Fig. 5. Pyrogram **A** is from a fragment of material found in the throat of a murdered child; **B** is from material found at the place where the murder was thought to have been committed (from where the body had been removed); and **C** is of material found on the suspect. Excepting a variation in the peak at 1140, caused by the varying extent to which the samples had been chewed, the three samples are in close agreement with one another, and agree with only one of the gums out of all of those available. (Also, an identity exists between thin-layer chromatograms of the organic dyes present in the samples.)

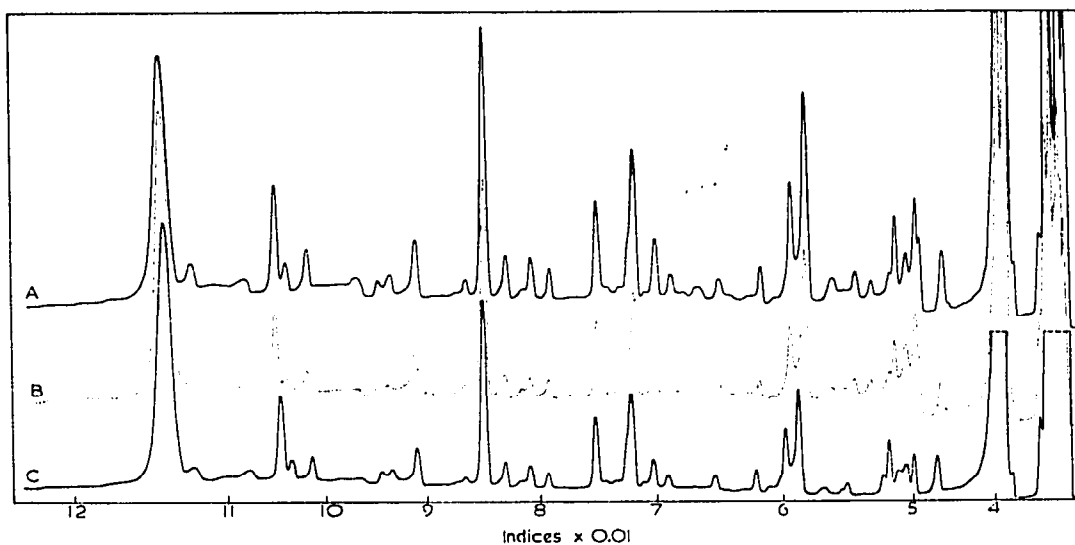


Fig. 5. Pyrograms of chewing gums from: (A) throat of murdered child, (B) scene from which the body had been removed, and (C) suspect.

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