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IDENTIFICATION OF WEATHERED PETROL RESIDUES BY HIGH-RESOLUTION GAS CHROMATOGRAPHY WITH DUAL FLAME IONISATION DETECTOR–HALL ELECTROLYTIC CONDUCTIVITY DETECTOR

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SUMMARY

A method is presented for the detection of severely weathered petrol residues in post-fire debris. The procedure involves the splitting of the capillary gas chromatographic (GC) column effluent between a flame ionisation detector and a Hall electrolytic conductivity detector to obtain the hydrocarbon and the sulphur chromatograms. The results showed it was possible to detect and identify petrol burned on cotton wool and weathered for 12 days. Positive identifications have been obtained by this method when applied to samples from cases of suspected arson where the GC–flame ionisation detection interpretations were inconclusive.

INTRODUCTION

Identifying a specific arson accelerant from the debris after a suspicious fire is not simple. Petroleum products such as petrol, white spirit, kerosene or diesel oil are frequently used by arsonists to initiate deliberate fires. These accelerants consist of highly complex mixtures of hundreds of hydrocarbons and other compounds which vary widely in their volatility and in their amounts from product to product. The detection of trace amounts of petroleum-based accelerants isolated from the residues after a fire can give rise to a number of problems since the accelerant suffers changes in composition[1,2] during the fire and by post-fire weathering, in addition there can be contamination of the recovered residue by material derived from debris materials[3–6].

The usual analytical approach is to obtain a chromatogram of the accelerant residue using a non-specific, flame ionisation detection (FID) system which is then matched with reference file chromatograms to identify the best fit. For distinguishing between different accelerant types, capillary gas chromatography (GC) has been recommended[7]. The chromatograms obtained from the fire residue samples are normally classified as giving either positive, negative or inconclusive results. While this approach has often proved extremely useful, it has inherent limitations. In particular,

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for severely post-fire weathered petrol residues, at trace levels many of the characteristic peaks or peak groups are either absent or masked by matrix interferences[8]. The application of a tandom technique such as GC–mass spectroscopy (MS) has been usefully applied to such complex residues[8,9]. However, it is expensive and may require an extensive data handling system to interpret the mass spectra.

It is well known that sulphur compounds in varying amounts are present in petrol[10]. Since many of these sulphur compounds are of higher molecular weight than the petrol hydrocarbons, it was considered that they should be relatively less affected by conditions of a fire and also to any subsequent weathering prior to sample collection. This idea is supported by the results obtained using FID and Hall electrolytic conductivity detection (HECD)[11] in parallel which has permitted positive identification of severely weathered petrol residues, steam extracted from cotton wool specimens.

EXPERIMENTAL

Samples, reagents and materials

Water was distilled and then passed through a Millipore Q2 filter. The solvents methanol and *n*-hexane, AnalaR grade were obtained from BDH. Materials used and their sources are: 2-methylbenzothiazole (Fluka), *n*-alkane and aromatic hydrocarbon calibration standards (SGE), and cotton wool, BPC grade (Eirecot–Robinson). All samples, petroleum products, samples of petrol, white spirit, kerosene and diesel oil, were obtained from local commercial sources.

Apparatus

The gas chromatograph (Carlo-Erba 4160 series) was equipped with a flame ionisation detector (Tracor Instruments Austin, TX, U.S.A.) and a Hall electrolytic conductivity detector, Model 700 (Tracor Instruments, Austin, TX, U.S.A.). The apparatus, all glass, for continuous steam distillation is shown in Fig. 1. The distillation apparatus was manufactured by Associated Glassblowers (Dublin, Ireland) and is a modification of the standard BP apparatus[12]. A Biral hot-wire air velocity meter was used.

Preparation of simulated fire residue samples

Wads of cotton wool (50 g) were soaked with fresh petrol (50 cm^3) poured on to the centre of the specimens. After a short soaking period (30 s) the specimen, held in a long tongs, was inserted into a muffle furnace set at 600°C. The specimens ignited almost instantaneously and were allowed to burn for 60 s. The specimens were removed from the furnace and the flames extinguished using a carbon dioxide fire extinguisher. The burned specimens were placed on wire mesh trays in a fume cupboard to weather for various time periods. To simulate the weathering conditions of an arson fire, the fume cupboard window was opened 1 cm from its work-base, to allow an air flow-rate of 171.9 l/min. Specimens were weathered for periods of 1, 7 and 17 h, 5, 10 and 12 days before isolation of the accelerant residues by steam distillation.

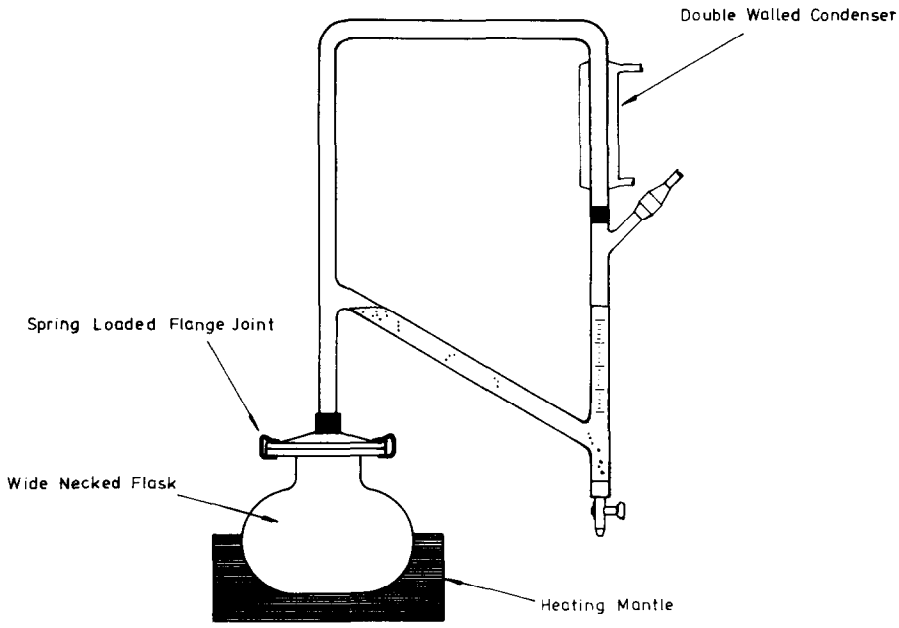

Fig. 1. Apparatus for continuous steam distillation.

Preparation of a laboratory evaporated petrol residue

For comparison with weathered fire residues, a 90% evaporated residue of petrol was prepared by placing 100 cm^3 of fresh petrol in an open evaporating dish and allowing it to evaporate at room temperature until 10 cm^3 remained.

Steam distillation

The steam distillation apparatus (Fig. 1) was used to isolate material from the laboratory prepared petrol fire residues. To improve the recovery of the more volatile components, a double walled water condenser was fitted. A wide neck bolt head reaction flask of one litre capacity was used to facilitate cleaning and easy removal of specimens. The flask was heated with an electrothermal mantle and the temperature controlled by a variable output transformer.

A prepared fire debris specimen was placed into the flask and 450 cm^3 of water added, the apparatus was assembled and steam distilled for one hour after the first drop of distillate had collected. After the prescribed distillation time the apparatus was allowed to cool and the recovered petrol residue, floating as a separate layer on the water was removed. A sample volume of 0.1 μl of each residue was chromatographed using the conditions described.

Chromatographic and detector conditions

GC–FID. The column used was a 15 m × 0.25 mm I.D. fused-quartz capillary wall-coated open tubular column coated with OV-101 liquid phase (SGE). The flame gases and their pressures were: hydrogen (0.5 kg/cm^2) and air (1.0 kg/cm^2). The carrier gas was helium at a flow-rate of 7 cm^3/min and the make-up gas was helium

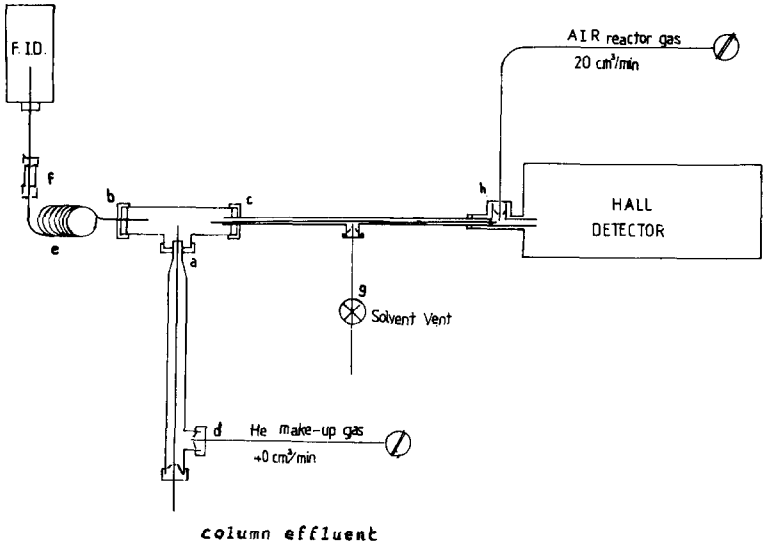

Fig. 2. Diagram of effluent splitter (individual items not to scale).

at a flow-rate of 30 cm^3/min. The injector and detector temperatures were 240 and 300°C, respectively. Temperature programme: 30°C to 240°C at 5°C/min held at 30°C for 3 min and at 240°C for 15 min. The recorder was a Hitachi dual pen (1 mV f.s.d.) with a record speed of 10 mm/min. The sample volume was 0.1 μl.

GC–HECD employed in the sulphur mode. For details see Operation and Service Manual, Tracor Instruments, TX, U.S.A.). The reactor gas was air at a flow-rate of 20 cm^3/min. The solvent was methanol, at a flow-rate of 0.5 cm^3/min. The ion-exchange resin was IRN-150–IRN-77 (1:1) (Tracor Instruments, TX, U.S.A.). The furnace temperature was 815°C. The reactor tube was 10 in. × 0.01 in. I.D. nickel tubing. Solvent venting was performed 3 min after injection by means of a three-way toggle valve.

Dual detection system incorporating FID and HECD

The simultaneous dual detection was achieved by splitting the column effluent with a simple effluent splitter as shown in Fig. 2. The column effluent and make-up gas were connected to the middle (a) of the effluent splitter while the exit ends were connected to the flame ionisation detector and Hall electrolytic conductivity detector at (b) and (c), to achieve a constant 1:1 split ratio the helium make-up gas flowed from behind the end of the capillary column which was inserted 10 mm into the splitter. The make-up gas was admitted through a 1/16 in. of stainless-steel T-piece (d) connected to 3 in. × 1/16 in. of stainless-steel tubing.

The column effluent and make-up gas were mixed prior to splitting to produce even dilution and appropriate flow-rates for each detector. A restrictor consisting of an 8 in. × 0.01 in. stainless-steel coil is fitted to network to allow for differences in back pressure between both detectors. The restrictor was connected via 1/16 in. stainless-steel Swagelok connection to a short piece of quartz capillary tubing inserted into the base of the flame ionisation detector.

The split column effluent to the Hall electrolytic conductivity detector for the selective detection of the sulphur-bearing compounds is mixed with air (h) and pyrolysed in the nickel tube held at 815°C. The available sulphur is converted probably to SO_2/SO_3. The SO_2/SO_3 dissolves in the methanol and the electrical conductivity is then measured. To protect the system from overload from low-molecular-weight hydrocarbons, venting is carried out through a toggle valve (g) which is closed after 3 min following the injection of a sample.

The Hall electrolytic conductivity detector Model 700 was designed for use with packed columns. Modification was necessary to couple it to a capillary column. This was achieved by replacing the quartz furnace tube with a 10 in. × 0.01 in. nickel tube thus reducing the overall dead volume to avoid significant loss in resolution or in linear response. A new design of Hall electrolytic conductivity detector Tracor Model 700 A is now commercially available which can be operated directly with capillary columns.

RESULTS AND DISCUSSION

The chromatograms shown in Fig. 3A–J were each obtained using the chromatographic conditions described with simultaneous dual FID–HECD. Petrol fire residues, weathered on cotton wool for various time periods (1 h to 12 days), isolated by steam distillation, were used to produce chromatograms shown in Fig. 3B–G.

Examination of chromatogram A, fresh petrol, shows a distinct peak pattern in the FID response to hydrocarbons which appears under the conditions used, in the region up to 19.5 min retention time. The HECD sulphur-selective mode chromatogram gives as independent "fingerprint" of the same petrol with a major peak at 17.3 min and a group of 4 minor peaks between 19.7 min and 20.7 min. The last peak in this group (20.7 min) is the same as 2-methyl-benzothiazol, denoted by mbt and appears in all petrol residue chromatograms. It should be noted that the GC–FID analysis shown in Fig. 3A, has no similar peak pattern in this region of the chromatogram.

The effects of post-fire weathering can be seen visually in the GC–FID analyses shown in Fig. 3B–G, and shows the loss of the low boiling compounds and the marked differences in composition as compared to the original petrol (Fig. 3A) shown by the shift in the chromatographic profile from right (low boiling compounds) to left (higher boiling compounds) with a good deal of peak distortion. It is evident from the examination of chromatograms in Fig. 3E, F and G that as weathering progresses the identification of petrol cannot be made using FID information alone, since the chromatographic profile now shifts into the diesel oil region.

By contrast, the sulphur selective chromatograms in Fig. 3B–G can be seen to be relatively insensitive to the influence of weathering. Fig. 3G (12 days weathered) shows an FID chromatogram which cannot be recognised as coming from petrol while the HECD chromatogram whilst somewhat depleted is nevertheless still recognisable and compares favourably with Fig. 3A (fresh petrol). Thus chromatographic patterns obtained from FID and HECD taken together give a greater diagnostic value, unattainable by FID alone. The fact that the HECD sulphur chromatogram reveals information about the less fugitive non-hydrocarbon composition of the petrol residues greatly enhances the value of this peak identification technique.

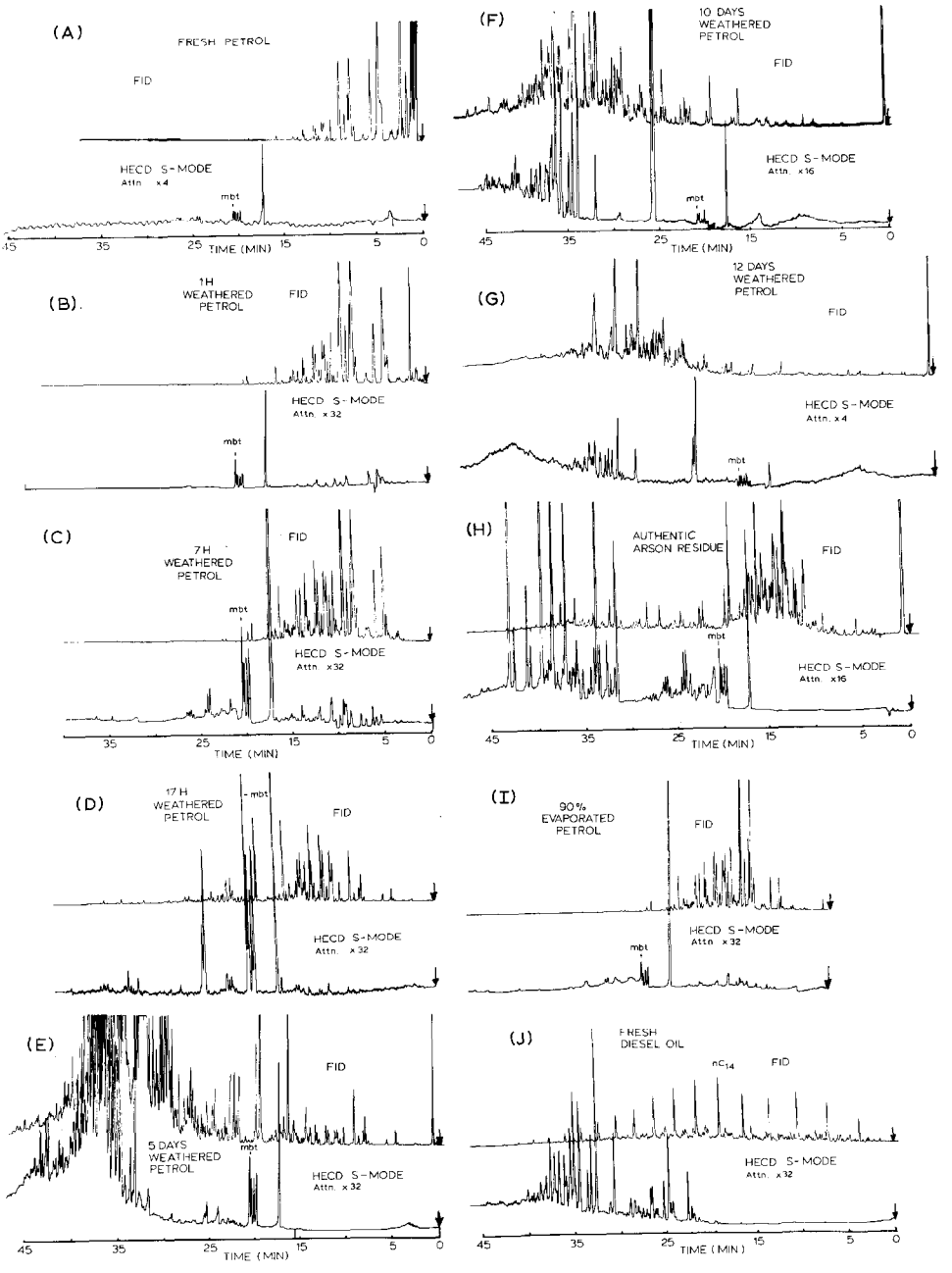

Fig. 3. Chromatograms of petrol and weathered petrol residues.

To discover if other common accelerants could be confused with, or even resemble, chromatograms of weathered post-fire petrol residues, white spirit, kerosene and diesel oil were chromatographed under the same conditions. White spirit and

kerosene gave only negligible responses in the sulphur-selective mode. Diesel oil however gave a sulphur chromatogram in the region of 22 to 40 min, shown in Fig. 3J. This chromatogram shows some resemblance in the higher boiling region only when compared to the more severely weathered petrol residues (Fig. 3E, F, G, and H). Considering that all petroleum distillates are overlapping fractions, differentiated only by their distillation cut points, it is not unreasonable that petrol contains small quantities of similar higher boiling sulphur compounds also present in diesel oil. Conversely, it is unlikely that diesel oil will contain any low boiling sulphur compounds generally found in petrol. This feature is illustrated in Fig. 3J by the absence of any sulphur compounds in the low boiling region (17.5 to 20.7 min). Therefore, with experience no difficulty should be expected when attempting to differentiate between weathered petrol and diesel oil residues.

APPLICATION OF DEVELOPED TECHNIQUES

Capillary GC with a simultaneous dual FID–HECD system has been used to identify the residues recovered from the debris samples of suspected arson fires. In one case the entire sample, which consisted of pieces of badly charred timber, clothing and some masonry material was extracted by steam distillation and the residue collected in 2 cm^3 of *n*-hexane which was then concentrated under a stream of nitrogen to approximately 50 μl. This recovered extract provided a very complex FID chromatogram, shown in Fig. 3H. No clear interpretation of the FID chromatogram alone was possible. However, the HECD chromatogram showing a major peak at 17.3 min and a group of 4 minor peaks between 19.7 and 20.7 min provided the necessary information to positively identify this residue as originating from a petrol.

Fig. 3I illustrates the peak pattern obtained from a 90% evaporated petrol residue. A comparison of Fig. 3I with Fig. 3A shows noticeable differences in FID peak patterns as a result of evaporation. If the FID peak pattern in Fig. 3I is matched with the other traces in Fig. 3, it appears to fall between Fig. 3B and C (1 h and 7 h weathered residues). This provides some indication of the significant loss of volatile material from these residues post fire and how unburnt petrol changes compared with evaporation. Fig. 3D–G represents a more significant loss of volatile material and indicate the advantage of early sample collection in a post-fire suspected arson situation.

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