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## Note

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### The analysis of diesel engine exhausts for low-molecular-weight carbonyl compounds

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This work constitutes part of a larger study into the nature of diesel engine exhaust emissions<sup>1</sup>. In order to obtain sufficient sample size for repetitive analyses, large volumes of exhaust were condensed at 0° and the resultant aqueous solutions were extracted with organic solvents<sup>2</sup>. The repeated use of the extracting solvents could not remove the brown coloration or burnt odour which the residues displayed.

Low-molecular-weight carbonyl compounds are known to be extremely soluble in water by virtue of ketal and hemiacetal formation<sup>3,4</sup>. The reaction between carbonyl compounds and 2,4-dinitrophenylhydrazine (2,4-DNP) is known to be an effective and virtually quantitative derivatization process which yields water-insoluble solids with sharply defined melting points<sup>5,6</sup>.

Low-molecular-weight carbonyl compounds have long been recognized as the eye irritating species present in exhausts from both spark and diesel ignition systems<sup>7</sup>. Detection and sampling techniques for the examination of source effluents for these low-molecular-weight carbonyl compounds have usually employed bisulfite or 2,4-DNP solutions as the trapping media and involved paper, thin-layer or gas chromatography (GC) to separate the various species of carbonyl-containing compounds<sup>8-10</sup>.

Recovery of aqueous carbonyl compounds with 2,4-DNP has been cited in many reports as reviewed by Papa and Turner<sup>11</sup>, but although quantitative in recovery, the subsequent analysis of the phenylhydrazones is inconsistent and inaccurate<sup>12,13</sup>.

A previously cited review<sup>11</sup> has detailed a new technique, which improves both reproducibility and accuracy, for the rapid GC analysis of 2,4-DNP derivatives. A slight modification of this method is applied to the separation and quantification of the low-molecular-weight carbonyl compounds found in the exhaust of a diesel passenger car.

## EXPERIMENTAL

The exhaust gases from a 1972 Mercedes Benz 220 diesel passenger car were passed through a pair of Freidrich condensers as shown in Fig. 1. The gases were

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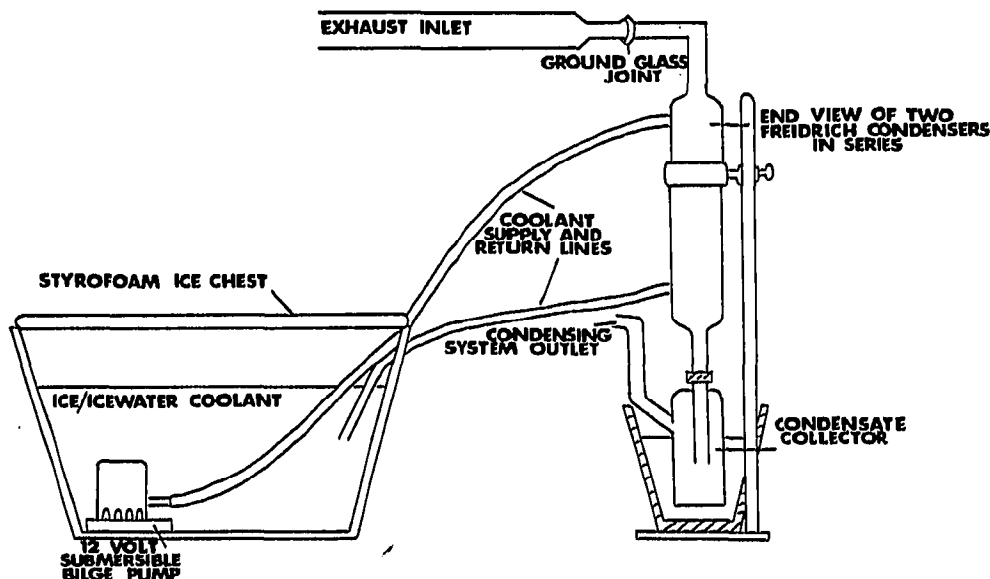


Fig. 1. The dual Freidrich condenser system.

condensed to form heterogeneous aqueous solutions of diesel soot and aqueous solutions of the organic combustion products. Table I lists the observations and measurements from the three exhaust sampling experiments cited in this work.

The aqueous condensates were filtered to remove the suspended particulate matter. The filtered particulates were air-dried prior to extraction and analysis for adsorbed organic materials. The resulting gold-coloured condensates were then extracted in separatory funnels in 500-ml aliquots with 4–25-ml portions of *n*-pentane and then with 8–25-ml portions of chloroform.

The aqueous residues remaining after solvent extraction were then placed in a boiling flask and distilled to give colourless liquids at 96° in 97% yields.

Aliquots of 20.0 ml of each of the clear distillates were reacted with excess

TABLE I

THE LOW-MOLECULAR-WEIGHT CARBONYL CONTENT OF DIESEL PASSENGER CAR EXHAUST

Experiment No.	Fuel burnt (gallons)	Volume of exhaust passed through condensers (l)	Volume of condensate (ml)	Carbonyl compound (g/kl)		
				Formaldehyde	Acrolein	Crotonaldehyde
1	27.6	25,080	2770	0.02	0.0008	0.00002
2	12.1	16,632	1200	0.03	0.0008	0.0032
3	12.2	18,893	1430	0.02	0.0005	0.0003

2,4-DNP reagent<sup>5,6</sup> and allowed to crystallize overnight in a refrigerator. The 2,4-DNP derivatives were recovered by filtration and air dried for several days.

The dry crystalline derivatives were then dissolved in 5.0 ml of chloroform and chromatographed on a special high-temperature column. As has been suggested by Papa and Turner<sup>11</sup>, the technique of "on-column" injection was used. Attempts to use a combined GC-mass spectrometry system to analyze the derivatives were unsuccessful and comparison of the retention times relative to an internal standard, anthracene, was necessary to prove the identity of the major derivatives.

The column used to achieve the separation of the 2,4-DNP derivatives was a 34 × 1/8 in. O.D. stainless-steel tube packed with 15% Dexsil 300 on Anakrom A, 90-100 mesh. The inlet pressure for the column was 28 p.s.i.g. and the outlet flow-rate 30 ml/min. The column temperature was programmed from 40° to 295° at 8°/min.

Quantitative data were obtained from the integrals provided by an Infotronics digital integrator Model CRS-208. Calibrations of the flame ionization detectors were accomplished with reference 2,4-DNP derivatives prepared as outlined<sup>5,6</sup>. The following formulae were used to calculate the quantities of carbonyl compounds present in 1000 l of exhaust:

$$\frac{\text{peak area}}{\text{response factor}} \cdot 500 \cdot \frac{\text{total vol. (ml) condensed}}{20.0} = \text{weight of 2,4-DNP derivative in total volume of condensed exhaust}$$

$$\frac{\text{weight (g)} \cdot 1000}{\text{mol. wt. of 2,4-DNP}} = \text{moles}$$

$$\frac{\text{moles} \cdot \text{mol. wt.}}{\text{total exhaust (kl)}} = \text{g/kl}$$

## RESULTS AND DISCUSSION

Fig. 2 shows the chromatograms obtained for the three exhaust conden-

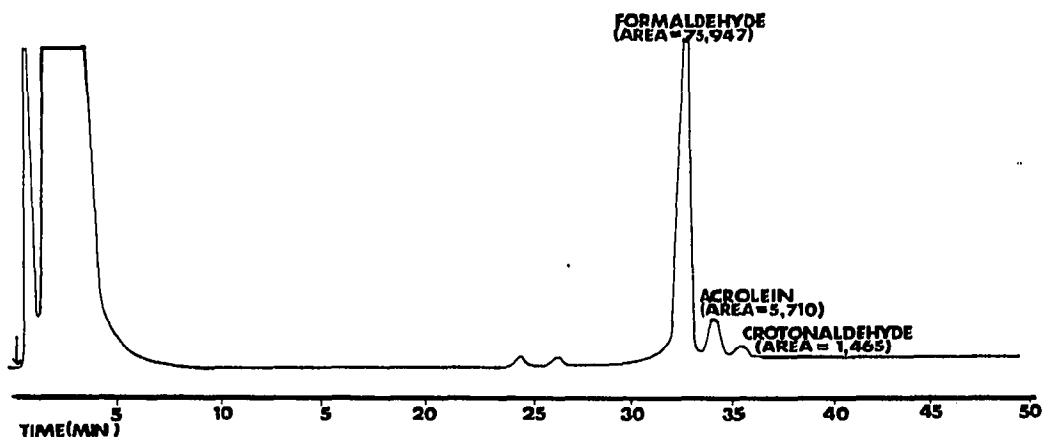


Fig. 2. Chromatogram obtained for sample from Experiment 2 in Table I. Sample size: 10  $\mu$ l in chloroform solution. Conditions: temperature programmed from 40° to 295° at 8°/min; flame ionization detector, 300°; carrier gas, helium; flow-rate, 30 ml/min; column, 34 × 1/8 in. O.D. stainless steel packed with 15% Dexsil 300 on Anakrom A, 90-100 mesh.

sation experiments tabulated in Table I. Table I gives the observed qualitative and quantitative composition of the exhausts with respect to low-molecular-weight carbonyl compounds.

The intimate contact of exhausted particulate matter and organic aqueous condensates does not appear to introduce any observable effects in either the qualitative or quantitative composition of the organic materials found in the liquid phase or adsorbed on to the particulate matter<sup>1</sup>.

The distillation of the aqueous residues concentrates the brown coloration in the boiling pot. The brown material is probably composed of tar-like materials. The precipitation of the 2,4-DNP derivatives from a clear, colourless solution minimizes contamination of the precipitate thereby simplifying the GC analysis. The distillation also ensures that components such as benzaldehyde (b.p. 178°), which is a known constituent of diesel exhaust, do not interfere with the analysis of the low-molecular-weight compounds<sup>1</sup>.

The source of the variations observed in crotonaldehyde concentration, as seen in Table I, is at present unknown. The analytical technique described in this report provides a suitable basis on which an in depth investigation into the relationships between fuel, engine parameters and load may be evaluated.

#### ACKNOWLEDGEMENT

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