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GLASS CAPILLARY GAS CHROMATOGRAPHY OF POLYNUCLEAR AROMATIC HYDROCARBONS IN AIRCRAFT TURBINE PARTICULATE EMISSIONS USING STATIONARY PHASES OF VARYING POLARITY

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SUMMARY

Polynuclear aromatic hydrocarbons isolated from particulate emissions of Pratt & Whitney JT3 and JT8 gas turbines were analysed by glass capillary gas chromatography on OV-25, Dexsil 300 and SE-54 stationary phases. By this method twenty major polynuclear aromatic hydrocarbons were characterized by comparison with reference substances. Base-line separation of isomeric benzo[fluoranthenes was achieved on OV-25. Triphenylene and chrysene were separated on Dexsil 300. It is also demonstrated that the quantitative determination of benzo[*a*]pyrene is inaccurate on SE-54. This appears to be due to an interfering compound, which can be eluted in one fraction with benzo[*ghi*]fluoranthene from Sephadex LH-20 by isopropanol. As all twenty major polynuclear aromatic hydrocarbons in aircraft turbine emissions are also emitted from other sources, only the ratios of their isomers can be used to characterize gas turbine emission profiles.

INTRODUCTION

Recently, polynuclear aromatic hydrocarbons (PAHs) originating from Pratt & Whitney JT3D3 gas turbines were analysed by glass capillary gas chromatography (GC) on the non-polar stationary phase OV-1¹. Owing to the complex nature of the PAH mixtures found in such samples, OV-1 fails to resolve some of the isomers including chrysene from triphenylene and benzo[*j*]fluoranthene from benzo[*b*]fluoranthene. The quantitative ratios of these isomers, however, are important in the investigation of the origin of PAHs found in urban areas.

Liquid crystal phases have been used for isomer separation². These phases have low coating efficiencies and temperature limits. However, a liquid crystal phase bonded to methylsilicone gum and coated on capillary columns allows resolution of all isomeric PAHs with the exception of two benzo[fluoranthenes³. In this work, stationary phases of low and medium polarity were employed in the analysis of PAHs from aircraft turbine particulate emissions by glass capillary GC.

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EXPERIMENTAL

Sampling

Samples were taken during test runs of aircraft equipped with Pratt & Whitney JT3D3 or JT8D9 gas turbines using high-volume samplers (HVS-1, Stroehlein, Dusseldorf, G.F.R.) fitted with filter heads of diameter 257 mm. Glass-fibre filters (No. 6, Schleicher & Schull, Dassel, G.F.R.) were employed for the precipitation of particulate matter at sampling rates of 50 m³/h. Filter heads were mounted on a frame situated 50 m behind the turbine duct. To prevent dust precipitation being interfered with by high airflow rates the filter head was enclosed in a steel hood open at the bottom. Samples were also taken from JT8D9 gas turbines during test runs on an engine testing stand.

Isolation of PAHs

Filters were dried over silica gel for 5 h, weighed and then extracted with toluene in a Soxhlet apparatus for 4 h. The toluene was evaporated off to a volume of 0.5 ml in a rotary evaporator and the PAHs isolated by clean-up on XAD-2⁴. A single clean-up was found to provide sufficiently pure PAH fractions. Further fractionation of the PAHs according to ring size was achieved by chromatography on Sephadex LH-20. The polymer (10 g) was slurried with isopropanol and packed into a column of internal diameter 2.5 cm. Toluene extracts were transferred to the top of the column and eluted with isopropanol. Fractions of 15 ml were collected automatically. All PAHs from phenanthrene to coronene were found to be desorbed from the column by 170 ml of isopropanol.

GC

Glass capillary columns of different lengths (25–90 m) having an internal diameter of 0.3 mm were drawn from Pyrex tubing with a glass-drawing machine (Shimadzu, GDM 1B). These were deactivated by leaching with 20% hydrochloric acid and high-temperature silylation⁵⁻⁷ and coated statically with stationary phases of either Dexsil 300, SE-54 or OV-25 (Supelco, Bellefonte, PA, U.S.A.). The PAH extracts were injected in the splitless mode and the glass liners in the injection port were cleaned frequently with chromic acid in order to avoid any discrimination of coronene or other high-boiling hydrocarbons. Furthermore, the injection port was maintained at a temperature of 290°C. Hydrogen was chosen as the carrier gas. A heating rate of 4°C/min was used for temperature-programmed GC runs. Isomeric benzofluoranthenes were partially resolved on long columns coated with SE-54 using a temperature programme from 110 to 280°C at 2°C/min.

RESULTS AND DISCUSSION

Approximately twenty polycyclic compounds were found as the major substances in the PAH profiles of aircraft turbine particulate emissions. These compounds were identified by comparison with pure reference compounds using GC. Columns with stationary phases of varying polarity were employed to avoid misidentifications. The twenty compounds identified are listed in Table I.

Fig. 1 displays glass capillary gas chromatograms of the PAH fraction isolated

from particulate emissions of JT3D3 gas turbines. Use of SE-54 (Fig. 1a) did not resolve benzo[*a*]pyrene from an interfering compound. Since this unknown substance is present in PAH emissions from other sources as well as in air particulate matter, quantification of benzo[*a*]pyrene on glass capillary columns coated with SE-54 is impractical. OV-25 and Dexsil 300 both coelute the unknown component with perylene, allowing accurate determination of benzo[*a*]pyrene and benzo[*e*]pyrene (Fig. 1b and c). The ratio of chrysene to triphenylene was determined on glass capillary columns coated with Dexsil 300. Use of OV-25 allowed baseline separation of benzo[*b*]fluoranthene, benzo[*j*]fluoranthene and benzo[*k*]fluoranthene, which was difficult to achieve on the other phases.

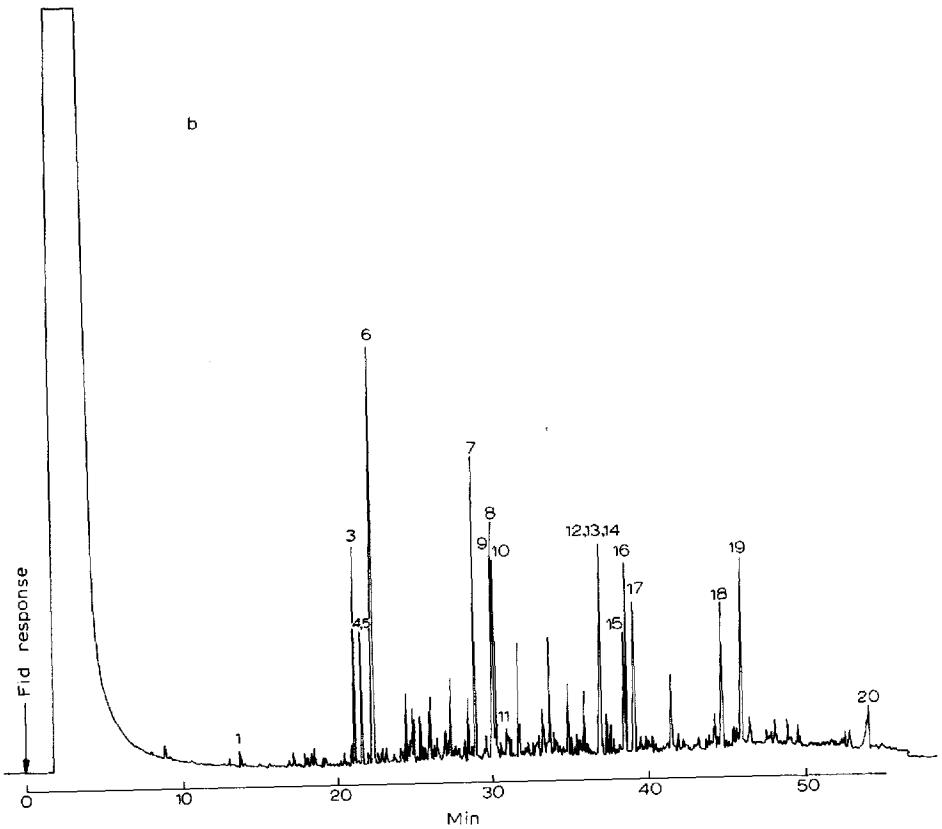
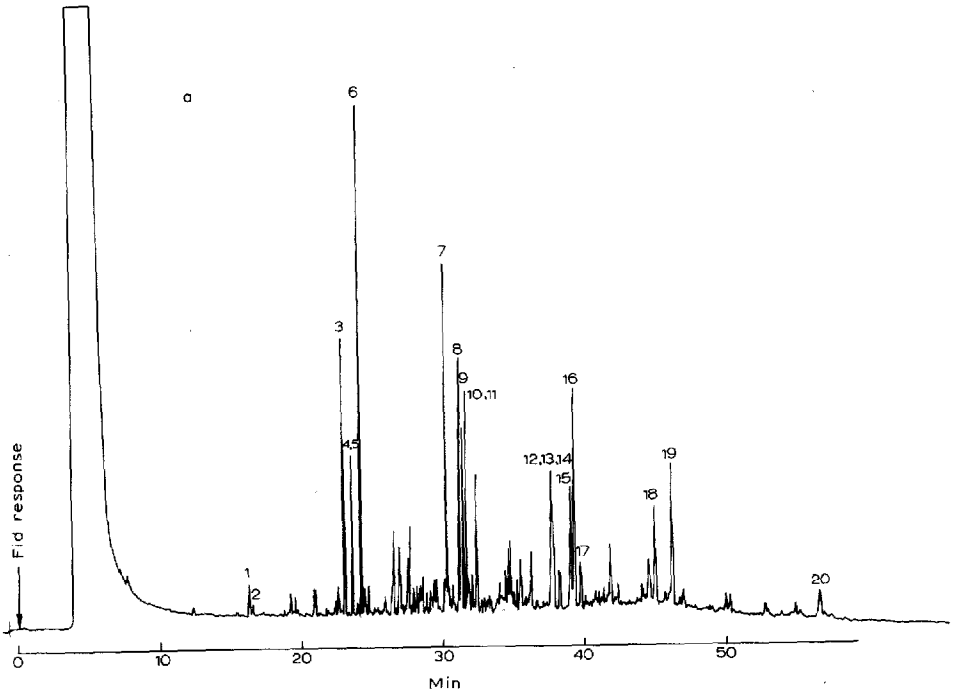
The amount of cyclopenta[*cd*]pyrene in gas turbine particulate emissions was variable. The JT3D3 gas turbines investigated released more cyclopenta[*cd*]pyrene than benz[*a*]anthracene or chrysene (Fig. 1a-c), but chrysene and benz[*a*]anthracene exceeded cyclopenta[*cd*]pyrene in all the JT8 gas turbine emissions tested so far. Fig. 2 shows the profile of PAHs isolated from the particulate emissions of one of the JT8D9 gas turbines.

Quantitative ratios of most of the PAHs in this profile are similar to those found in the emissions of JT3 turbines except that cyclopenta[*cd*]pyrene is almost completely absent. Peak 17 (Fig. 2) results from both perylene and the unknown interfering compound mentioned above. The mass spectrum of this compound, obtained by combined GC-mass spectrometry, consists of *m/e* 254 as the base peak and

TABLE I
TWENTY PAHs IDENTIFIED IN AIRCRAFT TURBINE PARTICULATE EMISSIONS

Peak number	Name of compound	Formula	Molecular weight
1	Phenanthrene	C ₁₄ H ₁₀	178
2	Anthracene	C ₁₄ H ₁₀	178
3	Fluoranthene	C ₁₆ H ₁₀	202
4	Acephenanthrylene*	C ₁₆ H ₁₀	202
5	Aceanthrylene*	C ₁₆ H ₁₀	202
6	Pyrene	C ₁₆ H ₁₀	202
7	Benzo[<i>ghi</i>]fluoranthene	C ₁₈ H ₁₀	226
8	Cyclopenta[<i>cd</i>]pyrene	C ₁₈ H ₁₀	226
9	Benz[<i>a</i>]anthracene	C ₁₈ H ₁₂	228
10	Chrysene	C ₁₈ H ₁₂	228
11	Triphenylene	C ₁₈ H ₁₂	228
12	Benzo[<i>b</i>]fluoranthene	C ₂₀ H ₁₂	252
13	Benzo[<i>j</i>]fluoranthene	C ₂₀ H ₁₂	252
14	Benzo[<i>k</i>]fluoranthene	C ₂₀ H ₁₂	252
15	Benzo[<i>e</i>]pyrene	C ₂₀ H ₁₂	252
16	Benzo[<i>a</i>]pyrene	C ₂₀ H ₁₂	252
17	Perylene	C ₂₀ H ₁₂	252
18	Indenol[1,2,3- <i>cd</i>]pyrene	C ₂₂ H ₁₂	276
19	Benzo[<i>ghi</i>]perylene	C ₂₂ H ₁₂	276
20	Coronene	C ₂₄ H ₁₂	300

* Acephenanthrylene and aceanthrylene were not available as pure reference substances, and peaks labelled 4 and 5 in the gas chromatograms are either one or both of the compounds.



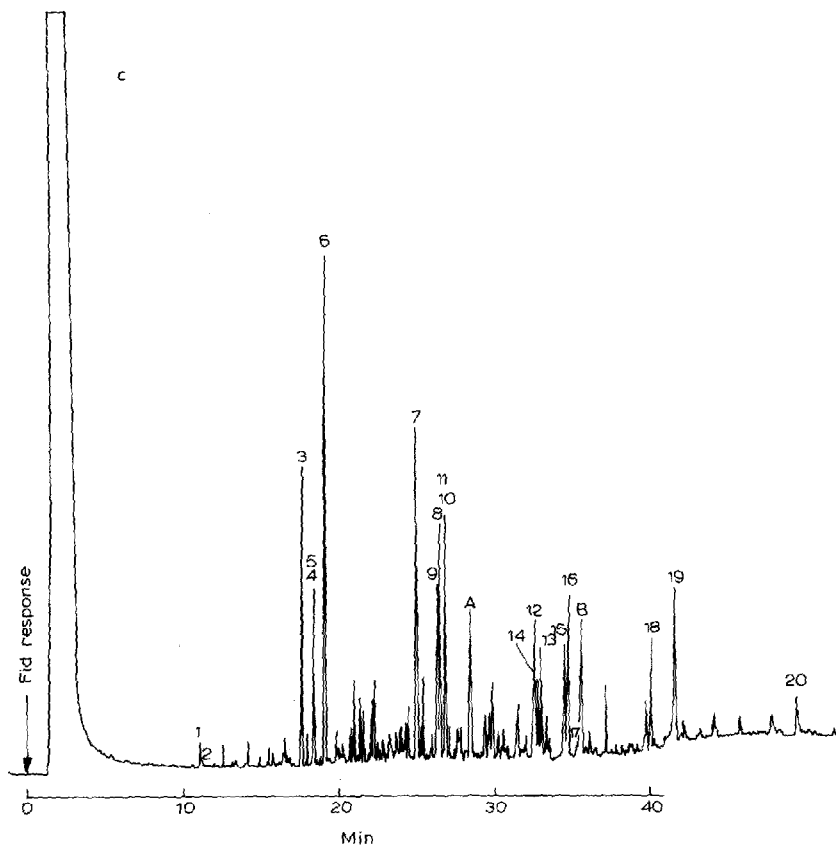


Fig. 1. PAH profiles of Pratt & Whitney JT3D3 gas turbine emissions. Peak numbers correspond to Table I. A and B are unknowns. For GC conditions see Fig. 2. Columns: a, 80 m \times 0.35 mm, SE-54; b, 40 m \times 0.30 mm, Dexsil 300 (peak 17 = perylene + unknown); c, 25 m \times 0.30 mm, OV-25.

shows only minor further fragmentation. Along with the fact that it is eluted with the PAH fraction during clean-up on XAD-2, this evidence suggests that the substance is of a polynuclear aromatic nature. Chromatography on Sephadex LH-20 with isopropanol as solvent leads to elution of this compound together with benzo[ghi]fluoranthene. The retention volume is *ca.* 15% smaller than for PAHs of molecular weight 252 (Fig. 3). Such behaviour is also observed in alkylated PAHs. Further investigations of the structure depend on the isolation of sufficient amounts of the substance (peak B, Fig. 3).

The PAHs found in aircraft turbine exhaust are also emitted from other sources, and so profiles can only be characterized accurately using ratios of isomers. All samples investigated in this work contained an excess of benzo[ghi]fluoranthene over chrysene. The ratio of benzo[b]fluoranthene to benzo[j]fluoranthene was found to be 1.1–1.9:1, with most values within the range 1.1–1.5:1. Benzo[ghi]perylene is always present in excess over indeno[1,2,3-*cd*]pyrene. Benzo[b]naphtho[2,1-*d*]thiophene has only been present as a trace or minor component in all the PAH profiles from gas turbine emissions investigated so far.

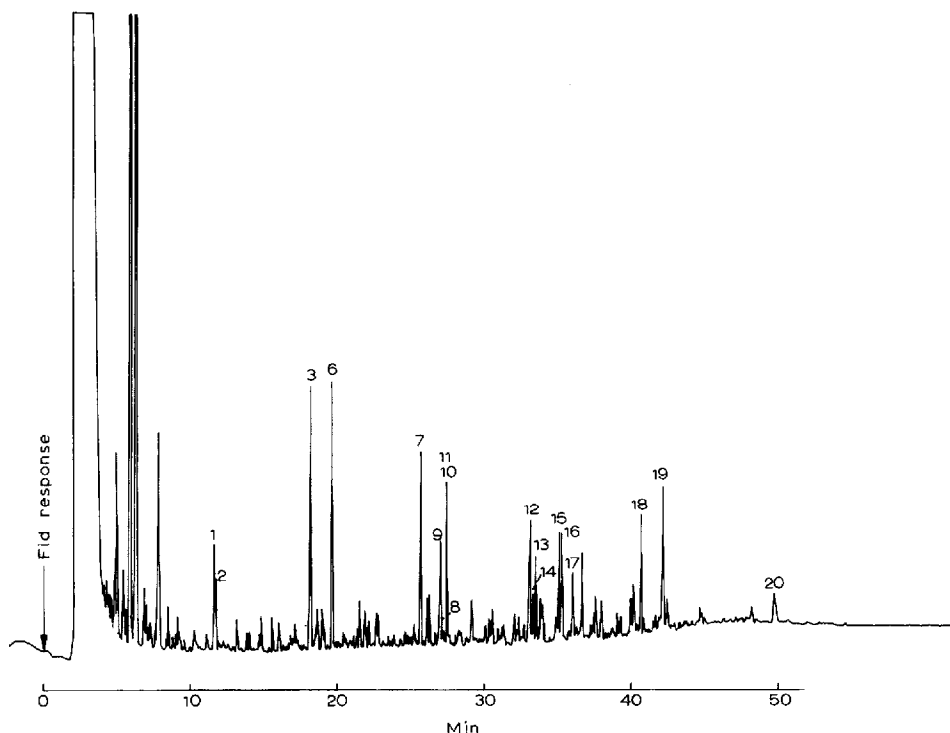


Fig. 2. PAH profile of Pratt & Whitney JT8D9 gas turbine particulate emissions. Column, 25 m \times 0.30 mm, OV-25. Peak numbers correspond to Table I. GC conditions: injector temperature, 290°C; splitless injection; temperature programme, 100–280°C; flame ionization detector (FID); carrier gas, hydrogen.

The original ratio of isomers emitted by aircraft turbine engines can undergo change in the atmosphere, since the reactivity and stability of the different PAHs are not identical. For example, benzo[*a*]pyrene disappears from PAH-carrying particulate matter with atmospheric exposure. This was also found in PAH profile analysis of particulate matter which had remained in contact with gas turbine exhaust for several seconds at elevated temperatures (60–100°C) prior to sampling. The profile of PAHs in the benzofluoranthene and benzopyrene region under these conditions is shown in Fig. 4. Benzo[*a*]pyrene (peak 16) has disappeared almost completely. Benzo[*j*]fluoranthene, benzo[*k*]fluoranthene and coronene also appear to have decreased slightly.

Finally, it was found that the more volatile PAHs (molecular weight 178–228) are vaporized in air and so can not be sampled with glass-fibre filters without a distortion of their original ratios. If particulate-adsorbed and vaporized PAHs are taken into account, fluoranthene and pyrene have an 20–30-fold excess over benzo[*e*]pyrene in gas turbine emissions. Total release of benzo[*e*]pyrene is in the range of 1–10 mg per metric ton of kerosene for Pratt & Whitney JT8D9 gas turbines. Accurate quantitative values, however, can only be obtained under standardized operating conditions.

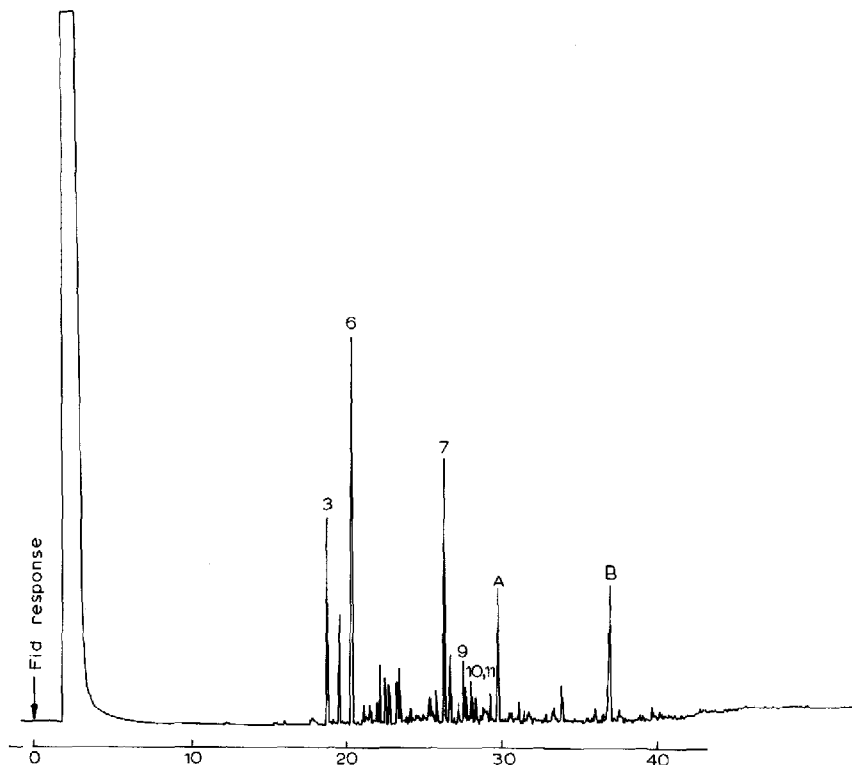


Fig. 3. Gas chromatogram of PAH fraction (51–62 ml) obtained after chromatography on Sephadex LH-20. Solvent, isopropanol; sample, same as in Fig. 1. For GC conditions see Fig. 2.

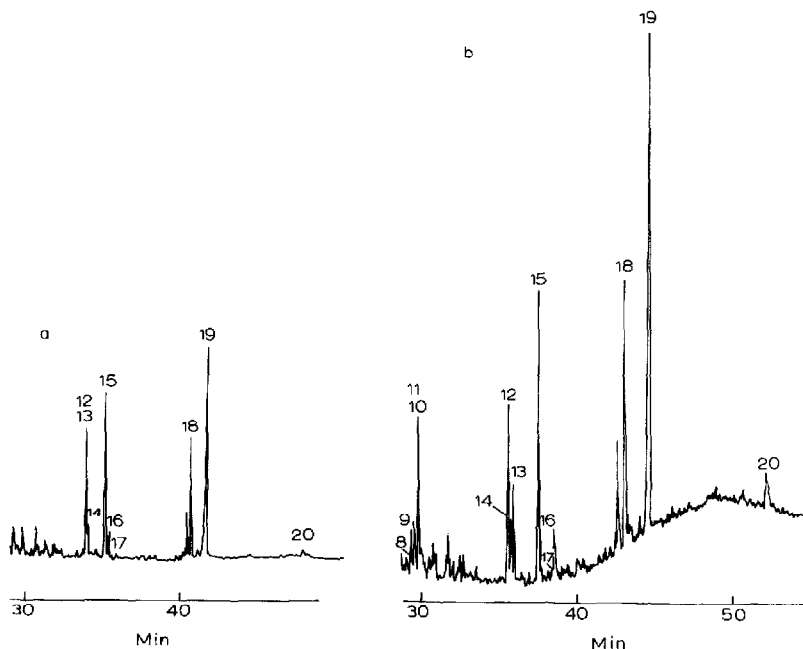


Fig. 4. Profile of non-volatile PAHs after contact of particulate emissions with hot exhaust gas from JT8D15 gas turbine. Columns: a, 30 m \times 0.30 mm, OV-1; b, 25 m \times 0.30 mm, OV-25. For GC conditions see Fig. 2.

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