CHROM. 17 650

# GAS CHROMATOGRAPHIC DETERMINATION OF TOTAL AROMATICS IN KEROSENE

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(Received January 4th, 1985)

## SUMMARY

A rapid and simple method for determining total aromatics in kerosene samples (b.p. 150–250°C) that contain less than 0.1% of olefins and/or heteroatomic compounds was developed; a 30% OV-275 on Diatomite S AW column was used at 190.3°C. Solute–solvent interactions are discussed in terms of Kováts retention indices and total molar polarization. The effect of temperature on the selectivity of separation was studied. The content of aromatics was determined with a relative standard deviation of 0.23%.

## INTRODUCTION

There have been several attempts to standardize methods for the evaluation of petroleum fractions. The concentration of aromatic hydrocarbons in kerosene fractions is an important criterion of their quality and therefore its knowledge is needed in order to be able to asses products and meet consumer specifications for aromatics. Although the determination of aromatics is of considerable industrial importance and some work has been published, it does not appear to have been solved satisfactorily so far. Various methods have been employed for this purpose. Currently used ASTM methods are based on different principles[1–3], but they are time consuming, laborious and/or of low precision. For example, the ASTM D1019-69/IP 145 method[2] has a precision of 2.6% and has recently become obsolete[4]. Snyder *et al.*[5] reported the direct mass spectrometric analysis of petroleum fractions boiling in the kerosene range. However, it requires approximately 2 h per sample and needs expensive instruments. Sautoni *et al.*[6] used a high-performance liquid chromatographic method for the determination of saturates, olefins and aromatics in hydrocarbon fractions with a distillation range of 60–271°C, involving a small-particle silica column and a low-polarity perfluorocarbon mobile phase. Gas chromatography (GC) has become the method most frequently used. Stuckey described the GC determi-

nation of aromatics in crude oil cuts boiling up to 180°C[7] and from 190 to 225°C[8]. He chose an open-tubular column coated with 1,2,3-tris(2-cyanoethoxy)propane (TCEP) as the stationary phase in both instances, followed by another open-tubular column containing DC-200 in the latter instance. Boer and Van Arkel[9] developed an automatic analyser using several columns in conjunction with flow switching and hold-up fractions for petroleum cuts with distillation end-points up to 200°C. The analysis time was 2 h. Cain[10] reported a comparison of various kerosene samples using a capillary column coated with silicone OV-101. Choubey and Mitra[11] used TCEP with a conventional column for the determination of aromatics in naphtha. Pesek and Blair[12] developed a GC procedure including backflushing for the determination of $C_8$ and higher molecular weight alkylbenzenes contained in petroleum naphtha. All the aromatic components were eluted in one peak. Recently, Herain[13] described the analysis of light kerosene cuts by combination of several techniques with capillary GC as the final step. His columns were coated with squalane, silicone SE-30 or OV-225 and TCEP. Norris and Rawdon[14] reported a supercritical fluid chromatographic method with flame-ionization detection for the determination of hydrocarbon types in petroleum liquids using liquified $CO_2$ as the mobile phase.

The objective of this study was to develop a simple, reliable and rapid method for the characterization of kerosene fractions boiling in the range 150–250°C for total aromatics, and to select conditions for their quantitative analysis.

EXPERIMENTAL

*Apparatus*

A Pye Model 104 temperature-programmed gas chromatograph with dual flame-ionization detectors (Pye Unicam, Cambridge, U.K.) was used. The columns employed were 160 × 0.2 cm I.D. and 300 × 0.25 cm I.D. glass tubes with nitrogen as the carrier gas at flow-rates of 20 and 15 ml/min, respectively. The samples were introduced with a 10- or 1-$\mu$l Hamilton microsyringe (Series 7001). The temperature of the oven was monitored using a Model R42/2 Lauda digital thermometer. A Pye Unicam PU4500 (capillary version) apparatus with dual flame-ionization detectors was also used. Both chromatographs were connected with a Pye Unicam PU4800 Chromatography Video Control Centre via universal analogue interfaces. The column employed was a 25 m × 0.20 mm I.D. WCOT SE-30 fused-silica capillary (SGE, North Melbourne, Australia). Helium of 99.996% purity (Air Products, New Malden, U.K.) was used as the carrier gas for capillary analyses at an inlet pressure of 1 bar and a splitting ratio of 1:50. A make-up tee was used to sweep the column eluents towards the detector at a flow-rate of 50 ml/min from the second injection port to prevent tailing. The injection port and detector were maintained at 260 and 300°C, respectively.

The recorder (0–10 mV) was obtained from Kipp en Zonen (The Netherlands). Also used were an SPE Model 15 EHG hydrogen generator (General Electric, Wilmington, DE, U.S.A.) and an Autolab Minigrator (Spectra-Physics, Santa Clara, CA, U.S.A.).

*Column packings*

Silicone OV-275 (Supelco, Bellefonte, PA, U.S.A.) was chosen as the stationary

phase. The packings were prepared in the usual manner by dissolving the stationary phase in acetone and slurrying it with 100–120-mesh Diatomite S AW (Pye Unicam). The slurry contained 30% (w/w) of the liquid phase. Columns containing 0.76 and 3.18 g of the liquid phase were pre-conditioned for 8 h at 200°C with the carrier gas flowing. Similarly, tetracyanoethylated pentaerythritol (TCEPE) (Supelco) was coated to 30% on Diatomite S AW and conditioned.

## Chemicals

n-Decane, n-dodecane and n-tetradecane (all puriss., standards for GC, purity at least 99.5% by GC analysis), 1,4-diethylbenzene (purum, purity at least 97%), 4-methylnonane (purum, purity as least 98%), 2-methylnonane, n-hexadecane, n-heptadecane, m-xylene, mesitylene, n-butylcyclopentane, n-pentylcyclohexane and acetone (all purum, purity at least 99%) and n-propylcyclohexane (practical grade, purity at least 95%) were supplied by Fluka (Buchs, Switzerland). n-Undecane, o-xylene, p-xylene and ethylbenzene (purity of all 99.92–99.97%) were products of Phillips petroleum (Bartsville, OK, U.S.A.). Toluene and n-butylbenzene (purities 99.7 and 96%, respectively) were supplied by Merck (Darmstadt, F.R.G.). Methane (grade 2) was a product of Airco Industrial Gases (Rivertone, NJ, U.S.A.). Benzene (purity 99%) was supplied by BDH (Poole, U.K.). n-Hexylbenzene (97%), m-ethyltoluene (99%) and 1-trans-1,4-dimethylcyclohexane were products of Aldrich (Gillingham, U.K.). Naphthalene (purified) was supplied by Hopkin and Williams (Chadwell Heath, U.K.).

## Kerosene samples

The kerosene samples were crude oil cuts of different origin (sample A and sample B), boiling between 150 and 250°C, distilled according to standard methods.

## Standard mixtures

For determining the response factors for aromatic hydrocarbons, calibration mixtures with aliphatics, n-dodecane (DD)–p-xylene (PX) (I) and n-tetradecane (TD)–n-butylbenzene (BB) (II), were prepared in the ratio of approximately 1:3 by precisely weighing and mixing 0.1978 g of DD and 0.0643 g of PX (I) and 0.1966 g of TD and 0.0797 g of BB (II).

To approximate the make-up of a kerosene hydrocarbon fraction, a mixture of saturated and aromatic hydrocarbons was prepared in such a way as to contain approximately 20% (v/v) of aromatics. The amount of each component included in the mixture was weighed precisely. The composition of the mixture is given in Table I. The response factors were calculated in the usual way[16]. In the kerosene-like mixture, common response factors were determined for the groups of aliphatics and aromatics and expressed relative to aliphatics.

## RESULTS AND DISCUSSION

The principle of the separation of aliphatic from aromatic hydrocarbons in mixtures is based on the selectivity of stationary phases usually termed "strongly polar", containing cyanoethyl groups such as 1,2,3-tris(2-cyanoethoxy)propane (TCEP)[6,7,11,13], thiodipropionitrile[17], N,N-bis(2-cyanoethyl)formamide

TABLE I

COMPOSITION OF ARTIFICIAL KEROSENE MIXTURE

Theoretical composition: sum of aromatics, 20.0% (v/v), *i.e.*, 23.07% (w/w); sum of aliphatics, 80.0% (v/v), *i.e.*, 76.93% (w/w). Found (mean values from six measurements with 0.23% relative standard deviation): sum of aromatics, 20.5% (v/v), *i.e.*, 23.63% (w/w); sum of aliphatics, 79.5% (v/v), *i.e.*, 76.37% (w/w).

| Compound | Density[15] (g/ml) | Volume (ml) | Weight (g) | Concentration (%) | |
|---|---|---|---|---|---|
| | | | | v/v | w/w |
| *Aromatics:* | | | | | |
| o-Xylene | 0.8802 | 0.50 | 0.4635 | 2.0 | 2.40 |
| p-Xylene | 0.8611 | 1.00 | 0.8771 | 4.0 | 4.55 |
| Ethylbenzene | 0.8670 | 0.50 | 0.4586 | 2.0 | 2.38 |
| n-Butylbenzene | 0.8601 | 1.00 | 0.8736 | 4.0 | 4.53 |
| Mesitylene | 0.8652 | 0.50 | 0.4515 | 2.0 | 2.34 |
| 1-Methyl-3-ethylbenzene | 0.8645 | 0.50 | 0.4496 | 2.0 | 2.33 |
| 1,4-Diethylbenzene | 0.8620 | 0.50 | 0.4410 | 2.0 | 2.29 |
| n-Hexylbenzene | 0.861 | 0.50 | 0.4354 | 2.0 | 2.26 |
| Total | – | 5.00 | 4.4503 | 20.0 | 23.08 |
| *Aliphatics:* | | | | | |
| n-Decane | 0.7300 | 3.00 | 2.1955 | 12.0 | 11.38 |
| n-Undecane | 0.7402 | 3.00 | 2.2315 | 12.0 | 11.57 |
| n-Dodecane | 0.7487 | 4.00 | 2.9863 | 16.0 | 15.48 |
| n-Tetradecane | 0.7628 | 3.00 | 2.2967 | 12.0 | 11.91 |
| 2-Methylnonane | 0.7281 | 3.00 | 2.1880 | 12.0 | 11.34 |
| 4-Methylnonane | 0.7323 | 4.00 | 2.9409 | 16.0 | 15.25 |
| Total | – | 20.00 | 14.8389 | 80.0 | 76.93 |

TABLE II

ELECTRON POLARIZABILITIES, TOTAL MOLAR POLARIZATIONS, KOVÁTS RETENTION INDICE AND SOME PHYSICAL PROPERTIES OF SOME AROMATIC HYDROCARBONS

| Compound | Mol. wt.[15] (g/mol) | B.p.[15] (°C) | Dipole moment[21], $\mu$ (D) | $\alpha_E$[*] (cm³ · 10²⁴) | $P$[**] (m³/mol · 10⁵) | I (i.u.) at column temperature | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | 150.6°C | 169.9°C | 190.3°C |
| Benzene | 78.12 | 80.12 | 0.0 | 10.4149 | 2.625 | 1391 | 1483 | 1576 |
| Toluene | 92.12 | 110.6 | 0.36 | 12.3123 | 3.336 | 1477 | 1550 | 1640 |
| o-Xylene | 106.17 | 144.4 | 0.62 | 14.1996 | 4.359 | 1645 | 1717 | 1819 |
| m-Xylene | 106.17 | 139.1 | 0.31 | 14.2612 | 3.789 | 1557 | 1629 | 1714 |
| p-Xylene | 106.17 | 138.3 | 0.0 | 14.2784 | 3.573 | 1549 | 1617 | 1706 |
| n-Butylbenzene | 134.22 | 183.0 | 0.36 | 17.8857 | 4.771 | 1704 | 1775 | 1868 |
| Mesitylene | 120.20 | 164.7 | 0.0 | 16.1876 | 4.079 | 1622 | 1682 | 1771 |

    [*] Electron polarizability[22], calculated from $\alpha_E = [(n^2-1)/(n^2+2)]3M/4\pi N\rho$, where $n$ is the refractive inde $M$ the molecular weight, $N$ Avogadro's number and $\rho$ the density (g/ml).
    [**] Total molar polarization[23], calculated from $P = (4\pi N/3)[(\alpha_E + (\mu^2/3kT)]$, where $k$ is Boltzmann's consta and $T$ the temperature (°K).
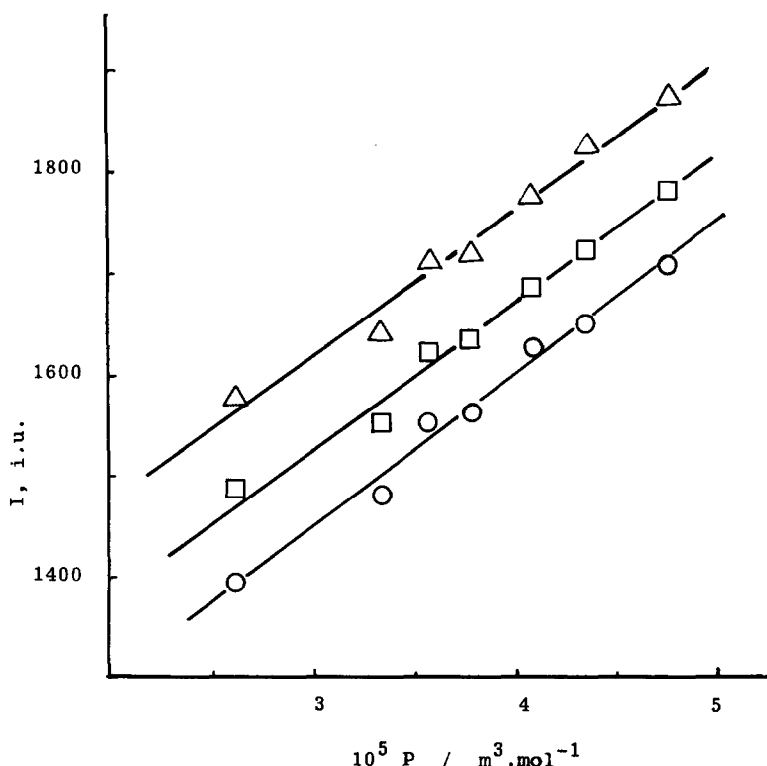
Fig. 1. Plot of total molar polarization ($P$) vs. retention indices of some aromatic hydrocarbons at temperatures of 150.6 (O), 169.9 (□) and 190.3°C (△). Column: 30% OV-275 on Diatomite S AW, 300 × 0.2 cm I.D.

(CEF)[12,18,19] and tetracyanoethylated pentaerythritol (TCEPE)[20]. The volatility of most of the stationary phases reported limits their use with higher boiling mixtures of aliphatic and aromatic compounds.

TCEPE was recommended[20] as a substitute for TCEP or CEF owing to its higher thermal stability, but this was found not to be sufficient for the analysis of kerosene fractions. Moreover, its selectivity for separations of aliphatics and aromatics was lower than that of the other stationary phases mentioned.

The selectivity of OV-275 for the separation of aliphatics and aromatics in complex mixtures was investigated in this work. In order to elucidate the nature of solute–solvent interactions affecting the retention behaviour of aromatics versus aliphatics, Kováts retention indices, electron polarizabilities and total molar polarizations were calculated for some aromatic hydrocarbons (see Table II). The forces involved in the retention of aromatics on OV-275 are a combination of induced and permanent dipole moments of the solutes on the one hand and the permanent dipole moment of the stationary phase on the other. The total molar polarization of solute molecules will be a measure of the retention order if a "strongly polar" stationary phase is used (see Fig. 1).

The effect of temperature on the selectivity was also studied; benzene was eluted after n-tridecane at 150.6°C and just before n-hexadecane at 190.3°C (see Fig. 2).
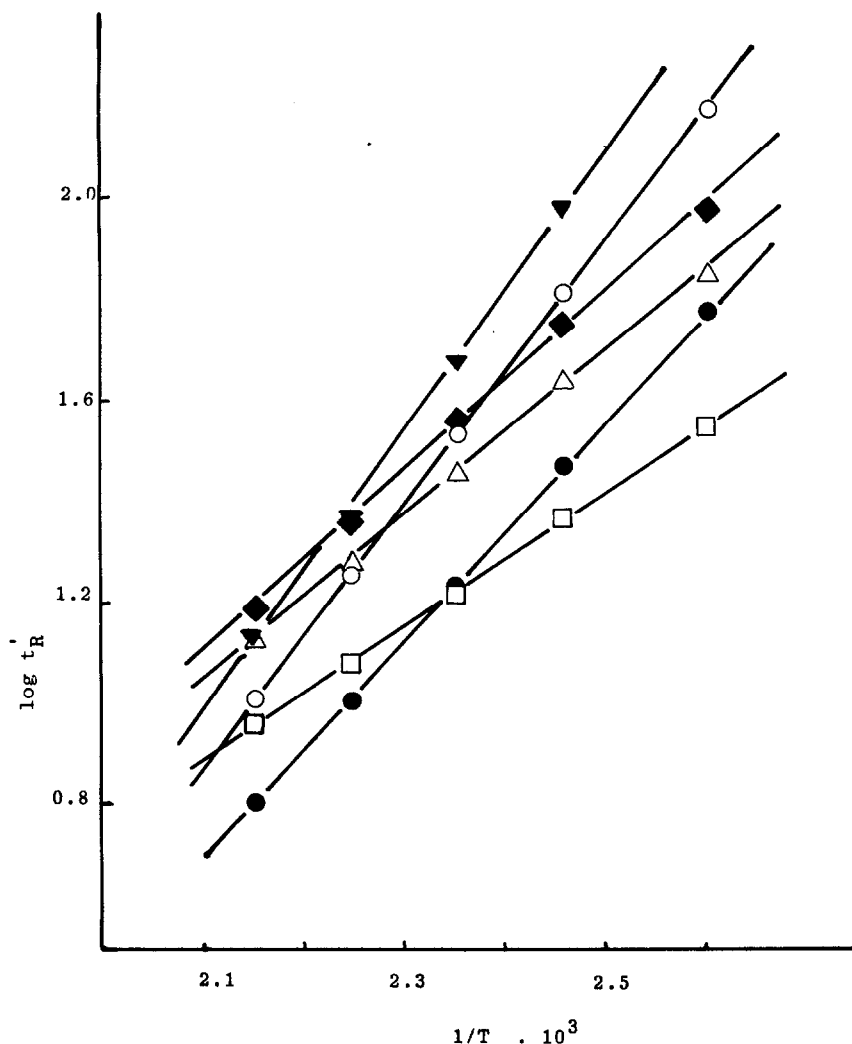
Fig. 2. Plot of temperature dependence of log (retention time) for benzene (□), n-tetradecane (●), p-xylene (△), mesitylene (◆), n-hexadecane (○) and n-heptadecane (▼). For conditions, see Fig. 1.

Kerosene fractions boiling in the range 150–250°C usually contain toluene in trace amounts (see Fig. 3), but xylenes are considered to be the first aromatic hydrocarbons to be present in significant amounts. Samples of cycloalkanes were found to elute more or less at the same retention times as those of the corresponding n-alkanes. Moreover, kerosenes with the boiling range mentioned above contain $C_9$–$C_{14}$ saturated hydrocarbons (see Fig. 3). Therefore, OV-275 may be suggested as a selective stationary phase for the determination of total aromatics in kerosene samples because p- and m-xylenes are eluted after n-heptadecane. However, there are some points that must be taken into consideration in order to clarify the scope, limitations and accuracy of the determination.
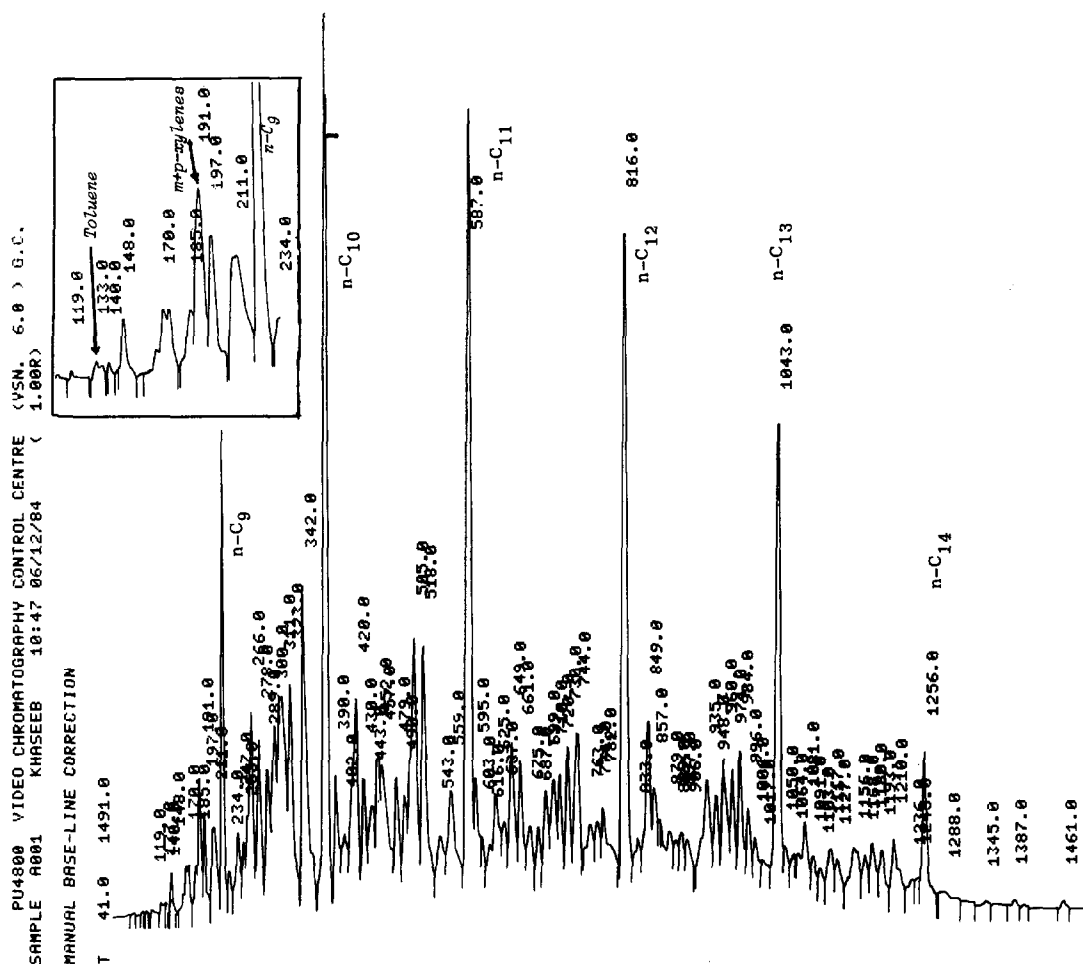
Fig. 3. Typical capillary gas chromatogram of kerosene fraction. Column: fused-silica, 25 m × 0.2 mm I.D., SE-30. Temperature: 80°C for 5 min then programmed to 200°C at 4°C/min. The inset represents an expansion of toluene and xylene elution.

A typical gas chromatogram for a kerosene sample on OV-275 at 190.3°C is shown in Fig. 4. The retention times of different monoaromatics and monoalkylnaphthalenes revealed that a run time of 25 min was sufficient to elute the aromatic hydrocarbons usually present in such boiling range fractions under the experimental conditions used in this work. The accumulation of integrated peak areas of aromatic hydrocarbons extended from the $m$- and $p$-xylene peak to the end of the run. The peak-area integration used was to slice the chromatogram just when the $m$- and $p$-xylene peak emerged and followed a straight baseline as shown in the shaded area in Fig. 4. It is immediately clear from Fig. 5 that the aromatics present in kerosene-like standard were baseline separated from the $n$-tetradecane peak. However, owing to the complex nature of kerosene samples, a baseline separation between aromatics
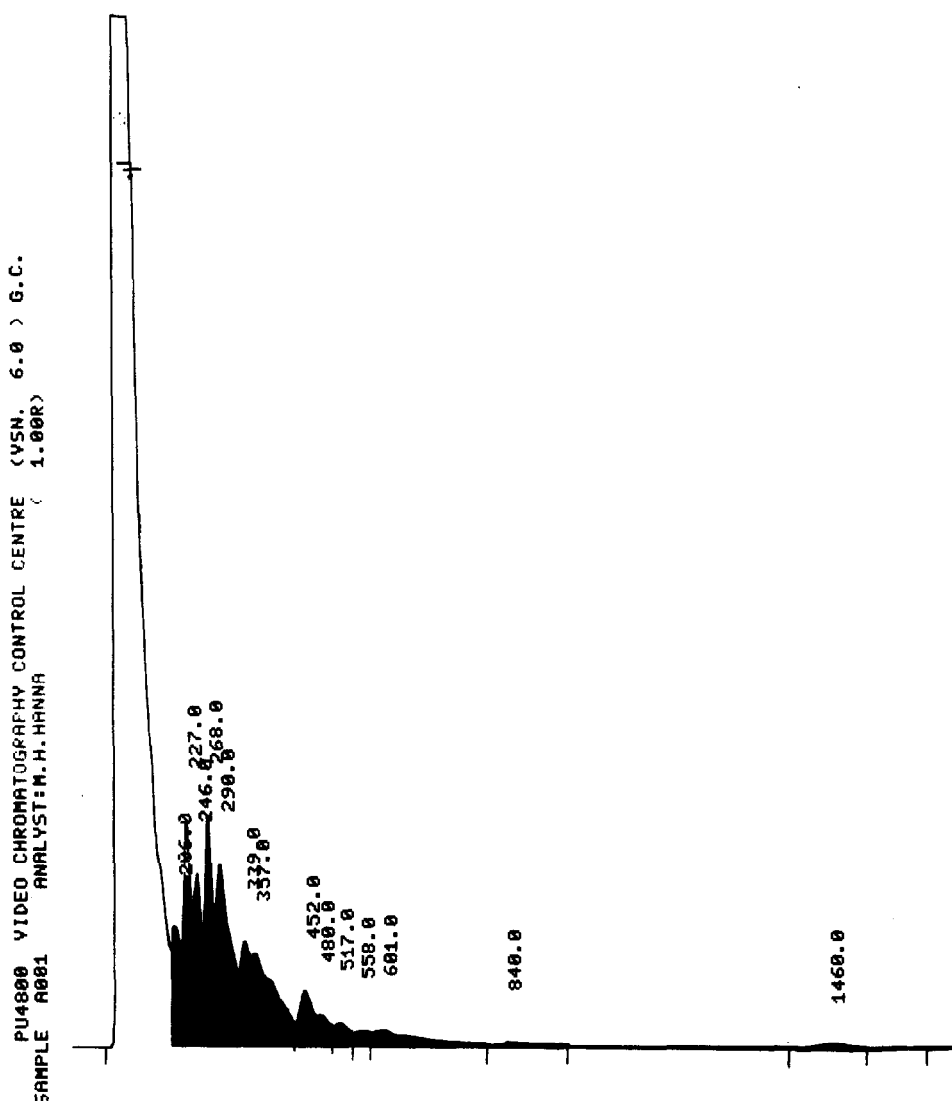
Fig. 4. Typical gas chromatogram of a kerosene sample. Column: 30% OV-275 on Diatomite S AW, 3 m × 0.2 cm I.D. Temperature, 190.3°C; flow-rate of $N_2$, 15 ml/min. The shaded part represents areas of total aromatics.

and saturated hydrocarbons cannot be expected. Nevertheless, slicing of the chromatogram was thought to be a good compromise to compensate for the loss in the *m*- and *p*-xylene peak area by the gain obtained by the tail of the saturated hydrocarbon peak.

The suggested compromise could be verified by using the facilities of the PU-4800 data system by expanding the regions concerned and performing several integrations for both the OV-275 and SE-30 capillary columns.
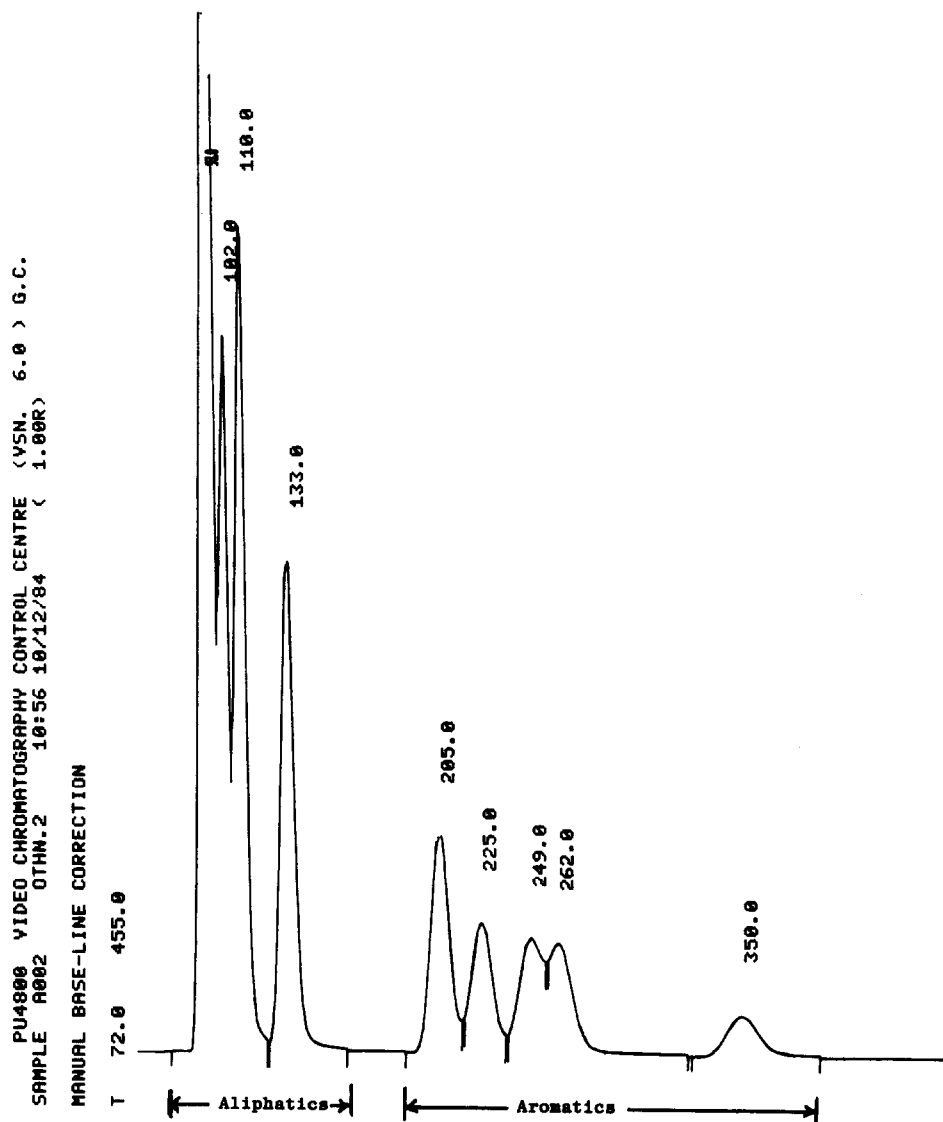
Fig. 5. Gas chromatogram of an artificial kerosene mixture. For conditions, see Fig. 4.

However, it should be emphasized that kerosene samples containing olefins at concentrations higher that 0.1% could not be analysed for their aromatic contents by this method. It can be anticipated that olefin and aromatic hydrocarbons peaks will overlap and the same limitation can be considered for oxygen-, nitrogen- and sulphur-containing compounds. If kerosene samples are pre-purified to remove all these components, the present method is applicable.

The thermal stability of OV-275 favoured the suggested procedure because

TABLE III

COMPARISON OF CONTENTS OF AROMATICS AND ALIPHATICS IN KEROSENE SAMPLES
BY GC AND ASTM METHODS

| Kerosene sample | Compounds | Content by GC method | | Content by ASTM method (%, v/v) |
|---|---|---|---|---|
| | | % (w/w)* | % (v/v) | |
| A | Aromatics | 22.56 | 21.4 | 22.1 |
| | Aliphatics | 75.44 | 78.6 | |
| B | Aromatics | 20.13 | 17.4 | 17.5 |
| | Aliphatics | 79.87 | 82.6 | |

* Mean values of five measurements.

there was a large difference between the maximum operating temperature of the stationary phase and the column temperature used.

Some papers[24,25] dealing with the response factors of hydrocarbons using flame-ionization detection showed that most aromatic and aliphatic hydrocarbons have response factors of $1.00 \pm 0.02\%$, and this was verified by experimental work in this laboratory on some aromatic and aliphatic hydrocarbon standards. Therefore, it was reasonable for the response factor to be taken as equal to 1.00 in this work.

The analysis of kerosene-like standard mixtures gave results with a relative standard deviation for aromatics of 0.23%. These encouraging results favoured the testing of the method with actual kerosene cuts. Two real samples of boiling range 150–250°C were analysed for total aromatics and the same samples were also analysed by the ASTM method using acid extraction[2]. As the latter method reports aromatics content as volume percent, the data obtained by our method as weight percent ought to be converted to volume percent for comparison. The differences in the densities of the aromatic hydrocarbons in the kerosene fraction are small; for example, it was found from several density readings (see Table I) that the average density of these compounds was $0.87 \pm 0.01$ g/ml and for saturated hydrocarbons it was $0.74 \pm 0.01$ g/ml. Hence weight percent values could be converted to the corresponding volume percent values, to a good approximation, by using above average densities. Table III shows a comparison of results obtained. The accuracy of the weight percent values for aromatics was 0.23% and that of the volume percent values was 2.3%.

The same analyses as obtained with the PU4800 data system were performed in parallel with a simple laboratory integrator (Autolab Minigrator). It was found that such a simple integrator can also provide data as good as those obtained with the sophisticated integrating system, the differences being within the limits of the precision of the method. Moreover, the Autolab Minigrator and some other commercially available integrators have the facility to simulate distillation calculations, and they can therefore be utilized for this purpose also.

CONCLUSIONS

This work suggests that 30% OV-275 on Diatomite S AW can be used as a

stationary phase for the GC determination of total aromatics in kerosene fractions boiling in the range 150–250°C. The analysis time is 25 min utilizing simple conventional columns and equipment. The kerosene samples should not contain more than 0.1% of S, O, N and/or olefinic compounds in order to achieve a 0.23% absolute accuracy for aromatics. It is considered that the present method is rapid, simple and reliable in comparison with existing standard methods.

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