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QUANTITATIVE ANALYSIS OF *n*-ALKANES IN KEROSENES BY CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

High resolution capillary gas chromatography (HRCGC) has been employed for quantitative estimation of *n*-alkanes in kerosenes having high and low contents of *n*-alkanes. Use of molecular sieve 5A with HRCGC is recommended, particularly for kerosenes having low (< 15%) contents of *n*-alkanes. The precision and accuracy of the method are high. It is shown that capillary gas chromatography provides a better distribution of the *n*-alkanes than packed column chromatographic analysis. The analysis time required was found to be significantly less compared to other methods, and the method can be recommended for routine *n*-alkanes analysis (concentrations from 5 to 35%).

INTRODUCTION

n-Alkanes (C₁₀–C₂₅) are extensively applied in the manufacture of detergents, fatty acids, alcohols, petroproteins and speciality chemicals like chlorinated and sulphochlorinated intermediates, etc. Low-boiling straight chain *n*-C₁₁–C₁₄ alkanes form the feedstock for the production of biodegradable detergent alkylates. Alkanes in the range C₁₂–C₂₀ can be fermented to proteins, while the range (\approx C₁₇ to C₂₅) is useful in the production of synthetic fatty acids. All these paraffins can be obtained from the appropriate distillate fractions of crude oils (mainly from kerosene and gas oil). Their recovery from petroleum fractions can be effected either by molecular sieve adsorption or by urea adduction. Based on the use of molecular sieves, at present there are seven commercial processes for the selective removal of *n*-alkanes from lighter and kerosene fractions. Six of those processes operate in the gas phase and one in the liquid phase, the Molex process (Universal oil product); all these processes require accurate analysis of *n*-alkanes in petroleum streams.

The direct analysis of *n*-alkanes in light and middle distillates of crude petroleum by traditional gas–liquid chromatography (GLC) is usually unsatisfactory because of the complexity. Several laboratory GC methods have been reported^{1–12} for the separation and analysis of *n*-alkanes in kerosene fractions, employing liquid- or gas-phase subtraction of *n*-alkanes by molecular sieve 5A. In practice, it has been found that molecular sieve 5A sometimes shows erratic behaviour, and in fact few

of the branched alkanes and aromatics are sorbed on molecular sieve 5A under analytical conditions. Hence there is a need to develop an alternative analytical method, without involving the molecular sieves.

With the advent of high resolution capillary columns (which are thermally stable) and modern data-processing techniques it should be possible to analyse the *n*-alkanes in petroleum streams without involving molecular sieves^{11,12}. As early as 1972¹¹, a direct analytical approach was reported for estimation of *n*-alkanes in kerosenes, employing a 50-m, Apiezon L capillary and an external standard method. The method did not require any data processor/integrator. Reference standards were prepared by blending high-purity *n*-alkanes in kerosene from which alkanes had been removed. Recently, Hine¹² used the capability of modern electronic integrators to analyse *n*-alkanes in kerosene and diesel oil mixed fraction on a fused-silica open-tubular bonded column (BP-1) with an area normalization technique. Both of these methods are applicable to kerosenes which are of intermediate base (characterization factor, K_{Uop} , 11.5–12.0), and having high contents of *n*-alkanes (>20%, w/w).

In this paper a simplified method for determination of total *n*-alkanes and their distribution in kerosenes is described which employs an open-tubular column and an up-to-date data-handling system. Analytical conditions are reported, which enable the analysis of kerosenes having low as well as high contents of *n*-alkanes. The use of molecular sieve 5A is unavoidable in the case of kerosenes having low contents of *n*-alkanes. The method is rapid and offers a precision and accuracy equivalent to, if not better than, that of other approaches used, and can be recommended for routine analysis of *n*-alkanes in kerosenes from various crude oils.

EXPERIMENTAL

A Perkin-Elmer Sigma 3b gas chromatograph equipped with a flame ionization detector was employed. High resolution capillary gas chromatography (HRCGC) was used to separate *n*-alkanes from the kerosene petroleum fractions. The OV-17 capillary column (WCOT type) was 40 m × 0.25 mm I.D. High-purity hydrogen was used as carrier gas at an average linear velocity of 10 cm/min, corresponding to a flow-rate of 0.3 ml/min. The injector and detector were set at 250 and 300°C respectively, to ensure complete vaporization of the heaviest component in kerosenes. The oven temperature was raised from 70 to 200°C at 4°C/min, after a 1-min hold at 70°C. For most kerosenes these programming conditions were found to be satisfactory; however, in some cases where the initial or final boiling point of the fraction varied, the conditions were changed accordingly. The volume of sample injected varied from 0.2 to 0.4 μ l with a splitting ratio of 320:1, thus ensuring that there was no saturation of the column and detector due to the large concentration of alkanes which may be present. The criterion for sample size was dependent on the concentration level of individual *n*-alkanes; the content of any *n*-alkane was never more than 10^{-8} g. In our experience, the introduction of higher contents of individual compounds generally overloads high resolution capillary columns.

Data handling

A Sigma 15 chromatographic data station supplied by Perkin-Elmer was used. It was set up to perform area-normalization calculation of the results. Baseline cor-

rection was performed according to the basepoint-to-basepoint mode. On each day before starting experimental work, 2-min blanks were performed to determine the area and base sensitivity for accurate peak detection. In this case, the area and base sensitivities were found to be slightly on the high side, 270 and 13 at 1×1 attenuation, thus settings of 250 and 10 were entered for all these analyses. Skim sensitivity, a criterion used by the system to determine the area of a tailing peak, was kept at default value, zero.

RESULTS AND DISCUSSION

Various non-polar open-tubular columns, WCOT (fused-silica or stainless steel) are suitable for separation of kerosene samples. In particular, SE-30 (fused silica, 12 and 50 m \times 0.25 mm I.D.), OV-17 (stainless steel WCOT, 40 m) and DC-550 (WCOT, 100 m) yielded useful data from kerosene samples. All these columns could resolve *n*-alkanes from other compounds; however, the total number of peaks obtained with a typical kerosene (140–270°C) varied with the analysis time. For the sake of brevity, the details are omitted here. Amongst these, a moderate column of 40 m \times 0.25 mm I.D. OV-17 was found to be satisfactory. It is interesting that around 250 peaks were obtained for a typical kerosene sample (140–270°C) on a 40-m OV-17 WCOT column, almost the same number as were obtained on a 100 m \times 0.25 mm WCOT, DC-550 column, within a reasonable analysis time of *ca.* 35–40 min. In our laboratory we prefer stainless steel WCOT columns over fused-silica ones for analysis of hydrocarbon fractions. With the latter columns, quite frequently a characteristic “Christmas tree” shape occurs for the chromatographic peaks^{13,14} due to an uneven air-flow pattern inside the oven and temperature fluctuations at the column inlet and outlet, etc. This observation sometimes lead to incorrect interpretation of the results. Moreover, in petroleum fraction analysis (such as gasoline and kerosenes) where not many polar compounds are involved in significant amount, the use of fused-silica columns offers no added advantage. Thus a 40-m OV-17 WCOT column was selected for this study.

To check the efficacy of the analytical column, the values of the Trenzahl number, Tz_{100} , and resolution rate, Tz_{100}/t_R , were determined. Under programmed temperature gas chromatographic (PTGC) conditions, the Trenzahl number and resolution rate for the pair *n*-C₁₁–*n*-C₁₂ were found to be 25 and 1.8 per minute respectively; the number of theoretical plates, *n*, and the capacity factor, *k*, for *n*-tetradecane were $104 \cdot 10^3$ and 15.3 respectively. These data indicate that the separation ability and capacity of the column is satisfactory in comparison with other columns and similar data published earlier (though not under identical conditions)^{15–17}. Recently, Hine¹² reported the use of a 25-m fused-silica open-tubular column for analysis of *n*-alkanes in a 1:1 mixture of kerosene and diesel oil (*n*-C₉–*n*-C₂₄) and observed a total of 450 peaks, whereas under our analytical conditions for a typical kerosene, C₉–C₁₅, we obtained around 250 peaks. From this, it may be concluded that any column providing around 230–240 peaks for a kerosene (boiling range 140–270°C) may give *n*-alkane, peaks sufficiently well separated from other components and thus reliable quantitative data. Minor interferences present in the case of kerosenes having more than 15% *n*-alkanes (1.1% at the level of 24.7% *n*-alkanes¹²) can be ignored since the level of interference would be within the range of precision and accuracy of the results reported.

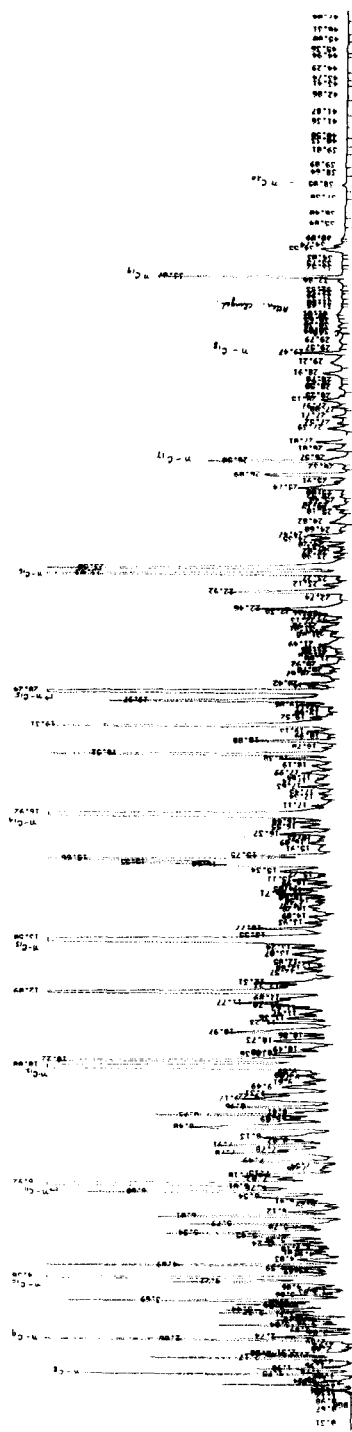


Fig. 1. Capillary gas chromatographic analysis of a kerosene having a high concentration of *n*-alkanes, obtained under PTGC conditions.

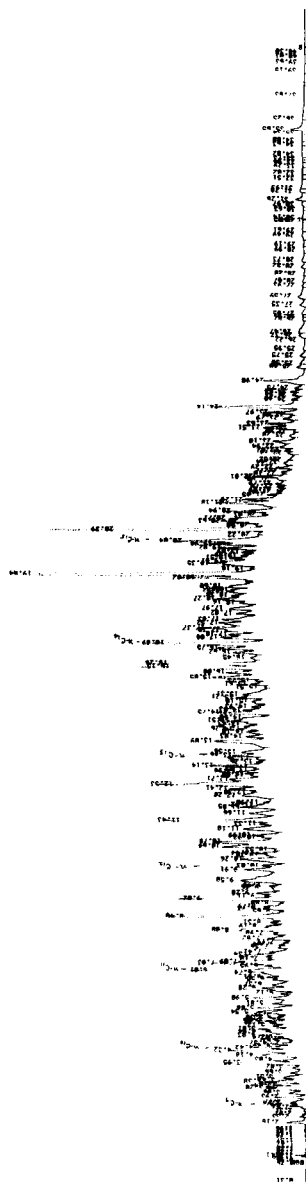


Fig. 2. Capillary gas chromatogram of a kerosene having a very low amount of *n*-alkanes.

Fig. 1 depicts the separation achieved for a kerosene sample having a high content of *n*-alkanes (> 20%). Under PTGC conditions, the *n*-alkanes could easily be recognized because they generally give large peaks spaced at regular intervals. It should be noted that other compounds like 2-methyl-dodecane and some isoprenoid hydrocarbons also occur in most kerosenes having large amounts of alkanes; isoprenoid hydrocarbons also exhibit a regular spacing in capillary chromatography on a non-polar phase. With kerosenes having low amounts of *n*-alkanes the situation is altogether different, as is evident from the chromatogram shown in Fig. 2. Assignment of the *n*-alkane peaks was very difficult, and the contribution from non-normal hydrocarbons at the positions of *n*-alkanes cannot be ignored. In such cases, the use of molecular sieve 5A for *n*-alkane subtraction is unavoidable. The estimation of *n*-alkanes in such kerosenes (naphthenic) could be performed by injecting the same volume of sample with and without molecular sieve, in capillary gas chromatography. In our chromatographic unit the subtraction of *n*-alkanes was carried out by replacing the injector liner with another glass liner packed with 2–3 cm molecular sieve 5A (50–60 mesh). The molecular sieve (pre-column) could be activated by heating the injector port at 320°C under an hydrogen carrier stream for 2 h. The activation of the molecular sieve bed was tested by injecting a pure *n*-alkane mixture (*n*-C₈–C₁₄). The calculation of the *n*-alkane content and distribution was much simpler and could be done by subtracting the percentage area obscured by other non-normal components from the percentage area of *n*-alkane peaks obtained. The positions of *n*-alkanes in a chromatogram without use of molecular sieves and of overlapping components in a chromatogram with molecular sieves could easily be recognized with the help of retention time and pattern recognition, since the overall absolute retention time did not differ much. This approach, using molecular sieves with area-normalized values, could reduce the level of error marginally. No correction factor was required, in contrast to other methods; only the enhancement of the percentage area of obscured peaks (non-normal hydrocarbons) due to loss of *n*-paraffins needs to be taken into account. Furthermore, the capillary chromatogram involves large numbers of peaks as compared to one from a packed column, thus making it easier to determine the *n*-alkanes under unfavourable conditions (Fig. 2). With this method we could analyse each *n*-alkane down to 0.5%. Thus it has the potential for estimation of non-sorbed *n*-alkanes in a kerosene stream obtained from a single stage molecular sieve subtraction process. A number of kerosene samples of widely ranging compositions, dominated either by alkanes (55–60%, branched to normal ratio varying from 0.5 to 1.5), cycloalkanes (70%) or aromatics to the extent of 40%, were tested and analysed successfully.

In the case of high resolution capillaries operated in split mode, it is necessary to use the instrument at maximum sensitivity (attenuation range 1 or 10). At high sensitivity, the number of noisy peaks becomes too large, and the integrator reads the noise as peaks if operated with default values of the area and base sensitivities. It is worthwhile to mention that the default values for noise rejection and slope sensitivity parameters given by manufacturers are normally the set points for intermediate chromatographic sensitivity, *e.g.*, Perkin-Elmer gives for the CDS-Sigma 15 the values 50 and 4 for area and base sensitivity at range 100 with flame ionization detection, and Hewlett-Packard gives for its 5880A, 3990A, integrators the value 0.04 min and 4 for the peak width and threshold respectively. Though it is well known

that, for reliable and accurate quantitative analysis, peak processing is a crucial parameter^{18,19}, in most cases the analyst employs automatic settings for peak detection and area determination. In our laboratory, experience with capillary gas chromatography (petroleum analysis) has shown that appropriate values of the area sensitivity (to identify a peak start and crest) to discriminate a real peak from a noise background and of the base sensitivity to detect the slope of the signal level (peak end-point and baseline) should be entered manually for accurate peak processing. The baseline treatment and tangential skimming of the rider peak can be done later on in some cases once the raw data have been obtained. Surprisingly, not many reports are available on these aspects, which are the key factors in the accurate quantitation of peaks obtained in capillary gas chromatography. Only recently there has been some deliberation on the validation of chromatographic software packages for computer systems used in analysis, processing of data, transferring of data for storage, etc. Benezra²⁰ demonstrated, when checking his chromatographic software CHROM (in-house development work at Burroughs Wellcome, NC, U.S.A.), that the acquisition and reduction of chromatographic data generated by CHROM were comparable to traditional manual methods (cut and weigh, peak height \times width at half-height and triangulation); no statistical difference between the areas determined by traditional methods and those determined by CHROM was observed. However, a very important observation was the variance which occurred in the computer-generated areas, which arose because thirteen individuals were allowed to set parameters that determined the beginning and end of a peak. There was almost no variance in the computer-determined areas provided the operating set points were the same.

It should be noted that it is easy to adjust all these parameters during the reprocessing of chromatograms having small numbers of peaks; however, in the case of kerosene where the capillary chromatogram may have more than 250 peaks some generalizations have to be made. In our work on *n*-alkane analysis in a kerosene, the integrator settings were selected so that any component present at 0.005% was not ignored, otherwise the overall small contribution due to several non-normal hydrocarbons was reflected as a significant contribution to the *n*-alkane concentration (in the case of area normalization). With more sensitive settings the raw data may become unwieldy. Hence optimization of these settings was carried out. In practice, it was found useful to determine the area and base sensitivities daily at two stages: at the initial oven temperature and at the final oven temperature, under PTGC conditions for a blank experiment. The values thus obtained were averaged out, and were entered into the system manually. During a temperature-programmed experiment the background signal gradually increases to produce a baseline with a "knee" in it. In such cases, baseline treatment using the basepoint-to-basepoint mode (code 2 for Sigma 15) is advisable and skim sensitivity at the default value (5%) was used in our quantitative calculations.

Table I presents the precision obtained for *n*-alkane analysis in a typical kerosene sample obtained from an Indian crude oil. Eleven analyses were performed by making replicate injections during a period of 1 week. The concentration of individual *n*-alkanes varied between 0.3 and 7% (w/w). The standard deviation was less than 0.1, and the coefficient of variation (C.V.) was within 6%. In order to define the accuracy of the method used, a series of determinations were made with specially prepared standard mixtures. Six synthetic mixtures were made by blending a high-

TABLE I

PRECISION OF QUANTITATIVE DATA FOR *n*-ALKANE ANALYSIS IN A COMMERCIAL KEROSENE

| Sample No. | <i>n</i> -Alkane | Concentration (% w/w) | Standard deviation | C.V. (%) |
|------------|-----------------------|-----------------------|--------------------|----------|
| 1 | <i>n</i> -Octane | 0.51 | 0.03 | 6.02 |
| 2 | <i>n</i> -Nonane | 1.26 | 0.03 | 2.28 |
| 3 | <i>n</i> -Decane | 3.36 | 0.08 | 2.26 |
| 4 | <i>n</i> -Undecane | 6.48 | 0.11 | 1.70 |
| 5 | <i>n</i> -Dodecane | 7.20 | 0.07 | 0.98 |
| 6 | <i>n</i> -Tridecane | 6.64 | 0.10 | 1.54 |
| 7 | <i>n</i> -Tetradecane | 4.64 | 0.11 | 2.27 |
| 8 | <i>n</i> -Pentadecane | 2.49 | 0.05 | 2.10 |
| 9 | <i>n</i> -Hexadecane | 1.19 | 0.03 | 2.31 |
| 10 | <i>n</i> -Heptadecane | 0.36 | 0.02 | 6.51 |

purity *n*-alkane concentrate (*n*-C₁₁-C₁₄) with varying proportions of denormalized fraction. The total *n*-alkane content blended ranged from 7 to 30% (w/w), thus representing almost the complete range of kerosenes. All six mixtures were analysed under the conditions given above, and the values are reported in Table II. The data indicate high accuracy (each of the six samples was analysed twice; the second time analysis being done 1 week after the first), deviating in the range of +5 to -7% from the true value. The precision and accuracy data in Table II suggest that the method is applicable to all sorts of kerosene fractions. It should be noted that the contribution from non-normal hydrocarbons to the *n*-alkanes (blended) was taken into account by analysing the denormalized cut used in all the six samples; it was significant in this case (5.2%). Use of an internal standard can also be made with this capillary gas chromatographic system. In our studies, two different mixtures prepared separately by mixing a kerosene with *n*-nonadecane as an internal standard (0.83 and 12.74 wt.%) were analysed. The data for total *n*-alkanes and their distribution were in good agreement, and the *n*-nonadecane was found to be 0.89 and

TABLE II

ACCURACY OF THE CAPILLARY GAS CHROMATOGRAPHIC METHOD

DN = Denormalized fraction; P = *n*-alkane concentrate (*n*-C₁₁-C₁₄); I and II are two different runs.

| Sample No. | Synthetic blend | Actual <i>n</i> -alkane concentration (% w/w) | Observed values (% w/w) | | Relative deviation (%) | |
|------------|-----------------|---|-------------------------|-------|------------------------|-------|
| | | | I | II | I | II |
| 1 | DN + P - 1 | 7.32 | 6.83 | 7.20 | -6.69 | -1.64 |
| 2 | DN + P - 2 | 10.86 | 10.97 | 11.42 | +1.01 | +5.16 |
| 3 | DN + P - 3 | 20.35 | 19.26 | 21.19 | -5.36 | +4.13 |
| 4 | DN + P - 4 | 23.70 | 23.96 | 24.18 | +1.10 | +2.03 |
| 5 | DN + P - 5 | 27.82 | 26.78 | 27.27 | -3.74 | -1.98 |
| 6 | DN + P - 6 | 31.18 | 32.75 | 31.33 | +5.04 | +0.48 |

TABLE III
COMPARISON OF DATA (wt.%) OBTAINED FOR *n*-ALKANES BY CAPILLARY GAS CHROMATOGRAPHY (CGC) AND THE UOP METHOD*

| Sample No. | <i>n</i> -Alkane | Sample A | | Sample B | | Sample C | | Sample D | | Sample E | |
|------------|----------------------------------|----------|-------|----------|-------|------------------|-------|----------|-------|------------------|-------|
| | | CGC | UOP | CGC | UOP | CGC | UOP | CGC | UOP | CGC | UOP |
| 1 | <i>n</i> -Octane | 0.98 | 1.27 | — | — | 0.91 (1.00) | 0.61 | — | — | — | — |
| 2 | <i>n</i> -Nonane | 4.23 | 5.12 | 4.20 | 5.16 | 1.83 (1.79) | 1.99 | — | — | — | — |
| 3 | <i>n</i> -Decane | 7.12 | 7.99 | 5.66 | 5.97 | 3.84 (3.73) | 3.62 | 6.81 | 7.92 | 7.23 (7.85) | 7.34 |
| 4 | <i>n</i> -Undecane | 7.96 | 8.10 | 5.90 | 5.66 | 5.52 (5.61) | 5.48 | 9.82 | 10.15 | 8.57 (8.61) | 8.47 |
| 5 | <i>n</i> -Dodecane | 5.84 | 6.63 | 5.83 | 5.96 | 5.81 (5.75) | 6.24 | 8.63 | 8.82 | 7.86 (7.95) | 8.76 |
| 6 | <i>n</i> -Tridecane | 3.45 | 3.57 | 5.52 | 6.81 | 5.61 (5.39) | 6.47 | 7.80 | 7.62 | 6.91 (6.75) | 8.38 |
| 7 | <i>n</i> -Tetradecane | 0.91 | 0.60 | 4.21 | 3.79 | 4.94 (4.69) | 4.57 | 1.72 | 1.28 | 2.07 (1.86) | 1.70 |
| 8 | <i>n</i> -Pentadecane | — | — | 2.16 | 0.95 | 3.52 (3.41) | 3.44 | 1.20 | — | 1.47 (1.34) | — |
| 9 | <i>n</i> -Hexadecane | — | — | 1.20 | — | 1.49 (1.39) | 1.47 | — | — | 0.57 (0.50) | — |
| 10 | <i>n</i> -Heptadecane | — | — | — | — | 0.67 (0.64) | 0.65 | — | — | — | — |
| 11 | Total <i>n</i> -paraffin | 30.49 | 33.28 | 34.68 | 34.30 | 34.14 (33.40) | 34.54 | 35.98 | 35.79 | 34.68 (34.86) | 34.66 |
| 12 | C ₁₁ -C ₁₄ | 18.16 | 18.90 | 21.46 | 22.22 | 21.88 (21.44) | 22.76 | 27.97 | 27.87 | 25.41 (25.17) | 27.31 |

* In the molecular sieve subtraction, UOP, method, the total *n*-alkane content obtained by the indirect in combination with the relative distribution procedure was adopted for an absolute distribution of the *n*-alkane concentrations. Values given in parentheses are duplicate data analysed 8 months earlier.

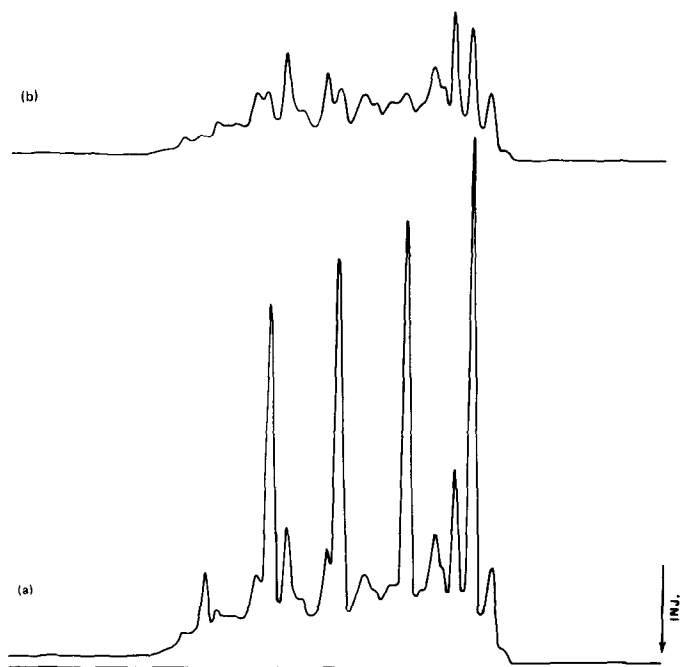


Fig. 3. Analysis of a kerosene fraction (165–250°C) on a SE-30 column before (a) and after (b) molecular sieve treatment.

12.58% (w/w) respectively. These data further indicate the high accuracy and also demonstrate that no fractionation of high boiling hydrocarbons occurs at the injector port.

Additional investigations were carried out on five kerosene range fractions; three were kerosenes from different Indian refineries, and two were narrow range fractions (165–250°C). These samples had been analysed earlier by the Universal Oil Products (UOP) method and Table III compares the quantitative data obtained by the two methods. Certain information revealed by this comparison is important and further illustrates the accuracy achieved by our method. The amounts of total *n*-alkanes determined by the UOP and our method were in excellent agreement except for one sample (A), and the summations of the data for *n*-C₁₁–C₁₄ were also in close proximity. The relative distributions for individual *n*-alkanes reveal slight deviations. As expected, the values for lighter *n*-alkanes (C₈–C₁₀) obtained by the present method are on the low side (volatiles are vaporized during storage) and heavier alkanes are relatively concentrated. Further, the distribution ratios given by the UOP method (subtraction by molecular sieve 5A and packed column analysis) are susceptible to error due to large interference caused by branched and cyclic alkanes and aromatics. Fig. 3a and b show the chromatograms obtained for a narrow range kerosene fraction on a SE-30 column (as prescribed by UOP) before and after molecular sieve treatment. It is clear from Figs. 1 and 3a, which provide the relative distribution of *n*-alkanes, that the former (Fig. 1) will provide the better distribution.

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