Journal of Chromatography, 101 (1974) 365–371

CHROM. 7794

GAS CHROMATOGRAPHIC DETERMINATION OF THE PARAFFIN AND NAPHTHENE CONTENT IN SATURATED HYDROCARBON DISTILLATES WITH POROUS LAYER OPEN TUBULAR COLUMNS OF MOLECULAR SIEVE 13X

N. L. SOULAGES and A. M. BRIEVA

Laboratorio Investigación y Desarrollo Y.P.F., Avda. Calchaqui Km. 23.5, Florencio Varela (Argentina)

(First received April 26th, 1974; revised manuscript received June 28th, 1974)

SUMMARY

The use of a molecular sieve 13X porous layer open tubular (PLOT) column in the determination of paraffins and naphthenes in dearomatized naphthas boiling up to 200° is described. The column was subjected to severe operating conditions and was used for more than 100 analyses at different times without signs of deterioration, demonstrating that these PLOT columns require minimal attention. Their superior resolving power in comparison with classical packed columns is discussed. The analysis time for C_5–C_{12} saturated hydrocarbons is 12 min, which represents a five-fold increase in the speed of analysis.

INTRODUCTION

The separation of the saturated hydrocarbons in naphthas into paraffinic and naphthenic fractions is of great importance in the petroleum industry, particularly at the present time with the increasing utilization of catalytic processes. In 1968, Brunnock and Luke[1] described the surprising property of molecular sieve 13X (MS-13X) to effect the separation of paraffinic and naphthenic hydrocarbons according to the carbon-number distribution in saturated fractions boiling up to 185°. Later publications[2–7] proposed different approaches to this analysis, some of which allowed the simultaneous determination of aromatic hydrocarbons and/or normal paraffins. In every instance, the separation of paraffins and naphthenes was carried out with a column similar to that described by Brunnock and Luke, *i.e.*, a column packed with MS-13X particles. The time required for elution and complete separation of hydrocarbons up to C_{11} was *ca.* 1 h.

We have successfully employed a porous layer open tubular (PLOT) column of MS-13X. With this column, the analysis time is considerably shortened and, at the same time, better resolution is obtained, which even allows the determination of some individual hydrocarbon components.

Several active solid stationary phases have been used in PLOT columns, *e.g.*,

graphitized carbon black[8,6], colloidal silica[9,10], fibrilar boehmite[11] and molecular sieve 5A[12], but no references were found to the use of MS-13X.

EXPERIMENTAL

Equipment

The analysis was performed on a Carlo Erba Fractovap Model D gas chromatograph equipped with an oven easily adapted to operate up to 450°, with a wide range of temperature programmes up to a maximum of 22°/min. The original flame ionization detector (FID) and electrometer were replaced by units of recent design, *i.e.*, a Type FID/D detector head and an SS 450/C electrometer, with improved quantitative behaviour. Peak areas were measured with an Infotronics CRS-100 integrator.

In order to homogenize the sample with the carrier gas thoroughly before the stream splitter, a glass tube filled with 30–60 mesh Chromosorb P was fitted at the injector.

A copper deoxygenator maintained at 600° and a U-tube filled with anhydrite and freshly activated MS-13X to dry the carrier gas were incorporated in the flow system just before the injection port.

Treatment of molecular sieve 13X

Powdered MS-13X (Linde) was treated with sodium hydroxide in order to reduce the acidic activity of the sieve and, at the same time, to improve the capacity to resolve saturates into paraffins and naphthenes of the same carbon number[1,7].

The procedure was as follows. A 10-ml volume of MS-13X was mixed with 50 ml of 3% sodium hydroxide solution in a centrifuge tube for 15 min. The MS-13X particles were then separated by centrifugation, the sodium hydroxide poured off and the residue washed at least five times with distilled water. During each rinse, the suspension was thoroughly dispersed by shaking and was later centrifuged.

The washed aqueous suspension was ground in a colloidal mill so as to give a particle size of 1–2 μm, ascertained by microscopic observation. The concentration of MS-13X in the suspension was assessed by evaporating to dryness an aliquot of solution and weighing the residue. A solution of a suitable concentration was obtained by evaporation or dilution of the original stock solution.

Preparation of PLOT columns

Two techniques can be used for the preparation of PLOT columns, the static[13,14] and the dynamic coating procedure[9,15]. The results indicated that the columns prepared by the dynamic coating procedure behaved in a superior manner and therefore the static coating procedure, which is more complicated, was abandoned. This does not imply that columns prepared by a more elaborate static technique might not perform as well as or better than those prepared by the dynamic technique.

The MS-13X concentration is not critical, and we obtained good performance with columns prepared with suspensions in the 5–10% (w/v) range. In a typical coating procedure, a 5 m × 0.5 mm I.D. stainless-steel tube, Type 304 (Superior Tube Co.), was connected to a 10-ml reservoir with a side entrance connected to a nitrogen cylinder through a needle valve to pressurize the filling tube. The MS-13X suspension

was thoroughly shaken and 5 ml were added to the receptacle and forced to pass through the column in 2–4 min by applying pressure. Owing to the instability of the aqueous dispersion, it is important that the passage is effected in a short time. Once the excess of the suspension had drained through, the nitrogen flow-rate was adjusted to 5 ml/min and allowed to run overnight in order to dry the column.

The column was conditioned with a temperature programme of 3°/min up to 450°, this temperature then being maintained for several hours with a nitrogen flow-rate of 1 ml/min.

RESULTS AND DISCUSSION

Separation of paraffins and naphthenes

The results obtained with a PLOT column operated with two different temperature programmes, the complete operating conditions being listed in Table I, are shown in Figs. 1 and 2. As the column resistance is very low, flow fluctuations of 20% between the initial and final temperatures occurred; this change in flow does not, however, greatly affect the baseline or the FID response.

TABLE I

CHROMATOGRAPHIC CONDITIONS

Condition	*Value*
Column dimensions	5 m × 0.5 mm I.D.
Column material	Stainless steel 304
Temperature programme	Fig. 1: 140–450° at 4.5°/min Fig. 2: 275–450° at 16°/min
Carrier gas	Nitrogen
Inlet pressure	0.15 kg/cm²
Linear velocity	10 cm/sec
Sample volume	0.2 µl
Splitting ratio	1:50
Injector temperature	250°
Detector	FID
Hydrogen flow-rate	10 ml/min
Oxygen flow-rate	250 ml/min

In the chromatogram shown in Fig. 1, the temperature programme began at 100° and increased slowly (4.5°/min) so as to give a detailed resolution which would allow not only the separation of paraffins and naphthenes, but also the identification of individual hydrocarbons; CH and MCP were completely isolated, and the normal paraffins from C_7 to C_{11} were resolved from the corresponding branched-chain isomers, thus allowing quantitative determinations to be made.

The identification proposed in Fig. 1 is based on a comparison with reference blends of pure hydrocarbons (Chemical Samples, Columbus, Ohio, U.S.A.) and should be considered to be a first approach, particularly in the case of several overlapping isomers. The precise identification of the hydrocarbons separated by the PLOT column could be obtained by mass spectrometry, as indicated by Brunnock and Luke[1].

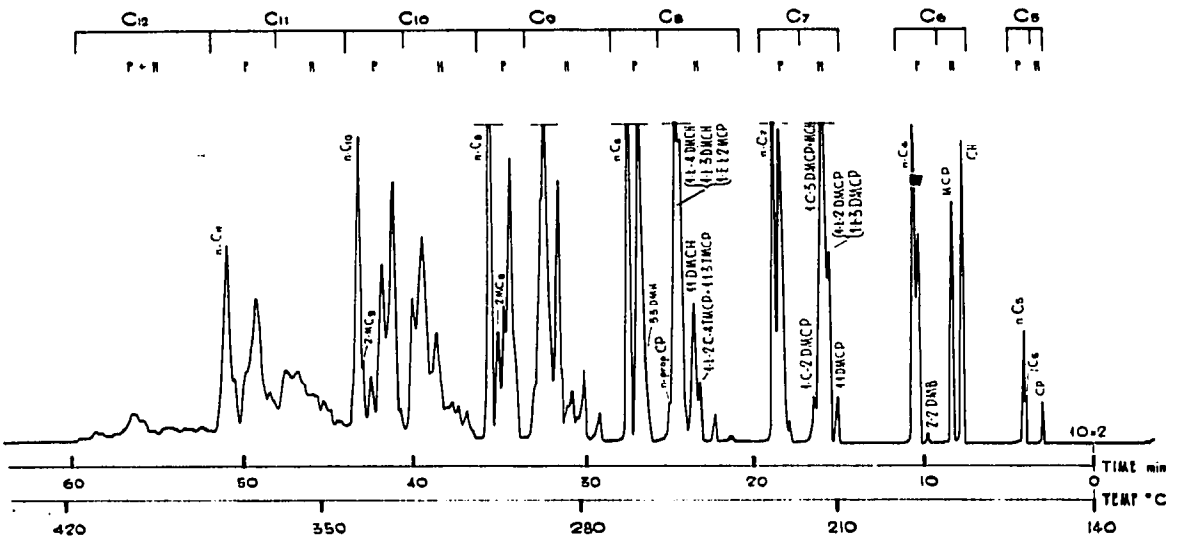

Fig. 1. Typical analysis of dearomatized naphtha with PLOT column of molecular sieve 13X. Conditions: see Table I. CP = cyclopentane; iC_5 = isopentane; $n\text{-}C_5$ = *n*-pentane; CH = cyclohexane; MCP = methylcyclopentane; 2-2 DMB = 2,2-dimethylbutane; $n\text{-}C_6$ = *n*-hexane; 1-1 DMCP = 1,1-dimethylcyclopentane; 1-t-3 DMCP = 1-*trans*,3-dimethylcyclopentane; 1-t-2 DMCP = 1-*trans*,-2-dimethylcyclopentane; 1-c-3 DMCP = 1-*cis*,3-dimethylcyclopentane; MCH = methylcyclohexane; 1-c-2 DMCP = 1-*cis*,2-dimethylcyclopentane; $n\text{-}C_7$ = *n*-heptane; 1-t-2-c-4 TMCP = 1-*trans*,2-*cis*,4-trimethylcyclopentane; 1-1-3 TMCP = 1,1,3-trimethylcyclopentane; 1-1 DMCH = 1,1-dimethylcyclohexane; 1-t-4 DMCH = 1-*trans*,4-dimethylcyclohexane; 1-t-3 DMCH = 1-*trans*,-3-dimethylcyclohexane; 1-E-t 2 MCP = 1-ethyl-*trans*,2-methylcyclopentane; n-prop.CP = *n*-propylcyclopentane; 3-3 DMH = 3,3-dimethylhexane; $n\text{-}C_8$ = *n*-octane; 2 MC_8 = 2-methyloctane; $n\text{-}C_9$ = *n*-nonane; 2 MC_9 = 2-methylnonane; $n\text{-}C_{10}$ = *n*-decane; $n\text{-}C_{11}$ = *n*-undecane.

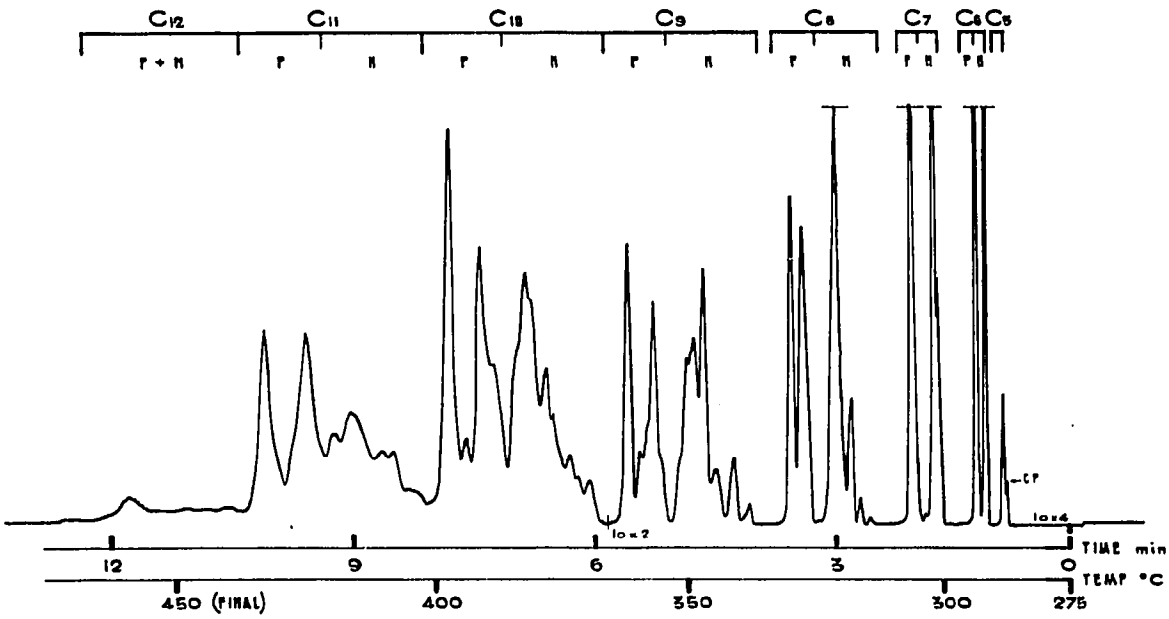

Fig. 2. Rapid analysis of paraffin/naphthene content. Conditions: see Table I.

Fig. 2 shows a rapid analysis of the same sample, which is recommended for routine determinations of the paraffin and naphthene contents. Beginning at 275° with a temperature programme of 16°/min, a good separation of hydrocarbons up to C_{12} was obtained in only 12 min.

Column performance

In the early stages of this work, our aim was to establish the stability and life expectancy of this type of PLOT column, in which the porous layer adheres to the inner wall of the tube only by naturally cohesive forces. We tested the column stability under normal operating conditions and also under extreme conditions such as long periods at 450° and at high linear flow-rates of carrier gas (30–40 cm/sec); these tests indicated a very stable porous film to be present.

A column employed for 2 months in the analysis of more than 100 samples of gasolines was taken off the chromatograph oven and stored with the ends open to the atmosphere for 1 month, and showed no deterioration in performance. These results show that this type of column can be employed in such analyses without undue precautions.

So far, we have not developed a column filling technique that will produce columns with reproducible resolution. Several columns apparently prepared with similar care were efficient in the separation of paraffins and naphthenes, but showed appreciable differences in resolving power. This is probably due to difficulties in the formation of a homogeneous porous film along the length of the tube. Those workers acquainted with the preparation of PLOT or capillary columns will know the difficulties involved in obtaining good columns, and that success is sometimes the result of the strict observation of very simple precautions.

Encouraged by the advantages of PLOT columns over packed columns in this type of analysis, we undertook a systematic study of all the steps pertaining to their preparation so as to eliminate errors that affect their quality.

Quantitative results

As previously stated, the carrier gas is deoxygenated and dehydrated immediately before the injection port. A first attempt to dehydrate the nitrogen with anhydrite did not result in the complete removal of the sharpening of the C_9-paraffin band. The "driving effect of water", as was defined by Boer and Van Arkel[7], disappears on the addition of MS-13X activated *in situ* at 400° by the passage of nitrogen previously dried over anhydrite.

We found no evidence of cracking reactions induced by trace amounts of oxygen in the carrier gas. Repeated tests using oxygen-free nitrogen and nitrogen which contained at least 5 ppm of oxygen, failed to reveal any differences. As PLOT columns permit a shorter analysis time, it is possible that the cracking of hydrocarbons is negligible owing to their short residence time in the column.

Table II summarizes the results of ten succesive analyses on the same sample made with nitrogen without deoxygenation, and the standard deviations for each particular group of hydrocarbons and for the total paraffin and naphthene content.

The higher standard deviation for the C_{11} and C_{12} fractions is partly ascribed to the difficulty in determining the integration end-point, and to small deviations in the baseline that the integrator cannot correct because of the continuous elution of hydrocarbons in this part of the chromatogram.

TABLE II

REPEATABILITY AND STANDARD DEVIATION

*Hydrocarbon**	*Mean (%wt.) (10 results)*	*Standard deviation*
N-C_5	0.18	0.03
P-C_5	0.62	0.03
N-C_6	3.00	0.12
P-C_6	3.63	0.10
N-C_7	7.02	0.13
P-C_7	6.24	0.08
N-C_8	9.27	0.05
P-C_8	8.62	0.07
N-C_9	11.30	0.09
P-C_9	9.98	0.11
N-C_{10}	9.38	0.18
P-C_{10}	12.40	0.10
N-C_{11}	5.99	0.13
P-C_{11}	9.30	0.30
N-C_{12}	3.07	0.29
N_{total}	49.21	0.19
P_{total}	50.79	0.19

* N = naphthenes; P = paraffins.

CONCLUSIONS

A very interesting and promising field in gas chromatography is the development of new column technology in order to achieve rapid analyses with high resolving powers. The increasing utilization of columns with small diameters filled with a support coated with a thin film of stationary phase, of capillary columns and of PLOT columns is particularly noticeable.

The separation of paraffins and naphthenes effected in a MS-13X PLOT column is an instance of the above: the time of analysis has been reduced five-fold, with improved resolution.

We consider that PLOT columns with the different types of adsorption materials now used in gas–solid chromatography will prove to behave in a similar manner. Recent results with PLOT columns of molecular sieve 5A for the separation of normal paraffins are very encouraging and will be the subject of a future paper.

REFERENCES

1 J. V. Brunnock and L. A. Luke, *Anal. Chem.*, 40 (1968) 2158.
2 J. V. Brunnock and L. A. Luke, *Anal. Chem.*, 41 (1969) 1126.
3 N. G. McTaggart, L. A. Luke and D. Wood, in R. Stock and S. G. Perry (Editors), *Gas Chromatography 1970*, Institute of Petroleum, London, 1971, p. 35.
4 N. G. McTaggart and L. A. Luke, *Erdöl Kohle, Erdgas, Petrochem.*, 9 (1971) 586.
5 R. M. Peterson and J. Rodgers, *Chromatographia*, 5 (1972) 13.
6 F. Garilli, L. Fabiani, U. Filia and V. Cusi, *J. Chromatogr.*, 77 (1973) 3.
7 H. Boer and P. van Arkel, *Chromatographia*, 4 (1971) 300.
8 I. Halász and C. Horváth, *Nature (London)*, 197 (1963) 71.
9 R. D. Schwartz, D. J. Brasseaux and G. R. Shoemake, *Anal. Chem.*, 35 (1963) 496.

10 R. D. Schwartz, D. J. Brasseaux and R. G. Mathews, *Anal. Chem.*, 38 (1966) 303.
11 J. J. Kirkland, *Anal. Chem.*, 35 (1963) 1295.
12 J. E. Purcell, *Nature (London)*, 201 (1964) 1321.
13 C. Horváth, *Ph. D. Thesis*, University of Frankfurt am Main, Frankfurt/M., 1963.
14 I. Halász and C. Horváth, *Anal. Chem.*, 35 (1963) 499.
15 J. G. Nikelly, *Anal. Chem.*, 44 (1972) 623.
16 G. C. Goretti, A. Liberti and G. Nota, *J. Chromatogr.*, 34 (1968) 96.