Journal of Chromatography, 349 (1985) 377–384
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 679

NAPHTHA ANALYSIS

THE ADVANTAGES OF A SPECIFIC OLEFIN TRAP

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SUMMARY

Quantification of olefins has always been a major problem in the analysis of naphthas with an upper cutting point of 200°C. Most existing methods for this task use an irreversible olefin trap, necessitating two injections for each analysis.

This paper describes the use of a newly developed, reversible olefin trap that performs group separation of olefins with carbon numbers greater than 5 from saturated hydrocarbons with carbon numbers less than 12. The combination of this trap with a standard paraffin-naphthene-aromatic analysis method enables a completely automated paraffin-olefin-naphthene-aromatic analysis to be carried out in 3 h, including the carbon number separation of all cyclic and acyclic olefins. Good accuracy and precision are achieved throughout.

INTRODUCTION

Naphtha analysis is of fundamental importance to the hydrocarbon processing industry for quality control (when buying and selling decisions have to be made) and for process control (analysis of reformer feedstock and reformate to ensure optimum reforming process conditions).

In 1970, Boer and Van Arkel[1,2] reported a method for naphtha analysis, based on multiple-column gas chromatography, that analysed paraffins, naphthenes and aromatics with boiling points up to 200°C. In 1980, Boer *et al.*[3] reported an improved paraffin-naphthene-aromatic (PNA) analysis that enabled naphtha samples with final boiling points up to 275°C to be analysed. It has been shown that for complex samples, such as olefin-containing naphthas, group separation is preferred over total separation of all components[4]. The rapid growth in the importance of olefin analysis in recent years has prompted the petrochemical industry to search for a reliable paraffin-olefin-naphthene-aromatic (PONA) analysis method. A logical way to achieve this aim is to extend the existing PNA analysis method (according to Boer's principle) with an olefin trap. Olefin traps can be divided into two categories: irreversible traps and reversible traps.

PONA analyses based on irreversible traps require two injections. The first run is used for a standard PNA analysis after all the olefins have been hydrogenated:

0021-9673/85/$03.30

Cyclo-olefins are converted to naphthenes, and *n*- and iso-olefins are converted to *n*- and iso-paraffins, respectively. The second run is used to adsorb the olefins irreversibly. The differences in the peak areas of paraffins and naphthenes in the two runs are
attributed to *n*- and iso-olefins and to cyclo-olefins, respectively. This approach has a number of major disadvantages:

(1) Long analysis times are required because two runs are necessary.

(2) The fact that the subtraction method has to be applied leads intrinsically to inaccurate results.

(3) Irreversible olefin traps, such as mercury perchlorate[5], are not inert (leading to ghost peaks and the corrosion of metal surfaces) and are not reusable.

Since many olefin traps are not reusable, the trap material has to be replaced after every PONA analysis, with the risk of introducing leaks into the system. Furthermore, it means that PONA analyses cannot be automated. Consequently, the development of a reversible olefin trap that allows trapped olefins to be released by thermal desorption has been regarded as a priority for the further development of PONA analysis methods. This would allow PONA analyses to be carried out with only one injection, resulting in a considerable reduction in analysis time. Ideally, the reversible olefin trap should retain all olefins with carbon numbers less than 12 and allow saturates (paraffins and naphthenes) with carbon numbers less than 12 to pass through unretarded.

This paper evaluates the performance of the Packard olefin trap (POLT: patent pending) and describes a complete quantitative PONA analysis.

EXPERIMENTAL

The experiments were performed on a Packard Model 412A PIANO analyser (Packard Instrument, Delft, The Netherlands) equipped with a Packard automatic sampling device (Model 940 One-Shot Sampler). Integration and data handling were performed on an SP4200 integration system (Spectra-Physics, Santa Clara, CA, U.S.A.).

RESULTS AND DISCUSSION

The principle of reversible olefin adsorption as applied in the newly developed olefin trap is as follows. The trap retards the olefins at 100°C. At this temperature, the saturates (paraffins and naphthenes) exhibit far less retention. When the saturates have been eluted from the trap, the flow is reversed and the trap temperature is raised to 150°C to release the olefins, which are detected as a single peak in backflush (Fig. 1). Under these conditions, olefins with carbon numbers greater than 5 exhibit longer retention times than *n*-undecane. Thus, the olefin trap employed here is a group-selective olefin adsorber.

If the principle of selective olefin retardation is to be applied in combination with a Molecular Sieve 13X column (which subsequently subdivides the olefins by carbon number and separates the *n*- and iso-olefins from the cyclo-olefins), it is necessary first to hydrogenate the olefins to their corresponding saturated analogues to prevent cracking of the olefins on the Molecular Sieve 13X column[6].

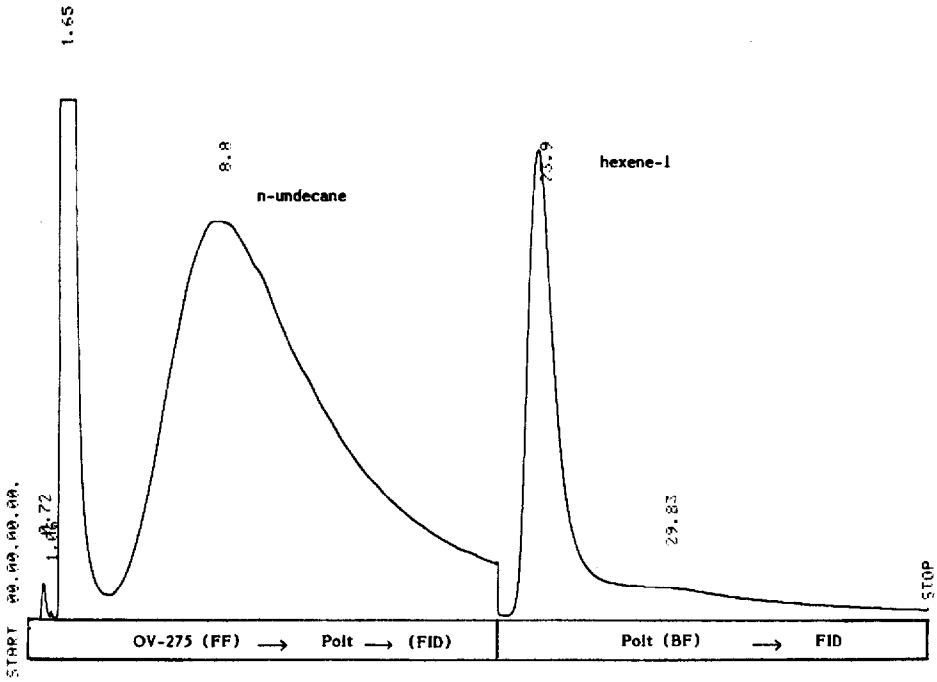

Fig. 1. Chromatogram showing retention of olefins at 100°C and subsequent release in backflush at 150°C.

The recovery of the olefins after trapping, thermal desorption, and hydrogenation on a platinum catalyst was examined with a quantitative reference sample containing 1-heptene, 1-octene and 1-decene in a hydrocarbon matrix consisting of paraffins, naphthenes and aromatics. It was found that the values obtained after trapping, desorption and hydrogenation were close to those determined by weighing (Table I).

A schematic flow diagram of the essential elements of a PONA analysis is shown in Fig. 2, and a flow diagram of the gas chromatographic separation scheme is shown in Fig. 3. The analytical process can be described as follows.

Pre-column

The OV-275 polar pre-column (dicyanoallyl silicone on Chromosorb) separ-

TABLE I

PERCENTAGE RECOVERY OF OLEFINS FROM THE SPECIFIC OLEFIN TRAP

Olefin	*Weighing (%, w/w)*	*Gas chromatographic run (%, w/w)*	*Recovery (%)*
1-Heptene	1.20	1.15	96
1-Octene	2.40	2.38	99
1-Decene	1.60	1.58	99

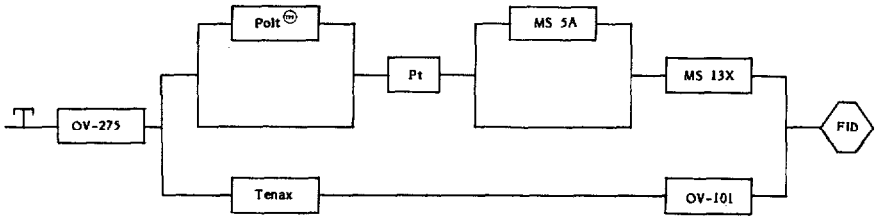

Fig. 2. Schematic flow diagram of the PIANO analyser.

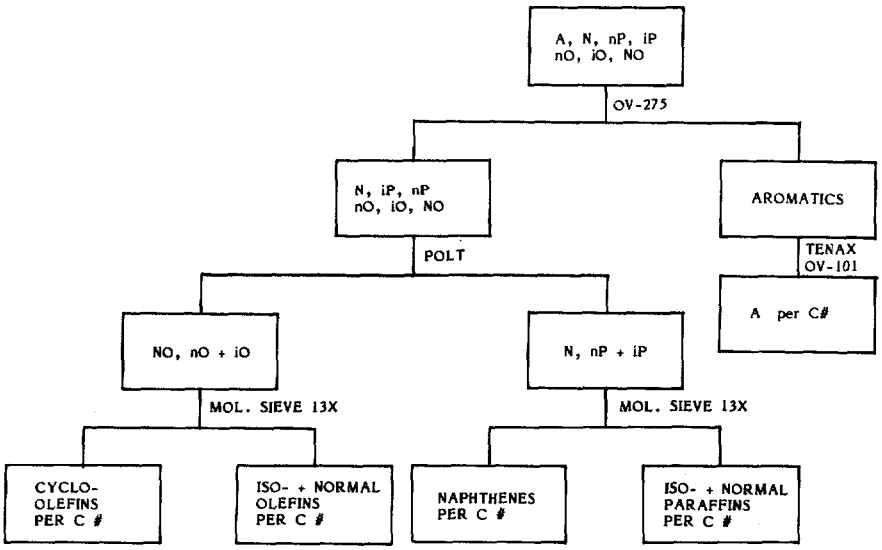

Fig. 3. Gas chromatographic separation scheme as applied in the PIANO analyser. A = aromatics, N = naphthenes, nP = normal paraffins, iP = iso-paraffins, nO = normal olefins, iO = iso-olefins, NO = naphthenic olefins (*i.e.* cyclo-olefins), C # = carbon number.

ates the aromatics from the olefins and saturates. On this column, the retention time of benzene exceeds the retention times of *n*-dodecane and undecenic isomers.

Boiling point column and Tenax trap

The OV-101 column (methyl silicone) is used to separate the aromatics further, according to their boiling points. The Tenax trap refocuses the aromatics prior to injection into the OV-101 column. The specific aromatic fractions that can be analysed have been described previously[3].

Olefin trap

A silver-containing macroporous copolymer of divinyl benzene and polystyrene that selectively removes the olefins from the saturates[7].

Molecular Sieve 13X column and reactor

The saturates are separated into groups by carbon number, *i.e.* the species of each particular carbon number are grouped together, but within each carbon number

grouping, the naphthenes and paraffins are eluted as two distinctly separate bands. This column is also used for the analysis of the olefins, which are first hydrogenated to their saturated analogues in a miniature reactor filled with a platinum catalyst.

The performance (accuracy and precision) of the system was established with the aid of a reference sample of known composition. Good figures for standard deviation were obtained and, equally important, the reported weight percentage com-

TABLE II

PERFORMANCE OF THE OLEFIN TRAP AS DETERMINED WITH THE PONA ANALYSER

δ = difference between the values obtained for the gas chromatographic run and the actual composition.

Olefin	*Percentage (w/w) as determined by weighing*	*Percentage (w/w) as determined by the PONA analyser*	δ
Cyclohexene	1.03	0.94	−0.09
1-Hexene	0.98	0.78	−0.20
1-Heptene	3.04	3.03	−0.01
1-Octene	6.10	6.23	+0.13
1-Nonene	6.07	6.13	+0.06
1-Decene	3.10	3.14	+0.04

TABLE III

REPEATABILITY FIGURES FOR A PONA ANALYSIS (REFERENCE SAMPLE)

Group of compounds	*Carbon No.*	*Mean of 20 runs*	*S.D.*	*Coefficient of variation*
Paraffins	5	1.88	0.011	0.60
	6	4.02	0.014	0.36
	7	6.19	0.012	0.19
	8	8.58	0.021	0.25
	9	8.37	0.018	0.21
	10	6.30	0.017	0.28
Olefins	6	0.94	0.009	1.00
	7	3.03	0.016	0.52
	8	6.23	0.015	0.24
	9	6.13	0.013	0.21
	10	3.14	0.009	0.29
Naphthenes	5	1.95	0.013	0.66
	6	4.07	0.014	0.33
	7	6.06	0.014	0.23
	8	6.85	0.017	0.24
Aromatics	6	2.14	0.017	0.80
	7	2.24	0.010	0.44
	8	4.09	0.043	1.04
	9	8.53	0.033	0.38

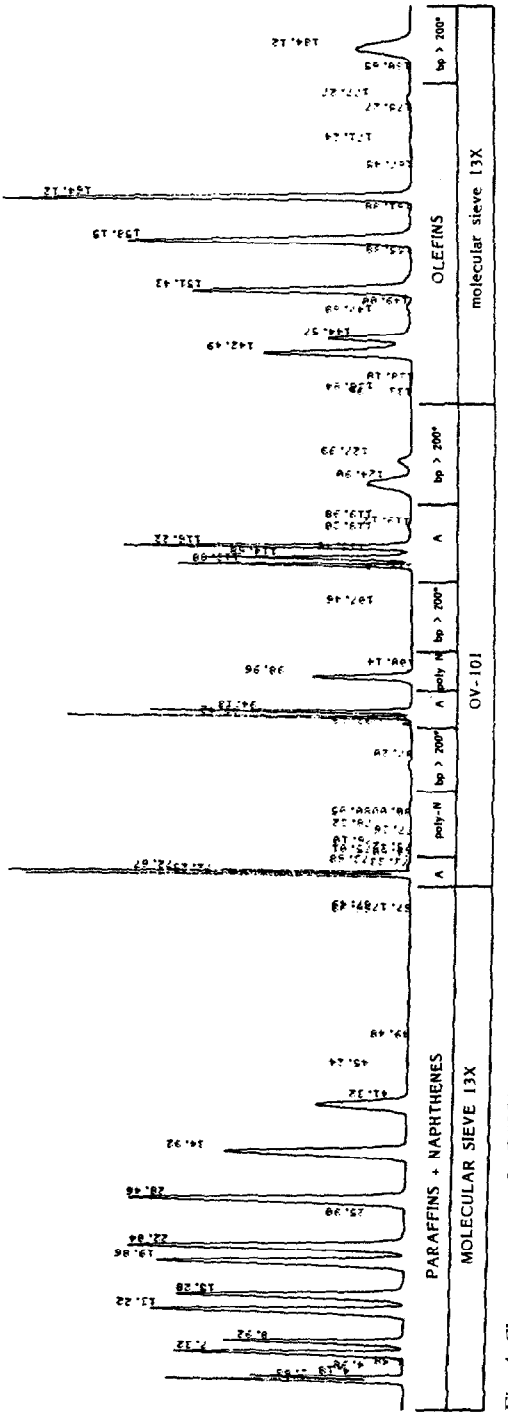

Fig. 4. Chromatogram of a PONA analysis reference sample.

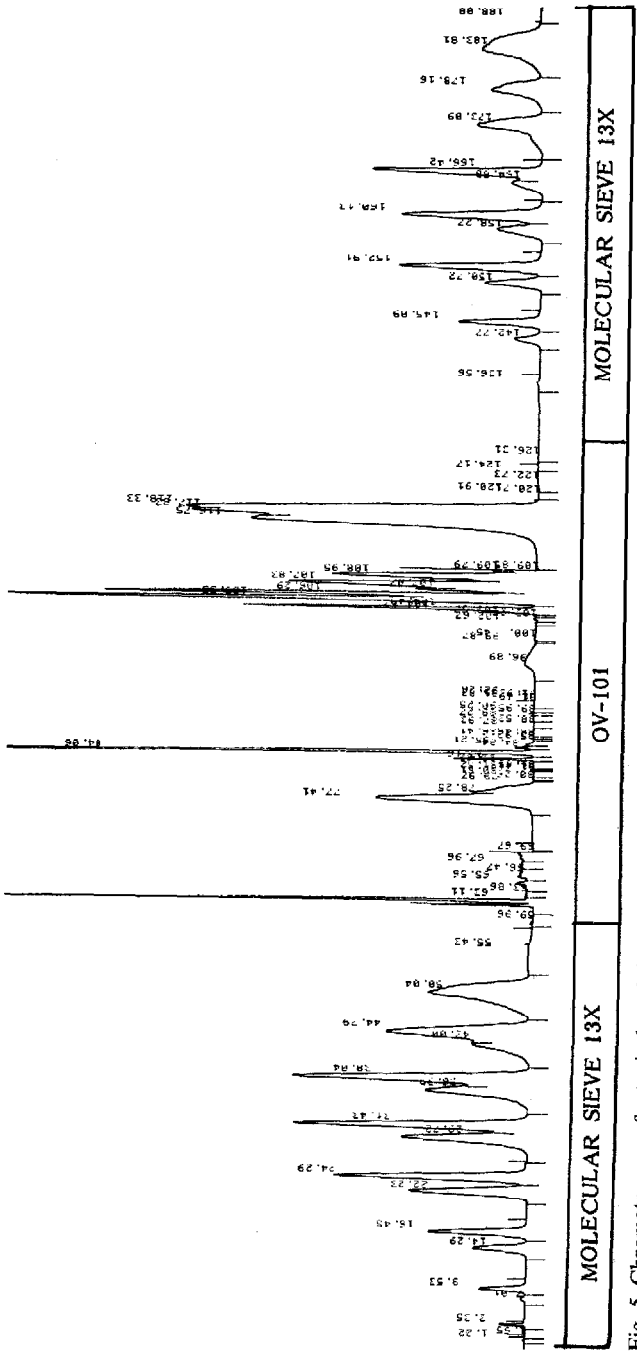

Fig. 5. Chromatogram of a typical naphtha analysis.

position was close to the actual sample composition, as determined by weighing (Tables II and III). Finally, Fig. 4 illustrates the analysis of a PONA reference sample and Fig. 5 illustrates the analysis of a typical naphtha sample.

CONCLUSIONS

The advantages of the multiple-column method presented in this paper are summarized below:

(1) Only one injection is required for each analysis.

(2) Reduced analysis times as compared to PONA analyses based on irreversible olefin traps are achieved. A typical PONA analysis now takes 3 h instead of 5 h.

(3) The analysis can now be performed completely automatically because the trap material does not have to be replaced.

(4) Accurate retention times can be obtained on the Molecular Sieve 13X column because water vapour is not needed for good trapping properties of the olefin trap (contrary to many other irreversible and reversible traps).

(5) The multiple-column PONA method enables group separation per carbon number without the need for identifying every single compound, in contrast to single-column capillary PONA analysis.

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