Note

Quantitative analysis of olefins in a light hydrocarbon mixture by bromination and gas chromatography using a methylsilicone column

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Because of their ability to polymerize over solid catalysts and adsorbents, olefins are undesirable impurities in many petrochemical feedstocks. The analysis of trace olefins in alkanes is an important procedure in the chemical laboratories of many petrochemical plants. The classical methods used to separate olefins are time-consuming, requiring long columns and the calculation of the bromine index[1]. The results obtained are somewhat uncertain because an average molecular weight must be assumed for the olefins in order to obtain their percentage from the bromine index. Furthermore, as the retention times of paraffins and olefins do not greatly differ, the small olefin peaks are usually overlapped by the larger paraffin signals. Thus, the accuracy of the analysis is impaired.

In the present note we report a fast, convenient technique for the separation of trace amounts ($< 0.5\%$, w/w) of olefins in light hydrocarbon cuts. This method includes bromination of the double bonds in the sample, followed by temperature-programmed chromatography. The technique has been tested with several solutions of olefins in alkanes. The results are promising.

EXPERIMENTAL

An Hewlett-Packard 5880A gas chromatograph equipped with a flame ionization detector and an on-column injection port was employed with nitrogen as the carrier gas. The column was fused silica (25 m × 0.2 mm I.D.) with methylsilicone (cross-linked phase, Ultra, Hewlett-Packard) as stationary phase. Both the injector and detector were kept at 200°C. Samples were injected with a 5-μl Hamilton syringe.

The reagents were sodium sulphite, bromine, carbon tetrachloride, n-hexane (olefin-free, confirmed by using the ASTM bromine index technique), n-hexane (technical grade, contaminated with alkanes and traces of alkenes) and a C_5–C_{11} paraffin

raffinate consisting of about 85%, w/w of C_5 and C_6 alkanes. A solution of bromine in carbon tetrachloride (*ca.* 0.25 mol/kg) was prepared to avoid handling liquid bromine.

Solutions containing between 0.05 and 0.4% (w/w) olefins in different alkanes were prepared for trial separations. A small portion (10 ml) of each solution was brominated with about the same volume of the bromine solution. The bromine added was always enough for the solution to remain pale yellow throughout the bromination. The solution was then kept in the dark for 10 min. This was essential to avoid photochemical reactions leading to bromination of the alkanes. After bromination, the excess of bromine was eliminated by adding 20 ml of saturated sodium sulphite solution and stirring for 1 min. Once the organic phase had separated, a 0.4-μl sample was injected into the gas chromatograph. In a typical experiment the oven was kept at 40°C for 6 min, then heated at a rate of 25°C/min to a final temperature of 130°C. The oven was kept at this temperature for 11 min. The complete experiment lasted about half an hour.

RESULTS AND DISCUSSION

For each group of olefins investigated (C_5 and C_6), the olefins brominated in positions 1,2 were the last to elute. Since 1,2-dibromopentane was eluted before any dibromohexane, separation of the two groups of peaks was simple. Although bromination of the double bond in branched olefins might result in the formation of enantiomeric pairs, these are not separable on a non-chiral column. Thus, the number of dibromoalkane peaks in our chromatograms should correspond to the number of olefins in our samples.

The results obtained are summarized in Table I. The response factor, F, was

TABLE I

RESPONSE FACTORS AND EFFECTIVE CARBON NUMBERS FOR C_5 AND C_6 OLEFINS

Values quoted for F are averages of five determinations. Deviations from the mean value were less than ± 0.01 in all cases.

Olefin	Solvent (%, w/w)	Olefin (%, w/w)	% area of dibromoalkane	Response factor, F	ECN
1-Hexene	n-Hexane (pure)	0.096	0.0866	0.90	5.40
1-Hexene	n-Hexane (pure)	0.360	0.323	0.90	5.40
1-Hexene	n-Hexane (technical)	0.160	0.145*	0.91	5.44
2-Methyl-1-pentene	C_5–C_{11}	0.122	0.110*	0.90	5.40
2-Methyl-1-butene	n-Hexane (pure)	0.013	0.0113	0.87	4.35
2-Methyl-1-butene	n-Hexane (technical)	0.075	0.066	0.88	4.40

* Overlapping of the dibromoalkane and an unidentified paraffin (probably C_{10} or C_{11}) peak. The area of the former was obtained by subtraction of the area of the unwanted peak.

calculated as the ratio of the percentage area under a dibromoalkane peak to the olefin content (%, w/w). The effective carbon number (ECN) is defined as nF, where n is the number of carbon atoms in the olefin. Very small amounts of monobromoalkanes (formed because of unavoidable exposure to light) may be eluted during the chromatography, but the area under their peaks is negligible compared with the dibromoalkane signals.

The experimental results show that, for the C_5 and C_6 olefins investigated, both the response factor and the effective carbon number depend only on the number of carbon atoms. Branched and linear olefins with the same number of carbon atoms exhibit the same values for F and ECN. This suggests that the response factor measured for one C_5 or C_6 olefin can be used for all C_5 or C_6 olefins.

It is obviously tempting to try to extrapolate our results to olefins with chain lengths other than C_5 and C_6. We note that, for the olefins investigated, bromination of the double bond reduces the effective carbon number by a constant factor equal to 0.6 units. Stenberg et al.[2] found that a variety of substituent groups reduce the ECN of a paraffin series by a constant factor. If those results hold for the dibromine substitution, the response factor for any dibromoalkane can be calculated as $F = (n - 0.6)/n$, where n is the number of atoms in the olefin.

We have employed the described technique to measure the olefin content in a petrochemical feedstock consisting of C_5–C_6 alkanes containing C_6 (mainly) and C_7 olefins. The olefin content determined in five samples was 2.66 ± 0.05% (w/w) olefins.

Research is currently underway in our laboratory to check the equation for F with a large number of olefins and to extend the technique to solutions containing higher percentages of heavier olefins.

CONCLUSIONS

We have presented a technique for the determination of olefins in light hydrocarbon cuts. The results obtained compare well with those from the classical bromine index technique. Our method is suitable for use in quality-control laboratories where a rapid analysis of olefins is required.

REFERENCES

1 *ASTM Standards, Bromine Index D-2710-77*, ASTM Committee D-2 Petroleum Products and Lubricants, Philadelphia, PA, 1977, Part 24, p. 604.
2 J. C. Stenberg, W. S. Gallaway and D. T. L. Jones, *Preprints, International Gas Chromatography Symposium, Lansing, MI, 1961*, pp. 159–184.