ELSEVIER

Journal of Chromatography A, 791 (1997) 197–202

JOURNAL OF CHROMATOGRAPHY A

Automatic gas chromatographic retention time matching applied to synthetic petroleum (Fischer-Tropsch) products, using HP Chemstation software

Kirk Snavely, Bala Subramaniam*

Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, KS 66045, USA

Received 21 April 1997; received in revised form 4 July 1997; accepted 9 July 1997

Abstract

Organic-phase liquid product of Fischer-Tropsch (FT) synthesis is analyzed in a GC and tentatively identified using Hewlett-Packard 3365 Chemstation data analysis software. The software matches retention times of peaks in a chromatogram to times listed in a calibration table. Five different tables are constructed using retention times obtained from the chromatography of standards as well as retention times calculated from temperature-programmed retention indices of gasoline compounds cited in the literature. From 57 to 77% of the approximately 90 peak identifications in an analysis are correct. The large number of compounds present in both the tables and in the FT sample hinders correct identification.

Keywords: Retention times; Petroleum products; Fischer-Tropsch prodcts

1. Introduction

Several manufacturers provide software for data acquisition, analysis and instrument control of gas chromatography. The software is typically capable of performing both qualitative and quantitative analysis of chromatograms. Qualitative analysis is based on retention time matching between peaks in the chromatogram and entries in a calibration table in the software. Retention indices, calculated from retention times or temperatures, have also been used for identification. Retention times and retention indices provide 'tentative' identification; positive identification requires the use of supplementary techniques such as GC–MS and GC–FT-IR which provide information about molecular structure. Retention data are used routinely for the reliable analysis of simple samples, such as water-borne pesticides [1].

The numerous peaks present in the chromatograms of complex hydrocarbon samples such as gasoline and Fischer-Tropsch (FT) synthesis products pose a challenge to proper identification when using retention data. Nevertheless, retention time matching has been used successfully to identify complex samples, and retention indices obtained for high resolution capillary columns have been suggested for use in 'tentative' identification of gasoline samples. Shiomi et al. [2] chromatographed naphtha and gasoline samples in a GC equipped with a single 50-m nonpolar capillary column and flame ionization

*Corresponding author.

0021-9673/97/$17.00
PII S0021-9673(97)00775-9

detection (FID). They identified 236 compounds in the premium gasoline sample with software ('PONA', Shimadzu) that matched absolute retention times and, for smaller peaks, matched relative retention times as well. Compound identity was verified by GC–MS, retention time matching to standards, and type discrimination by sulfonation trapping of unsaturates. Johansen et al. [3] used experimentally generated relative retention times for identification of compounds in a gasoline sample.

White et al. [4] measured temperature-programmed retention indices (I_P values) for 366 gasoline range compounds (C_1–C_{18}) in standards, using a Supelco Petrocol™ DH column, with excellent reproducibility. When White et al. applied their table to the qualitative analysis of a synthetic gasoline, they found good agreement between the tabulated and experimental I_P (an average absolute deviation of 0.31 index units, with a maximum deviation of 2.02 index units) and suggested that the tabulated I_P could be used for 'tentative' identification of compounds in gasoline and other samples, chromatographed using analytical conditions identical to theirs.

The success of others in using retention data to tentatively identify gasolines motivated the current investigation, which used the table of I_P of White et al. along with experimental data to construct calibration tables of retention times in the 3365 Chemstation software (Hewlett-Packard). The tables were subsequently used for the computer identification of peaks in an FT organic phase product chromatogram.

2. Conditions

2.1. Standards

The following standard mixtures, containing a total of 110 different compounds, were chromatographed: low boiling point calibration sample no. 2 (5080-8768) (Hewlett-Packard, San Fernando, CA, USA); qualitative reference reformate standard (4-8268), olefins mix (4-4589), and alcohols mix (lot no. LA-45540) (Supelco, Inc., Bellefonte, PA, USA). The four mixtures contained, respectively, C_5–C_{18} normal alkanes, C_5–C_9 normal and *iso*-alkanes, C_5–C_{10} 1-, 2-, and 3-alkenes, and C_1–C_8 primary, secondary and branched alcohols. Fischer-Tropsch (FT) organic phase product, provided by the University of Kentucky (USA), was chromatographed under the same conditions as the standards.

2.2. Apparatus

Chromatograms were generated using a 5890 Series II GC (Hewlett-Packard, Wilmington, DE, USA) configured with a Petrocol™ DH capillary column (100 m×0.250 mm, 0.5-μm film) (Supelco, Bellefonte, PA, USA) connected to a flame ionization detector (FID). This column is identical to that used by White et al. [4]. The industrial-grade helium used as carrier gas, obtained from Air Products and Chemical (Lenexa, KS, USA), flowed through a high-capacity gas purifier (2-3800, Supelco) prior to entering the GC. HP 3365 Series II Chemstation software (B.01.02) (Hewlett-Packard) was used for integration and peak identification as well as for control of the GC.

The analytical conditions used by White et al. [4] were employed, with an increase in the upper temperature limit from 220 to 275°C in order to elute C_{30} hydrocarbons present in the FT sample. The temperature was programmed from 30°C (0 min) to 275°C at 1°C/min. A column head pressure of 70 p.s.i.g. produced a carrier gas linear velocity of 31.5 cm/s at 30°C, identical to the velocity reported by White et al. [4]. Additional details may be obtained elsewhere [5].

3. Results and discussion

3.1. Experimental I_p

Experimental temperature-programmed retention indices were calculated for comparison to those of White et al. [4]. A database of retention times (t_R) was generated by chromatography of the standards. Peak identities in the resulting chromatograms were obtained by GC–MS (except for reformate), by retention time matching to simpler standards containing one or a few compounds, and (for alkene and reformate standards) by visual comparison to the vendors' chromatograms from nonpolar columns (which had identified peaks). The experimental and

vendor chromatograms were very similar in appearance. For the reformate standard, peaks identified in the vendor chromatogram which were very small and poorly resolved were not included in the study.

The t_R values were converted into retention temperatures (T_R) using the temperature program. Temperature-programmed retention indices, $I_P(x)$, were calculated using the following equation [6]:

$$I_P(x) = 100z + 100\frac{T_R(x) - T_R(z)}{T_R(z+1) - T_R(z)} \quad (1)$$

where x is a compound eluting between two normal alkanes with carbon numbers z and $z+1$ and $T_R(x)$ is the column temperature when x elutes from the column.

The experimental I_P were compared with tabulated I_P for compounds present in both the standards and the table of White et al. [4] (the table of White et al. did not include any oxygenates). In Fig. 1, the difference in I_P (ΔI_P = experimental I_P − White et al. I_P) is plotted against the I_P of White et al. Only normal alkanes were present in the standards below C_4 (400) and above C_{10} (1000). Hence, no I_P were calculated for these ranges. The average absolute difference between our I_P values and the tabulated I_P values from White et al. is 0.60 I_P units and the maximum absolute difference is 2.5. These deviations compare favorably with the inter-laboratory precision (1.0 and 1.2 average absolute deviation, 2.4 and 3.6 maximum absolute deviation) among the three laboratories employed in the research of White et al. The systematic deviation apparent in Fig. 1 (negative in this case) was also noted by White et al. The tabulated I_P values were generated in one of the laboratories. The I_P measured in the other two laboratories were on average one unit lower and one unit higher, respectively, than the tabulated I_P.

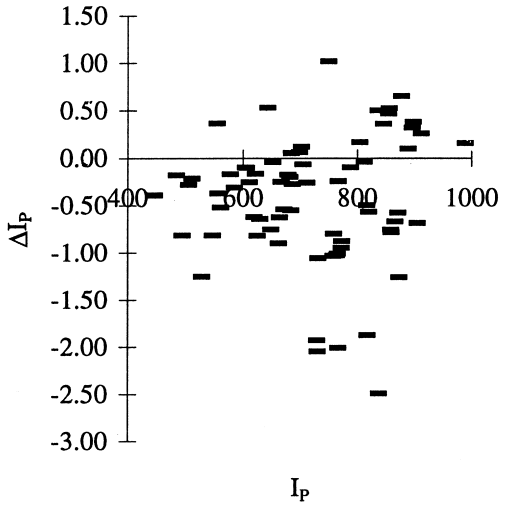

Fig. 1. Comparison of experimental and tabulated temperature-programmed retention indices (I_P).

Sixty-five out of the 70 deviations presented in Fig. 1 are less than 1.5 units, the maximum tolerance recommended by White et al. for use of their table in qualitative analysis of gasoline and other samples. The small difference in I_P also suggests that the peak identification of some of the standard peaks via visual matching was relatively accurate.

3.2. Performance of software

After confirming the reproducibility of the I_P, chromatograms of standards and UK (University of Kentucky) FT organic phase product were superimposed using Chemstation in order to visually determine which of the 110 standard compounds were present in the FT sample. (This procedure was analogous to the retention time matching performed by the software.) This set of compounds was referred to as 'common'. The rest of the FT sample chromatogram was labeled 'unknown'. It is noteworthy that the identities of the five major C_{12} peaks, obtained from manual identification of their spectra from a GC/MS scan of the FT product, agreed with the general fingerprint identities of the major peaks for the lower carbon numbers, obtained from matching to standards via superposition of chromatograms. Fig. 2 shows the 'fingerprint' pattern characteristic of the major peaks in the FT product at each C_{4+} carbon number, from an FID chromatogram. The primary alcohol in Fig. 2 is of carbon number *n*-3 (1-octanol in this case).

Five calibration tables as follows were created using the White et al. table of I_P and the database of experimental retention times.

(A) t_R calculated from tabulated I_P for all compounds present in the White et al. table; experimental t_R for compounds not present in the White et al. table (i.e. alcohols and some *iso*-alkanes).

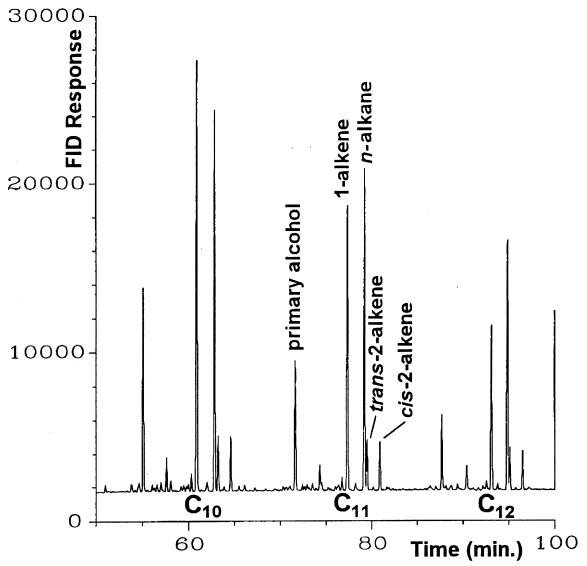

Fig. 2. Fingerprint compounds in FT product chromatogram.

(B) Calibration Table A with experimental t_R of the common compounds substituted for t_R calculated from tabulated I_P.

(C) Calibration Table A with dienes, cyclics and aromatics removed.

(D) Calibration Table B with dienes, cyclics and aromatics removed.

(E) Experimental t_R of the 110 standard compounds.

The contents of these calibration tables and their nomenclature are as follows. For Table A, the table of I_P from White et al. was first converted into a table of retention temperatures, using Eq. (1) and the experimentally determined T_R values for the C_5–C_{18} normal alkanes. The calculated T_R were then converted into t_R using the temperature program. While it is risky to eliminate the dienes, cyclics and aromatics from consideration (Tables C and D), these compounds were expected to be either absent from the FT product or else present in very small amounts [7]. In addition, this investigation was exploratory in nature and the goal was to maximize the accuracy of 'tentative' identification. The calibration tables were subsequently entered into separate methods in the Chemstation.

Following construction of the calibration tables, the performance of the Chemstation for the identification of the UK FT product was assessed by integrating the FT chromatogram using each of the five calibration tables, changing the reference compounds several times for calibration Tables A and B to improve identification. Integration is required to generate the retention times used for comparison to the times in the calibration table. In the calibration table, any entry can be identified as a reference compound. Reference compounds were chosen from prominent peaks in the chromatogram of the FT sample. When the Chemstation searches for a reference peak in the chromatogram, it chooses the largest peak within the time window centered on the retention time given in the calibration table.

Fig. 3 shows how the Chemstation uses the reference compounds with the calibration table to identify peaks. It first constructs an *XY* plot of the reference peak times (Fig. 3a). *X*, the retention time listed in the calibration table, is used to search for the reference compound peak in the integrated chromatogram. When this peak is found, its actual time is stored as *Y*. Then the *XY* points are connected by line segments and this segmented line is used to convert the non-reference peak times in the cali-

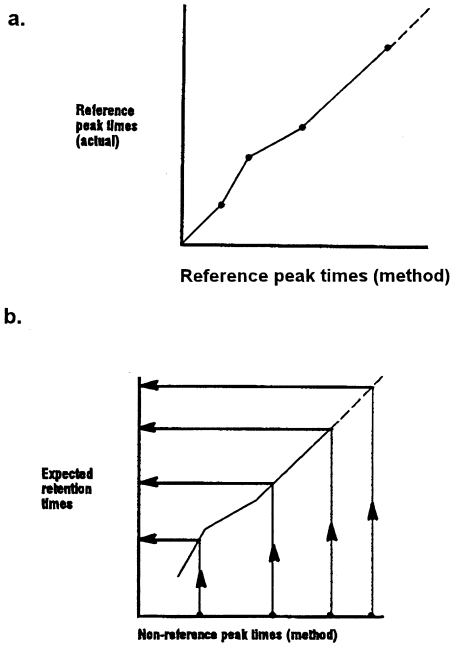

Fig. 3. Time correction process of Chemstation: (a) finding the reference peaks; (b) finding the non-reference peaks [8].

bration table into expected retention times (Fig. 3b), which are used to search for the remaining peaks. The system works better if reference peaks are chosen which bracket and span the chromatogram, thereby minimizing errors from extrapolation and interpolation.

The results of the integrations are given in Tables 1 and 2. These integrations used a time window of 5%; the results were similar for a time window of 2%. The letters in the first row of Tables 1 and 2 refer to the Chemstation calibration tables listed previously. The numbers in the row of column headings of A and B in Table 1 refer to individual integrations. Each numbered integration used a different set of reference compounds, as indicated by the variation in 'x' pattern from one numbered column to the next. The 'Reference Compounds' column contains compounds used as reference compounds in the calibration table (an 'x' in the row means the compounds in that row were used for reference for that integration). For each integration, all of the reference compounds were correctly identified.

Incorrectly identified compounds were placed into two categories. The row labeled 'Misidentified' refers to common peaks that were misidentified. The row labeled 'Not Present' refers to unknown peaks identified as standard compounds that were not common. In other words, the standard peak did not match any peak in the FT chromatogram when superimposed. As shown in Table 1, the FT sample was integrated four times with calibration Table A, using a different set of reference compounds each time. The '% Correct' in this case did improve from about 58 to roughly 68% when the reference compound switch from 1-alkene to *n*-alkane occurred at C_7 rather than at C_{11}. When the calibration table which had experimental t_R substituted for tabulated t_R was used for identification, integration results were not affected by the set of reference compounds chosen (compare integrations 1 and 2 of B in Table 1).

Variations in calibration tables and reference compounds did improve the performance of the Chemstation identification over a range from 57 to 77% correct. However, this improvement was still considered inadequate for use in identification. Two separate conclusions were drawn from this work. First, the large number of compounds present in the calibration tables tends to hinder correct identification. Often, the correct assignment for a misidentified compound was in an adjacent row of a table. Removal of dienes, cyclics and aromatics from the table reduced the number of misidentified com-

Table 1
Performance of Chemstation identification using complete I_P table

	A				B	
	1	2	3	4	1	2
Reference compounds						
Primary alcohol (C_1–C_8)	x		x		x	x
1-Alkene (C_5–C_6)			x	x	x	
n-Alkane (C_7–C_{17})			x	x	x	
1-Alkene (C_5–C_{10})	x	x				x
n-Alkane (C_{11}–C_{17})	x	x				x
Cis-2-alkene (C_5–C_9)	x	x				x
3-Methylhexane			x	x		
2-Methylheptane			x	x		
Ethylbenzene			x	x		
Identification						
Correct identification	50	53	60	61	59	61
Misidentified	24	23	15	16	12	14
Not present	13	14	13	12	14	13
Total	87	90	88	89	85	88
% correct	57	59	68	69	69	69
% not present	15	16	15	13	16	15

Table 2
Performance of Chemstation identification using partial I_P table and table containing only standard compounds

	C	D	E
Reference compounds			
Primary alcohol (C_1–C_8)	x	x	x
1-Alkene (C_5–C_6)	x		x
n-Alkane (C_7–C_{17})	x		x
1-Alkene (C_5–C_{10})		x	
n-Alkane (C_{11}–C_{17})		x	
Cis-2-alkene (C_5–C_9)		x	
3-Methylhexane	x		
2-Methylheptane	x		
Ethylbenzene	x		
Identification			
Correct identification	57	61	73
Misidentified	10	9	3
Not present	17	17	20
Total	84	87	95
% correct	68	70	77
% not present	20	20	20

pounds for the FT sample (compare 'Misidentified' results of C and D in Table 2 to those of A and B in Table 1).

Second, the large number of compounds present in the sample also obstructs proper identification. The table with the smallest number of compounds, Table E, consisting entirely of experimental t_R values, had the highest number of errors (20) involving identification of compounds known to be missing from the sample. When the Chemstation searches for a peak, it uses a window centered on the estimated retention time of the table compound. Even though the standard compound peak may not be present in the sample (no superposition of standard and sample chromatogram peak), with a complex sample such as FT product, there may still be a large number of peaks in the window to choose from.

A calibration table was subsequently created in Chemstation for use in our laboratory which provided reliable identification of the major compounds in the FT product. The table included most of the compounds eluting before hexane and the fingerprint compounds (the five major peaks at each carbon number, see Fig. 2) eluting after hexane. The region of the chromatogram eluting before hexane contained relatively few peaks (23 peaks) compared to the rest of the chromatogram and hence did not hinder peak identification due to its complexity. At each carbon number for C_{7+}, two of the five major peaks (primary alcohol and 1-alkene) were chosen as reference peaks in the table. Since these peaks were relatively large, they were successfully identified as reference peaks by the software. The regular spacing between them aided in the correct identification of the other three fingerprint compounds at each carbon number.

4. Conclusion

Retention time matching via Chemstation chromatography software does not produce reliable 'tentative' identification of a majority of the products of Fischer-Tropsch synthesis. In the current investigation, accurate qualitative analysis is hindered by one or both of two factors. The large number of compounds necessarily present in the calibration table of the software creates the potential for incorrect matching to entries adjacent to the correct entry. Conversely, the large number of compounds present in the complex sample creates the potential for matching to compounds present in the table but not in the sample, as the program searches the numerous peaks within a window centered at the retention time of the table entry. A simpler calibration table which produced accurate identification of the major peaks in the FT product was subsequently created.

The success of Shiomi et al. [2] in identifying gasoline and naphtha might be due to the use of relative retention times for small peaks or to the difference in sample. Perhaps the tabulated I_p of White et al. [4] would work with software that converted retention times to retention indices, then matched these to the tabulated I_p. However, when converted to retention times and used with the HP 3365 Chemstation software, the tabulated I_p do not provide accurate 'tentative' identification of FT product.

Acknowledgments

The financial support of the Department of Energy (Grant DE-FG22-92PC92532) is gratefully acknowledged. In addition, we are grateful to Dr. B.H. Davis (University of Kentucky Center for Applied Research) for providing us with FT product samples.

References

[1] M.A.H. Franson (Managing Editor), Organochlorine pesticides (6630)/liquid-liquid extraction GC method, in: Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC, 1995, Part 6000, p. 114.
[2] K. Shiomi, M. Shimono, H. Arimoto, S. Takahashi, J. High Resolut. Chromtogr. 14 (1991) 729.
[3] N.G. Johansen, L.S. Ettre, R.L. Miller, J. Chromatogr. 256 (1983) 393.
[4] C.M. White, J. Hackett, R.R. Anderson, S. Kail, P.S. Spock, J. High Resolut. Chromtogr. 15 (1992) 105.
[5] W.K. Snavely, M.S. Thesis, University of Kansas, 1996.
[6] M.L. Lee, F.J. Yang, K.D. Bartle, Open Tubular Column Gas Chromatography, John Wiley & Sons, New York, 1984.
[7] J. P Hackett, G.A. Gibbon, J.A. Feldman, J. Chromatogr. Sci. 23 (1985) 285.
[8] HP 3365 Series II Chemstation (DOS Series), Reference Manual Volume II, Part No. G1202-90200, Hewlett-Packard, USA, 1992.