PONA Analysis on GSBP-PONA Column

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1. Introduction

Gasoline, either naphtha, cracked or reformulated, contains large number of hydrocarbons including isomers. Because of complex compositions, the analysis of individual components is a challenging technique. ASTM D 5374 and D5374-92 give methods of detailed hydrocarbon analysis (DHA) for gasoline and other petrochemical applications. This specified DHA is done on high resolution capillary column, a 100% poly(dimethylsiloxane) column. Because of its specifically important role in DHA, this column is often called PONA column. Common PONA columns are either 0.20mm x 50m x 0.5um or 0.25mm x 100m x 0.5um.

Various software and methods have been developed for such PONA and DHA applications. There are two techniques for these applications. One is based on multi-dimensional GC, and other is based on high resolution chromatography. Both techniques use retention times of individual hydrocarbons to identify and quantify each composite separated. As the number of the composites of a gasoline can be as many as 500, the peak identification becomes very difficult and is very critical step for DHA. Often peak identification can be errant. Intensive labor effort is then taken to manually correct errors in peak identification.

Among various softwares for ASTM D5134, the software called PONA developed by Beijing Chromtech Institute uses an algorithm of retention index to identify peaks. Because retention index is relatively insensitive to the variations from columns, instruments and methods, this software is able to automatically and correctly identify each peak with great confidence. Even though this algorithm improves accuracy of peak identification, it still requires minimum variations in column dimension, column retention time, column efficiency and column selectivity.

This application note describes a FCC gasoline application on an GSBP-PONA column. This GSBP-PONA column replicates the performances of HP-PONA column, an industrial fleet column, including column selectivity, column dimension and retentions. Under the same instrumentation condition, the software PONA produces the same result as the one obtained from an HP-PONA column for this application.

2. Experimental

2.1 Column:

The column used is an GSBP-PONA column, 0.20mm x 50m x 0.5um, coated with GsBP-1 stationary phase, part number 9002-PONA, obtained from GS-Tek Inc., Newark, DE 19713, USA. The column temperature limits are -60C to 325/350C. Prior to each run, column was conditioned at 280C for 4hr.

2.2 Instrumentation conditions:

Instrumentation conditions are listed in Table I.

Table I the instrumentation conditions

Gas Chromatography	Agilent 6890 GC with ALS
Raw date acquisition	HP-Chemstation
Inlet	250C, s/s, split flow 140ml/min
Carrier	Nitrogen
Column head pressure	99kpa varied
Detector	FID, 300C
Oven	35C 10min, 0.5C/min to 60C, 2C/min to 180C, 10+min
Sample	A FCC gasoline sample
Injection	1ul

2.3 Column retention time calibration

Constant pressure mode was used for carrier flow. Column head pressure was adjusted to have n-Pentane retention time around 9.75+-0.1min as holdup time prior to sample injection.

For a comparison, the analysis was repeated on an HP-PONA column at the same instrumentation conditions.

3. Software

3.1 DHA and PONA analysis

PONA software from Beijing Chromtech Institute, Beijing, China was used in a PC with OS Microsoft 95 or above. It uses the following formula (1) to calculate the retention index of all individual peaks.

$$RIi = ((RTi-Rtref\_Cn)/(Rtref\_Cn+1-Rtref\_Cn) + Cn) * 100 \qquad (1)$$

RIi： Retention index of composite i
RTi： Retention time of composite i
Cn ： Reference peak of carbon n
Cn+1： Reference peak of carbon n+1
Rtref_Cn ：Retention time of reference peak Cn
Rtref_Cn+1：Retention time of reference peak Cn+1

Retention time of reference peaks can be searched automatically based on empirical database built-in the PONA software

3.2 Calculation of Octane Number:

Two octane values defined by RON and MON are calculated as

$$RON = Cr + Fr \sum_{i=1}^{i=N} Ai\ Wi \qquad (2)$$

$$MON = Cm + Fm \sum_{i=1}^{i=N} Bi\ Wi \qquad (3)$$

Cr : given constant, RON
Fr : given correlation factor, ROM
Cm : given constant, MON
Fm : given correlation factor, MON
Ai : correlation coefficient of i^{th} hydrocarbon, RON, listed in calibration table
Bi : correlation coefficient of i^{th} hydrocarbon, MON, listed in calibration table
Wi : weight percentage of i^{th} , measured by DHA
N : total number of peaks measured by DHA

3.3 Calculation of Carbon/Hydrogen（C:H）ratio:

$$C{:}H = \sum_{i=1}^{i=N} (C{:}H)i\ Wi \qquad (4)$$

(C:H)i : Carbon/Hydrogen of i^{th} hydrocarbon
Wi : weight percentage of i^{th} , measured by DHA
N : total number of peaks measured by DHA

3.4 Calculation of Specific Gravity (D):

$$D = \sum_{i=1}^{i=N} Di\ Wi \qquad (5)$$

Di : Specific Gravity of i^{th} hydrocarbon
Wi : Weight percentage of i^{th} , measured by DHA
N : Total number of peaks measured by DHA

3.5 Data Analysis：

Once the separation of each composite in a gasoline sample is completed, the raw data of DHA was generated by HP Chemstation or similar data acquisition software. The raw data includes peak retention time, area and/or area percentage. The file format of the raw data file used in this PONA software is .D.

After completion of the chromatography run, the PONA reads the raw data file, and automatically identify the reference peaks (as many as to 13) from assigned one of three databases for three types of gasoline. Manual correction of the reference peaks is only as needed for the first run. Once the reference peaks are correctly identified, the software can automatically calculate all physically and chemically values described in 3.1 to 3.4. The report file can be either printed or transferred for a customized report.

4. Result

Fig 1 shows the comparable chromatograms of a FCC gasoline sample on GSBP-PONA and HP-PONA columns. It is clearly that the GSBP-PONA exhibits a small retention time difference from the HP-PONA column, however, the peak elution order and relative peak height ratios are essentially same. Even for this retention time difference, the PONA software is able to identify all peaks in both chromatograms. The physical properties calculated are listed in table II for the results from two PONA columns.

Table II Calculated physical properties

Column	GSBP-PONA	HP-PONA
No. of peaks identified	300	301
Calculated RON	87.26	87.15
Calculated MON	78.18	78.07
C:H	7.33	7.34
Specific density	0.8064	0.8062

All other calculated values are listed in the table III.

Table III PONA analysis report of a FCC gasoline sample

PONA Columns	GsBP	HP	GsBP	HP
Compositions	Wt%	Wt%	V %	V %
P (Normal Paraffin)	3.29	3.28	3.68	3.67
I (Iso Paraffin)	25.81	25.69	28.37	28.20
O (Olefin)	9.14	9.40	10.08	10.40
N (Naphtha)	15.74	15.72	16.20	16.19
A (Aromatic)	46.02	45.91	41.67	41.54

5. Conclusion

Based on the above results and same instrumentation conditions used, it can conclude that both GSBP-PONA and HP-PONA are essential identical. GSBP-PONA column has produced almost same result as HP-PONA has.

6. Order Guild

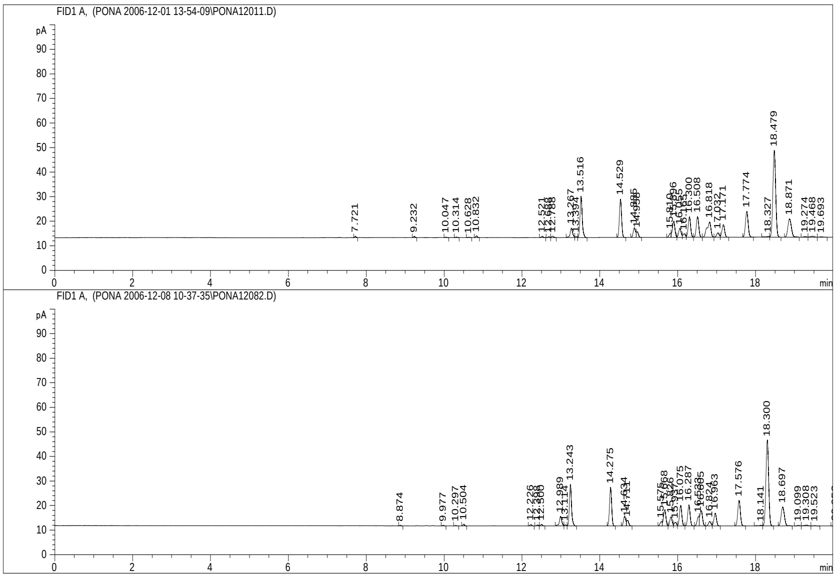
Table IV lists the suggested parts for PONA application.

Table IV Suggested parts for PONA analysis

Item	Description	P/N
1	PONA software	9001-PONA
2	GSBP-PONA	9002-PONA
3	Gasoline Reference Sample, 1ml	9003-PONA

7. Other applications of GSBP-PONA column

The other applications of GSBP-PONA column would be the separations of natural gas, pesticides, and VOC.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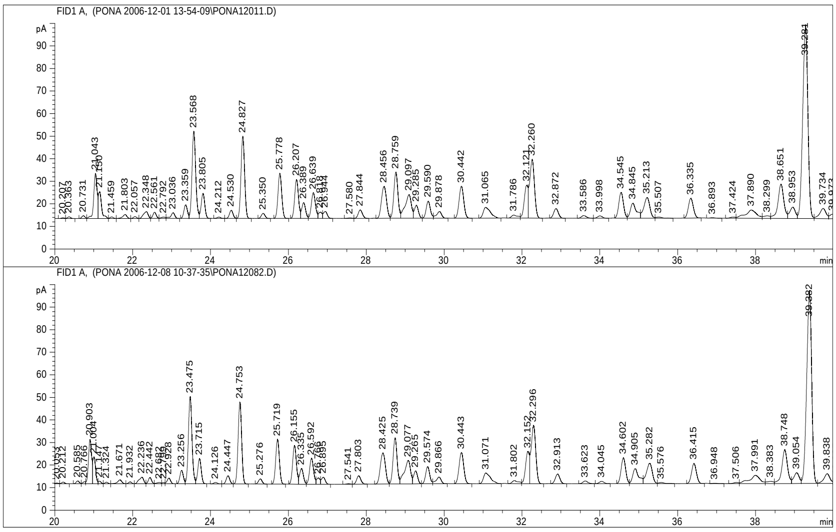
FID1 A, (PONA 2006-12-08 10-37-35\PONA12082.D)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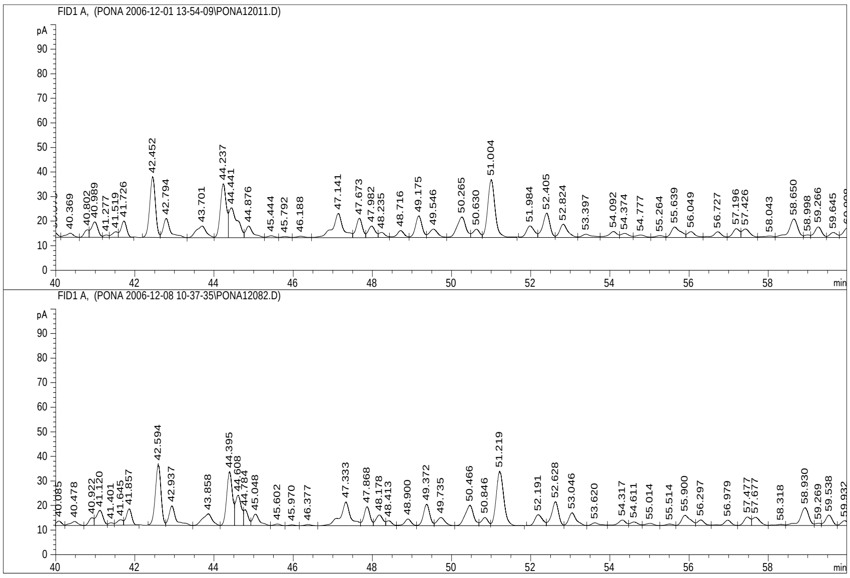
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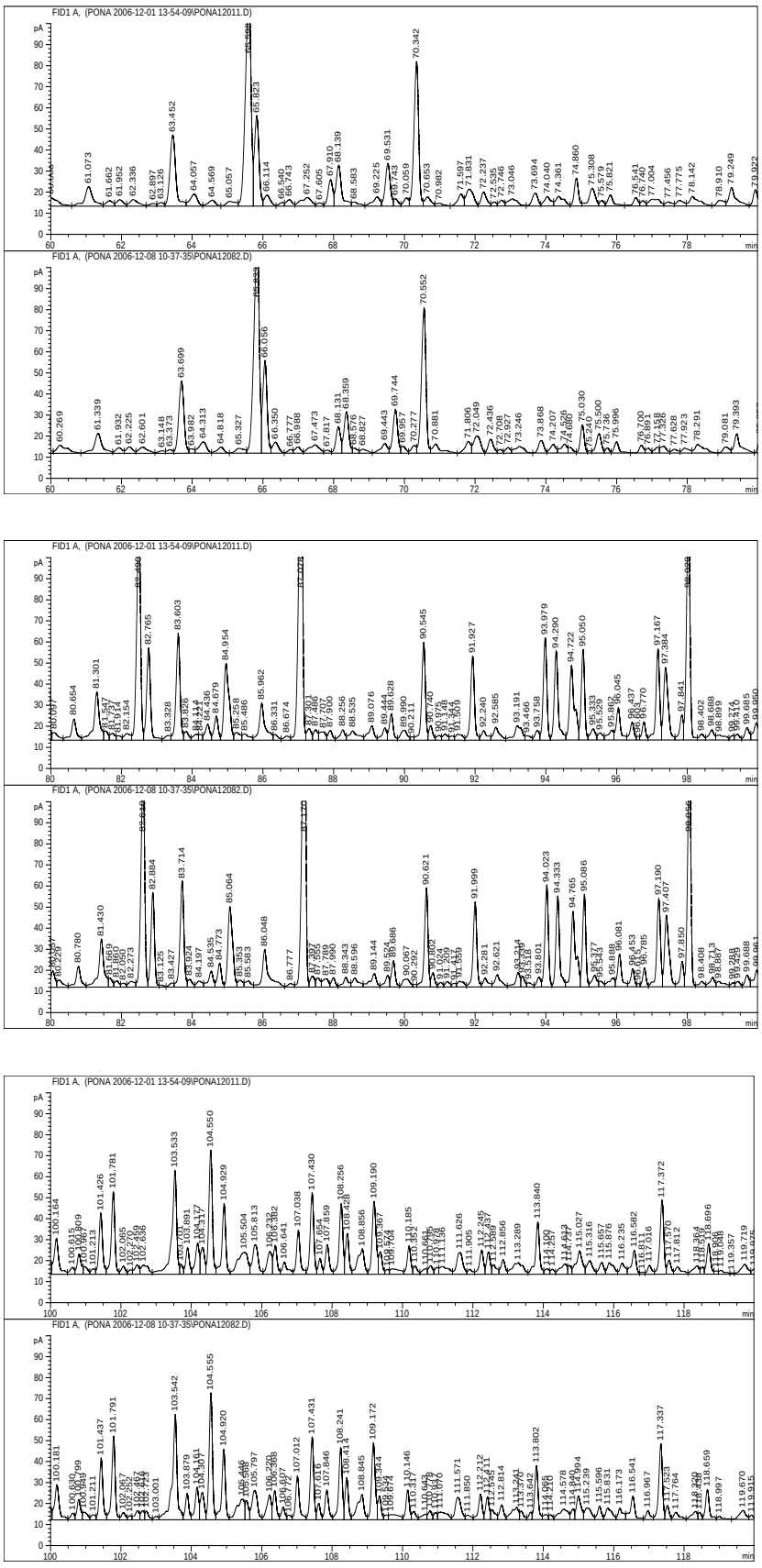

Fig. 1, Chromatograms of a FCC gasoline sample on an GSBP-PONA column and an HP-PONA column. Top, GSBP-PONA; bottom, HP-PONA. Instrumentation condition is shown in Table I.