GAS CHROMATOGRAPHIC PREDICTION OF POLY-AROMATICS RETENTION INDICES IN PETROLEUM CRUDE OIL SAMPLE BASED ON RETENTION INDICES MATCHING

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Abstract

Gas chromatographic prediction of poly-aromatics retention indices in a petroleum crude oil based on matching with reported retention indices on the same stationary phases under a similar temperature program was studied. The bases of the matching with reported retention indices for peaks identifications were mentioned. Deconvulated software was used to separate the overlapped poly-aromatic peaks.

Keywords: Poly-aromatics; Gas chromatography; retention indices; deconvulated software.

1. Introduction

In a petroleum crude oil sample, the problem of identification of individual isomers is generally related to their multi-componentity on one hand, and the lack of standard reference materials on the other hand. Moreover, the calculation methods for retention indices using molecular structure descriptors, quantum chemical, connectivity and topological parameters [1-4] as well as most recently published papers on using accurate quantitative structure relationship of these isomers by projection pursuit [5] and semi-empirical topological method [6] are not accurate enough for identification. Furthermore, numbers of published methods have been concerned in poly-aromatics identifications. [7-9]

Kovats retention index, which has been widely used, is an important parameter in isothermal and programmed GC. Studies on retention index have been fully reviewed by several authors. [10-12] The identifications based on Kovats retention indices matching not only for the same column under the same conditions [13] but also for the same stationary phase under similar conditions were reported as a more accurate method. [14] It is clearly possible to acquire Kovats retention indices from data obtained under temperature programmed conditions and to apply these data in qualitative analysis. Moreover, it is easier to recognize peaks on chromatograms acquired at two linear temperature programs than at different isothermal temperatures. [14] The aim of the present work is to predict the retention times of some poly-aromatics in petroleum crude oil sample based on matching with the reported retention indices for these compounds on the same stationary phase and similar or the same column under a similar operating conditions as a more accurate prediction method than many of the published methods based on molecular descriptors. To overcome on limited resolution power of the given capillary a deconvulation software was used to separate the overlapped peaks of the investigated compounds.

2. Experimental

Perkin-Elmer Claurs 500 equipped with FID detector and split type injector was used for the analysis. Injection was performed manually. Data handling was carried out by Perkin-Elmer Total Chrom software. To achieve the target crude oil analysis in one GC running; separation was preformed on a 60 m x 0.25 μm x 0.32 I.D. 100% poly-dimethyl-siloxane fused silica column (Rtx-1). Helium was employed as carrier gas at a flow rate of about 2 ml/min. One ramp temperature program was used; the column oven temperature was at 80 ºC and raised at 5 ºC/min. to 300 ºC and held for

50 min. the injector and detector temperatures are maintained at 320 ºC and 0.1 µl sample size is injected with split ratio 50:1. Crude oil sample is provided by AGIBA Co. - Egypt. Its chromatographic analysis is shown in Fig.1.
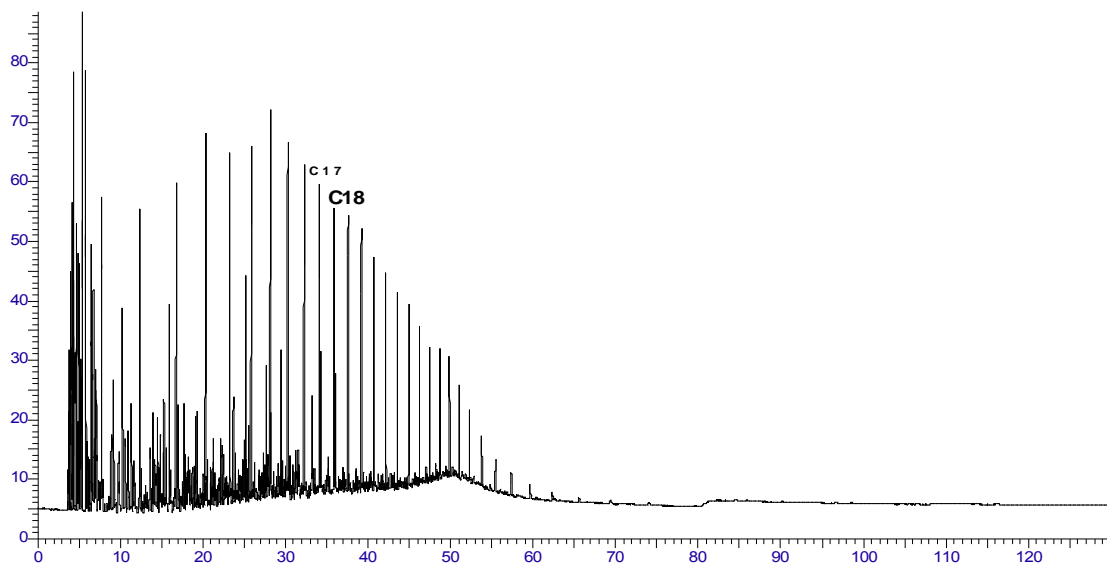

Fig. 1: The chromatogram of the investigated AGIBA crude oil.

3. Results and discussions

The identification of the investigated poly-aromatics (Fig. 2) in the given crude oil sample by the matching with the reported Kovats retention indices on the same stationary phase under similar conditions based on the following pervious reported results:
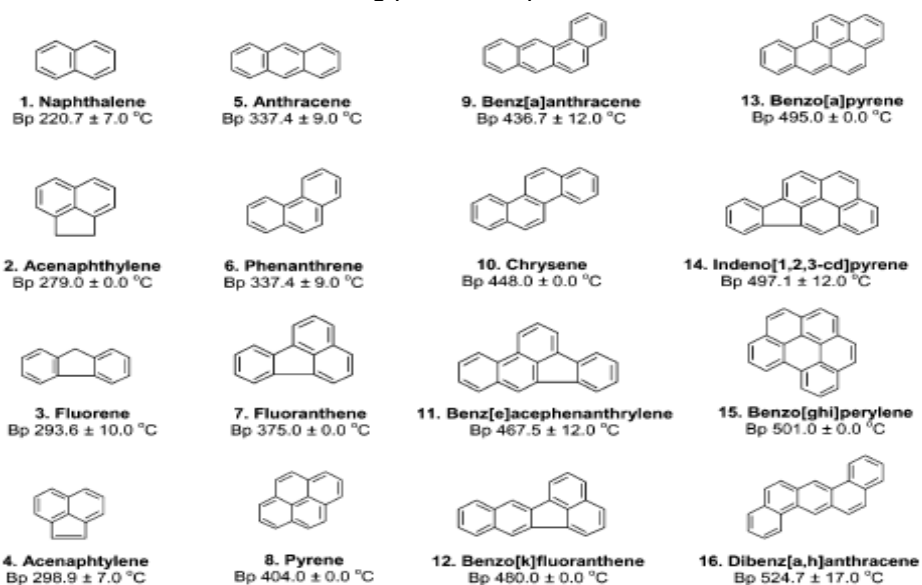

Fig. 2: the structure and boiling point of the investigated poly-aromatics.

(i) From the point of view of quantitative structure–activity/property relationship (QSAR/QSPR) model, e.g. a molecular electronegativity–distance vector (MEDV) [7] , which based on the activity of the eluant with respect to the stationary phase, for the same stationary phases under two different temperature programs, it is expected that MLR derived equation has the same constants. This means that the derived QSAR equation for the poly-dimethyl-siloxane stationary phase under temperature program of Dumitrescu, Buda, et al. [15] can be used in the prediction the retention indices on the same used Rtx-1 100% poly-dimethyl-siloxane stationary under similar or the same temperature program.

(ii) Chen et al. [14] used a Qbasic-designed software based on integration procedure for the prediction of retention indices from data determined under various temperature conditions in GC. They were obtained similar values for Kovats retention indices under different temperature programs on OV-101

stationary phase. Taking into consideration the calculation procedure was based on two thermodynamic constants characterizes for the OV-101 stationary phase.

(iii) The calculated retention index under different temperature programming conditions is almost unaffected by operating parameter and column size. For conformation, table 1 shows the retention indices of naphthalene on some reported stationary phases. These stationary phases have the same composition 100% poly-dimethysiloxane but under different temperature programs and column dimensions with H_2 and He as carrier gases. It can be observed that, the retention index of naphthalene ranges from 1150-1159 on the reported capillaries regardless to the column length, diameter, the type of the carrier gas and the different one ramp temperature programs. The most similar program for the used is that on OV-1 [15] and SE-52 [16] as shown in table 1. Accordingly, the obtained retention indices values for the poly-aromatics on this OV-1 column [15] (table 2) were used for matching-identifications of these compounds on the employed 100% poly-dimethyl-polysiloxane Rtx-1 60 m x 0.25 μm x 0.32 mm ID.

Table 1 Kovats retention indices for naphthalene on some reported non-polar poly-dimehyl-siloxane capillary columns [19]

	Ret. Index	Column
OV-1	1159	Column: 50 m x 0.25 μm; carrier gas H_2; temperature program T_{start}: 100°C; at 4°C/min: T_{end}: 275°C. [15]
OV-1	1150	Column: 50 m x 0.25 μm; carrier gas H_2 ; temperature program: T_{start}: 80°C; at 5°C /min. T_{end}: 275°C. [15]
OV-1	1155.1	Column: 50 m x 0.2 mm; temperature program: 35°C at 5.min; T_{end}: 280°C. [15]
DB-1	1157	Column: 60 m x 0.32 mm x 0.25 μm; Carrier gas He. temperature program 35°C at 4°C/min, 2°C/min, 230°C at 25 min. [20]
DB-1	1153	Column: 50 m x 0.32 mm; temperature program: T_{start}: 50°C; 3°C/min T_{end}: 250°C. [20]
DB-1	1155	Column: 50 m x 0.32 mm; temperature program: T_{start}: 50°C; 3 C/min T_{end}: 250°C. [21]
OV-101	1159	Column: 50m x 0.32 mm; temperature program: 50°C at 0.1 min, 4°C/min, 225°C at 30 min. [22]
OV-101	1156	Column: 110 m x0.25 mmx0.20 μm; carrier gas He; temperature program: 1°C/min; T_{start}: 35°C; T_{end}: 200°C. [22]
DB-1	1155.	Column: 60. m x 0.32 mm; carrier gas He; temperature program: 50°C at 0.1 min, 4 °C/min, 250°C at 5 min. [23]
OV-1	1157.1	Column: 30 m x 0.3 mm x 1.1 μm; temperature program: 35°C at 5 min, 4°C/min.T_{end}: 250°C. [24]
OV-1	1157	Column: 24m x 0.3 mm x 1.1 μm; temperature program: 35°C at 5 min, 4°C/min; T_{end}: 250°C. [24]
SE-30	1159	Column: 50 m/ 0.5 mm. He; temperature program: 40°C at 3 min, 3K/min;; T_{end}: 170°C. [25]
Methyl-Silicone	1158	Column: 30 m x 0.32 mm x 0.25 μm; carrier gas He; temperature program: 60°C at 2 min, 2°C/min, 250°C at 5 min. [25]
SPB-1	1156	Column: 60m/0.25 mm/0.25 μm; carrier gas He; Temperature program: 35 °C at 10. min. 2 °C/min, 235°C at 40 min. [26]
SE-52*	1150	Column: 65. m x: 0.3 mm; carrier gas N_2; Temperature program: T_{start}: 100°C; at 1.8 C/min till T_{end}: 300°C [16]

Table 2 Kovats retention indices for poly-aromatics on reported OV-1 capillary column under one ramp temperature program. [15]

Compound	Ret. index	Compound	Ret. index
Anthracene	1709[a]	Chrysene	2323
	1709[b]		2333
Acenaphthylene	1402	Benz[e]acephenathrylene	2609
	1395		2600
Flourene	1522	Benzo[k]flouranthene	2605
	1525		2615
Acenaphthene	1429	Benzo[a]pyrene	2679
	1434		2668
Phenathrene	1700	Indeno[1,2,3-cd]pyrene	2910
	1700		2920
Fluoranthene	1960	Benzo[ghi]perylene	2959
	1954		2969
Pyrene	2000	Diben[a,h]anthracene	2916
	2000		2927
Benzo[a]anthrathene	2327		
	2317		

[a] *H2; Phase thickness: 0.25 μm; Tstart: 80°C at 5 C/min ; Tend: 275°C*, [b] *H2; Phase thickness: 0.25 μm; Tstart: 100°C; at 4 C/min Tend: 275°C*

The detailed analysis of petroleum mixture is a very difficult task and required for special gas chromatographic configuration and software. Resolution capability of chromatographic capillaries columns is limited even with longer capillary column. The separations suffer from a considerable numbers, even with n-alkanes, of overlapping which effect on quantitative and qualitative analysis. It frequently happens that the best separation still does not allow a satisfactory detection and quantisation of all components. Accordingly, a commercial Peak Fitting Module software [17] was used for deconvolution of single peak data for peaks overlaps. The procedure and the operation steps of PFM have been reported. [18] The theoretically identified deconvulated poly-aromatic compounds are shown in chromatograms Figs. 3-9.
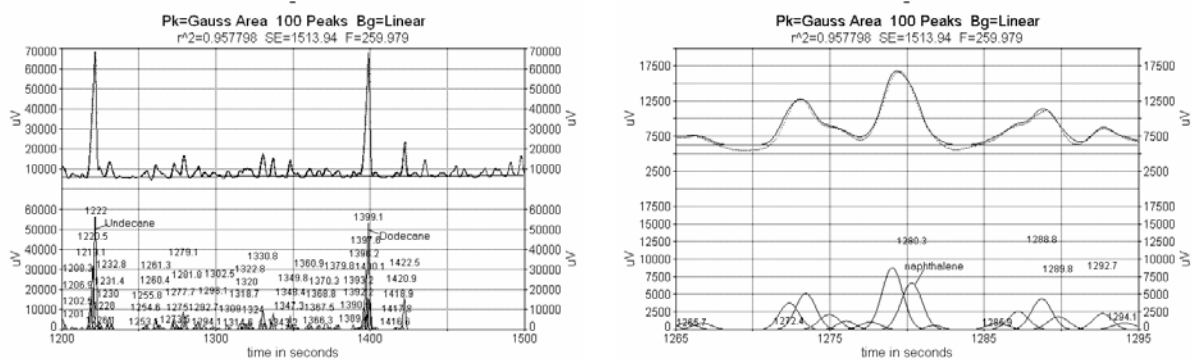

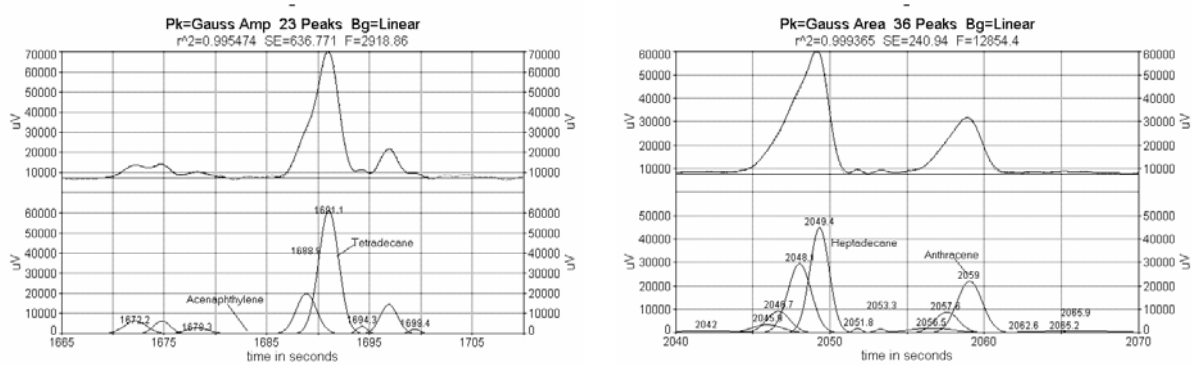Fig.3: The deconvulated chromatogram for the theoretically identified naphthalene.

Fig. 4: The deconvulated chromatogram for the theoretically identified acenaphthylene and anthracene.
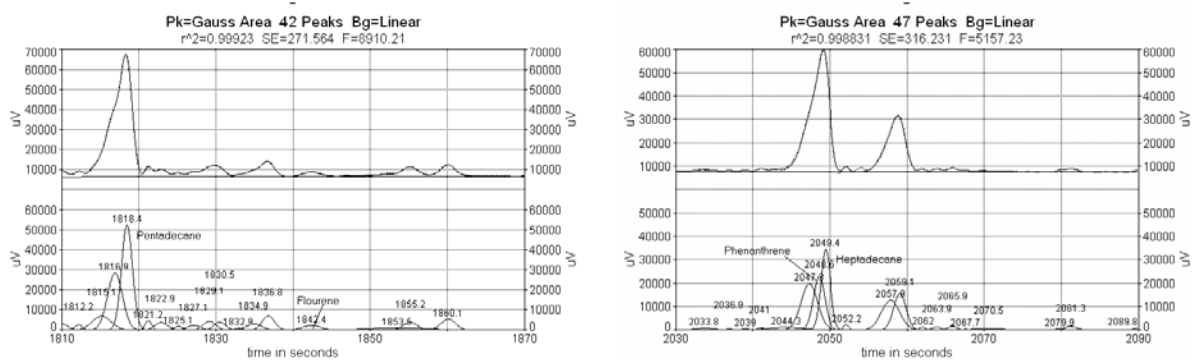

Fig. 5: The deconvulated chromatogram for the theoretically identified flourene and phenanthracene.
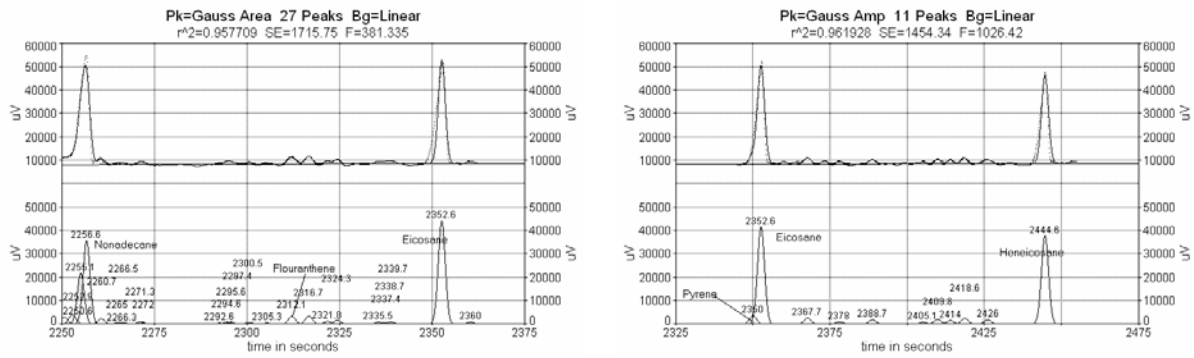
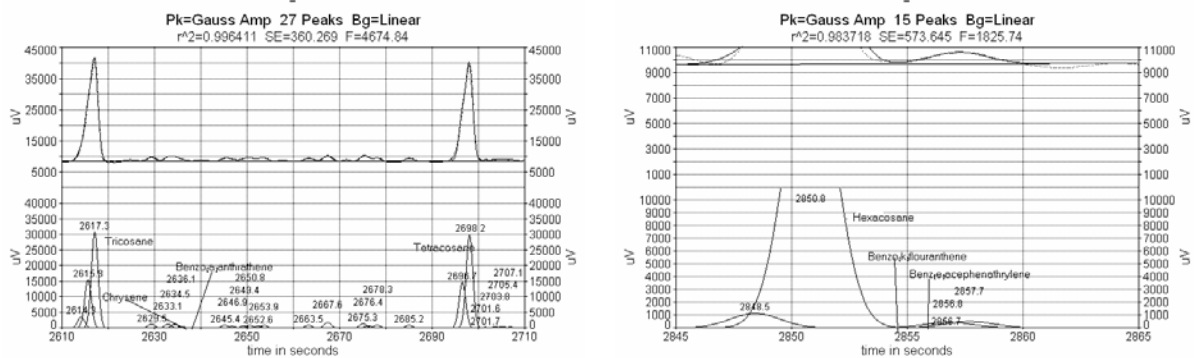Fig. 6: The deconvulated chromatogram for the theoretically identified flour-anthene and pyrene.

Fig. 7: The deconvulated chromatogram for the theoretically identified four poly-aromatics members.
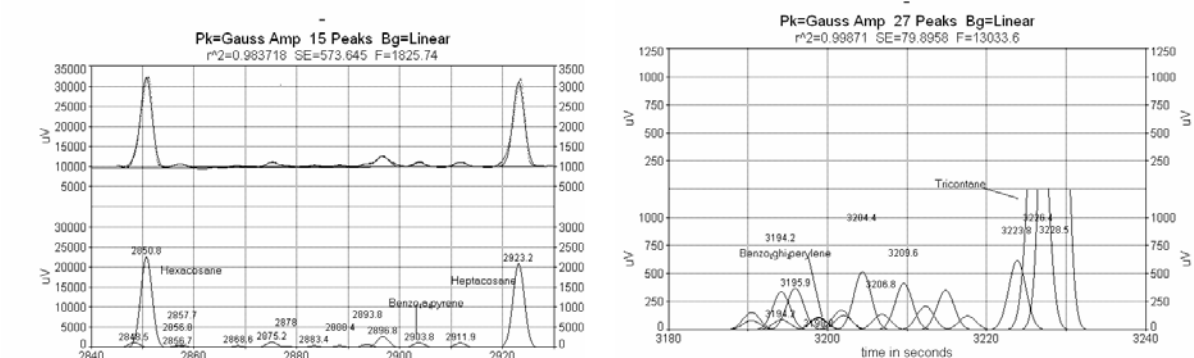

Fig. 8: The deconvulated chromatogram for the theoretically identified benzo[a] pyrene and benzo[ghi] perylene.
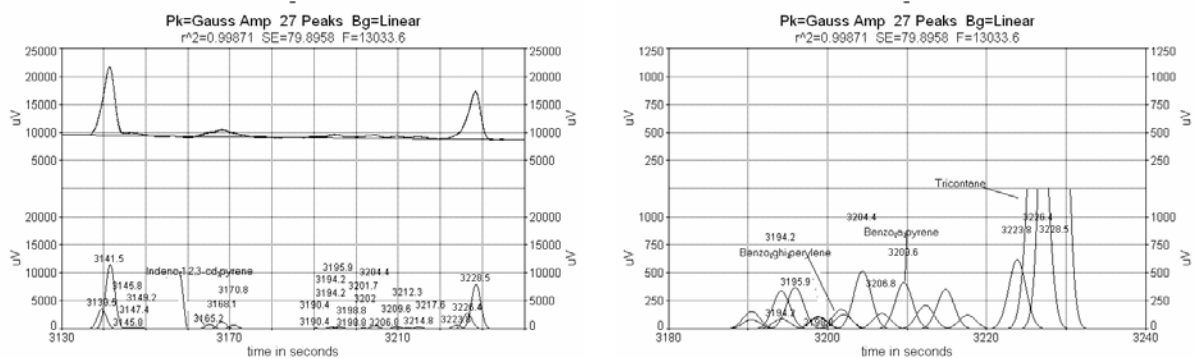

Fig. 9: The deconvulated chromatogram for the theoretically identified three polyaromatics members

4. Conclusions

The identifications based on matching with the reported Kovats retention indices on the same stationary phase under the same or a similar gas chromatographic programming conditions were used for prediction of Kovats retention indices of well separated poly-aromatics peaks in petroleum crude oil sample. The used identified method was confirmed by the previously reported results.

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