

# Gas Chromatographic Analysis of Petroleum Associated Condensate Oil with Simultaneous Determination of Some Characteristic Physical Parameters

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## Abstract

A method is developed for the analysis of associated condensate by capillary gas chromatography (GC) with simultaneous determination of its major physical characteristic parameters. The method aims at the qualitative and quantitative determination of C<sub>2</sub>–C<sub>36</sub> alkanes, methylcyclopentane, cyclohexane, methylcyclohexane, benzene, toluene, ethylbenzene, xylenes, and 1,2,4-trimethylbenzene. This composition is according to the petroleum companies demand. The method is used for the simultaneous determination of the condensate average molecular weight, density, carbon-to-hydrogen ratio, and boiling range. The data obtained by the method has a good agreement with those obtained by other methods. The literature methods cited later used a simulated distillation method to obtain the hydrocarbon distribution spectrum of the given condensate sample. The obtained results revealed that the GC capillary method used is most rapid and accurate for achieving the demanded analytical report.

## Introduction

Condensate oil is a petroleum fraction associated with a gasometer natural gas sampling for gas chromatography (GC) analysis in PVT studies of condensates. It is composed mainly of natural occurring hydrocarbons, which are grouped into paraffins (P), naphthenes (N), and aromatics (A). The Petroleum Companies demanded analysis is for paraffins, C<sub>1</sub>–C<sub>36</sub>; for naphthenes, methylcyclopentane, cyclohexane, and methylcyclohexane; and for aromatics, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, and 1,2,4-TMB. The analysis demanded not only involves quantitative determination of the sample components, but also some characteristic physical properties such as average molecular weight (M), density (d<sup>20</sup>), boiling point range, volatility, carbon to hydrogen ratio (C/H), and other characteristics.

The capillary gas chromatography (CGC) (1) method for hydrocarbon analysis can provide quantitative data for the condensate individuals that are the basis for calculating its characteristic physical parameters. The CGC method for hydrocarbon

analysis is not a new technique. But the CGC method is mainly used to determine the chemical groups and individual hydrocarbons, and it is rarely utilized to simultaneously obtain more characteristic parameters, which are determined by using conventional techniques. Most of these methods are not for routine analysis due to time constraints, unreliable quantitative data, and high cost instruments, and they are unable to obtain other parameters. Other analytical methods used for quantitative determination of individuals and/or chemical group type composition of complex hydrocarbon mixture are the fluorescent indicator adsorption method (2), mass spectrometry (3), GC–mass spectrometry (4–6), infrared spectroscopy (7–9), nuclear magnetic resonance (10–12), high-performance liquid chromatography (13,14), supercritical fluid chromatography (15,16), and multidimensional gas chromatography (17–20).

The aim of this work is to study a most rapid and accurate method for analysis the condensate oil sample with the simultaneous determination of its characteristic physical parameters, according to the petroleum companies' demand, by only one GC running. This is taking into consideration that 5–7 condensate analyses are required per petroleum company sample.

## Experimental

### Samples

The identification blends; *n*-C6–*n*-C11, *n*-C14, *n*-C16; benzene, toluene, ethylbenzene, *p*+*m*+*o*-xylenes, 1,2,4-TMB, cyclohexane and methylcyclohexane were purchased from Aldrich Co. (St. Louis, MO) Pye-unicam retention indices library and detailed analysis (21) of gasoline range hydrocarbons are used also in identification of isomers-retention distance (i.e., start and end) for each *n*-alkane. Condensate samples provided by Khalidi Co. (Egypt).

### Instrument and conditions

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 plus Arneil software (this software has the ability to transfer the data from the chromatogram to the Excel-sheet, simultaneously, just the run end). To achieve the target condensate analysis in one GC running; separation was performed on a 100 m × 0.25 μm × 0.25 i.d. PIONA fused silica column (*Rtex*). Helium was employed as carrier gas at a flow rate of approximately 2 mL/min. A two stage temperature program

**Table I. Densities and Molecular Weights for the Condensate Oil Hydrocarbons Used in the GC Calculations**

| Component          | M. Wt.  | Density (g/cm <sup>-1</sup> at 60°F) |
|--------------------|---------|--------------------------------------|
| Methane            | 16.043  | 0.2997                               |
| Ethane             | 30.07   | 0.3558                               |
| Propane            | 44.097  | 0.5065                               |
| <i>i</i> -Butane   | 58.123  | 0.5623                               |
| <i>n</i> -Butane   | 58.123  | 0.5834                               |
| <i>i</i> -Pentane  | 72.15   | 0.6238                               |
| <i>n</i> -Pentane  | 72.15   | 0.6305                               |
| Hexanes            | 86.18   | 0.6631                               |
| M-C-Pentane        | 84.16   | 0.7533                               |
| Benzene            | 78.11   | 0.8820                               |
| Cyclohexane        | 84.16   | 0.7827                               |
| Heptanes           | 100.204 | 0.6875                               |
| M-C-Hexane         | 98.19   | 0.7740                               |
| Toluene            | 92.14   | 0.8734                               |
| Octanes            | 114.231 | 0.7063                               |
| Ethylbenzene       | 106.17  | 0.8735                               |
| <i>m+p</i> -Xylene | 106.17  | 0.8671                               |
| <i>o</i> -Xylene   | 106.17  | 0.8840                               |
| Nonanes            | 128.285 | 0.7212                               |
| 1,2,4-TMB          | 120.19  | 0.8797                               |
| Decanes            | 142.285 | 0.7780                               |
| Undecanes          | 147     | 0.7890                               |
| Dodecanes          | 161     | 0.8000                               |
| Tridecanes         | 175     | 0.8110                               |
| Tetradecanes       | 190     | 0.8220                               |
| Pentadecanes       | 206     | 0.8320                               |
| Hexadecanes        | 222     | 0.8390                               |
| Heptadecanes       | 237     | 0.8470                               |
| Octadecanes        | 251     | 0.8520                               |
| Nonadecanes        | 263     | 0.8570                               |
| Eicosanes          | 275     | 0.8620                               |
| Heneicosanes       | 291     | 0.8670                               |
| Docosanes          | 305     | 0.8720                               |
| Tricosanes         | 318     | 0.8770                               |
| Tetracosanes       | 331     | 0.8810                               |
| Pentacosanes       | 345     | 0.8850                               |
| Hexacosanes        | 359     | 0.8890                               |
| Heptacosanes       | 374     | 0.8930                               |
| Octacosanes        | 388     | 0.8960                               |
| Nonacosanes        | 402     | 0.8990                               |
| Tricontanes        | 416     | 0.9020                               |
| Unitricontanes     | 430     | 0.9060                               |
| Dotricontanes      | 444     | 0.9090                               |
| Tritricontanes     | 458     | 0.9120                               |
| Tettratricontanes  | 472     | 0.9140                               |
| Pentatricontanes   | 486     | 0.9170                               |
| Hexatricontanes    | 506     | 0.9180                               |

**Table II. Exemplified-Simultaneous GC Compositional Report of the Condensate Sample with Calculated Physical Characteristics and its Comparison with other Methods**

| Component                                 | Wt%      | Mole %  |
|---|----------|---------|
| Methane                                   | 0.000    | 0.000   |
| Ethane                                    | 0.000    | 0.000   |
| Propane                                   | 0.350    | 0.940   |
| <i>i</i> -Butane                          | 0.547    | 1.116   |
| <i>n</i> -Butane                          | 1.859    | 3.793   |
| <i>i</i> -Pentane                         | 2.370    | 3.895   |
| <i>n</i> -Pentane                         | 2.961    | 4.866   |
| Hexanes                                   | 6.904    | 9.500   |
| Methylcyclopentane                        | 1.412    | 1.989   |
| Benzene                                   | 1.467    | 2.227   |
| Cyclohexane                               | 1.019    | 1.436   |
| Heptanes                                  | 9.054    | 10.714  |
| Methylcyclohexane                         | 5.933    | 7.165   |
| Toluene                                   | 6.254    | 8.048   |
| Octanes                                   | 5.978    | 6.205   |
| Ethylbenzene                              | 0.610    | 0.681   |
| <i>m+p</i> -Xylene                        | 5.016    | 5.602   |
| <i>o</i> -Xylene                          | 0.963    | 1.075   |
| Nonanes                                   | 5.833    | 5.392   |
| 1,2,4-trimethylbenzene                    | 1.230    | 1.213   |
| Decanes                                   | 6.332    | 5.277   |
| Undecanes                                 | 4.831    | 3.897   |
| Dodecanes                                 | 3.537    | 2.605   |
| Tridecanes                                | 3.531    | 2.393   |
| Tetradecane                               | 2.563    | 1.600   |
| Pentadecanes                              | 2.525    | 1.453   |
| Hexadecanes                               | 2.082    | 1.112   |
| Heptadecanes                              | 1.818    | 0.909   |
| Octadecanes                               | 1.581    | 0.747   |
| Nonadecanes                               | 1.286    | 0.580   |
| Eicosanes                                 | 1.337    | 0.576   |
| Heneicosanes                              | 1.094    | 0.446   |
| Docosanes                                 | 0.998    | 0.388   |
| Tricosanes                                | 0.946    | 0.353   |
| Tetracosanes                              | 0.824    | 0.295   |
| Pentacosanes                              | 0.799    | 0.275   |
| Hexacosanes                               | 0.720    | 0.238   |
| Heptacosanes                              | 0.715    | 0.227   |
| Octacosanes                               | 0.709    | 0.217   |
| Nonacosanes                               | 0.495    | 0.146   |
| Tricontaines                              | 0.406    | 0.116   |
| Unitricontaines                           | 0.363    | 0.100   |
| Dotricontaines                            | 0.281    | 0.075   |
| Tritricontanis                            | 0.189    | 0.049   |
| Ttettratricontanis                        | 0.124    | 0.031   |
| Pentatricontanis                          | 0.125    | 0.030   |
| Hexatricontanis+                          | 0.031    | 0.007   |
| Total sum                                 | 100.000  | 100.000 |
| <i>Condensate Sample characteristics:</i> |          |         |
| Average molecular weight:                 | 145.9924 | 144*    |
| Density (g/cm <sup>-3</sup> at 60°F)      | 0.76518  | 0.7760  |
| C/H                                       | 8.00     | 8.40    |

\* By using other methods: Bench-calibrated instruments models density meter-DMA 4500-HP and CRYETTE WR (made in USA) for measurement density and molecular weight, respectively. Elemental analyzer for C, H measurement model HERAEUS (micro-analytical center-Cairo university).

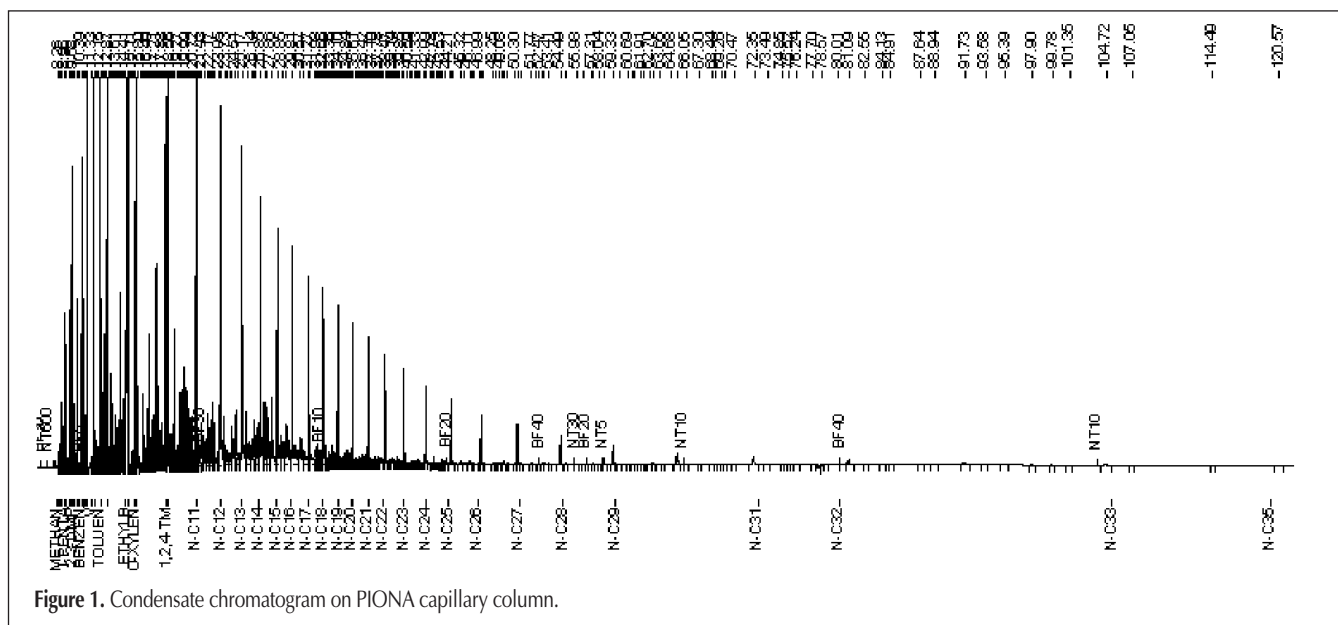


Figure 1. Condensate chromatogram on PIONA capillary column.

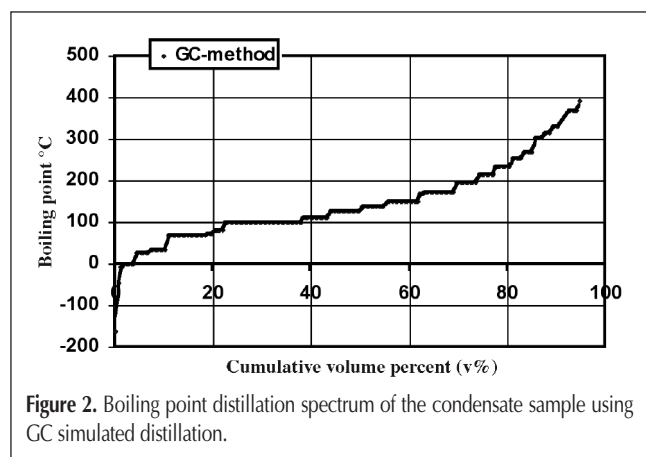


Figure 2. Boiling point distillation spectrum of the condensate sample using GC simulated distillation.

was used; the column oven temperature was at 100°C, raised at 5°C/min to 150°C, then raised at 50°C to 300°C, and held for 50 min. The injector and detector temperatures were maintained at 300°C, and 0.1 µL sample size was injected with split ratio 30:1.

## Results and Discussion

The chromatogram of condensate sample is shown in Figure 1. The required condensate *n*-alkanes, naphthenes, and aromatics are identified using the injected external standards; otherwise, the start and the end of the isomers retention distance is determined for each *n*-alkane using the hydrocarbon retention indices library. The mass percent ( $m_i$ ) values of the condensate individuals and groups were calculated with respect to the following reference *n*-alkanes: *n*-C<sub>6</sub> (C<sub>2</sub>–C<sub>9</sub>), *n*-C<sub>10</sub> (C<sub>10</sub>–C<sub>13</sub>), and *n*-C<sub>14</sub> (C<sub>14</sub>–C<sub>36</sub>). Software mass vs. area relationships (as injected external standard [5 *m/v*] in *n*-pentane solvent) were then multiplied by the relative response factor calculated according to D 4626 practice and normalized:

$$F_i = \left( \frac{(C_{aw} \times C_n) + (H_{aw} \times H_n)}{C_n} \right) \times 0.83905 / C_{aw} \quad \text{Eq. 1}$$

In the resulting equation:  $F_i$  = relative response factor for a hydrocarbon type group of a particular carbon number;  $C_{aw}$  = atomic weight of carbon, 12.011;  $C_n$  = number of carbon molecules in the group;  $H_{aw}$  = atomic weight of hydrogen, 1.08;  $H_n$  = number of hydrogen molecules in the group.

Then the required characteristic parameters of the condensate sample are calculated from the following relationships:

$$M = \sum_{i=1}^n m_i M_i / 100 \quad \text{Eq. 2}$$

$$C/H = \sum_{i=1}^n m_i (C/H)_i / 100 \quad \text{Eq. 3}$$

$$d^{60} = \sum V_i d_i^{60} \quad \text{Eq. 4}$$

$$V_i = (m_i / d_i^{60}) / \sum m_i / d_i^{60} \quad \text{Eq. 5}$$

Where  $m_i$  = mass percent of hydrocarbon *i*;  $V_i$  = volume percent of hydrocarbon *i*;  $M_i$  = molecular weight of hydrocarbon *i*; and  $d_i^{60}$  = density of hydrocarbon *i* at 60°F.

These parameters are calculated automatically by the software, just the run end. A condensate sample containing hydrocarbons ranging in carbon number from 3 to 36 was analyzed by the described method (Tables I and II). The compared data were determined by other methods: molecular weight, C/H, density. The validity of this software was also checked by agreement between topping distillation value of C<sub>12</sub>+% (= 53.5%) and the chromatogram calculated value (= 55%) for a condensate sample.

Xue Hui-feng et al. (24) used the GC simulated distillation method, cumulated volume percent vs. boiling point, to get the

boiling point spectrum of naphtha. This method was confirmed by Engel distillation (ASTM D-86). It is found that the GC simulated distillation method has two main advantages compared to physical distillation method, which are: (i) it is not affected by the surrounding conditions and (ii) it provides more detailed information. A similar software GC simulated distillation method was used to plot b.p. vs. cumulated V% of the condensate individuals to show its distribution spectrum. Figure 2 shows that the condensate distillation spectrum is characterized by graduated flats according to the individual contents. The two main flats correspond to C<sub>6</sub> and C<sub>7</sub>. The spectrum ends at C<sub>32</sub> where the b.p.s. of C<sub>33</sub>–C<sub>36</sub> is under mm pressure. Initial boiling point start at ethane. It can be observed that this spectrum has intermediate characteristics between these of naphtha (22) and medial distillates (23).

## Conclusion

The GC PIONA column, computerized Perkin Elmer calculated software, and Arnel-data transfer software were used as bases for construction of accurate and rapid GC method for the compositional analysis of the petroleum condensate oil with simultaneous calculations of its physical properties. This is based on using the *n*-C<sub>6</sub>, *n*-C<sub>10</sub>, and *n*-C<sub>14</sub> external standards as references for wt% calculations taking into consideration the variations in response factor between the reference *n*-alkane and the given condensate component according to D 4626 practice. Boiling point distillation spectrum of the condensate sample was obtained using GC simulated distillation method as a previously confirmed technique.

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