# High resolution gas chromatography: fingerprint of Cuban oils from Pina and Puerto Escondido fields

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Key words: finger print, crude oil, peak ratios, star diagram, reservoir geochemistry.

**RESUMEN**. La huella dactilar mediante Cromatografía Gaseosa Capilar de Alta Resolución fue obtenida para 18 muestras de crudos de petróleo cubano de dos yacimientos: 9 de Pina y 9 de Puerto Escondido. El análisis fue realizado usando columna capilar DB-1 (J&W), de 30 m de largo x 0, 2 5 mm de diámetro interior y 0,25 µm de película de fase estacionaria, así como un programa de temperatura adecuado y paquetes de programas para procesamiento de los datos cromatográficos. Por medio de la huella dactilar ampliada de las muestras fue posible resaltar las pequeñas diferencias en su composición que permitieron seleccionar relaciones de picos adecuadas para graficar en coordenadas polares y obtener los diagramas de estrella para cada muestra. La comparación de estos diagramas permitió apreciar diferencias y semejanzas de composición dentro de cada yacimiento y además, comparar los yacimientos entre sí. Esta técnica es muy usada en la obtención de datos para estudios de geoquímica de reservorios, por ser rápida, confiable y sencilla. Los resultados correspondientes a diferencias promedio de relaciones de pico entre 2 y 5 % para análisis duplicados, demuestran buena reproducibilidad acorde con lo que ha sido reportado. Diferencias mayores, de hasta 40 % en Puerto Escondido y entre 10 y 41 % en Pina, fueron obtenidas. Estos resultados indican variaciones en la composición química de las muestras analizadas dentro de los yacimientos estudiados, o sea, falta de continuidad de los fluidos en ellos. No obstante, fue posible agrupar algunas muestras de Puerto Escondido con una diferencia promedio para las relaciones de pico seleccionadas de alrededor de 5 a 6 % e incluso menores que 5 %. Los resultados dejan espacio al interés de profundizar los estudios de la geoquímica de reservorios en estos yacimientos.

**ABSTRACT**. High Resolution Gas Chromatography fingeprint was obtained for 18 crude oil samples of two Cuban fields: 9 from Pina and 9 from Puerto Escondido. A 30 m x 0.25 mm internal diameter and 0.25 µm film thickness DB-1 (J&W) capillary column as well as a suitable temperature program and chromatographic software were used. By means of a wider view of sample fingerprints, small differences in composition were highlighted and proper peak ratios for polar plot to obtain each sample star diagram were allowed to select. Diagram comparison shows similarities and differences in composition within each field and between them. This technique is often used to obtain data for reservoir geochemistry studies because it is fast, confident and simple. The obtained average peak ratio differences for duplicated analysis of 2-5 % show good reproducibility according to those that have been reported. Higher differences up to 40 % in Puerto Escondido and between 10-41 % in Pina were obtained. These results show variations in chemical composition between the analyzed samples within the studied fields, in fact, lack of continuity for the fluids in them. Nevertheless, it was possible to group some samples from Puerto Escondido with an average difference for the selected peak ratios between 5-6 % and also lower than 5 %. The obtained results leave an open space to the interest in deepening the reservoir geochemistry studies in these reservoirs.

## INTRODUCTION

High Resolution Gas Chromatography has been for years a useful tool for reservoir continuity studies. The obtained chromatograms are unique fingerprints that have been also useful for identifying: pipelines leaks, oil spills, nonproductive reservoir zones, etcétera.

Kaufman and col.[1,2] have use a novel technique based on the calculation of selected peak ratios and its polar plot. This technique has been also useful to diagnose source rock origin, maturity or water washing.[3] The identification of individual reservoir units is based on the knowledge of the chemical composition of the fluids. In general, it is commonly found that oils within a continuous reservoir have a uniform hydrocarbon composition and oils in separate reservoirs almost always have measurable compositional differences. The critical point is that the differences between the oils are usually small, due to their similar geologic history within a Field. Bulk property analyses such as gravity, viscosity, ext, may not be successful in the detection of these small differences, not so molecular composition techniques, such as gas chromatography, which is a particularly powerful tool with an excellent analytical reproducibility.[4,5]

In recent years gas chromatography fingerprint results applied to reservoir fluid continuity studies have been successfully compared with some other from spectroscopic techniques such as FTIR (Fourier transformed infrared) and SUVF (synchronous ultraviolet fluorescence).[6]

Cuban oils have been studied during the last fifteen years. Characterizations, family classifications by means of biomarkers and maturity and biodegradation studies have been done.[7] Also cluster analysis, has been reported for Pina´s oils.[8]

The main purpose of this work was to compare some Cuban oils from Pina and Puerto Escondido fields using Kaufman's technique and in general to obtain compositional information of these oils by means of the gas chromatographic analysis, as an analytical aid for further geochemistry studies.

## EXPERIMENTAL

Nine crude oil samples from Pina Field and nine from Puerto Escondido from different wells were studied.

Geochemical properties (Table 1), were obtained by standard procedures: API gravity by hidrometer method,[9] W % sulphur by quartz volumetric method.[10] Asphaltenes were precipitated with n-pentane and maltenes were fractionated using a silica-alumina column by elution liquid chromatography using solvents with increasing polarities, to yield saturates (paraffins), aromatics and resins (SARA).

Gas chromatographic analysis, were done in a CP 9001 Chrompack chromatograph with a 30 m x 0,25 mm and 0,25 µm film thickness (J&W), DB-1 capillary column. The conditions were set as follows: injector temperature- 300 °C, detector temperature- 320 °C, oven column program- 30 °C during 5 min, 30-50 °C at 20 °C/min, 50-160 °C at 2 °C /min, 160-310 °C at 20 °C/ min, and 5 min at 310 °C .

Data were analyzed automatically by software Maestro II, Version 2.4 of Chrompack International B.V. 1995.

Chromatograms were analyzed individually by:

- sequential numeric identification of the peaks in the whole run.
- visual inspection: variations in height of adjacent or very close peaks.
- calculation of height ratios of the selected peaks, that compensates variations in baseline shifts and injection volume.
- calculation of average results from four runs.
- Polar plot of 12 peak ratios for Pina and 11 for Puerto Escondido that involves naphtenes, aromatics and isoparaffins.

## RESULTS AND DISCUSSION

It was observed differences between Pina and Puerto Escondido oils (Table 1). Pina oil is lighter and has less sulfur an asphaltene content than Puerto Escondido's. It is also more paraffinic. This results are in agreement with typical fingerprints [Fig. 1 (a) Pina and (b) Puerto Escondido]. In Pina it can see the resolved paraffin peaks higher than in Puerto Escondido, and on the other hand higher unresolved compounds sign (UCM) corresponding with the heavy end part of the sample is clearly seen in Puerto Escondido chromatogram. Highlighted small peak differences in a typical chromatogram portion is observed too [Fig. 1 (c)].

Due to the observed compositional differences between Pina and Puerto Escondido oils, selected peak ratios were different in each case. The obtained average differences between selected peak ratios for duplicated analysis of the same oil were between 2-5 % and showed good reproducibility in agreement with those that has been reported for the oil fingerprinting technique using capillary chromatography.[3] shows typical repeatability results obtained in this work. Higher differences were obtained for the comparison of different oil samples in each field that reflects differences in relative hydrocarbon composition for the oils rather than analytical error (Table 2).

**Table 1**. Different well fluids characteristics from Pina (P) and Puerto Escondido (PE) fields.

| Field /Reservoir | API | S | Asphalthenes | Saturates (Paraffins) | Aromatics | Resins |
|---|---|---|---|---|---|---|
| | | | | (w%) | | |
| PE/4 | 11.3 | 6.06 | 34.11 | 22.28 | 20.09 | 23.52 |
| PE/5 | 12 | 6.4 | 18.37 | 19.56 | 37.87 | 24.2 |
| PE/6 | 11.9 | 6.54 | 18.56 | 20.62 | 36.62 | 24.2 |
| PE /7 | 11.3 | 6.63 | 21.13 | 22.23 | 31.51 | 25.13 |
| PE/8 | 13.8 | 6.41 | 19.13 | 19.46 | 36.98 | 24.43 |
| PE/9 | 8.6 | 6.23 | 16.73 | 21.66 | 37.71 | 23.9 |
| PE/10 | 10.7 | 6.64 | 18.6 | 21.8 | 33.9 | 25.7 |
| PE/11 | 12.09 | 6.77 | 17.79 | 20.22 | 36.33 | 25.66 |
| PE/12 | 11 | 5.84 | 16.05 | 18.91 | 43.25 | 21.79 |
| P/2 | 25.7 | 2.59 | 5 | 41.63 | 41.29 | 12.08 |
| P/3 | 34.9 | 1.37 | 5.5 | 45.91 | 38.31 | 10.28 |
| P/21 | 35.1 | 1.54 | 1.35 | 37.45 | 51.29 | 9.91 |
| P/103 | 16.6 | 2.36 | 5.9 | 34.29 | 44.51 | 15.3 |
| P/104 | 21.1 | 2.74 | 2.86 | 34.37 | 48.92 | 13.85 |
| P/110 | 19.9 | 2.41 | 9.4 | 32.72 | 44.86 | 13.02 |
| P/115 | 26.5 | 2.79 | 5.8 | 39.92 | 41.73 | 12.55 |
| P/121 | 20.6 | 2.72 | 5.68 | 38.41 | 49.13 | 6.78 |
| P/129 | 31.7 | 1.59 | 3.8 | 45.85 | 40.35 | 10 |

API gravity  S Sulphur content.

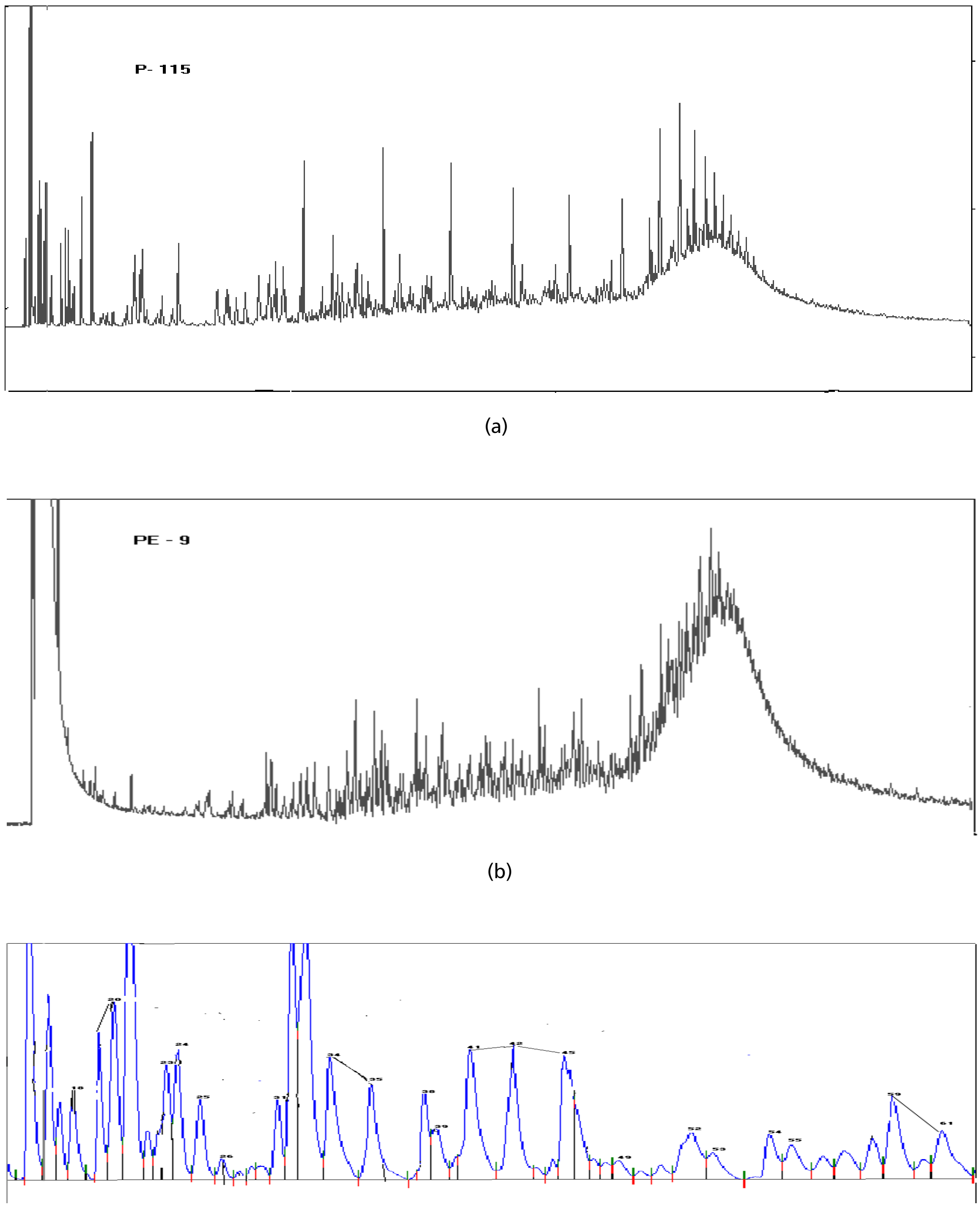


***Fig. 1.*** *Typical gas chromatograms (fingerprints): (a) from Pina (P-115), (b) from Puerto Escondido (PE-9) and (c) highlighted gas chromatogram portion.*

Table 3 shows the obtained peak ratios for the different Pina's samples . Average peak ratio differences higher than 10 and up to 41 % can be seen in Pina's star diagrams (Figures 2 y 3). Even P-103 and P-104, with similar shape (Fig. 3) has average peak ratio differences about 15 %. On the other hand, polar plot of Puerto Escondido's results (Table 4) is a clear evidence of one group with mostly similar shape: PE wells 5, 6, 7, 9, 11, 12 (Fig. 4) and three wells (4, 8, and 10), significantly different between them with more than 15 % difference (Fig. 5). The first six samples could be separated into two groups: PE (5, 6, 9) with peak ratio average differences about 5-7 % and PE (7, 11, 12) with peak ratio average differences lower than 5 %.

These results show reservoir compartmentalization (lack of continuity) in the studied fields, specially in Pina, where each sample has clear compositional differences from the other, shown in the obtained star diagrams. Puerto Escondido wells 7, 11 and 12, probably belongs to the same reservoir. This fact could explain the obtained peak ratio differences within analytical reproducibility for these samples.

## CONCLUSIONS

Gas chromatograms (fingerprints), from Pina and Puerto Escondido oil samples from different wells were obtained and show dif-

**Table 2.** Typical repeatability of peak height measurements (from PE-12).

| Run | 19/20 | 35/34 | 42/41 | 42/45 | 61/59 |
|---|---|---|---|---|---|
| 1 | 0.721 | 0.751 | 2.813 | 0.802 | 0.500 |
| 2 | 0.715 | 0.730 | 0.932 | 0.800 | 0.518 |
| 3 | 0.704 | 0.739 | 0.940 | 0.809 | 0.521 |
| 4 | 0.685 | 0.750 | 0.935 | 0.812 | 0.502 |
| X | 0.706 | 0.742 | 0.936 | 0.806 | 0.510 |
| R (%) | **4.473** | **2.813** | **1.043** | **1.602** | **3.048** |

**Table 3.** Selected peak ratios (four runs average) for Pina samples (P-n).

| PR | P-2 | P-3 | P-21 | P-115 | P-121 | P-129 | P-103 | P-104 | P-110 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.473 | 1.216 | 0.887 | 1.152 | 1.176 | 0.885 | 3.04 | 2.826 | 3.221 |
| 2 | 0.601 | 0.568 | 0.479 | 0.594 | 0.668 | 0.61 | 0.605 | 0.646 | 0.622 |
| 3 | 1.035 | 1.227 | 1.116 | 1.098 | 0.984 | 1.153 | 0.847 | 1.01 | 1.086 |
| 4 | 1.018 | 1.095 | 1.129 | 0.995 | 1.076 | 1.346 | 1.166 | 1.034 | 1.239 |
| 5 | 0.741 | 0.793 | 0.958 | 0.841 | 1.092 | 0.913 | 1.107 | 0.926 | 1.188 |
| 6 | 1.168 | 1.125 | 0.893 | 1.007 | 0.801 | 0.772 | 0.931 | 1.032 | 0.8 |
| 7 | 1.686 | 1.783 | 1.429 | 1.557 | 1.476 | 1.439 | 2.572 | 2.196 | 2.328 |
| 8 | 0.696 | 0.779 | 0.831 | 0.748 | 1.041 | 0.94 | 0.975 | 0.762 | 1.023 |
| 9 | 0.919 | 1.015 | 0.838 | 1.028 | 1.195 | 1.585 | 1.221 | 1.102 | 1.187 |
| 10 | 1.326 | 1.398 | 1.584 | 1.799 | 1.461 | 1.52 | 1.366 | 1.56 | 1.707 |
| 11 | 0.821 | 0.788 | 0.596 | 0.638 | 0.786 | 1.014 | 0.504 | 0.49 | 0.406 |
| 12 | 1.281 | 1.543 | 2.157 | 0.937 | 1.067 | 1.634 | 0.897 | 0.98 | 1.384 |

PR Peak ratio.

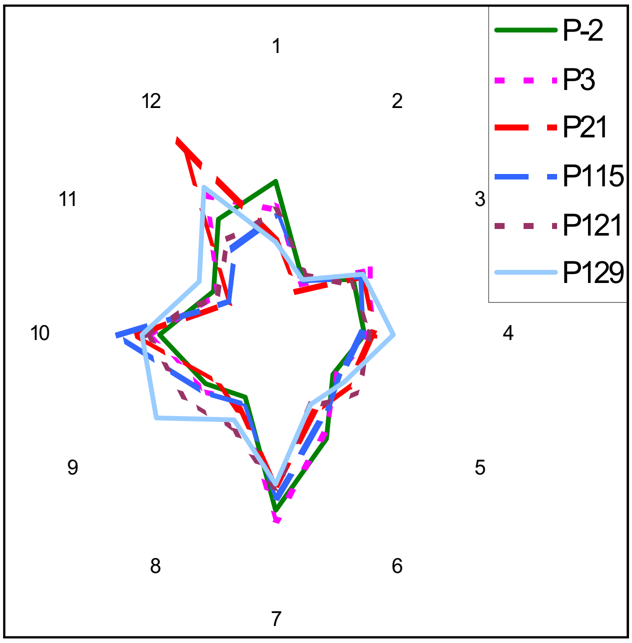


*Fig. 2. Star diagram for six Pina samples (P-2, P-3, P-21, P-115, P-121, P-129).*

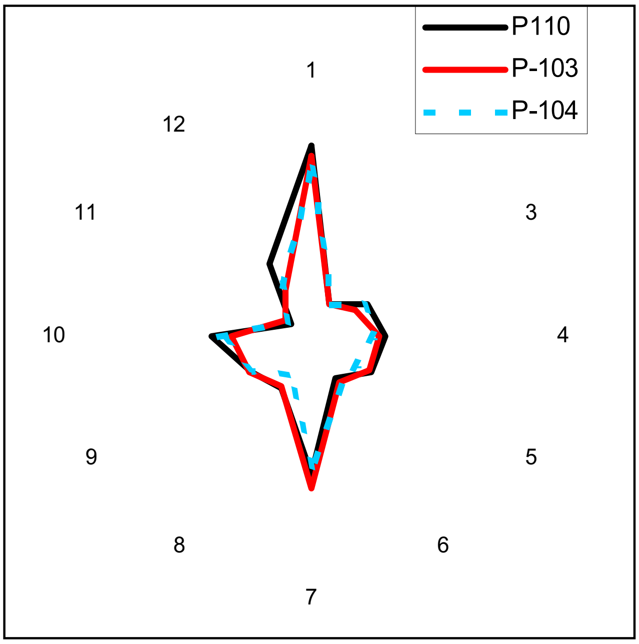


*Fig. 3. Star diagram for three Pina samples (P-103, P-104, P-110).*

ferences in composition between the different samples. Selected peak ratios were polar plot and the corresponding Star Diagrams obtained, show reservoir compartmentalization in both Fields. Nevertheless, in Puerto Escondido Field at least three wells show very similar composition, that reminds that they possibly belong to the same reservoir.

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**BIBLIOGRAPHY**

1. Kaufman R.L., Ahmed A.S., and Hempkins W. B., A New Technique For

**Table 4.** Selected peak ratios (four runs average) for Puerto Escondido samples (PE-n).

| PR | PE-5 | PE-6 | PE -7 | PE-9 | PE-11 | PE-12 | PE-4 | PE-8 | PE-10 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.44 | 0.38 | 0.49 | 0.40 | 0.47 | 0.47 | 1.33 | 0.31 | 1.17 |
| 2 | 0.62 | 0.68 | 0.68 | 0.61 | 0.65 | 0.71 | 0.76 | 0.52 | 0.76 |
| 3 | 0.85 | 0.95 | 0.82 | 0.87 | 0.78 | 0.83 | 0.74 | 0.82 | 0.85 |
| 4 | 0.72 | 0.70 | 0.71 | 0.71 | 0.77 | 0.74 | 0.76 | 0.68 | 0.75 |
| 5 | 0.89 | 0.95 | 0.94 | 0.93 | 0.91 | 0.94 | 0.81 | 1.01 | 0.79 |
| 6 | 0.84 | 0.86 | 0.84 | 0.88 | 0.81 | 0.81 | 0.58 | 1.13 | 0.54 |
| 7 | 0.51 | 0.53 | 0.50 | 0.50 | 0.52 | 0.51 | 0.49 | 0.52 | 0.48 |
| 8 | 1.08 | 1.04 | 0.86 | 0.97 | 0.82 | 0.77 | 0.16 | 1.52 | 0.50 |
| 9 | 0.97 | 0.96 | 0.97 | 0.95 | 1.01 | 1.02 | 0.10 | 0.98 | 0.92 |
| 10 | 0.63 | 0.64 | 0.63 | 0.66 | 0.69 | 0.72 | 0.41 | 0.80 | 0.38 |
| 11 | 0.60 | 0.64 | 0.69 | 0.63 | 0.69 | 0.70 | 1.15 | 0.49 | 1.16 |

PR Peak ratio.

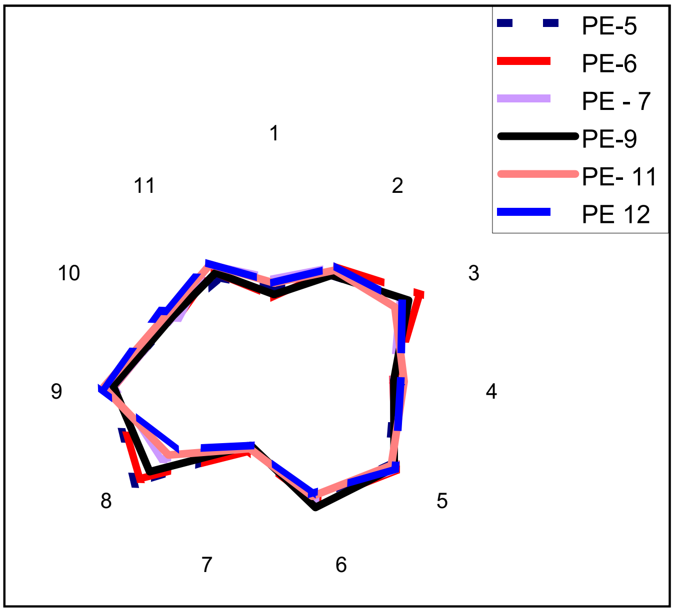


*Fig. 4. Star diagrams for six Puerto Escondido samples (PE- 5, PE- 6, PE- 7, PE- 9, PE- 11, PE- 12).*

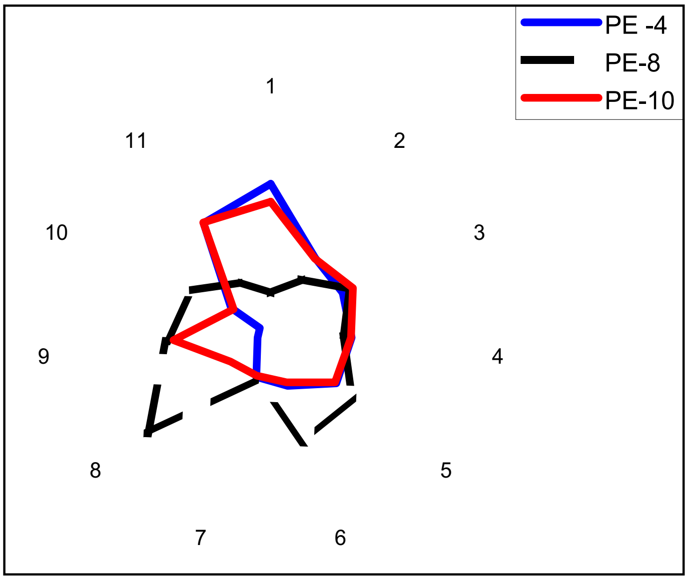


*Fig. 5. Star diagrams for three Puerto Escondido samples (PE- 4, PE- 8, PE- 10).*

The Analysis of Commingled Oils And Its Application To Production Allocation Calculations, Proceedings Indonesian Petroleum Association Sixteenth Annual Convention, 247-267, 1987.
2. Kaufman R.L., Ahmed A.S., Elsinger R. J., Gas Chromatography As A Development And Production Tool For Fingerprinting Oils From Individual Reservoirs: Applications in the Gulf of Mexico, GCSSPM Foundation Ninth Annual Research Conference Proceedings, 263- 282, 1990.
3. Magnier C., Trindade L.A.F., **Rev. Latin Am. Geoq. Org. , 5**, 25- 37, 1999.
4. Holba, A.G., L.I. P. Dzou, J.J. Hickey, *et al.*, Reservoir geochemistry of South pass 61 Field, Gulf of México: Compositional Heterogeneities reflecting filling history and biodegradation, **Org. Geochem., 24**, 1179-1198, 1996.
5. Hwang R.J., Ahmed A.S. and Moldowan J.M. Oil composition variation and reservoir continuity: Unity Field, Sudan, **Org. Geochem., 21**, 171-188, 1994.
6. Permanyer A., Doufi C., Lachcini A., Lamontage J., Kister J., FTIR and SUVF spectroscopy applied to reservoir compartmentalization: a comparative study with gas chromatography fingerprints results, **Fuel, 81**, 861-866, 2002.
7. Magnier C., Moretti I., Lopez J. O., Gaumet F., Lopez J. G., Letouzey J., Geochemical characterization of source rocks, crude oils and gases of Northwest Cuba, **Marine and Petroleum Geology, 21**, 195-214, 2004.
8. Castro O., Pascual O., Díaz L., Llabre G. Clasificación de los Petróleos en el Yacimiento Pina mediante Técnicas de la Estadística Multivariada, **Revista Latinoamericana de Geoquímica Orgánica, 6**, 40-52, 2002.
9. ASTM D 1298: Density, Specific Gravity or API Gravity of Petroleum Crude Oil and Petroleum Products.
10. GOST 1437: Acelerated Method for Sulfur Determination.