

## ESTIMATION OF API GRAVITY BY QUANTITATIVE GAS CHROMATOGRAPHY FOR SELECTED OILS OF BRAZILIAN BASINS

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API gravities strongly impact the economic viability of oil fields because physical properties of oil affect oil value and its production (e.g. Tissot and Welte, 1984; Peters & Moldowan, 1993). Furthermore, even after decision has been made to develop a field, API gravity continues to impact the production strategy, since variations of this property must be considered for optimal well location and completion. However, API gravity generally cannot be measured by conventional methods before production tests because of the small amount of oil extracted from cuttings and core samples during drilling. Quantitative gas chromatography, a technique that is used to analyze volatile organic compounds, can be proposed as a technique to quickly estimate the API gravity of oils with acceptable precision. The main advantage of its use is that the amount of sample required is minimal. It can be fast and bring many benefits to a quick evaluation during well drilling and testing when the amounts of crude oil available are small. In addition, gas chromatography accounts for the large range of compounds and molecular weights present in oils.

The aim of this study was to develop a gas chromatographic method to quantify petroleum fractions ranging from 7 to 40+ carbon atoms in Brazilian oils and to estimate oil API gravities, using two newly developed macros compatible with the Agilent Chemstation.

GC analyses were performed with a Hewlett-Packard 6890 series II gas chromatograph equipped with an on-column injector and a flame ionization detector (FID). A retention gap and fused silica DB-5 phenyl/methyl polysiloxane capillary column (20 m x 0.25 mm x 0.1  $\mu$ m) were used. The oven temperature was programmed from 35°C to 340°C at a heating rate of 2.5°C/min. Helium was used as carrier gas at a constant flow of 2.8 mL/min. Around 10mg of sample were diluted in 1mL of carbon disulphide. A standard mixture containing *n*-paraffins from 5 to 28 carbon atoms (*Analytical Controls, part number 59.50.101A*) dissolved in CS<sub>2</sub> was used to calibrate retention times and to calculate response factors.

Two macros have been developed for quantification of the GC traces. The first one runs on a standard containing some pure *n*-alkanes from *n*-C<sub>5</sub> to *n*-C<sub>28</sub>. This macro calculates the response factor that is applied to all whole-oil samples. The second macro gives

cumulative mass percentage results of slices of the chromatogram delimited by the peaks of *n*-paraffins (including hump) observed in the oil. A final reported value of total cumulative mass is obtained, and the difference between this value and the injected mass is attributed to the amount of sample retained inside the chromatographic column, which corresponds to the non-eluted compounds representing sample loss. Furthermore, quantitative GC with the macro provides the mass fraction of the pre-selected peaks (*n*-paraffins, pristane, phytane) as well as the mass fraction of the sum of all resolved peaks and the hump (UCM) area. Oil density is estimated by calculating a weighted average, i.e., the summation of the products of mass fraction and density values for each slice of the chromatogram:

$$\sum_{i=1}^n \rho_i \times w_i, \text{ where } \rho_i \text{ and } w_i \text{ are the density and mass fraction respectively of each "i" slice.}$$

API gravities can then be calculated from the estimated whole-oil density.

To ascertain that the analytical conditions and the macro that calculates the response factor provide correct results, six samples of the standard mixture containing *n*-paraffins from *n*-C<sub>5</sub> to *n*-C<sub>28</sub> were analyzed. Mean, standard deviation, % standard deviation for the six response factors were calculated and the results were considered adequate since the % standard deviation was less than 3%. These tests attest the repeatability of the results and the correct data processing of the developed macro.

The optimized method was applied to a set of Brazilian oils with a wide range of API gravities (8 to 45°), ranging from non-biodegraded to intensely biodegraded oils. Our results showed an excellent correlation between estimated and measured API gravities for each oil family that was investigated. To achieve this, specific exponential functions defining the relationship between pseudo-densities and slices along the GC trace have been numerically fitted for each oil family. The results of this study corroborated the usefulness of applying quantitative gas chromatography in the geochemical assessment of oils including their physical and chemical properties.

## REFERENCES

- Peters, K. E. and Moldowan, J. M., 1993. *The Biomarker Guide*. Prentice-Hall, Englewood Cliffs, N J, 363 p.
- Tissot, B.P., Welte, D.H., 1984. *Petroleum Formation and Occurrence*. Springer, New York. 699 p.