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Full Length Article

APPI(+)-FTICR mass spectrometry coupled to partial least squares with genetic algorithm variable selection for prediction of API gravity and CCR of crude oil and vacuum residues

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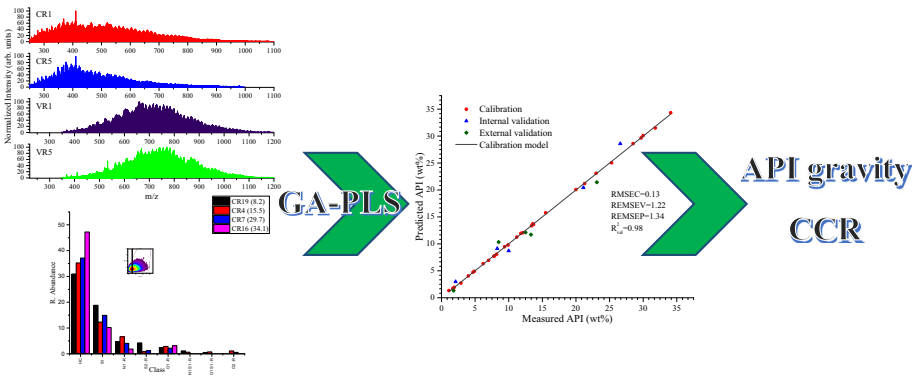
HIGHLIGHTS

- APPI(+) FT-ICR mass spectra coupled to GA-PLS allowed to predict API gravity and CCR of crude oils.
- The procedure saving time and it requires little amount of sample.
- The models GA-PLS were robust and presenting high predictive capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

Positive-ion mode atmospheric pressure photoionization, APPI(+), with Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) was coupled to a Partial Least Squares (PLS) regression and genetic algorithm variable selection (GA-PLS) methods to estimate the API gravity and Conradson Carbon Residue of Colombian crude oil and vacuum residues (VR) samples. It was observed compositional differences between the crude oils, especially increase in relative abundances of the HC Class with API gravity. Principal Component Analysis (PCA) allowed distinguish crude oils and vacuum residues according to their API gravity value. GA-PLS calibration model provide root mean square error (RMSEC) of 0.13 and 0.33 for API gravity and CCR, respectively. The results here obtained allow to use FT-ICR MS data for quantitative analysis of crude oils and their fractions.

1. Introduction

Crude oil is a mixture of organic compounds rich in hydrocarbon that have accumulated in subterranean reservoirs. Crude oil varies dramatically in its properties depending on its origin. Crude

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oils are formed principally by paraffinic, naphthenic or aromatic hydrocarbon families and the composition of these compounds give them different physicochemical characteristics [1–4]. Vacuum residue (VR) is defined as the fraction of petroleum that does not evaporate under vacuum in a distillation process. It is known that VRs are a mixture of hydrocarbons and compounds with heteroatoms species (S, N and O) and metals. Effective production and utilization of these heavy fractions of petroleum requires better understanding of their chemical composition, including molecular weight distribution and physicochemical properties like the American Petroleum Institute gravity (API gravity) and Conradson Carbon Residue (CCR). The wide range of compounds present in crude oil implies great difficulties in the characterization of their physicochemical properties such as density, carbon residue, viscosity, Saturates, Aromatics, Resins and Asphaltenes (SARA) composition, among others [5,6].

API gravity is an arbitrary measure of how heavy or light is the crude oil and its fractions compared to water. API gravity is an inverse measure of the density relative to that of water (also known as specific gravity). API gravity is generally measured using reference methods given by ASTM D4052-96 [7] (American Standards for Testing and Materials) and ISO 12185 [8]. On the other hand, CCR is a test to measure the amount of carbonaceous residue remaining after the crude oil or its fractions is undergoing to evaporation and pyrolysis. CCR provide an indication of the relative tendency to crude oil coke formation. For its determination, the methodology ASTM D4530 [9] is the most used. Despite these methods are widely used and considered reliable, there is a general consensus about some inherent problems in these tests: long time of analysis, large amount of samples, impracticable automation and pollutants. In addition, these measurements do not allow to know about the chemical composition of the sample.

In last years, many studies have used spectroscopic and spectrometric techniques coupled to chemometrics approach due to its intrinsic advantages (non-destructive method, compatible efficiency and quickness) in comparison with conventional methods recommended by ASTM. In crude oil characterization, FTIR [10–15] has been the technique most used. However, in recent years Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been gaining importance for analysis of crude oil and their fractions, especially because provides unique molecular-level information which allow detailed analysis of its structure (qualitative information as molecular weight, aromaticity, Compound classes, etc.). [16–23]. Petroleomics have as fundamental goal to link such detailed structural analysis of crude oil to its properties [19]. Therefore, the combination of chemical analysis by FT-ICR MS with chemometric procedures such as PLS can be a powerful tool for predicting physical-chemistry properties [24,25] such as API gravity and CCR.

The partial least squares (PLS) method is the most frequently used to build multivariate models from first-order spectroscopic and spectrometric data. PLS relate two data matrices, X and Y, by means of a linear model; where X contains the spectroscopic or spectrometric variables (instrumental responses) and Y the property of interest to be modeled. Multivariate model can be built using entire spectral data of spectrum. However, if spectral data have a large number of variables, some of these can affect the performance of the model. Therefore, it is necessary to select the best variables associated with the property of interest [9,26].

Several approaches to select the best variables have already been used in some studies, showing proficient to generate models that are more stable and robust. Variable selection methods differ by the procedure performed for selection of the spectral region. The two variables selection approaches, coupled with to partial least squares (PLS), most used are interval partial least squares (iPLS) and genetic algorithm (GA) [9,26]. Genetic Algorithms (GA) are a global search empirical inspired on the natural evolution of species and in the natural biological process. Essentially, a GA generates a population of possible solutions to the problem being solved and then submit these solutions to the evolution process. The main advantages of GAs are their robustness and applicability in a wide variety of problems, including analytical chemistry [27]. In the current study, we demonstrate that APPI(+) FT-ICR MS may be coupled to PLS using genetic algorithm variable selection to predict API and CCR in crude oils and heavy fractions as vacuum residue (VR).

2. Experimental section

2.1. Samples

In this study, forty Colombian crude oils (21) and vacuum residues (19) samples were used. API gravity and CCR of the crude oils and vacuum residues were measured by Colombian Petroleum Institute (ICP) according to the standards of the American Society for Testing and Materials, ASTM D70 [28] and ASTM D4530, respectively. Table 1 presents ranges and statistical data of API gravity and CCR values of the samples studied here.

2.2. Sample preparation

High-performance liquid chromatography (HPLC)-grade (Sigma-Aldrich Chemical Co.) solvents were used. Crude oil samples were diluted with toluene a concentration from 0.1 to 0.5 mg mL^{-1} and vacuum residues samples from 0.5 to 1.0 mg mL^{-1}. Prior to FT-ICR MS analysis, samples were sonicated for 5 min.

2.3. APPI(+) FT-ICR mass spectrometry

FT-ICR mass spectrometry analysis was performed on a SolariX 15 T mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with an APPI source, with a Krypton photoionization lamp (10.6 eV), and operated in positive (+) mode. The front and back trapping voltages in the ion cyclotron cell were set at +0.70 and +0.50 V, respectively. Samples were infused at a flow rate of 350 μL/h using a syringe pump via an APPI II source. Ions accumulated for 40 ms in a collision cell. The time-of-flight (TOF) was set to 700 ms to transfer the ions to an ICR cell by electrostatic focusing ion guide operating at 4 MHz and 350 V_{p-p} rf amplitude. The ICR cell was previously calibrated using a NaTFA (sodium trifluoroacetate) solution (from 200 to 1100 Da). Each spectrum (200–1100 Da) was acquired by accumulating 100 scans of time-domain transient signals in 4 mega-point time-domain data sets.

2.4. Mass calibration

APPI(+) FT-ICR mass spectra were internally recalibrated using a homologous series of alkylated compounds using the Data Analysis Software 4.2 (Bruker Daltonics, Billerica, MA). Mass spectra were further recalibrated using the PetroOrg software (The Florida State University). Resolving power at m/z 400 higher than 600,000, and mass accuracy less than 1.0 ppm, provided unambiguous molecular formula assignments for singly charged molecular ions with relative abundance above 1%. Elemental formulas were assigned based on m/z values within 1 ppm error range.

2.5. Data analysis

Prior to build the models, PetroOrg software is used for elemental formula assignments and then the data set was arranged as a