APPLICATION NOTE

Determination of SARA (Saturates, Aromatics, Resins and Asphaltenes) in bitumen by HPTLC

A-101.1

Keywords

Densitometry, heavy petroleum products

Introduction

Chemical properties of most petroleum products are determined by chemical families rather than by individual molecules. One group analysis is known as SARA (**Saturates, Aromatics, Resins and Asphaltenes**) or hydrocarbon group type analysis. It is used in petro chemistry to determine the quality of a product, evaluate variables for their conversion processes, elucidate reaction pathways and kinetics, and obtain insights into the processability of the feed, or the quality of the finished products.

Scope

This HPTLC method can be applied to SARA analysis of a wide variety of fossil fuel products, which include, among others, heavy-petroleum products with a boiling point higher than that of diesel, e.g., heavy residual, bitumen, refining products, base oils, asphalts, hydro-liquefaction products, tars, pitches, and other pyrolysis products.

Required or recommended devices

Automatic TLC Sampler 4 or Linomat 5, Automated Multiple Development (AMD 2), TLC Visualizer, TLC Scanner 4, Chromatogram Immersion Device III, TLC Plate Heater, and visionCATS software

Chemicals / reagents / solvents

Tetrahydrofuran (THF) without stabilizer; dichloromethane (DCM) stabilized with ethanol; *n*-heptane HPLC grade

Derivatization reagent

Reagent name: berberine

Preparation: 12 mg of berberine chloride dissolved in 200 mL of methanol
Note: the reagent should be stored protected from light

Use: dip the plate into the reagent (speed 3, time 0), and then dry the plate for 10 min at 30°C.

Sample

Test solution of bitumen is prepared at 1 mg/mL in THF.
Note: If needed, samples are heated to about 80°C to reduce their viscosity.

Standards

Standard solution is prepared at 1 mg/mL in THF.
Note: Standards are samples with known composition that are representative of each type of product to be. Bitumen standard was provided by Dr. V. L. Cebolla (CSIC, Zaragoza, Spain).

Chromatography

Stationary phase: HPTLC Si 60, 20 x 10 cm (Merck), **without fluorescent indicator**
Plates are **pre-washed** with THF and air-dried in a fume hood for 10 min at room temperature

Sample application: 0.5 and 5.0 µL of each *Test solution* and 0.1 to 25 µL of the *Standard solutions* are applied as 4 mm bands, track distance 6.0 mm, 10 mm from lower edge of plate. First application position is 20 mm from the left edge of the plate.

Development: Automated Multiple Development (AMD 2) with a 3 step gradient

	THF (%)	DCM (%)	*n*-heptane (%)	Developing distance (mm)	Drying time (min)
1	0	0	100	60	2
2	0	100	0	40	2
3	100	0	0	20	5

Documentation: With the TLC Visualizer under white light and under UV 366 nm.

Densitometry: With TLC Scanner 4 and visionCATS software in absorption mode (prior to derivatization) at 280 nm using a D2 lamp (slit 4 x 0.2 mm) for Asphaltenes, Resins and Aromatics; and in fluorescence mode (after derivatization) using an Hg lamp at UV 366/>400 nm (slit 4 x 0.2 mm) for Saturates; evaluation via peak height or area, Michaelis-Menten-2 regression.

Evaluation: **Prior to derivatization**: UV measurement at 280 nm (slit 4 x 0.2 mm) allows a detection of Asphaltenes, Resins and Aromatics. For a semi-quantitative analysis of Aromatics, Resins and Asphaltenes only the tracks corresponding to sample application volumes of 0.5 µL should be considered, as the linear range of detection for these groups is between 0.01-1 µg.

After derivatization: the plate section containing the peak developed with *n*-heptane (Saturates) is scanned in fluorescence mode at UV 366/>400 nm (slit 4 x 0.2 mm). The fluorescence signal is proportional to the mass of Saturates in the sample. For semi-quantitative analysis of Saturates only the tracks corresponding to sample application volumes of 5 µL should be considered, as the linear range of detection for this group is between 0.01-10 µg.

Results

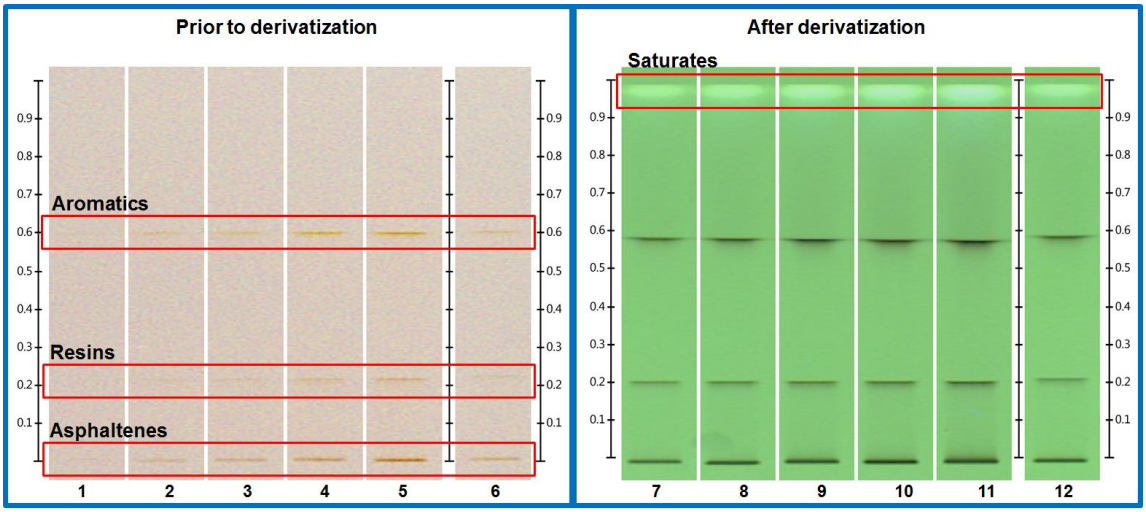

Fig. 1 Left: Plate under white light prior to derivatization (enhanced: contrast 4.0, exposure 0.018 s), right: Plate under UV 366 nm after derivatization. Tracks 1-5: standard applied in different volumes (0.1-1 µL); Track 6: sample (0.5 µL); Tracks 7-11: standard applied in different volumes (3.5-10.0 µL); Track 12: sample (5.0 µL).

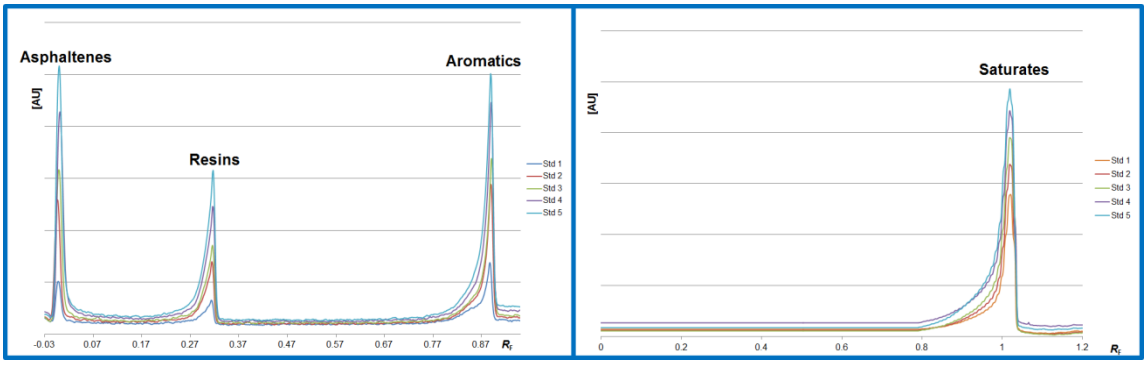

Fig. 2 Left: Densitograms of Asphaltenes, Resins, Aromatics at different concentrations (absorption at 280 nm); right: Densitograms of Saturates at different concentrations (fluorescence with Hg lamp at UV 366/>400 nm).

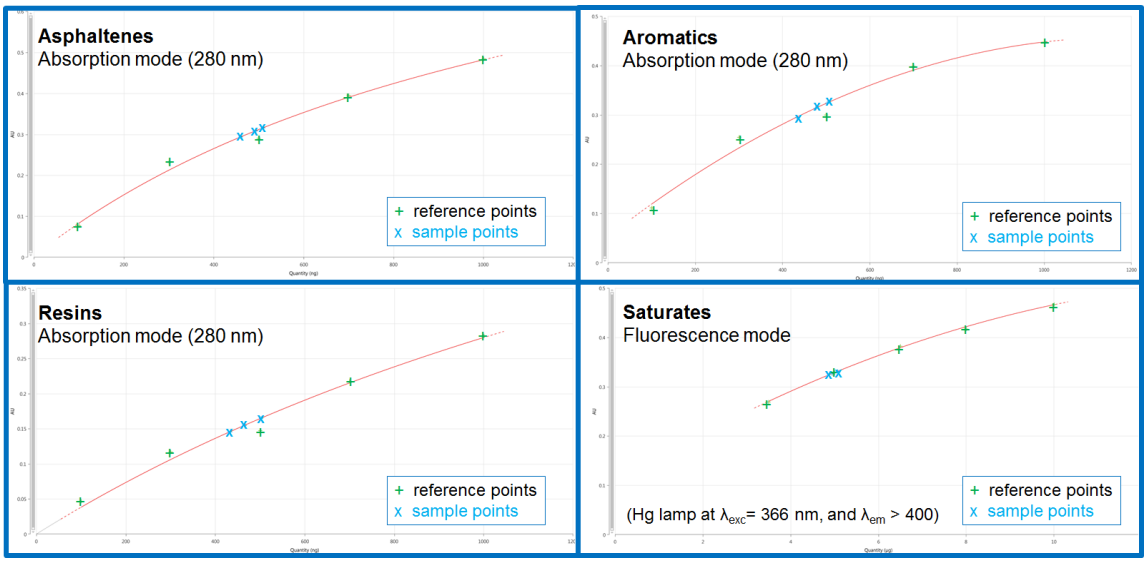

Fig. 3 Calibration curves of each chemical family (peak height vs. quantity). Prior to derivatization: Asphaltenes from 5.0 to 60.0 ng; Resins from 15.1 to 151.0 ng; Aromatics from 63.3 to 633.0 ng. After derivatization with berberine: Saturates from 581.0 ng to 1.7 µg.

Table 1: Results obtained for one bitumen sample (triplicate)

	Asphaltenes	Resins	Aromatics	Saturates
Application 1	51.0 µg/mL	151.7 µg/mL	636.4 µg/mL	166.0 µg/mL
Application 2	49.3 µg/mL	140.4 µg/mL	603.1 µg/mL	164.1 µg/mL
Application 3	46.0 µg/mL	130.8 µg/mL	548.1 µg/mL	168.5 µg/mL
Average	48.8 µg/mL	141.0 µg/mL	595.9 µg/mL	166.2 µg/mL
Standard deviation	5.2 %	7.3 %	7.4 %	1.3 %

Literature

[1] M. Matt, E.M. Gálvez, V.L. Cebolla, L. Membrado, R. Bacaud, S. Pessayre. J Sep Sci 26 (2003) 1665–1674