



Asphaltene content by the in-line filtration method



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HIGHLIGHTS

- The in-line filtration method to determine asphaltene content takes less than 10 min.
- The method has high repeatability and a detection limit of 13 ppm of asphaltenes.
- The method uses a standard HPLC instrument and filters that are widely available.
- Results correlate with results obtained using traditional gravimetric techniques.

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ABSTRACT

In this work, we report the development of an improved analytical method for the evaluation of asphaltene content. This method uses high performance liquid chromatography (HPLC) but, instead of using a conventional column, it uses a commercially available filter to retain the precipitated asphaltenes that are to be quantified. The in-line filtration method represents a significant improvement with respect to previous methods that use a column packed with an inert packing material to perform the analysis, being more repeatable and reproducible with better sensitivity and as a consequence, lower detection and quantification limits. Additionally, the improved method works at lower flow rates making possible the use of a larger variety of different HPLC detectors and opening the possibility to directly couple it with other analytical techniques such as GPC, MS, ICP that require low flow rates. Filters are commercially available, cheaper, and show low variability that drives a more consistent performance than inert/handmade columns. This in-line filtration method requires small amounts of sample and can take less than 10 min. These characteristics make the use of filters an excellent candidate for monitoring processes in the oil industry where evaluation of asphaltenes is important.

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1. Introduction

Asphaltene precipitate during production and refining operations, causing significant losses to the oil industry every year. For example, remediation costs due to asphaltene precipitation in on-shore wells can be around one-half million dollars and significantly more in off-shore wells [1]. In downstream operations, the cost associated with crude oil fouling due mainly to asphaltene precipitation in the pre-heat trains was estimated to be in the order of \$4.5 billion 15 years ago [2]. This last estimate did not consider the impact that fouling might have in other units of the refinery.

Since asphaltene fouling has a great impact in the petroleum industry, it is important to develop tools to evaluate the tendency toward asphaltene precipitation of crude oils and petroleum

related materials. Equally important, but significantly more difficult is to find ways to estimate the potential amount of asphaltene that can precipitate. This knowledge plays a key role in the designing and monitoring of different processes in the oil industry.

Asphaltene content determination traditionally relies on the precipitation of asphaltene using large amounts of solvent and involves filtration of the precipitated material. These traditional methodologies have low repeatability and reproducibility, requiring at least several hours to perform. Recently, new faster techniques based on filtration have been developed [3–6]. Two of them [3,4] are based on proprietary equipment and use spectroscopy measurements in the ultraviolet–visible (UV–vis) range to determine asphaltene content. In these instruments, plugging can be an issue when high asphaltene content samples or unstable ones are tested. Additionally, it has been reported that when UV–vis absorbance of asphaltene is employed to measure asphaltene concentrations, calibration constants correlate to the average associated molar masses of the asphaltene. This can lead to

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significant errors in the asphaltene concentration [7]. On the other hand, on-column methods also rely on filtration and use regular high performance liquid chromatography (HPLC) equipment [5,6]. In these methods, asphaltenes are precipitated and retained in an inert column, redissolved with an appropriate solvent and are quantified using an Evaporative Light Scattering Detector (ELSD). These methods allow not only the determination of asphaltene content, but also can be used to evaluate the asphaltene solubility profile of crude oils and processed materials [8,9]. In particular, by using the asphaltene solubility profile and solubility fraction methods it has been possible to estimate the stability of crude oils and products [8,9], reactivity of residues toward hydroprocessing [10], and fouling in downstream operations [11]. Rather recently, their application has been extended to high temperatures [12].

On-column separation of asphaltenes was first reported by Boduszynski et al. [13]. Heptane, toluene, and pyridine were used to extract coal liquids deposited onto an inert column packing. Later, a similar technique (sequential extraction fractionation – SEF) was applied to separate petroleum residue into different solubility fractions [14]. In 1987, Kingsley [15] patented a sequential process for carbonaceous materials in which for the first time, the sample is injected into a stream of solvent instead of being previously deposited on the column. The introduction of HPLC to perform the measurements [5,6] simplified the determination and had a clear advantage over the use of proprietary instruments in terms of being easily available in most laboratories. However, the use of “inert” columns still poses several limitations for the practical applications of the methods based on this technology.

Inert columns used in the experiments are filled using the “tap-fill” method for packing of rigid solids [16]. Unfortunately, the “tap-fill” method produces highly variable columns that lead to lower reproducibility and repeatability. They also degrade with time due to irreversible asphaltene adsorption and formation of preferential channels and require frequent replacement and/or cleaning. Additionally, the columns have a relatively large volume (>10 mL) that lead to broad peaks which in turn, reduces the sensitivity. To keep the peaks as narrow as possible, relatively large flow rates (>3 ml/min) are required which limit the type of detector that can be used. These large flow rates make difficult the coupling of these methods with other analytical techniques such as Gel Permeation Chromatography (GPC), Mass Spectrometry (MS), and Inductively Coupled Plasma (ICP). The large volume also increases the pressure differential across the HPLC lines, shortening maintenance cycles and lowering life times for seal, valves, and piston pumps.

To overcome the above-mentioned limitations, a improved method was developed to determine asphaltene content. This method uses an in-line filter and is faster, more repeatable and reproducible with better sensitivity and lower detection limit than the on-column techniques. In this work, we present experimental data to support the use of filters instead of Teflon-filled columns for the determination of asphaltene content. The comparison with the old on-column method clearly shows that the use of a filter instead of a column is a significant advance in the reliability of asphaltene testing with important consequences in the practical application of these types of analytical methods.

2. Experimental section

2.1. Sample selection and materials

80 different crude oils and processed materials were used during this work. These materials were selected based on availability and asphaltene content. For these samples, gravimetric asphaltenes were extracted using a modification of the ASTM D6560 test

[17]. In this modified version, a 1/20 sample/n-heptane ratio is used, and the blend is filtered at 80 °C. The precipitated material was washed using hot heptane prior to drying and weighing.

Methylene chloride, toluene, methanol, and n-heptane HPLC grade solvents were purchased from Fisher Scientific and used without further purification. Filters were bought from Restek Corporation and IDEX Health & Science LLC.

2.2. Asphaltene determination by the in-line filtration method

Fig. 1 shows a scheme of the method. In a standard experiment, for samples with estimated asphaltene (extracted with heptane) content larger than 1 wt%, a solution of 1 wt% of the sample in dichloromethane or toluene (if the sample is highly paraffinic) is used. For samples with estimated asphaltene contents lower than 1 wt%, a solution of 10 wt% is prepared. For gravimetric asphaltenes, a solution of 0.1 wt% is prepared. No further preparation of the sample is required. The solution is injected into a flow of heptane and passed through a filter. A typical injection volume is 4 μ L. Heptane induces the precipitation of asphaltenes as soon the sample enters into contact with the heptane. Precipitated asphaltenes are retained by the filter while maltenes pass through it reaching the detector. Then, the mobile phase is switched to a solvent with a high solvent power (i.e. dichloromethane/methanol 90/10 v/v). This blend redissolves the asphaltenes, and as they reach the detector, they are quantified. This procedure is similar to the one

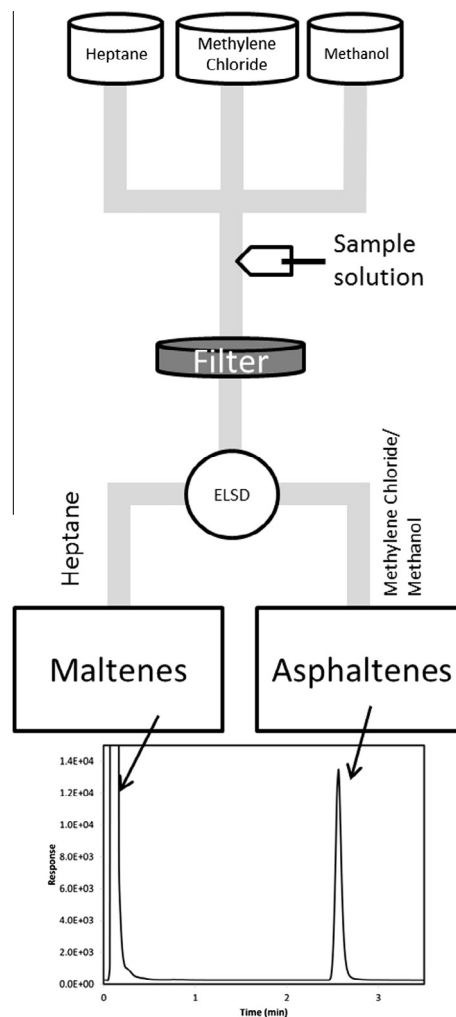


Fig. 1. Scheme of the in-line filtration method.

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