



# A liquid chromatography–atmospheric pressure photoionization tandem mass spectrometric method for the determination of organosulfur compounds in petroleum asphalt cements



Géssica Domingos da Silveira<sup>a,b</sup>, Henrique Faccin<sup>a,b</sup>, Luis Claussen<sup>a,b</sup>, Rayane Bueno Goularte<sup>a,b</sup>, Paulo C. Do Nascimento<sup>a,b</sup>, Denise Bohrer<sup>a,b</sup>, Margareth Cravo<sup>c</sup>, Leni F.M. Leite<sup>c</sup>, Leandro Machado de Carvalho<sup>a,b,\*</sup>

<sup>a</sup> Department of Chemistry, Federal University of Santa Maria (UFSM), Santa Maria-RS, Brazil

<sup>b</sup> Graduate Program in Chemistry, Federal University of Santa Maria (UFSM), Santa Maria-RS, Brazil

<sup>c</sup> Centro de Pesquisa e Desenvolvimento “Leopoldo Américo Miguez de Mello (CENPES), PETROBRAS, Rio de Janeiro, RJ, Brazil

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## ABSTRACT

We present a sensitive liquid chromatography–atmospheric pressure photoionization tandem mass spectrometric (UHPLC-APPI-MS/MS) method for the determination of selected organosulfur compounds in Brazilian asphalt cements. It was possible to detect 14 organosulfur compounds of different classes where sulfoxides and sulfones presented higher sensibility in ionization than thiophenes and aromatic sulfides. A dopant-assisted APPI method was also tested, however, when chromatographic flow rate was optimized a decrease in signal was observed for all compounds. PAHs were tested and ruled out as possible interfering compounds and the matrix effect of asphalt cements was within an acceptable range for the quantification of organosulfur compounds. The proposed method was found to have satisfactory linearity and accuracy with recoveries between 83.85 and 110.28% for thianaphthene and 3-methylbenzothiophene, respectively. Therefore, the method allowed the characterization of organosulfur compounds in Brazilian asphalt cements and demonstrated changes in the amount quantified in asphaltenic and maltenic fractions after the RTFOT + SUNTEST aging process.

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## 1. Introduction

Interest in characterization of organosulfur compounds has increased in the last years as they are present in crude petroleum and consequently in its derived products such as asphalt cements [1]. Thus, the determination of these compounds in asphalt cements is important from scientific and technological viewpoints, since sulfur species are considered precursors of the asphalt oxidation reaction. The oxidation reaction can cause changes in the physicochemical and rheological properties of asphalt cements and interfere with the performance and durability of the asphalt pavement [2,3]. Furthermore, some organosulfur compounds are derived from polyaromatic hydrocarbons (PAH) and have very similar physicochemical properties that may hamper

their chromatographic separation [4,5]. The polycyclic aromatic sulfur heterocycles (PASHs) are by far the most investigated sulfur compounds in petroleum, but sulfides and thiophenes may have some potential as marker compounds in matrices derived from petroleum such as asphalt cements. Mainly because of their oxidation to sulfoxides in photochemical reactions [6], these compounds may change their pattern and concentration yielding information on important parameters such as the maturity of a crude oil [5]. Moreover, sulfones and sulfoxides has been investigated in bitumen and oil shales after artificial maturation process and the samples were found to contain sulfur speciation dominated by oxidized sulfur forms (sulfoxides and sulfones) [7].

Among the available analytical tools in the literature, chromatographic methods are preferred for the identification and characterization of organosulfur compounds in complex matrices such as petroleum derived products [8,4]. More recently, comprehensive two-dimensional gas chromatography has been used to investigate speciation of organic sulfur in petroleum [8]. Nevertheless, volatile compounds can be characterized and analyzed only semi-quantitatively using these methods [9]. Although GC

\* Corresponding author at: Department of Chemistry, Federal University of Santa Maria (UFSM), Santa Maria-RS, Brazil, P.O. Box 5051, 97105-970, Santa Maria-RS, Brazil.

E-mail address: [lemacarvalho@gmail.com](mailto:lemacarvalho@gmail.com) (L.M. de Carvalho).

and GC/MS are powerful analytical tools for the characterization of volatile sulfur compounds, these techniques have some limitations in determining organosulfur compounds in petroleum mainly due to interference caused by PAHs [10,11]. Liquid chromatography coupled to mass spectrometry can overcome these interference problems and allow the analysis of less volatile sulfur compounds [11]. More recently, Al-Zahrani and co-workers characterized sulfur compounds in crude oil and diesel by GC using sulfur chemiluminescence detection (SCD) [12]. The method involved a liquid-phase microextraction demonstrating that a GC approach in complex matrices requires usually a more sophisticated pretreatment step.

Among the detection systems available for liquid chromatography, tandem mass spectrometry (MS/MS) has gained attention for the identification and confirmation of several organosulfur compounds despite the difficulty of their ionization. Rudzinski and co-workers [13,14] reported an HPLC method using a variant of coordination ion spray in which Pd(II) in methanol was introduced into the electrospray ionization source (ESI) of an ion trap mass spectrometer for the determination of e.g. dibenzothiothiophene, thianthrene, 4,6-dimethyl-dibenzothiothiophene and others in crude oils. Rudzinski and Rai [11] developed a high-performance liquid chromatography with atmospheric pressure chemical ionization (APCI)/tandem mass spectrometry method with post column addition of tropylium cations prior to APCI/MS to determine 3- and 4-ring organosulfur compounds in Arabian crude oil with high sensitivity. Organosulfur compounds are difficult to ionize by ESI and APCI sources because they provide soft ionization and PASH are not amenable to the normal mechanisms of ion formation. PASH are not easily protonated or deprotonated so coordination with a charged metal can allow their determination using ESI and APCI sources.

A more recent ionization method for liquid chromatography is atmospheric pressure photoionization, which was described for the first time in 2000 by Robb and co-workers [15] including the ionization and determination of a diphenyl sulfide standard. The technique is able to ionize those molecules that are poorly amenable to the normal mechanisms of ESI and APCI sources [16]. Purcell and collaborators compared ESI and APPI sources in the analysis of sulfur compounds in crude oil by Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) and showed that APPI produced more ions and was able to ionize samples without requiring chemical derivatization [17].

The identification and elucidation of unknown sulfur compounds in asphalts can be considered a complex issue. Moreover, it would be always considered a partial approach, since there are a large and unpredictable number of organosulfur molecules in the matrix. Therefore, a possible and realistic way of studying the aging process of asphalts could be the choice of known majority sulfur classes and the use of commercial synthetic standards for a qualitative and quantitative interpretation of the phenomena. Considering that these sulfur classes have been described in asphalt fractions (e.g. maltenes, asphaltenes, resins) obtained from cements of different sources, we decided for modeling the classes involved in the aging processes of asphalts. Some of the analytes studied in this work, such as dibenzothiothiophene, 4,6-dimethyldibenzothiothiophene, 3-methyl benzothiothiophene, 4-methyl dibenzothiothiophene, thianthrene, benzo (a) naphto [2,3 -d] thiophene have been found in Arabian oil and its derivatives [11,14]. According to Green [11], the presence of such sulfur compounds could be associated with aging processes of the cements used for paving. Thus, the aim of the present study was the development and validation of an UHPLC–MS/MS method using APPI as the ion source for the determination of selected organosulfur compounds in Brazilian petroleum asphaltic cements. Moreover, characterization of selected organosulfur compounds in these matrices has been little described to date, so that some sulfur compounds were cho-

sen as markers of the main functional groups present in asphaltic matrices (sulfides, sulfoxides, sulfones and thiophenes).

## 2. Materials and methods

### 2.1. Chemicals and solutions

All chemicals employed in this investigation were of analytical grade purity (at least 95% purity) and were used without further purification. The standards dimethyl sulfoxide, butyl sulfoxide, di-*p*-toluyl sulfone, methyl phenyl sulfoxide, benzyl sulfone, thianthrene, thianaphthene, 4-methyl benzothiothiophene, 3-methyl benzothiothiophene, 4,6-dimethyl dibenzothiothiophene, benzo (a) naphto [2,3-d] benzothiothiophene, dibenzothiothiophene, dodecyl sulfoxide, diphenyl sulfide, hexyl sulfide and butyl disulfide were purchased from Sigma-Aldrich® (St. Louis, MO, USA). The standards of PAHs tested as possible interferents anthracene, benzo (a) pyrene, benzo (b) fluoranthene, benzo (G, H, I) perylene and fluorene were purchased also from Sigma-Aldrich® (St. Louis, MO, USA); benzo (k) fluoranthene and the NPAHs 1-nitropyrene and nitrofluorene were purchased from Fluka (Buchs, Switzerland). Methanol and acetonitrile (LC–MS grade) were obtained from Panreac (Castellar del Vallès, Spain); dichloromethane was of Chromasolv® HPLC grade and supplied by Sigma-Aldrich (St. Louis, MO, USA); toluene was obtained from Merck® (Darmstadt, Germany). Water was purified using a Milli-Q Ultra Pure Water System (Merck Millipore, Darmstadt, Germany).

The Standard reference material, SRM 1582, was from the American National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) and it consists of a crude oil that provides a typical specimen of an oil matrix for use in developing analytical methods.

Standard stock solutions ( $1\text{ g L}^{-1}$ ) of the individual compounds were prepared by dissolving appropriate amounts of substances in HPLC grade dichloromethane. All the solutions were stored in amber glass recipients at  $-6^\circ\text{C}$  until their use. The working solution was prepared by diluting the individual solutions with methanol (LC–MS grade) to obtain a mix of the organosulfur compounds.

### 2.2. Ultra high performance liquid chromatography (UHPLC) and mass spectrometry (APPI-MS/MS)

An Agilent® 1260 Infinity UHPLC–MS chromatography system (Santa Clara, CA, USA) with automatic injection, which was able to operate at pressures up to 600 bar, was used for chromatographic separations. Separations were performed in a Poroshell 120 C18 column (Agilent Technologies®) with dimensions of  $3.0\text{ mm} \times 100\text{ mm}$  packed with  $2.7\text{ }\mu\text{m}$  superficially porous particles. Water (A) and Methanol (B) were used as the mobile phase at a constant flow rate ( $0.800\text{ mL min}^{-1}$ ) according to the following gradient program: 34% B (0.0–0.8 min); 45–86% B (0.8–6.4 min); 86–100% B (6.4–6.6 min); and 100% B (6.60–10.0 min). The chromatographic column was maintained at  $40^\circ\text{C}$  and conditioned daily using the initial conditions of the elution program for 20 min prior to use in the experiments. After the conditioning period,  $5\text{ }\mu\text{L}$  of the working solutions were automatically injected. The compounds were ionized by a krypton lamp on an APPI PhotoMate (Agilent Technologies®, Santa Clara, CA, USA) source and subsequently analyzed in an Agilent 6430 Triple Quadrupole mass spectrometer operating in the *selective reaction monitoring* (SRM) mode with a resolution of  $0.7\text{ m/z}$  (FWHM).

After finishing the gradient program, a time of 4.0 min was adopted for re-equilibrating the system, which was based on the time required to reestablish the initial pressure.

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