



# Speciation of organic sulfur compounds using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry: A powerful tool for petroleum refining



Bárbara M.F. Ávila<sup>a,\*</sup>, Vinícius B. Pereira<sup>a</sup>, Alexandre O. Gomes<sup>b</sup>, Débora A. Azevedo<sup>a,\*</sup>

<sup>a</sup> Universidade Federal do Rio de Janeiro, Instituto de Química, LAGOA-LADETEC, Ilha do Fundão, Rio de Janeiro, RJ 21941-909, Brazil

<sup>b</sup> Petrobras, CENPES/PDEDS/TAP, Ilha do Fundão, Rio de Janeiro, RJ 21941-909, Brazil

## HIGHLIGHTS

- Sulfur compounds play an important role in naphthenic corrosion.
- Sulfur compound speciation was performed in two oils with no pre-treatment.
- Many classes were identified due to the two separation mechanisms of GC × GC.
- Thiols, sulfide and disulfides were detected in one sample, and none in the other.

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## ABSTRACT

Sulfur compounds are among the most important heteroatomic constituents of petroleum. These compounds are undesirable because they increase emulsion stability, cause corrosion, contaminate catalytic processes of refining, and determine color and odor of final products. Also, sulfur compounds play an important role in naphthenic corrosion, which occurs via chemical reaction of naphthenic acids with iron; sulfur limits corrosion through formation of a surface film of FeS, but this formation does not occur for all classes of sulfur compounds. Hence, their speciation is important. In this work, qualitative and semi-quantitative characterization of organic sulfur compounds were performed in two petroleum samples with no pre-treatment using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC-TOFMS). Total sulfur content (ASTM D 4294) was 1.91% and 0.96%, on mass %, while °API was 33.1 and 19.6 for sample #1 and sample #2, respectively. Regarding cyclic sulfur compounds, one sample showed a total concentration of 60,363  $\mu\text{g g}^{-1}$  of whole oil, while the other sample showed a total concentration of 4,740  $\mu\text{g g}^{-1}$ . Further, sulfides, disulfides, and thiols were detected only in sample #1; total concentration was 1,372  $\mu\text{g g}^{-1}$ . Thus, total concentration of all sulfur compounds for sample #1 was 61,735  $\mu\text{g g}^{-1}$ . These data illustrate the potential of the GC × GC-TOFMS technique for molecular characterization and semi-quantification, in this case sulfur speciation, of complex samples, such as petroleum.

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## 1. Introduction

Sulfur compounds are among the most important heteroatomic constituents of petroleum. These compounds occur mainly as thiols, sulfides, disulfides, thiophenes, and benzo-, dibenzo-, and benzonaphthothiophenes. The rising demand for transportation fuels in combination with changing feedstock supplies leads refiners to

process heavier and more sour crude oils [1,2]. Sulfur compounds are responsible for problems in storage, blending, and processing of crude petroleum fractions in refinery operations. Typical problems caused by these compounds include catalyst poisoning and deactivation, high hydrogen consumption in processing, and corrosion of equipment [3].

Due to these adverse events, removal of sulfur compounds or their conversion to less deteriorative compounds is an important step in refining. Different groups of sulfur-containing compounds generally show differing behavior with respect to catalyst poisoning, equipment corrosion, and sulfur-removal processes, such as

\* Corresponding authors. Tel.: +55 21 2562 7488; fax: +55 21 2260 3967.

E-mail addresses: [barbaramfavila@yahoo.com.br](mailto:barbaramfavila@yahoo.com.br) (B.M.F. Ávila), [debora@iq.ufrj.br](mailto:debora@iq.ufrj.br) (D.A. Azevedo).

hydrodesulfurization. Knowledge of desulfurization reactants and products is useful for optimization of sulfur removal processes. Besides, development of novel catalysts requires detailed knowledge of the molecular structures of the sulfur-containing compounds present in crude oil and intermediate products [4–6]. Therefore, speciation of these compounds is necessary, as it would provide important information and allow differentiation between oil types.

Further, sulfur compounds play an important role in naphthenic corrosion, a type of corrosion caused by naphthenic acids during petroleum refining. This corrosion occurs via chemical reaction of naphthenic acids with iron; sulfur limits corrosion through formation of a surface film of FeS, because there is competition between the two kinds of processes, naphthenic attack and hydrogen sulfide attack [7,8].

Corrosion engineers tend to use total sulfur as a measure of reactivity of sulfur compounds in crude oil; however, at best, this is a poor method for estimating the probability of the presence of a sulfur compound, due to difficulties in analysis of this kind of analyte. Total sulfur content reveals nothing about its reactivity. For example, H<sub>2</sub>S and alkanethiols are very reactive toward iron, producing the FeS protective layer. By contrast, other organic sulfur compounds, such as the thiophene family, have little reactivity toward iron [8]. This is why speciation of sulfur compounds is so important.

Many authors investigate sulfur compounds in petrochemical samples using various techniques, such as gas chromatography-atomic emission detection (GC–AED) [9,10], gas chromatography-flame ionization detection (GC–FID) [11], gas chromatography–mass spectrometry (GC–MS) [11–13], gas chromatography–sulfur chemiluminescence detection (GC–SCD) [14], among others. Due to the lack of resolution and peak capacity of complex matrices analyzed using GC (gas chromatography), many coelutions are observed. Therefore, owing to two separation mechanisms of analytes, comprehensive two-dimensional gas chromatography (GC × GC) provides much more information and separation power than 1D-GC. Use of GC × GC is recently reported for identification of sulfur compounds [2,4,5,15–25]. The majority of these studies use selective detectors, such as sulfur chemiluminescence detector (SCD) [2,5,15–17,19,20,23,25] and atomic emission detector (AED) [4,18]. Few studies use GC × GC–TOFMS, and the principal approach is qualitative analysis of the sulfur species [4,22–25].

Thus, the aim of this work is speciation of organic sulfur compounds in petroleum samples using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC–TOFMS), with no pre-treatment or fractionation, avoiding any compound loss, and semi-quantification. Many of these compounds are volatile compounds, and some are in trace amounts in a complex sample such as crude oil.

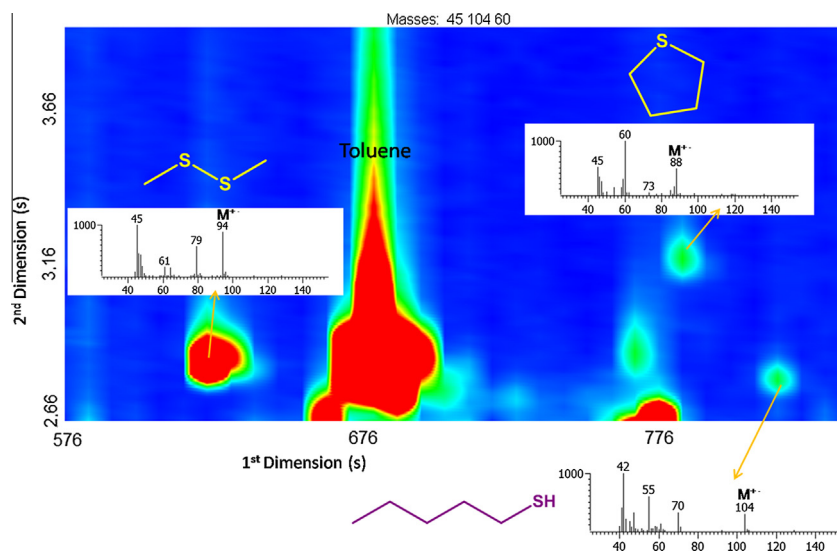
## 2. Experimental

### 2.1. Samples and standards

Two samples were supplied by CENPES/PEDS/TAP, Petrobras (Brazil) with different characteristics. Total sulfur content (ASTM D 4294) was 1.91% for sample #1 and 0.96 % for sample #2, on mass %; the °API are 33.1 and 19.6 for samples #1 and #2, respectively. Approximately 100 mg of each sample were weighed directly on a vial followed by addition of *n*-tetracosane-d<sub>50</sub> and pyrene-d<sub>10</sub> standard solution (1 mL) at 10 ng μL<sup>-1</sup> and 14 ng μL<sup>-1</sup>, respectively. *n*-Tetracosane-d<sub>50</sub> and pyrene-d<sub>10</sub> were acquired from Cambridge Isotopes Laboratories (Andover, MA, USA), for use as internal standards for semi-quantification of sulfur compounds. 2-Methyl-1-butanethiol, 1-pentanethiol, 1-octanethiol, cyclohexanethiol, cyclopentanethiol, ethyl-methyl-sulfide, diphenyl-sulfide, and tetrahydrothiophene were used as authentic standards for identification purposes. The standards were obtained from Sigma–Aldrich (Brazil) and were GC-reagent grade (purity ≥98%).

### 2.2. GC × GC–TOFMS

The GC × GC–TOFMS system was a Pegasus 4D (Leco, St. Joseph, MI, USA), which is an Agilent Technologies 6890 GC (Palo Alto, CA, USA) equipped with a secondary oven and a non-moving quad-jet, dual-stage modulator. Data acquisition and processing were carried out using ChromaTOF™ software version 4.44 (Leco Corp., St. Joseph, MI, USA). The GC column set consisted of a HP-5 ms (Agilent Technologies), 5%-phenyl-95%-methyl-siloxane (30 m, 0.25 mm i.d., 0.25 μm d<sub>f</sub>) as the first dimension (1D) and a BPX-50 (SGE), 50%-phenyl-50%-methyl-siloxane (1.5 m, 0.1 mm i.d.,



**Fig. 1.** Selected region of GC × GC–TOFMS *m/z* 45 + 60 + 104 extracted ion chromatogram (EIC) of sample #1, showing dimethyl-disulfide, tetrahydrothiophene and 1-pentanethiol.

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