



# Method development and validation for sulfur determination via CS molecule in petroleum green coke by high resolution continuum source molecular absorption spectrometry



Adriana Simane Camera<sup>a</sup>, Patrícia Passos Arcênio<sup>a</sup>, Waldemar de Oliveira Pacheco Filho<sup>a</sup>, Tatiane de Andrade Maranhão<sup>a</sup>, Fernando Jorge Santos de Oliveira<sup>b</sup>, Vera Lúcia Azzolin Frescura<sup>a,\*</sup>

<sup>a</sup> Departamento de Química, Campus Trindade, Universidade Federal de Santa Catarina, 88040-900 Florianópolis, SC, Brazil

<sup>b</sup> Petróleo Brasileiro S. A., Gerência de Meio Ambiente, Av. Almirante Barroso, 81, 20031-004 Rio de Janeiro, RJ, Brazil

## ARTICLE INFO

### Article history:

Received 5 December 2016

Received in revised form 11 May 2017

Accepted 25 June 2017

Available online 27 June 2017

### Keywords:

Petroleum green coke

Sulfur

Molecular absorption spectrometry

Method validation

## ABSTRACT

Development and validation of a method for determination of sulfur via CS molecule in petroleum green coke samples by high resolution continuum source molecular absorption spectrometry (HR-CS MAS) is the aim of this work. The protocol adopted for the method validation followed criteria based on international guidelines. Optimizations and determination of the analyte in the samples were carried out at the wavelength 258.0330 nm, at the same spectral interval of the analytical line of Tl. Slurry prepared using Triton X-100 (0.05% v/v) without the use of HNO<sub>3</sub>, is proposed as a simple and fast sample treatment. Chemical modifier KOH (1.0% m/v) was important to promote the formation and stabilization of CS molecule. Pyrolysis and Vaporization temperatures were optimized using different compounds, ammonium sulfate, L-cysteine monohydrochloride and thiourea aqueous solutions, and also certified reference material, NIST 2718, and petroleum green coke. Compromise temperature conditions were 1000 °C and 2600 °C, for pyrolysis and vaporization, respectively. Aqueous calibration with thiourea presented the best condition and was chosen for the determination of the analyte. The obtained concentrations of sulfur in coke samples were between 6.20 mg g<sup>-1</sup> and 9.40 mg g<sup>-1</sup>. The following parameters were evaluated as validation protocol: accuracy, precision, linearity, limits of detection and quantification, sensitivity, selectivity, robustness, working range and measurement uncertainty. Weighted least square (WLS) method was employed to estimate LOD and LOQ, since it leads to lower final uncertainty. The evaluation of the validation parameters, especially the measurement uncertainty, confirmed the satisfactory performance of the method.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Petroleum refining process is one of the main activities responsible for polluting gas emission, containing many hazardous compounds including different species of sulfur, leading to several detrimental consequences, such as acid rain, which is harmful to forests, crops, water bodies and eventually jeopardizing human healthy. To minimize the release of this element and to meet new tendencies for clean production, refineries nowadays employ hydrodesulfurization units to remove sulfur from final products; gasoline, diesel, kerosene, jet fuel and fuel oils. However, the removal of many hazardous elements is not accomplished for wastes and by-products during petroleum processing, and these residues can contain high concentration of sulfur, resulting in damage to

environment [1–4]. One by-product, generated in large amount by refining process is coke. Many different types of coke are produced and because the high energy content it is been proposed as alternative raw material in a variety of process. To ensure that processes using coke from petroleum industry are environmental friendly and avoid potential risks the characterization regarding the hazardous content, including sulfur is required [5–7].

Sulfur determination in petroleum coke usually can be achieved by application of official methods EPA method 8085 Compound-Independent Elemental Quantitation of Pesticides by Gas Chromatography with Atomic Emission Detection, for solid samples, ASTM D 6376 Standard Test Method for Determination of Trace Metals in Petroleum Coke by Wavelength Dispersive X-ray and ASTM D-1552 Standard Test Method for Sulfur in Petroleum Products by High Temperature Combustion and Infrared (IR) Detection or Thermal Conductivity Detection (TCD) [8–10]. Determination of sulfur also has been achieved by

\* Corresponding author.

E-mail address: [vera.bacunan@ufsc.br](mailto:vera.bacunan@ufsc.br) (V.L.A. Frescura).

different techniques, including UV–Vis spectrophotometry [11–13], inductively coupled plasma mass spectrometry (ICP-MS) [14–16] and inductively coupled plasma optical emission spectrometry (ICP OES) [17–20]. All these techniques require a sample treatment, either by digestion or extraction, to make it suitable to be inserted into the introduction system of the instrument.

High resolution continuum source molecular absorption spectrometry (HR-CS MAS), an alternative method, has been widely applied for sulfur determination, measuring the absorbance of molecules of the analyte using flame (F) or graphite furnace (GF) atomizers and different sample introduction systems. Graphite furnace makes it possible the introduction of the samples with a minimum treatment, slurry sampling, or even without any procedure, direct solid sampling [20–27]. In this work, our aim was to develop a method for determination of sulfur in petroleum green coke by GF-HR-CS MAS with a simple and fast sample treatment, slurry technique, which offers excellent advantages such as reducing in time preparation, contamination, losses of the analyte and residues generation [28–30]. The molecular species measured for sulfur determination was CS at the wavelength 258.0330 nm using chemical modifier KOH to promote the formation and stabilization of the molecule, a new approach developed by Arcênio et al. [31], and permanent modifier W to protect the surface of the furnace platform and extend its lifetime [32,33]. A protocol for validation of the method is also proposed with the following parameters established: accuracy; precision; linearity; limits of detection and quantification; sensitivity; selectivity; robustness; working range and measurement uncertainty [34–41].

## 2. Experimental

### 2.1. Instrumentation

All measurements for method development and sulfur determination were carried out in a high resolution continuum source atomic absorption spectrometer, model ContrAA 700 (Analytik Jena, Jena, Germany) equipped with a high pressure xenon short arc lamp emitting a continuous spectrum at a range from 190 to 900 nm. The instrument is also equipped with a double echelle monochromator (DEMON) aligned to a linear charge-coupled device (CCD) detector with 512 pixels. Sample introduction was performed using an autosampler model MPE 60 (Analytik Jena). Transversal graphite furnace recovered with pyrolytic graphite and integrated platform of pyrolytic graphite was the atomizer. Tungsten permanent modifier was employed and the program for its thermal deposition is shown in Table 1. Argon (99.998 % purity) was used as protection and purge gas during the measurements.

The spectral interval of CS molecule band is located from 257.8894 nm up to 258.1752 nm, corresponding to the same spectral interval of Tl, whose secondary atomic line, 258.0140 nm with a relative intensity is 4.8%, does not overlap the molecule signal. The determination of CS molecule was carried out at the wavelength 258.0330 nm, following the graphite furnace temperature program presented in Table 2. Iterative background correction (IBC) mode was used.

Sample pretreatment was carried out using an agate mortar and pestle, a ball mill, model MM200, (Retsch, USA) and nylon sieve cloth 45

**Table 1**  
Graphite furnace temperature program for thermal deposition of tungsten (W) on the graphite platform by HR-CS MAS.

Temperature (°C)	Ramp (°C s <sup>-1</sup> )	Hold (s)	Ar flow rate (L min <sup>-1</sup> )
80	6	20	2.0
90	3	20	2.0
110	5	10	2.0
350	50	20	2.0
1300	300	10	2.0
1300	0	5	0
2300	1500	4	0
2450	500	4	2.0

**Table 2**

Graphite furnace temperature program used for sulfur determination via CS molecule in petroleum green coke slurries using platform coated with W and chemical modifier KOH by HR-CS MAS.

Step	Temperature (°C)	Ramp (°C s <sup>-1</sup> )	Hold (s)	Ar flow rate (L min <sup>-1</sup> )
Dry	100	6	20	2.0
Dry	120	3	25	2.0
Pyrolysis	1000	300	20	2.0
Auto-zero	1000	0	5	0
Vaporization	2600	FP <sup>a</sup>	3	0
Clean out	2650	500	4	2.0

<sup>a</sup> Full POWER.

µm, Genesis Global JP Pet 120.34 W PW = 110 cm, Guarulhos, SP, Brazil).

### 2.2. Reagents, standards and samples

High purity water at a resistivity of 18.2 MΩ cm was obtained in a system, Milli-Q (Millipore, Bradford, MA, USA) and used to prepare all samples and solutions. Calibration curves were prepared using an inorganic salt, Ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Merck KgaA, Darmstadt, Germany), and two organic compounds, thiourea (CH<sub>4</sub>N<sub>2</sub>S, Quimibrás Indústria, Rio de Janeiro, Brazil) and L-cysteine monohydrochloride (C<sub>3</sub>H<sub>8</sub>ClNO<sub>2</sub>S, Sigma-Aldrich, Fluka, St. Louis, USA). Non-ionic detergent Triton X-100 (Sigma-Aldrich, Fluka) 5% v/v solution was employed to stabilize the solid particles of the green coke in the slurry. Certified reference material of green coke NIST 2718 (National Institute of Standards & Technology, USA) and green coke samples from a Brazilian oil company were employed in the development of this method. Permanent modifier W was deposited on the surface of the graphite platform by injection of 40 µL of a 1.0 g L<sup>-1</sup> solution of tungsten (Spex Industries, INC, USA) and submission to the temperature program described in Table 1. The procedure was repeated 25 times resulting in a 1.0 mg mass layer of the modifier. Additionally a 1.0% m/v KOH (Sigma-Aldrich, Fluka, St. Louis, USA) solution was used as chemical modifier.

### 2.3. Sample preparation and analytical procedures

Sample pretreatment was carried out by grinding the petroleum green coke using a mortar and pestle and, after that sieving it to obtain a thin powder with 45 µm particle size in order to increase the contact area and improve the stability of the slurry. To avoid fractionation of the analyte a representative amount of the samples was grinded and made pass through the sieve with no particles left over. Certified reference material NIST 2718 was powdered in a ball mill to assure the same particle size of the real samples.

Slurry sample preparation was accomplished by weighing 10.0 ± 0.1 mg of the sample or certified material directly into polypropylene tubes (NEST Biotechnology Co. Ltd., China) using a Microbalance (model AG 204, Mettler, Toledo, Switzerland) and addition of 0.05% v/v of Triton X-100 and water. For petroleum green coke the final volume was 10 mL and for certified reference material, 25 mL. The solutions were manually stirred to promote the suspension of the particles and prior the instrument pipetting the solution in the sampling cup was stirred six times with a Pasteur pipette to assure its homogenization.

Pyrolysis and vaporization temperatures were optimized for ammonium sulfate, L-cysteine monohydrochloride and thiourea calibration solutions as well as for the petroleum green coke and certified reference material slurries. The volumes inserted into the graphite tube were 20 µL of the sample or calibration solution and 10 µL of the modifier. The stability of the analyte in the calibration solutions was evaluated with and without addition of HNO<sub>3</sub> and the calibration concentrations were 5, 10, 15, 20 and 25 mg L<sup>-1</sup>, besides the blank.

Download English Version:

<https://daneshyari.com/en/article/5139131>

Download Persian Version:

<https://daneshyari.com/article/5139131>

[Daneshyari.com](https://daneshyari.com)