



Feasibility of high-resolution continuum source molecular absorption spectrometry in flame and furnace for sulphur determination in petroleum products

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ABSTRACT

For the first time, high-resolution molecular absorption spectrometry with a high-intensity xenon lamp as radiation source has been applied for the determination of sulphur in crude oil and petroleum products. The samples were analysed as xylene solutions using vaporisation in acetylene-air flame or in an electrothermally heated graphite furnace. The sensitive rotational lines of the CS molecule, belonging to the $\Delta v = 0$ vibrational sequence within the electronic transition $X^1\Sigma^+ \rightarrow A^1\Pi$, were applied. For graphite furnace molecular absorption spectrometry, the Pd + Mg organic modifier was selected. Strong interactions with Pd atoms enable easier decomposition of sulphur-containing compounds, likely through the temporal formation of Pd_xS_y molecules. At the 258.056 nm line, with the wavelength range covering central pixel ± 5 pixels and with application of interactive background correction, the detection limit was 14 ng in graphite furnace molecular absorption spectrometry and 18 mg kg⁻¹ in flame molecular absorption spectrometry. Meanwhile, application of 2-points background correction found a characteristic mass of 12 ng in graphite furnace molecular absorption spectrometry and a characteristic concentration of 104 mg kg⁻¹ in flame molecular absorption spectrometry.

The range of application of the proposed methods turned out to be significantly limited by the properties of the sulphur compounds of interest. In the case of volatile sulphur compounds, which can be present in light petroleum products, severe difficulties were encountered. On the contrary, heavy oils and residues from distillation as well as crude oil could be analysed using both flame and graphite furnace vaporisation. The good accuracy of the proposed methods for these samples was confirmed by their mutual consistency and the results from analysis of reference samples (certified reference materials and home reference materials with sulphur content determined by X-ray fluorescence spectrometry).

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1. Introduction

Sulphur is the most abundant heteroatom in crude oil and the element most often determined in materials from the petroleum industry. Crude oil can contain from 0.01 up to 10% sulphur, which is concentrated in heavier fractions and residues during distillation [1–4]. Even lighter fractions, such as gasoline or naphtha, can contain 0.02–0.1% of sulphur [4]. Sulphur compounds create a lot of trouble in refineries: corrosion of industrial devices, poisoning catalysts and sediment precipitation. They also worsen properties of final products, including colour, odour and susceptibility to ageing and stimulate corrosive action [1,4–6]. In addition, sulphur compounds contained in automotive fuels poison automotive catalysts and have a detrimental impact on the environment, because they cause acid rain, earth erosion, lung diseases and chemical weathering of statues and buildings. To protect the environment, the admissible sulphur content

in fuels has been significantly decreased [7]. Now in European Union countries, the limits in gasoline and diesel oil are equal to 0.0010% m/m [8,9], which represents a decrease of two orders of magnitude over the last 10 years. To fulfil this severe requirement, crude oil refineries have developed desulphurisation processes [10,11].

Numerous analytical techniques have been used for sulphur determination in petroleum products, including gravimetry [12], volumetry [13], square-wave voltammetry [14], ion chromatography [15], two-dimensional gas chromatography [16] and total reflection X-ray fluorescence [17]. However, the most widespread are X-ray fluorescence with energy [15,18,19] or wavelength dispersion [20–23], as well as combustion techniques with detection using fluorescence in ultraviolet [24,25] or microcoloumetry [26,27]. In addition, mass spectrometry with ionisation in inductively coupled plasma [28–30] and optical emission spectrometry with excitation in inductively coupled plasma [31–34] have been used for sulphur determination in crude oil or petroleum products. Sulphur determination using multi-elemental techniques is complementary to the determination of nickel and vanadium, which are the most abundant metals in crude oil [19,31–33].

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Atomic absorption spectrometry is not used for direct sulphur determination, as sulphur atomic lines lie in the vacuum ultraviolet and the element forms stable molecules resistant to atomisation below 3000 °C. However, conventional atomic absorption spectrometry has been applied for the determination of sulphur in indirect ways. For example, by measuring of barium over precipitate of barium sulphate, following addition of excess barium solution and conversion of sulphur compounds into barium sulphate [35].

Another interesting method of indirect analysis with conventional medium-resolution spectroscopy was intentional formation of sulphur compounds and measurement of their absorption using specific radiation from hollow cathode lamps or radiation of conventional continuum sources. Some examples of such analysis are listed in Table 1 [36–38]. This topic was reviewed in detail by Welz et al. [39].

Strong molecular absorption bands can be found in the ultraviolet spectra of sulphur-containing samples, vaporised in a flame or in a graphite furnace [38–45]. The spectra were attributed mainly to diatomic sulphur compounds (e.g., CS [38–45], SH [40,43] and S₂ [44,45]), but the generation of C_nS_m and SO_x was also taken into account [44,45]. A very strong absorption was registered below 230 nm (of unknown origin) and around 260 nm (attributable to CS). A weak group of absorption bands, ascribed to SH molecules, was found around 325 nm [40,43].

The door to new possibilities in non-metal determination has been opened with the introduction of high-resolution molecular absorption spectrometry with a high-intensity xenon lamp as the continuum radiation source (HR-CS MAS) [39–41]. As the vaporisation of measured species takes place at the high temperature of traditional AAS atomisers (flame or graphite furnace), the technique is also known as flame molecular absorption spectrometry (FMAS) or graphite furnace molecular absorption spectrometry (GFMAS) [39]. A few papers dealing with sulphur determination using these new techniques have appeared in the last few years [42,43,46–48]. In the flame technique, the characteristic concentration was 125 mg kg⁻¹ at 258.056 nm (90 mg kg⁻¹ at 257.599 nm) and the detection limit was 2.3 mg L⁻¹. In the graphite furnace technique, the characteristic mass was 12 [47] or 18 ng [48], whereas the detection limit was 2.3 [47] and 15 ng [48] (Table 1). However, none of the mentioned papers deal with the analysis of samples of petroleum origin. The aim of this work was the evaluation of the possibilities and limitations of HR-CS MAS with vaporisation in a flame or in a graphite furnace for sulphur determination in petroleum products after their dissolution in xylene.

The important fact that has to be taken into account when analysing petroleum products is rich and unknown speciation of sulphur. It can be present in crude oil in more than ten thousands different structures, including sulphides, disulphides, polysulphides, mercaptans, thiophene and its various derivatives, as well as condensed structures of high molecular weight [1,49]. Xylene is an

effective solvent for petroleum products and the chosen step of samples preparation for analysis (dilution in xylene) did not appear to be prone to an analyte form effect. The high efficiency of dissolution and relatively low dissolution coefficient are important from the point of view of the relatively low sensitivity of HR-CS MAS in sulphur determination [39–43,47,48]. It would be expected that, during analysis of organic samples dissolved in xylene in a flame or in a graphite furnace, the CS molecule is easily generated and absorbs radiation at the selected wavelength. On the other hand, the data on the difficulty of unification of the behaviour of various organic analyte forms should also be considered [50,51].

One of the important issues in analytical techniques using a graphite furnace is the application of chemical modifiers. The chemical modifiers applied in the literature devoted to sulphur determination by GFMA are listed in Table 1 [36–38,47,48]. Some differences in authors' opinions were noted. For example, Ferreira et al. [48] successfully used pyrolytically coated graphite tubes, but Tittarelli and Lavaroto did not obtain any sulphur signal when using similar pyrolytically coated graphite [38]. Heitmann et al. [47] regarded the use of 4% methane in argon necessary to improve the formation of CS, while Ferreira et al. [48] did not observed any significant effect of methane on analysis. Furthermore, Tittarelli et al. [38] claimed that methane inhibited reactions between sulphur compounds and carbon coming from graphite, making CS formation impossible. Moreover, Heitmann et al. [47] and Ferreira et al. [48] generated coatings of graphite with refractory carbides, zirconium carbide and tungsten carbide, respectively. Ferreira et al. [48] stated that this tungsten coating was advantageous because it reduced the contact of the analyte with the graphite furnace, preventing CS₂ formation.

In this work, different chemical modifiers were investigated, including palladium in an organic form, which was successfully used in the determination of other analytes in xylene solutions of petroleum products [50,51].

2. Experimental

2.1. Instrumentation and its operation

A commercially available high-resolution continuum source absorption spectrometer ContrAA 700 (Analytik Jena, Jena, Germany) was used in the work. It was equipped with a high-intensity xenon short-arc lamp operating in "hot-spot" mode as a radiation source, a high-resolution double monochromator consisting of a prism and an echelle grating and a linear charge-coupled device array detector with 588 pixels, 200 of which were available for analytical purposes [40,41]. The spectrometer covered a wavelength range from 189 to 900 nm, of which a spectral interval of up to one nanometre could be recorded simultaneously with a high linear

Table 1
Literature data on sulphur determination using GFMA.

Radiation source	Required analyte form (wavelength, nm)	Solvent	Furnace surface coating	Modifier	Comments	Detection limit	Reference
Hollow cathode lamp		Water	Uncoated graphite	To bind sulphur during drying and ashing steps various metals were added to measured solution	Better results for uncoated tubes		36
-Fe	-AlS (219.18)					-6 mg kg ⁻¹	
-Pt	-InS (243.7)					-2 mg kg ⁻¹	
-W	-SnS (273.6)					-5 mg kg ⁻¹	
H ₂ lamp	GeS (285.0; 215.2)	Water	-	-	Characteristic mass: 600 ng		37
D ₂ lamp	CS (257.6)	Xylene	Uncoated graphite	-	No sulphur signal for pyrolytically coated furnace	10 mg kg ⁻¹ in solution	38
Xe lamp	CS (258.056)	Water	ZrC	4% methane in argon and Ca in solution	Characteristic mass: 12 ng	2.3 ng S absolute	47
Xe lamp	CS (258.033)	Water	WC	40 µg Pd in solution	-4% methane in argon–non efficient -Ca and Mg modifiers were also evaluated -Characteristic mass: 18 ng	15 ng S absolute (30 mg kg ⁻¹ in solid sample)	48

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