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Quantitative on-line analysis of sulfur compounds in complex hydrocarbon matrices

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ABSTRACT

An improved method for on-line measurement of sulfur containing compounds in complex matrices is presented. The on-line system consists of a specifically designed sampling system connected to a comprehensive two-dimensional gas chromatograph (GC × GC) equipped with two capillary columns (Rtx$^{®}$-1 PONA × SGE BPX50), a flame ionization detector (FID) and a sulfur chemiluminescence detector (SCD). The result is an unprecedented sensitivity down to ppm level (1 ppm-w) for various sulfur containing compounds in very complex hydrocarbon matrices. In addition to the GC × GC-SCD, the low molecular weight sulfur containing compounds such as hydrogen sulfide (H_2S) and carbonyl sulfide (COS) can be analyzed using a thermal conductivity detector of a so-called refinery gas analyzer (RGA). The methodology was extensively tested on a continuous flow pilot plant for steam cracking, in which quantification of sulfur containing compounds in the reactor effluent was carried out using 3-chlorothiophene as internal standard. The GC × GC-FID/-SCD settings were optimized for ppm analysis of sulfur compounds in olefin-rich (ethylene- and propylene-rich) hydrocarbon matrices produced by steam cracking of petroleum feedstocks. Besides that is primarily used for analysis of the hydrocarbon matrix, FID of the GC × GC-FID/-SCD set-up serves to double check the amount of added sulfur internal standard which is crucial for a proper quantification of sulfur compounds. When vacuum gas oil containing 780 ppm-w of elemental sulfur in the form of benzothiophenes and dibenzothiophenes is subjected to steam cracking, the sulfur balance was closed, with 75% of the sulfur contained in the feed is converted to hydrogen sulfide, 13% to alkyl homologues of thiophene while the remaining 12% is present in the form of alkyl homologues of benzothiophenes. The methodology can be applied for many other conversion processes which use sulfur containing feeds such as hydrocracking, catalytic cracking, kerogen evolution, bio-waste pyrolysis, supercritical water treatment, etc.

1. Introduction

Heavy conventional (i.e. petroleum) and unconventional (i.e. shale oils) fossil oils usually contain considerable amounts of chemically bound heteroatom containing (sulfur, nitrogen, oxygen) compounds. The sulfur containing compounds especially have a significant impact on both the reactivity and the utilization strategy of fossil resources [1]. For instance, in steam cracking sulfur containing compounds are reported to reduce CO yields and coke formation, however on the other side sulfur containing compounds have a detrimental effect on the reactor material [2]. Crude oil derivatives contain elemental sulfur in concentrations from 0.1 wt% in light crude distillates, going up to 10 wt% in heavier fractions such as bitumen and tar sands [3]. Usually a considerable amount of the present sulfur is in the form of non-aromatic species such as thiols (also referred to as mercaptans) and sulfides, with the majority being heterocyclic structures containing a thiophenic ring such as alkyl homologues of thiophenes, benzothiophenes, dibenzothiophenes, and naphtobenzothiophenes [4,5]. Pyrolysis or combustion of these molecules can lead to a significant production of hazardous sulfur containing compounds, such as hydrogen sulfide and sulfur dioxide, exerting negative effects both on the process and product performance, as well as the environment by contributing to air pollution [4,6,7]. Obtaining accurate data on the speciation of organic sulfur constituents of various streams, and in particular understanding its behavior during pyrolysis, combustion or any other chemical process is of primary importance [1,3].

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Accurate quantitative analysis of sulfur compounds presents a difficult task. Sulfur compounds are highly reactive and will adsorb onto untreated or non-passivated metal surfaces, therefore, it is very important to use properly deactivated transfer lines, injection port liners, sample valves and sample loops [6,10,11]. To prevent adsorption of sulfur containing compounds it is very important that sulfur inert coated tubings (Sulfinert®, Restek®) are used for the tubing before and after the reactor. Stainless-steel materials and surfaces have been found undesirable for the sampling and transferring of volatile organic sulfur compounds. Exposure of sulfur compounds to these surfaces leads to the rapid loss of the most reactive compounds [12], which is especially the case when sulfur concentrations in gas mixtures are higher than 5 ppmv [13]. When testing for trace amounts of sulfur in hydrocarbon samples, large injection volumes (300 μl) may be required to attain adequate sensitivity for ultra-low levels of sulfur. This can be especially problematic when using detectors such as the pulsed flame photometric detector (PFPD), where co-elution of the analyte and solvent contribute to hydrocarbon quenching and interference, which may result in erroneous results. In contrast to flame photometric detector (FPD) detectors, the SCD can selectively detect trace ppb and even lower levels of volatile sulfur compounds in various matrices without suffering from any quenching or interference from the matrix [14,15]. Another very important factor for a proper analysis of sulfur containing compounds in complex hydrocarbon samples is column selection, such as fused silica or PLOT special columns for low level sulfur analysis. When performing both qualitative and quantitative sulfur speciation in hydrocarbon streams, understanding the potential sample composition helps to determine column separation requirements relative to molecular weight and elution temperatures [16]. One of the proven approaches for analyzing ppb level sulfur compounds by GC is to use a thick film capillary column such as 100% polydimethylsiloxane Rtx®-1 [17]. Thick film Rtx-1 type stationary phases are universally used for sulfur measurement due to their exceptional inertness. Their stability at high temperature even for thick stationary phase films allows these columns to separate volatile as well as less volatile sulfur compounds. Fused silica possesses low acidity, high surface area, reasonable thermal stability and sulfur tolerance, and hence is suitable for high temperature reactions [8].

Various analytical techniques have been applied for characterization of sulfur containing compounds in different matrices such as in environmental air [10,15,18–20], natural and syngas [21–23], highly concentrated ethylene and propylene streams [9,23], heavy crude oils and its distillates [7,24–28], as well as unconventional and renewable feedstocks such as shale [14] and pyrolysis oils [29]. These typically include one-dimensional gas chromatography (GC) coupled to different detectors such as mass spectrometer (MS) [10], flame ionization detector (FID), thermal conductivity detector (TCD) [27], sulfur chemiluminescence detector (SCD) [15,18,21], flame photometric (FPD) and pulse flame photometric detector (GC-PFPD) [26,30], Fourier transform ion cyclotron resonance mass spectrometry [26]. Also comprehensive two-dimensional gas chromatography (GC × GC) coupled to the PFPD [28] and SCD [7,10,14,15,18–31] have been proposed and demonstrated. Catalan et al. [31] used permeation tubes and GC-PFPD to determine the minimum detection limit (MDL), the Hubaux–Vos detection limit (xD), the absolute instrument sensitivity (AIS), and the sulfur detectivity (Ds) for hydrogen sulfide (H_2S), carbonyl sulfide (COS), sulfur dioxide (SO_2), methyl mercaptan (CH_3SH), dimethyl sulfide (DMS), carbon disulphide (CS_2), and dimethyl disulphide (DMDS) in concentrations varying from 0.36 ppb (v/v) up to 1.5 ppm (v/v) in nitrogen matrix. Nielsen and Jonsson [10] applied solid-phase micro extraction (using the 75-mm Carboxen–polydimethylsiloxane fiber coating) at 22 °C for 20 min, in combination with GC–MS to quantify nine (carbon disulfide, carbonl sulfide, diethyl sulfide, ethylmethyl sulfide, hydrogen sulfide, propanethiol, mehtanethiol, dimethyl disulfide and dimethyl sulfide) volatile sulfur compounds found in complex gaseous samples collected at a biogas-production plant and a sewage treatment plant. Andersson et al. [21] optimized the GC-SCD for on-line trace level light sulfur analysis in hydrocarbon matrices and used it to understand to which degree and in which form sulfur is released from the alkali promoted MoS_2 catalysts and incorporated into the liquid products during the synthesis of higher alcohols from syngas.

Hyphenated techniques such as GC × GC in combination with the SCD and flame ionization detector (FID) have gained a lot of attention in analyzing sulfur containing compounds in complex hydrocarbon matrices [7,14,24,25,29]. Because of the two-dimensional separation a significantly increased chromatographic resolution is achieved, resulting in roof-tile structured 2D chromatograms that significantly improve chemical-class separation and interpretation [32–34]. Dijkmans et al. [14,24] used full power of GC × GC-SCD to resolve and detect different groups of sulfur compounds such as thiols, sulfides, benzothiophenes, dibenzothiophenes in both conventional and unconventional petroleum fractions, gas and shale oils respectively. Kida et al. [25] applied GC × GC-SCD to understand the changes in alkylated thiophenes, benzothiophenes and dibenzothiophenes during supercritical water upgrading of heavy crude oil. Mahe et al. [7] applied a high temperature normal and reversed configured GC × GC chromatography hyphenated to a SCD to obtain a quantitative sulfur compounds speciation in heavy petroleum cuts. All these methods first collect the samples off-line before analyzing them, which makes the procedure tedious and error prone.

This study utilizes the power of the GC × GC in combination with the SCD to detect and measure ppm levels of sulfur containing compounds in olefin-rich (ethylene- and propylene-rich) hydrocarbon matrices produced by steam cracking of petroleum feedstocks. In addition to GC × GC-SCD, detection of low molecular weight sulfur containing compounds such as hydrogen sulfide was conducted using a thermal conductivity detector of a so-called refinery gas analyzer (RGA-TCD). On-line quantitative comprehensive experimental data is obtained based on GC × GC-SCD and RGA-TCD chromatograms, as well as by using well-chosen internal standards, i.e. 3-chlorothiophene for SCD and nitrogen for TCD detector. In addition, hydrocarbon matrix was analyzed using a combination of GC × GC-FID and RGA set-ups and multiple internal standards, i.e. nitrogen for RGA and methane for GC × GC-FID. The methodology provides excellent reproducible quantitative measurements with a relative standard deviation of 5% and was tested for both well-defined surrogates and real industrial feedstocks, i.e. vacuum gas oil. Although demonstrated for steam cracking the approach is universally applicable.

2. Material and methods

2.1. Chemicals and standards

Standard compounds and reagents used in this study were of GC grade. Heptane was procured from Thermo Fisher Scientific (Belgium) with a minimum purity of 99%. Dimethyldisulfide (DMDS) was obtained from Sigma-Aldrich® (Belgium) with a minimum purity of 99%, while 3-chlorothiophene and benzothiophene were also purchased from Sigma-Aldrich® (Belgium) with a minimum purity of 98%. Hexane was obtained from Chem-Lab (Belgium) with a minimum purity of 99%. Ethane of N25 grade (minimum purity of 99.5%) was provided in 50 l cylinders by Air Liquide (Belgium), while analytical gases (N_2, He, CO_2) were also purchased from Air Liquide (Belgium) with a minimum purity of 99.999%.