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Application of a quantitative structure retention relationship approach for the prediction of the two-dimensional gas chromatography retention times of polycyclic aromatic sulfur heterocycle compounds

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ABSTRACT

Information on the sulfur classes present in petroleum is a key factor in determining the value of refined products and processing behavior in the refinery. A large part of the sulfur present is included in polycyclic aromatic sulfur heterocycles (PASHs), which in turn are difficult to desulfurize. Furthermore, some PASHs are potentially more mutagenic and carcinogenic than polycyclic aromatic hydrocarbons, PAHs. All of this calls for improved methods for the identification and quantification of individual sulfur species. Recent advances in analytical techniques such as comprehensive two-dimensional gas chromatography (GC × GC) have enabled the identification of many individual sulfur species. However, full identification of individual components, particularly in virgin oil fractions, is still out of reach as standards for numerous compounds are unavailable. In this work, a method for accurately predicting retention times in GC × GC using a QSRR (quantitative structure retention relationship) method was very helpful for the identification of individual sulfur compounds. Retention times for 89 saturated, aromatic, and polyaromatic sulfur-containing heterocyclic compounds were determined using two-dimensional gas chromatography. These retention data were correlated with molecular descriptors generated with CODESSA software. Two independent QSRR relationships were derived for the primary as well as the secondary retention characteristics. The predictive ability of the relationships was tested by using both independent sets of compounds and a cross-validation technique. When the corresponding chemical standards are unavailable, the equations developed for predicting retention times can be used to identify unknown chromatographic peaks by matching their retention times with those of sulfur compounds of known molecular structure.

1. Introduction

The majority of organosulfur compounds in crude oils and their industrial conversion products are polycyclic aromatic sulfur heterocycles (PASHs). Information on the sulfur classes present in petroleum is a key factor in determining the value of such streams. The reason for this is clear as sulfur compounds participate in many undesirable processes such as catalyst poisoning [1–3], corrosion [4,5] and environmental pollution [6,7]. Furthermore, it is known that carcinogenic and mutagenic effects for some PASHs are higher than for analogous PAH compounds [8–10]. For example, benzo[2,3]phenanthro[4,5-bcd]thiophene was found to be more carcinogenic than benzo[a]pyrene [11]. However, the most disturbing fact is that the feedstocks processed in refineries around the world are becoming heavier and the total sulfur concentration as well as the fractional contribution of PASHs is increasing. Therefore, deep hydrodesulfurization (HDS) technology must be implemented to reduce levels of sulfur in finished products [6]. While many groups of sulfur compounds are moderately easy to remove, some PASH classes, such as dibenzothiophenes, are particularly resistant towards desulfurization [12,13]. Powerful analytical separation and speciation are necessary to determine which isomers are unaltered and at what concentrations they are present. Gas chromatography (GC) with a sulfur-specific detector has been the preferred characterization technique for the detailed analysis of sulfur compounds in petroleum. However, detailed separation cannot be obtained using conventional GC because of the lack of chromatographic resolution [14–17].

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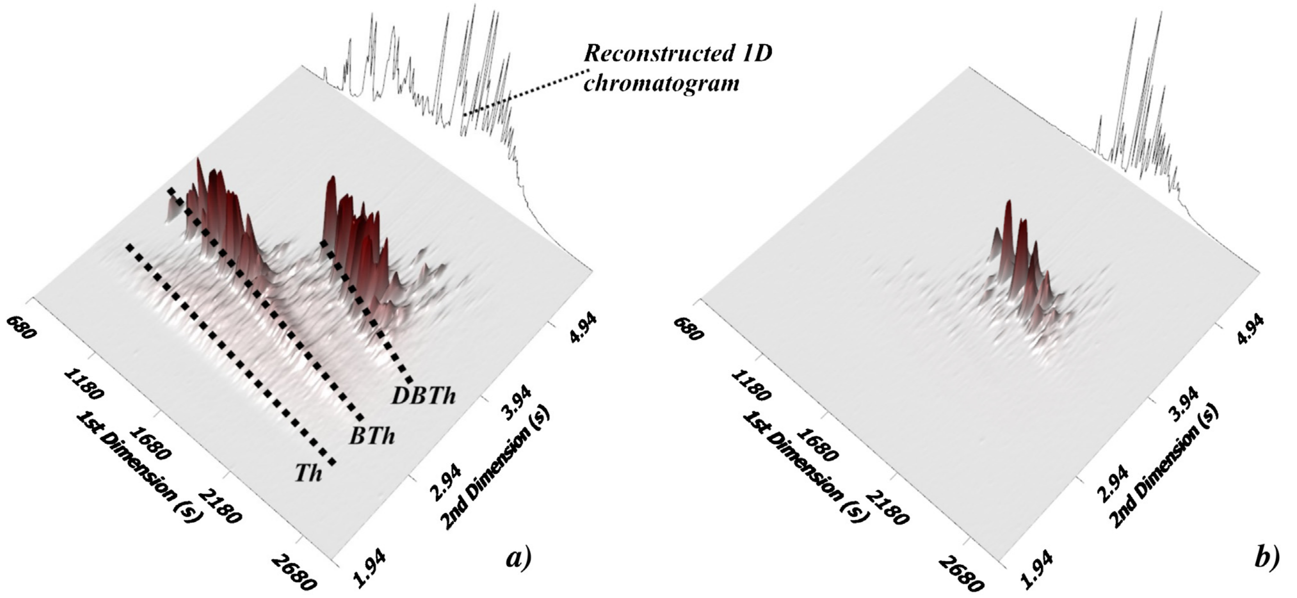

Fig. 1. Examples of chromatograms of an oil sample by GC × GC-SCD before (a) and after (b) desulfurization. The *x*-axis of the GC × GC chromatogram is the volatility-based retention time (s), the *y*-axis is the polarity-based retention time (s) and the *z*-axis is the detector (SCD) response. The signal axes are set at the same threshold for both (a) and (b).

Comprehensive two-dimensional gas chromatography (GC × GC) offers huge potential for the examination of complex mixtures (such as petroleum products) due to its superior chromatographic resolving power. Moreover, this method is characterized by improved detection limits due to the focusing of analytes during the modulation process, and the structured nature of chromatograms, where compounds are arranged according to their chemical group and their numbers of carbon atoms [18–20]. Fig. 1 shows examples of two-dimensional chromatograms of sulfur in petroleum samples before and after hydrodesulfurization. It is clearly seen (Fig. 1a) that thiophenes (Th), benzothiophenes (BTh), and dibenzothiophenes (DBTh) form three bands that are almost parallel to one another. This band arrangement demonstrates the orthogonality of the separation mechanisms in the two dimensions, as the peaks are distributed across the separation plane and effectively occupy the available separation space. After hydrodesulfurization (Fig. 1b), only compounds resistant to this process (dibenzothiophenes) are left in the sample. Detailed information on the distribution of such compounds can serve as an important basis for improving desulfurization technology. In spite of the great advances that accompany the use of GC × GC, the full identification of many individual sulfur species, particularly in virgin oil fractions, remains a problem, as standards for numerous compounds are unavailable. Although the molecular structure can often be deduced from mass spectral fragmentation patterns using GC × GC coupled with time-of-flight-mass-spectrometry (GC × GC-TOFMS), the large numbers of compounds having very similar structures present in oil fractions makes the identification and assignment process very tedious. A method for correctly predicting retention times or indices would be useful for the identification of individual sulfur compounds.

Earlier studies have shown that it is possible to predict the gas chromatographic retention characteristics of sulfur compounds in crude oil—based samples using a quantitative structure-retention relationship (QSRR) [21,22]; both of these studies used a single dimension of GC and employed atomic emission detection. Other works have applied QSRR to model one-dimensional GC separations of chlorinated pesticides and organohalides [23], saturated esters [24], alkyl benzenes [25], polyhalogenated biphenyls [26], and hydrocarbons found in gasoline [27]. Ren et al. reported the use of a QSRR model for the prediction of GC × GC retention of polychlorinated biphenyl congeners, but only models for the first dimension are shown [28]. The aforementioned GC × GC retention data were later modelled by D'Archivio et al., [29] who predicted retention behavior of solutes for both dimensions using various regression approaches. An alternative approach to predicting retention times is to model the thermodynamic parameters of the separation; this approach has been demonstrated for the prediction of GC × GC retention times for alkyl phosphates on ionic columns [30] and for alkanes, ketones, and alcohols on a more conventional column set [31]. QSRR modeling has also been applied to one-dimensional thermodynamic GC data of alkanes, alcohols, and alkyl halides, to expand data to new molecules [32]. Despite the potential represented by previous work, a QSRR model for the prediction of retention behavior of sulfur-containing compounds in two-dimensional chromatography has not been reported.

The main attraction of the QSRR modeling approach, in comparison to other methods used for the prediction of retention characteristics in GC × GC, is that it can be used without the laborious and expensive process of generating a great deal of experimental data. The QSRR modeling results obtained in this work for the primary column are comparable with the other QSRR models reported in the literature for sulfur-containing hydrocarbons. A short review of QSRR models is summarized in Table 1. Implementing the secondary separation and hence the QSRR modeling of secondary retention times may simplify the process of proper identification of sulfur compounds as well as supporting lab operators during the generation of classification templates used in GC × GC data reporting. An excellent comprehensive review of QSRR applications was written by K. Heberger, and covers the period between 1996 and 2006 [33].

The work presented herein demonstrates that QSRR can be used to successfully predict the retention of sulfur-containing compounds in GC × GC, including the second dimension. GC × GC data for 89 model compounds representing sulfur compounds found in crude oil are shown. The model is validated and results showing predicted *vs.* experimental retention times are presented.