Novel simple method for quantitation of nitrogen compounds in middle distillates using solid phase extraction and comprehensive two-dimensional gas chromatography

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HIGHLIGHTS

► Identification and quantitation of N-compounds in middle distillates is achieved.
► The method is based on SPE fractionation followed by GC × GC-NCD.
► The fractionation avoids the overlapping between basic N-compounds.
► Results were compared with ASTM-4629 reference method and they closely resemble.
► The method provides a distribution of organic N-compounds in middle distillates.

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ABSTRACT

Nitrogen speciation in crude oil and its fractions has become an important issue due to the undesirable effects of nitrogen compounds during important petroleum refining processes. In this work, a comprehensive two-dimensional gas chromatography method with a nitrogen chemiluminescence detector (GC × GC-NCD) was used for the speciation and quantification of nitrogen compounds in middle distillates. The developed method is based on an extraction of nitrogen compounds from the hydrocarbon matrix followed by their fractionation using solid phase extraction (SPE). Two fractions were collected thus minimizing misidentifications; the first one contained anilines, indoles and carbazoles and the second one contained pyridines, quinolines and acridines. An excellent agreement for total nitrogen content was found between the results obtained with the present method and those from the American Society for Testing Materials (ASTM) method. Good recoveries, repeatability and low detection limits (LOD), in a range from 10 to 20 µg L^{-1}, were also achieved.

1. Introduction

Nitrogen-containing compounds that occur in crude oil adversely affect many of the important petroleum processes such as hydrocracking and hydrotreating; for instance, due to their polarity and basicity, these compounds may poison the catalysts used in hydrocracking, catalytic cracking and reforming, through interactions with acid sites of catalysts. In addition, although nitrogen-compounds (N-compounds) are present in low concentrations in typical feedstocks, they have a negative influence on product stability [1,2]. Moreover, these compounds often have carcinogenic and mutagenic activities [3] and they are precursors of nitrogen oxides which are responsible for air pollution [4].

Most of the nitrogen that occurs in petroleum is present as organic compounds, mainly multiple aromatic heterocyclic rings. The N-compounds have been classified into two different groups; neutral and basic. Basic N-compounds usually cover pyridines, quinolines and acridines, while neutral nitrogen species include pyrroles, indoles, carbazoles and benzocarbazoles. The current economic and oil reserve conditions worldwide have increased the necessity of processing heavy oils with a much higher nitrogen content. Therefore, detailed knowledge of the type and concentration of N-compounds present in petroleum products is clearly needed to optimize the hydrodenitrogenation process (HDN) in order to improve the elimination of nitrogen in middle distillates. Moreover, the low reactivity of nitrogen makes HDN the most challenging hydrotreatment reaction, while the high reactivity of the N-compounds inhibits the hydrodesulfurization (HDS) process [5,6].

Gas chromatography (GC) hyphenated with specific detectors has been widely used for the speciation of N-compounds in middle

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distillates. Detectors such as atomic emission (AED) [7] or mass spectrometry (MS) [8,9] have been widely used to determine hetero-atoms containing compounds, as they have enough sensitivity to detect low concentration levels in complex samples. However, owing to their high sensitivity and selectivity, nitrogen chemiluminescence (NCD) and nitrogen phosphorus detectors (NPD) have been the most widely used for nitrogen speciation [10]. The main advantage offered by the NCD compared to the AED, MS and NPD is that the response to nitrogen compounds is equimolar [11,12]; therefore, quantification of the N-compounds is found to be easier since it is not necessary to have all the standards.

Recent studies in characterization of N-compounds in fuel have demonstrated the advantages of comprehensive two-dimensional gas chromatography (GC × GC) over conventional gas chromatography. GC × GC accomplishes better separations than GC, reducing the peak overlapping of N-compounds that occurs in diesel samples [13] and therefore achieving better identifications and quantifications. However, despite the great resolution of GC × GC, fractionation of the nitrogen species is still necessary because of the overlap of some nitrogen families. Usually the N-compounds are separated into basic and neutral types. However, for complex samples this separation is not enough as in the basic fraction, pyridines, anilines, quinolines and acridines overlap.

In this study, a simple and reliable method to identify and quantify the organic N-compounds that occur in middle distillates has been developed. It is based on SPE to separate specific nitrogen families which overlap even in GC × GC chromatography. In the first part of this study, first and second dimension columns used in GC × GC were optimized. Then, optimization of the SPE fractionation is described, underlining the advantages of SPE over other separation techniques. Finally, N-compounds were determined in different samples and the results obtained for total N content were compared with those found by the ASTM-4629 reference method.

2. Experimental

2.1. GC × GC-NCD setup

The GC × GC-NCD system consisted of a 7890 GC (Agilent Technologies) fitted with a N_2 quad jet thermal modulator (LECO), a nitrogen chemiluminescence detector (NCD) 255 Dual Plasma (Agilent Technologies) and a split/splitless injector (model 7683 Autosampler Injector). Four different sets of columns were tested (Table 1) and set A was chosen due to its better results; chromatographic conditions are listed in Table 2. The acquisition of the data was performed with the NCD and processed with Leco-ChromaTOF software (v 4.32).

2.2. GC × GC-TOFMS setup

The GC × GC system was the same as indicated in Section 2.1. The time of flight mass spectrometry (TOFMS) system was a Pegasus IV TOFMS (LECO, St. Joseph, MI, USA); chromatographic conditions are also those listed in Table 2. Identification of compounds was performed by comparison with the NIST 2.0 (2008) library.

2.3. Total nitrogen content

Total nitrogen content was determined according to ASTM-4629 [14]. A TN 3000 Nitrogen total analyzer (Thermo Electron Corporation) was used to measure total nitrogen content.

Table 1
Sets of columns tested for GC × GC-NCD.

Set	First column	Second column
A	DB-1 (30 m × 0.25 mm × 0.25 μm)	BPX-50 (1 m × 0.10 mm × 0.10 μm)
B	DB-1 (30 m × 0.25 mm × 0.25 μm)	ZB-1701 (1 m × 0.10 mm × 0.10 μm)
C	HP-Innowax (30 m × 0.25 mm × 0.25 μm)	Equity-1 (1 m × 0.25 mm × 0.25 μm)
D	DB-1 (30 m × 0.25 mm × 0.25 μm)	IL-59 (1 m × 0.10 mm × 0.08 μm)

ZB-1701, 14% cyanopropylphenil–84% dimethylpolysiloxane. Phenomenex, USA.
DB-1, dimethylpolysiloxane, J&W Scientific, Folsom, CA, USA.
HP-InnoWax, polyethyleneglycol. J&W Scientific, Folsom, CA, USA.
BPX-50, 50% phenyldimethylsiloxane, SGE, Courtaboeuf, France.
Equity-1, dimethylpolysiloxane, Supelco, PA, USA.
IL-59, 1,12-di(tripropylphosphonium)dodecane bis(trifluoromethane-sulfonyl)imide, Supelco, Bellefonte, USA.

2.4. Standards and samples

A standard solution containing 13 N-compounds purchased from Sigma–Aldrich and Acros (see Table 3) was used to check the viability of the extraction of basic and neutral species in order to determine the reproducibility and the recovery of the method. The standard solution was prepared by dissolving the commercial N-compounds in light cycle oil (LCO) free of nitrogen, covering a concentration range from 1 to 4.7 ppm N. To obtain LCO free of nitrogen, a weighed amount of LCO was loaded to the top of a glass chromatographic column packed with activated silica gel; n-hexane was added to the column to elute non-aromatic and aromatic compounds, while the N-compounds were trapped in the top of the column. The n-hexane from the collected fractions was completely removed by evaporation with the rotary evaporator, and residues (LCO) were weighed. This was performed with the aim of reproducing the matrix effect of the samples.

Several middle distillate samples with different nitrogen content were collected from different industrial Repsol YPF complexes.

2.5. Sample preparation

N-compounds were extracted and separated into basic and neutral fractions by SPE which was adapted from Wiwel et al. [15]. Separation was achieved using silica 0.5 g SPE cartridges (J.T. Baker); these were used once and discarded. 1 mL of sample was applied to the silica SPE column. The hydrocarbon matrix was eluted from the column with 9 mL of n-hexane whereas the nitrogen-containing compounds were trapped on the silica SPE-column. Aniline, indole and carbazole compound classes were eluted off the column with 9 mL of dichloromethane while pyridine, quinoline and acridine compound classes were eluted with 6 mL of acetone. The recovered fractions were evaporated in a nitrogen atmosphere to 1 mL.

3. Results and discussion

3.1. Optimization of the GC × GC-NCD method

Four sets of columns were tested in order to accomplish a good separation of N-compounds (Table 1). As shown in Fig. 1, the separation of the 13 N-compounds from the standard solution was achieved with the four tested sets of columns. However, none of these sets provided a good separation of the N-compounds when diesel samples were analyzed, due to their complexity. In fact, column set C presented the worst separation between anilines and quinolines. Column sets B and D, involving a more polar second