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New benchmark for basic and neutral nitrogen compounds speciation in middle distillates using comprehensive two-dimensional gas chromatography

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Abstract

This paper reports an analytical method for the comprehensive two-dimensional gas chromatography (GC × GC) separation and identification of nitrogen compounds (N-compounds) in middle distillates according to their types (basicity). For the evaluation of the best chromatographic conditions, a non-polar × polar approach was chosen. The impact of the second dimension (stationary phase and column length) on the separation of basic and neutral N-compounds was evaluated by mean of two-dimensional resolution. This study revealed that the implementation of polar secondary column having free electron pairs improves drastically the separation of N-compounds. Indeed, the presence of permanent dipole-permanent dipole interactions between neutral N-compounds and the stationary phase was enlightened. The comparison of two different nitrogen chemiluminescence detectors (NCD) was also evaluated for GC × GC selective monitoring of N-compounds. Owing to higher resolution power and enhanced sensitivity achieved using developed chromatographic and detection conditions, it was possible to identify univocally and to quantitate N-compounds (i) by class of compounds and (ii), within a class, by carbon number. Finally, quantitative comparison of GC × GC-NCD with conventional gas chromatography illustrates the benefits of GC × GC leading to an excellent correlation with results obtained by American Society for Testing Materials (ASTM) methods for the determination of basic/neutral nitrogen ratio in diesel samples.

Keywords: Comprehensive two-dimensional gas chromatography; Time of flight mass spectrometry; TOF-MS; Nitrogen chemiluminescence detector; NCD; Nitrogen-containing compounds; Middle distillates

1. Introduction

N-compounds naturally occur in petroleum samples and refining products. In diesel fuels, most of the nitrogen results from the blending of straight run distillates and cracked products of heavier feedstocks having high nitrogen content [1]. N-compounds are mainly present in gas oils in the form of basic (pyridine, acridine and quinoline) and neutral (indol and carbazole) compounds.

N-compounds are subject to more and more attention. Indeed, they are well known to have an adversely effect on the stability of fuel during the storage [2]. Besides, they are the precursors of nitrogen oxides (NO_X) which are released after combustion and responsible for acid rain [3]. Moreover, owing to their low reactivity, neutral N-compounds are refractory to hydrodenitrogenation (HDN). On the other hand, owing to their high reactivity, basic N-compounds exhibit a strong poisoning activity towards catalyst of hydrodesulfurization (HDS) [4] which may lead to products which do not meet the specifications. Thus, there is a growing need to better understand the HDN process in order to achieve a better elimination of nitrogen and sulfur in middle distillates. Further improvement in diesel hydrotreatment will rely on detailed molecular analysis of N-compounds.

Two methods of analysis providing different levels of detail have been normalized to obtain the nitrogen level in gas oil. The first one (ASTM D-4729) consists in the evaluation of total nitrogen and the second one (ASTM D-5291) relies on the measurement of basic N-compounds.

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Table 1
Operating conditions and columns associations for GC × GC-NCD experiments

System	First column	Second column	Column oven programmation	Carrier gas (nature; pressure)
A	SPB-5[a], 30 m × 0.25 mm × 1.0 μm	BPX 50[b], 1.0 m × 0.1 mm × 0.1 μm	60–260 °C; 3 °C/min (10 min)	He; constant flow, 1.4 mL/min
B	SPB-5[a], 30 m × 0.25 mm × 1.0 μm	BPX 70[c], 1.0 m × 0.1 mm × 0.2 μm	60–260 °C; 3 °C/min (10 min)	He; constant flow, 1.4 mL/min
C	SPB-5[a], 30 m × 0.25 mm × 1.0 μm	Solgel Wax[d], 1.0 m × 0.1 mm × 0.2 μm	60–260 °C; 3 °C/min (10 min)	He; constant flow, 1.4 mL/min
D	SPB-5[a], 30 m × 0.25 mm × 1.0 μm	Solgel Wax[d], 1.6 m × 0.1 mm × 0.2 μm	60–260 °C; 3 °C/min (10 min)	He; constant flow, 1.4 mL/min

[a] (5% Phenyl)methyl polysiloxane, Supelco (St Quentin-Fallavier, France).
[b] (50% Phenyl)polysilphenylene-siloxane, SGE (Courtaboeuf, France).
[c] (70% Cyano)propyl polysilphenylene-siloxane, SGE (Courtaboeuf, France).
[d] Solgel Wax (polyethylene glycol), SGE (Courtaboeuf, France).

High-resolution mass spectrometers (HR-MS) such as Fourier transform ion cyclotron resonance MS (FT-ICR-MS) is now recognized as a powerful tool to resolve thousands of species, including N-compounds, in a single run without preseparation step [5]. However, quantitation is limited by variation in ionization efficiency and competition for protons among various neutrals in the original sample [5].

As such methods cannot make simultaneously identification and quantification of N-compounds present in petrochemical samples, gas chromatography (GC) hyphenated with specific detectors such as atomic emission detectors (AED) [6–11], nitrogen chemiluminescence detector (NCD) [12–14] and MS [15–18] have been widely used. Unfortunately nitrogen detection by AED is subject to interference with the hydrocarbons of the matrix [1] and cannot be used for the study of N-compounds at low nitrogen level, unless prior separation occurs. Informative detectors, such as mass spectrometer (quadrupole, ion trap), are not sensitive enough to achieve detection of N-compounds at low concentration. Moreover, their low resolution do not permit to extract, identify univocally and quantify selectively N-compounds in complex matrices such as petrochemical samples. Owing to its high sensitivity (limit of detection below 3 pg N/s) and good selectivity (ratio of N/C signals higher than 10^7 measured for the same injected concentration) the chemiluminescence detection has been the most widely used detector for nitrogen speciation.

However, GC suffers from a lack of resolution leading to the co-elution of basic and neutral nitrogen fractions which could not be solved by usual informative detectors (quadrupole, ion trap MS); indeed, indol and quinoline, acridine and carbazole coelute and fragment into the same ions. One way to improve peak capacity of conventional separation techniques is to add another separation dimension.

During the past decades, comprehensive two-dimensional gas chromatography (GC × GC) has been introduced in order to achieve a full characterization of complex mixtures [19,20]. In GC × GC, the entire sample is submitted to two online GC separations involving different properties of analytes, i.e., the volatility related to the carbon atom number and the polarity related to the chemical group. The orthogonality of the separation is achieved by using two columns of different selectivities connected in series through a cryogenic modulator that traps, focuses and reinjects the effluent from the first column into the second one. The major advantage of GC × GC over conventional GC relies on its increased resolution power as the peak capacity in GC × GC is the product of the peak capacity of each separation column [21]. Another interesting feature of GC × GC is the refocusing effect of the modulator prior to the second dimension separation which offers a ca. 5 times higher sensitivity [22].

In a recent paper, the hyphenation of GC × GC with nitrogen chemiluminescence detection (GC × GC-NCD) has been reported to achieve the identification of various N-compounds in a diesel fuel [23]. In this study Wang et al. showed that under the chosen operating conditions, the coelution of basic and neutral N-compounds prevents their identification and quantitation; thus, for quantitative purpose, they assumed that basic N-compounds are removed through hydrotreatment so that indol and carbazole derivatives present in the diesel sample after hydrotreatment could be directly quantified by external calibration.

This paper reports the setting and analysis of all the classes of N-compounds in middle distillates by comprehensive two-dimensional gas chromatography hyphenated with a NCD detector. The first part of this study is devoted to the evaluation of NCD detectors from Antek and Sievers companies based on asymmetry and peak width. The second part aims at the evaluation of the best separation conditions and is based on the investigation of several sets of columns with different stationary phases. The last part is dedicated to the comparison of GC × GC-NCD results with methods commonly used in the petroleum industry i.e., total nitrogen, basic nitrogen and GC-NCD.

2. Experimental

2.1. GC × GC setup

The GC × GC system consists in a modified 6890 chromatograph (Agilent Technologies, Massy, France). The CO_2 dual jets modulator was built in-house as described by Beens et al. [24] and was installed inside the GC oven for GC × GC experiments. Modulation occurred at the beginning of the second column. In order to prevent boiling points discrimination during injection, 0.5 μl sample analyses were carried out with a direct on-column injector (Agilent Technologies, Massy, France) which was programmed from 90 to 260 °C with a 70 °C/min temperature gradient. All experiments were carried out at a constant flow of 1.4 mL/min.

Non-polar column (SPB-5) was used for the first dimension and four different secondary columns were investigated (Table 1).