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Determination of nitrogen-containing polycyclic aromatic compounds in diesel and gas oil by reverse-phase high performance liquid chromatography using introduction of sample as detergentless microemulsion

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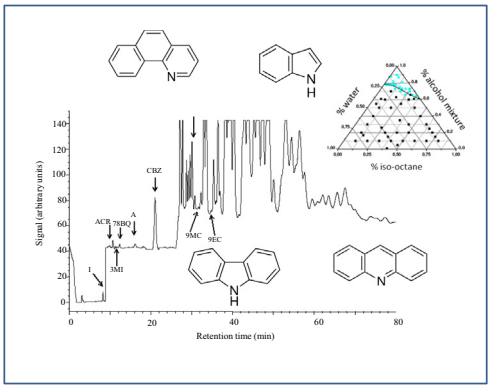
HIGHLIGHTS

- Microemulsified diesel and gasoil were introduced into HPLC system.
- Basic and neutral NPACS were determined altogether.
- Minimum sample preparation required for screening complex samples.
- Effective detectable concentration of NPACs in fuels in the mg L^{-1} level.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbazoles, quinolines, indoles, pyrroles, anilines and acridines are nitrogen-containing polycyclic aromatic compounds (NPAC) that contribute to deteriorate fuels affecting storage stability, causing problems to motor engines and poisoning automotive catalysts. Carbazole, 3-ethylcarbazole, 9-ethylcarbazole, 9-methylcarbazole, quinoline, benzo[*h*]quinoline, indole, 3-methylindole, acridine and N,N-dimeth ylaniline were separated and quantified in diesel and gas oil by reverse-phase high performance liquid chromatography with fluorimetric detection and molecular absorption photometric detection using introduction of fuel samples as detergentless microemulsion (DME). The DME is composed by ethanol, propan-2-ol, water and iso-octane in specific proportions to stabilize the organic samples. The introduction of sample in the DME simplifies the procedure since it avoids extraction of the analytes and enables the determination of basic and neutral NPAC altogether. The limits of quantification for the analytes in the DME were in μg L^{-1} order (ng range for 10 μL of injected volume). Satisfactory analyte recoveries were achieved (between 89.5% and 108.7%). Results were found to be comparable using or not using 7-methylindole and N-methylpyrrole as internal standards (since these were not found in the analyzed samples). Studies showed homogeneity of the analytes in the DME after mechanical stirring (at 7200 rpm for 5 min).

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Stability studies indicated results with coefficients of variation below 3%. The method is adequate for a rapid screening of NPACs in petroleum samples.

1. Introduction

Despite all of the efforts to enable efficient and cleaner energy sources, petroleum is still the primary raw material for fuels. Since it heavily contributes for environmental pollution, strict laws have emerged limiting the presence of certain substances, such as mercury and sulfur-containing compounds, in the composition of petroleum derivatives [1–4]. The nitrogen content in petroleum may account up to 0.10% in weight and it is present in a myriad of forms including as nitrogen-containing polycyclic aromatic compounds (NPAC) [5,6].

The presence of nitrogen-containing compounds in petroleum derived fuels might result in the decreasing of their stability, reducing storage time by inducing formation of gum through polymerization reactions. Such gum causes problems to the engines and poison automotive catalysts, promoting the increasing NOx emissions by combustion [5,6]. NPACs are frequently found in petroleum samples as trace contaminants and may appear throughout the boiling range of the petroleum fractions with more pronounced concentration in the heavier fractions [5,6]. The structure of the more frequently found NPACs includes the indolic ones (carbazoles and benzocarbazoles) and quinolinic ones (quinoline and benzoquinolines), respectively extracted in the neutral and basic fractions of petroleum, besides acridines, pyrroles and anilines. From the viewpoint of monitoring the quality of raw materials and products from the petrochemical industry, it is necessary to develop analytical methods for the identification and quantification of these species even if they are present in trace quantities.

The search for new analytical methods must focus not only in the quality of the results but also on practical aspects that reduces sample preparation time and complexity. In general, for NPACs in petroleum fuels, complex procedures and time consuming protocols are used to enable their determination, in general including separating the neutral from the basic fraction of analytes. However, in practice, procedures are hard to replicate and leads to inconsistent results.

Okumura and Stradiotto [7] proposed the determination of neutral nitrogen compounds in gasoline and in diesel by differential pulse voltammetry using a glassy carbon electrode. Analyte preconcentration was made using solid phase extraction (SPE) in a sequence of silica gel columns modified to retain acid compounds and basic compounds, allowing the elution of the neutral fraction. Limits of detection (LOD) in the $\mu g\ L^{-1}$ level and recoveries (in analyte fortified diesel samples) varying from 88% to 90% were achieved. Cheng et al. [8] identified NPACs in residual fluid catalytic cracking diesel oil by treating diesel with H_2SO_4 and ethanol. The extracted NPACs were recovered using four chromatographic columns and different eluents. Quinolines, carbazoles, indoles and anilines and other NPACs were identified by mass spectrometry (MS) producing qualitative information. Laredo et al. [9] studied the distribution of basic and non-basic nitrogen compounds along distillation curves of atmospheric gas oil and light cycle oil using gas chromatography (GC) with MS detection. Quinoline, indole and carbazole derivatives were found in atmospheric gas oil while aniline, indole and carbazole derivatives were found in light cycle oil. Sauvain et al. [10] determined acridines and carbazole in diesel exhaust particulates by GC–MS. The clean-up procedure consisted of SPE and liquid chromatographic fractionation on silica phases followed by liquid–liquid extraction. Determination was made by high performance liquid chromatography (HPLC) with a polyvinylbenzene copolymer column with recovery values below 80%. Mao et al. [11] identified quinolines and acridines using particle beam HPLC–MS and HPLC with molecular absorption photometric detection. Nitrogen bases were isolated from a Brazilian diesel distillate by acid extraction and determined. Benzoquinolines were identified as the major nitrogen containing group in this basic fraction. By using neutral mobile phases, benzoquinoline homologues were separated, enabling rapid class characterization as well as preparative HPLC isolation of individual benzoquinoline homologues. Kamata et al. [12] used GC for the determination of methylbenzo[c]acridines. These analytes were oxidized to formylbenzo[c]acridines with periodic acid in dimethyl sulfoxide. The formylbenzo[c]acridines were then reacted with p-fluoroaniline and the formed Schiff bases that were detected (down to 20 pg) by GC with electron-capture detection. The method was not applied in fuel samples. Da Luz et al. [13] have used SPE in combination with HPLC with fluorimetric detection for the sensitive determination of six basic azaarenes (benzo[*h*]quinoline, 7,9-dimethylbenzo[*c*]acridine, 9-amino-1,2,3,4-tetrahydroacridine, 9-methylacridine, acridine, and dibenzo[*aj*]acridine) in jet fuel. SPE was performed using a strong cation exchange sorbent to separate the basic and the neutral fractions. The absolute LOD values were between 2 and 21 pg. For samples fortified with analytes ($6.0\ \mu g\ L^{-1}$ final concentration) recoveries were from 92% to 107% except for 9-amino-1,2,3,4-tetrahydroacridine, which presented a 68% recovery. Da Luz et al. [6] also determined five acridines in diesel after submitting samples to a SPE with a cationic phase. Analytes were separated by capillary zone electrophoresis, using an acidic background electrolyte, and detected by molecular absorption photometric detection. Concentration of analytes into the capillary (through analyte stacking) enabled LOD values at the $mg\ L^{-1}$ level [6]. Nascimento et al. [14] developed a method to determine oxygen and nitrogen containing PAC (including acridine and quinolone among the seven NPACs studied) in asphalt mixtures using HPLC–MS chemical ionization at the atmospheric pressure. Samples were fractionated into asphaltenes and maltenes, then the fraction of maltenes was separated into acidic, basic and neutral fractions. Limit of quantification (LOQ) of $0.5\ \mu g\ L^{-1}$ for acridine and $4.6\ \mu g\ L^{-1}$ for quinolone were achieved. Recoveries were between 85% and 120% for quinolone and between 86% and 121% for acridine (depending on the analyzed fraction). In real samples, quinoline was quantified in the acidic fraction ($102.2\ mg\ kg^{-1}$) and in the basic fraction ($63.6\ mg\ kg^{-1}$). Belyaeva et al. [15] developed a colorimetric test to determine N-methylaniline in dodecane and in gasoline based on the reaction between the analyte with potassium ferricyanide fixed onto alumina solid substrate. The LOD was of 0.014%, indicating screening potential of the procedure. Dijkmans et al. [16] quantified sulfur and nitrogen PAC in shale oil using two dimensional GC (GC × GC) and the combination of four different detection systems: flame ionization detector (FID), sulfur chemiluminescence detector (SCD), nitrogen chemiluminescence detector (NCD) and time of flight mass spectrometry (TOF-MS). A complex protocol was used using different sample preparation procedures depending on the target analytes. The substances were detected by structural class and by carbon number. Among the nitrogen containing compounds found in shale oil (in weight percent) included the indoles (1.11%), quinolines (0.60%), anilines (0.47%), acridines (0.03%) and carbazoles (0.47 wt%). Camarão