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Analysis of neutral nitrogen compounds in diesel oil by direct injection high-performance liquid chromatography–mass spectrometry–ultraviolet spectrometry methods

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Abstract

An analytical methodology has been developed for the direct analysis of neutral nitrogen compounds in diesel oil by HPLC with subsequent detection using MS and/or photodiode-array UV spectrometry. By diluting diesel oils with one volume of hexane, diesel samples could be injected directly onto an alumina analytical column and then eluted with a gradient mobile phase consisting of hexane and dioxane. Nitrogen compounds were selectively retained on the alumina column, eluted using LC, and then detected by particle beam LC–MS or UV at 254, 270 and 290 nm. Two Brazilian and one Arabian diesel distillates were investigated. Alkylcarbazoles and alkylindoles were identified as the major neutral nitrogen components. Structural identification was accomplished by combination of electron impact MS and UV analyses. The concentration of carbazoles and indoles was estimated using calibration standards of carbazole and indole, respectively.

1. Introduction

It has been known for sometime that nitrogen compounds in petroleum adversely affect many of the important petroleum refining processes that are important in industry [1]. Many different nitrogen compounds, even at very low concentration levels (ppm), may poison the catalysts used in cracking and hydrocracking reforming processes presumably through interactions with the acid sites of these catalysts [2]. Because of the deleterious effects that nitrogen-containing compounds exhibit numerous studies have been conducted leading to the isolation, characterization and identification of the nitrogen compounds extant in petroleum [3–8]. Generally, both basic and neutral (non-basic) nitrogen compound types are found in petroleum distillates, with the neutral nitrogen compounds usually being the predominant entity types. The basic nitrogen compounds can be obtained by acid (HCl or H_2SO_4) extraction of the oil [8], while the neutral nitrogen compounds can be isolated

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through adsorption to an active adsorbent [8] like activated aluminum oxide. Although many of the established methods for the analysis of nitrogen-containing compounds in petroleum are effective, they often are time consuming and labor intensive. This is partially attributable to the lack of selectivity and sensitivity with respect to both separation and detection. As a result, extensive sample clean-up is usually necessary prior to analytical measurements. For instance, gas chromatography coupled to mass spectrometry (GC–MS) is widely used in the petroleum industry to monitor nitrogen compounds [9–11]. The high separation power of GC when coupled with MS detection has made this methodology particularly successful for analyzing samples of a complex nature, such as diesel oils. Nevertheless, certain non-volatile and polar compounds are not suitable for GC and further, to eliminate matrix interference, sample clean-up is essential. Because of the extreme complexity of petroleum products, very little attention has been given to the direct analysis of diesel oils by either gas or liquid chromatography. Our work explored the possibility of direct analysis of diesel oils by selective normal-phase liquid chromatography (LC) so that oil samples can be quickly screened for nitrogen compounds without labor-intensive sample preparation. Our results are therefore reported below.

Three samples were investigated: a Brazilian diesel oil (laboratory distilled), a Brazilian light cycle oil, and a commercial Arabian straight run diesel. In a previous study [12], we reported the isolation and identification of major nitrogen compounds in the three diesel samples by particle beam LC–MS and UV spectrometry. Alkyl carbazoles were identified as the major neutral nitrogen compounds in the Brazilian and Arabian straight run diesel samples [12], while alkyl indoles were the major neutral nitrogen compounds in the light cycle oil sample [13]. Alkyl benzoquinolines were identified as the major basic nitrogen compounds in the Brazilian diesel sample [12,13]. The results obtained in the present work are comparable to those obtained previously [12,13] and demonstrate the potential application of this direct analysis methodology to these very complex mixtures.

2. Experimental

2.1. Materials

The Brazilian diesel and light cycle oil were provided by Petrobras, Brazil. The Brazilian diesel sample was laboratory distilled at Petrobras with a boiling range of 200–400°C. The total nitrogen content of this sample was approximately 700 ppm. The Brazilian light cycle oil (boiling range: 206–314°C) contained approximately 2000 ppm of total nitrogen. The Arabian straight run diesel was also provided by Petrobras, Brazil. This sample had a boiling range of 171–377°C and contained approximately 102 ppm of total nitrogen, while reference standards of carbazole, indole, acridine and benzo[*h*]quinoline were purchased from Aldrich and were analytical grade. Chemical structures of these compounds are shown in Fig. 1. All other chemicals were obtained from commercial sources and were at a minimum reagent grade. All solvents were HPLC grade.

2.2. Sample preparation

Prior to high-performance liquid chromatography (HPLC), all samples were diluted with one volume of hexane and solutions were ana-

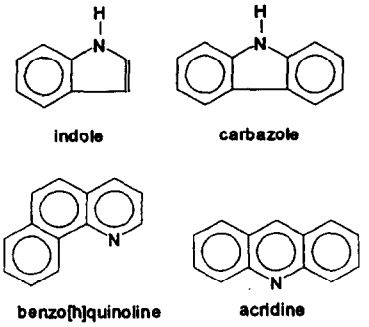

Fig. 1. Chemical structures of the nitrogen compounds investigated.

lyzed directly by HPLC–UV or particle beam LC–MS.

2.3. HPLC

HPLC–UV analyses were conducted using a Hewlett-Packard Model 1090 liquid chromatograph equipped with a gradient solvent pump, an autosampler and a photodiode-array detector. Samples were monitored at 254, 270 and 290 nm and UV spectra were collected at a scan range of 220–400 nm. LC–MS analyses were conducted using a Hewlett-Packard Model 1050 gradient solvent pump, a Hewlett-Packard Model 1050 autosampler and a Hewlett-Packard Model 5989A MS Engine (mass spectrometer) equipped with a particle beam interface. Full-scan electron impact (EI) mass spectra were obtained using 70 eV electron energy. The ion source temperature was 250°C and the analyzer temperature was 120°C. The interface was maintained at 50°C at a carrier gas (helium) flow of 50 p.s.i. (1 p.s.i. = 6894.76 Pa). The instrument was optimized by adjusting nebulizer and helium flow using flow injection analysis of a carbazole standard. Under the normal-phase HPLC conditions, the ion source pressure was approximately $1 \cdot 10^{-4}$–$2 \cdot 10^{-4}$ Torr (1 Torr = 133.322 Pa).

Normal-phase HPLC separations of oil samples were achieved on a Spherisorb alumina (5 μm, 250 × 4.6 mm) column using gradient elution at 0.7 ml/min. Elution solvent A was hexane and solvent B was hexane–dioxane (50:50). The linear gradient program was: 0 min, 100% A; 20 min, 100% A; 120 min, A–B (90:10).

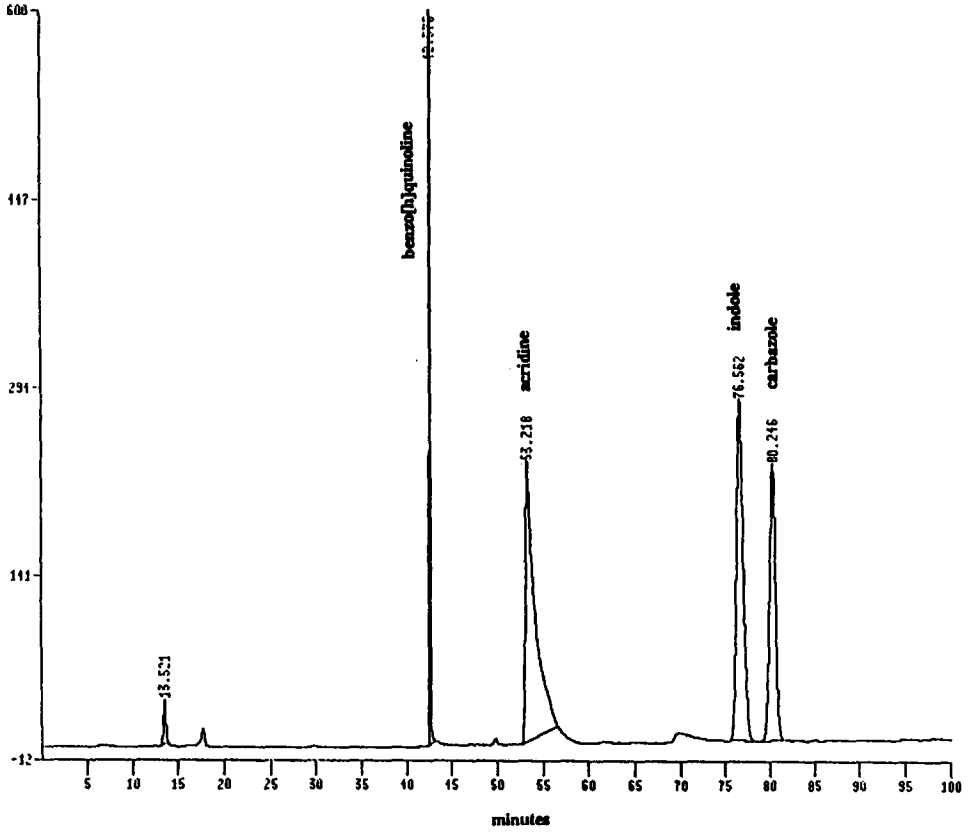

Fig. 2. HPLC–UV chromatogram (254 nm) of a standard mixture. Injection volume: 5 μl.

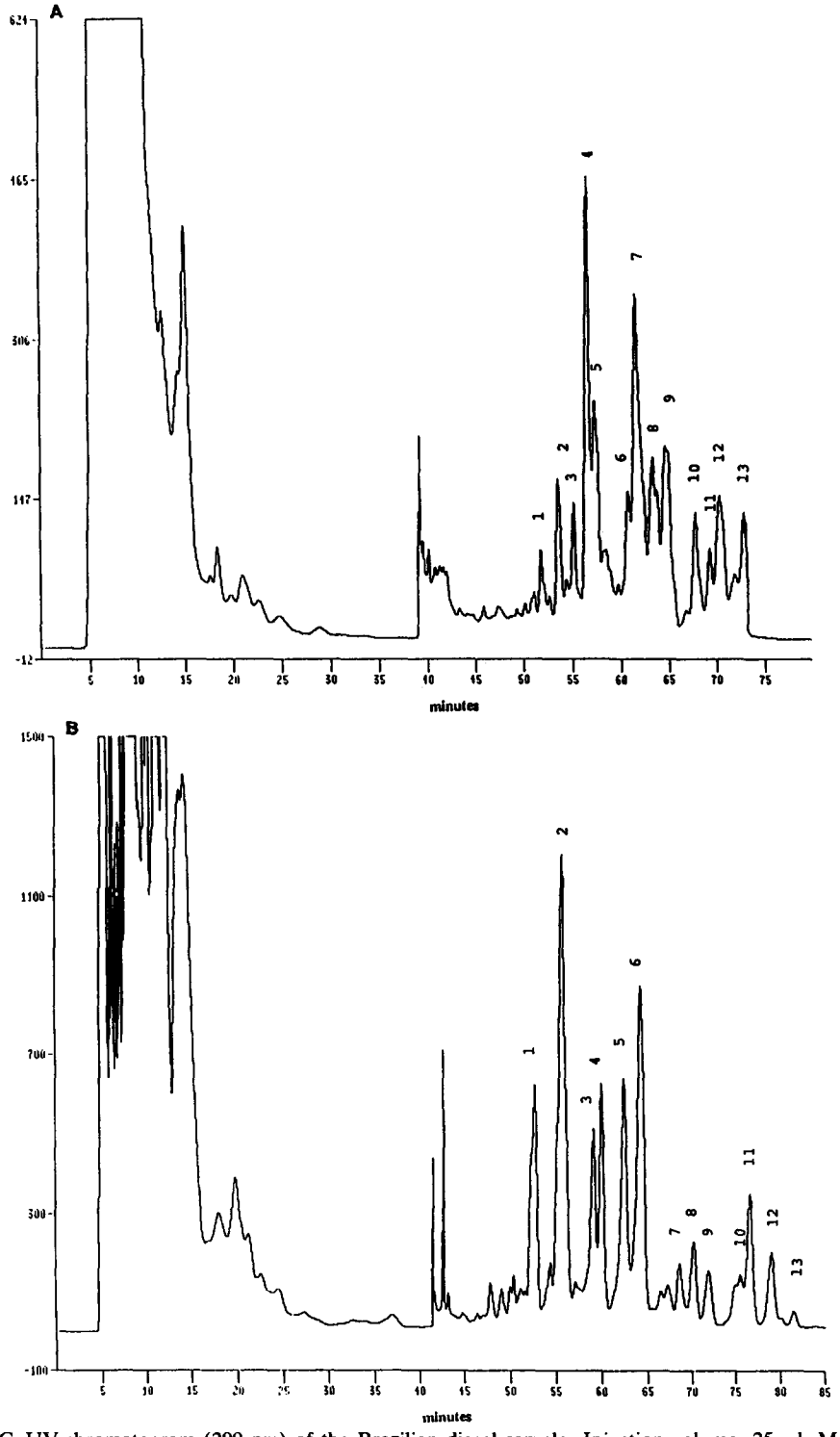

Fig. 3. (A) HPLC–UV chromatogram (290 nm) of the Brazilian diesel sample. Injection volume: 25 μl. Major alkylcarbazole peaks are numbered (1–13). (B) HPLC–UV chromatogram (270 nm) of the Brazilian light cycle oil sample. Injection volume: 25 μl. Major alkylindole and alkylcarbazole peaks are numbered (1–13).

2.4. Estimation of the concentrations of carbazoles and indoles

The concentrations of carbazoles and indoles in oil samples were estimated by HPLC–UV at 290 and 270 nm, respectively, using external calibration. External calibration standards of carbazole and indole were prepared in hexane at 500 ppm and analyzed with the samples. Because of the long HPLC runtime, the quantitation was based on a single-point calibration using peak area. The detector linearity was demonstrated over a range of 10–500 mg/l for both carbazole and indole using isocratic elution (to shorten the analysis time). Based on the detector response for the lowest calibration standard (10 mg/l), a ppm method detection limit was a reasonable estimation for both carbazoles and indoles in diesel samples.

3. Results and discussion

Neutral nitrogen compounds in petroleum products are frequently isolated by normal-phase column chromatography using activated aluminum oxide [8]. While hydrocarbons and other interfering components have very little or no retention on the column, the nitrogen compounds are selectively retained and can be eluted with stronger normal-phase solvents (e.g. chloroform, methylene chloride). This principle can certainly be extrapolated onto the analytical scale where nitrogen compounds can be analyzed directly using an HPLC analytical column without precolumn concentration enrichment.

In this work, we investigated four classes of compounds: carbazoles, indoles, benzoquinolines and acridines. The separation of a standard mixture containing these four reference standards is shown in Fig. 2. Neutral nitrogen compounds (carbazole and indole) retained significantly longer on the alumina column than the basic nitrogen compounds (benzo[*h*]quinoline and acridine). This separation was used successfully to monitor carbazoles and indoles in oil samples. On the other hand, because of the relatively short retention times, benzoquinolines and acridines were not adequately separated from the matrix polyaromatic hydrocarbons and the interference from the matrix militated against using direct injection methods for these basic nitrogen compounds. Thus the method

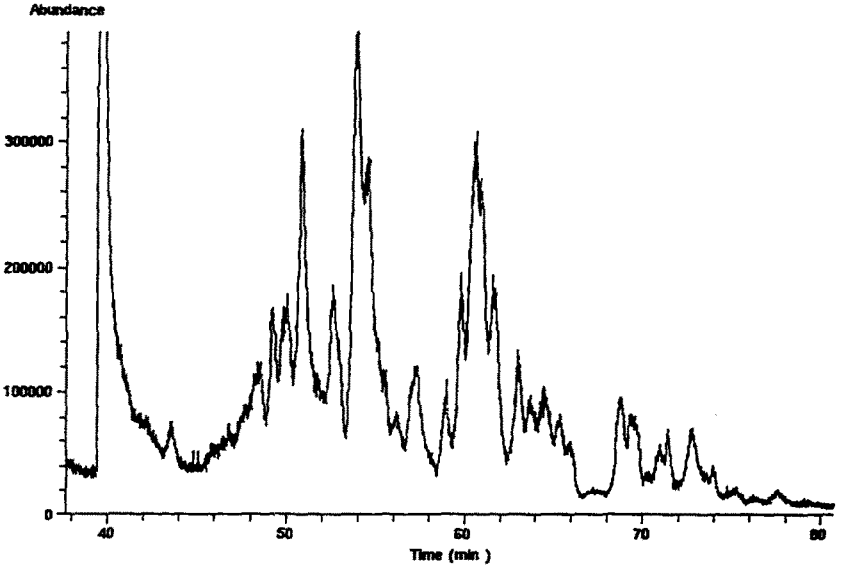

Fig. 4. Total ion chromatogram of the Brazilian diesel sample. Ion source temperature: 250°C; scan range: 110–250 u; injection volume: 50 μl.

developed in this work is more useful for the neutral nitrogen compounds than for the basic nitrogen compounds. (Because of the polar nature of the basic nitrogen compounds, reversed-phase HPLC is the preferred separation technique.) HPLC–UV analyses of the Brazilian diesel and light cycle oil are presented in Fig. 3. As shown, hydrocarbons were eluted with hexane during the first 30–35 min, while the neutral nitrogen compounds were retained and eluted with a gradual increase of the mobile phase strength (through gradient elution). Although the runtime was relatively long (100 min), peak broadening was not severe and adequate quantitation was achieved.

Approximately 13 major peaks were observed at 290 nm in the Brazilian diesel sample (Fig. 3A). They were identified as the C_1–C_5-carbazoles (mostly methyl and multiple methyl substitutions). The identification was based on EI-MS and UV spectrometry of each peak. The m/z values of molecular ions were used to differentiate carbazole homologues. The LC–MS total ion chromatogram of this sample is presented in Fig. 4. Extracted ion chromatograms of m/z 181, 195, 209, 223 and 237 are presented in Fig. 5, showing the distribution of C_1–C_5-carbazoles. Full-scan EI mass spectra of selected peaks are shown in Fig. 6. Although there were ion contributions resulting from fragmentation of

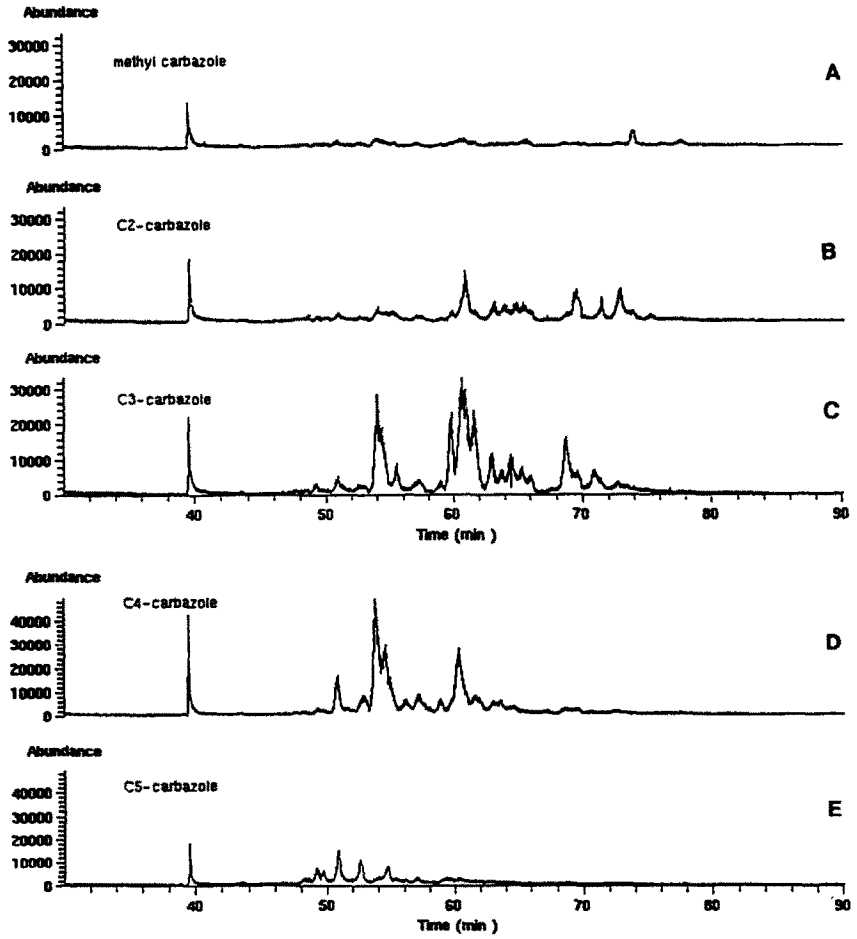

Fig. 5. Extracted ion chromatograms [m/z 181 (A), 195 (B), 209 (C), 223 (D) and 237 (E)] of the Brazilian diesel sample.

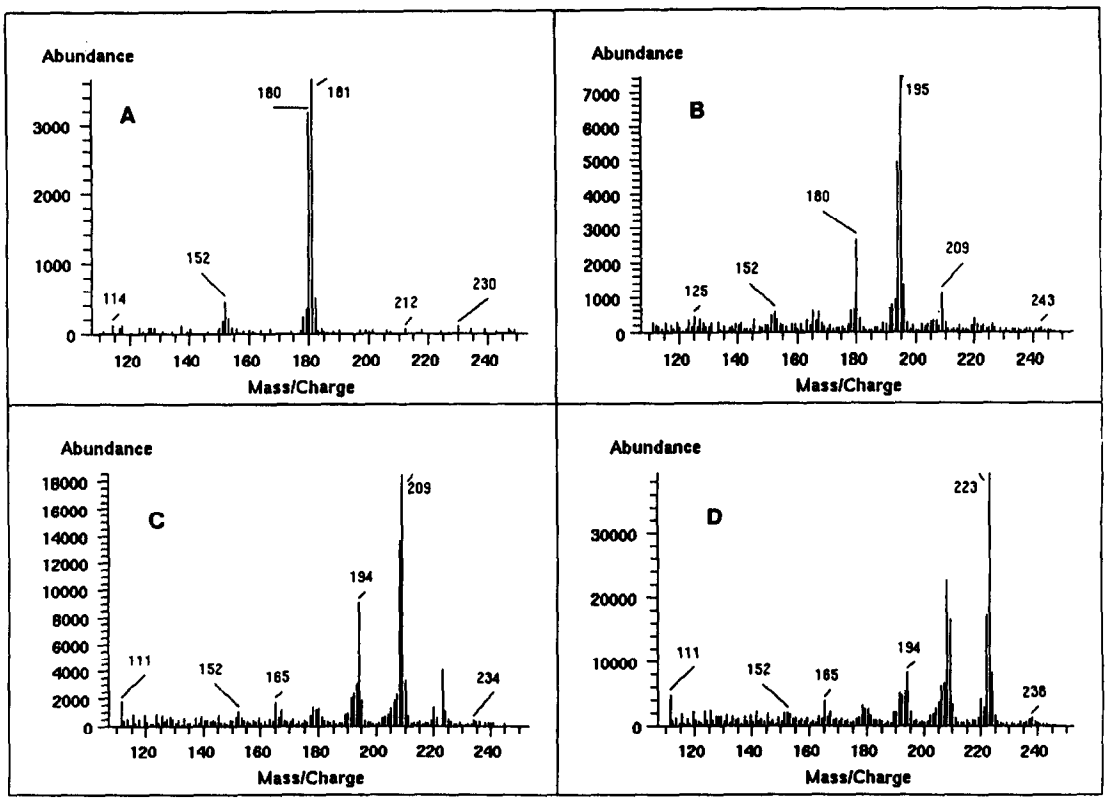

Fig. 6. Full-scan LC–EI-MS mass spectra of (A) methyl carbazole, (B) C_2-carbazole, (C) C_3-carbazole and (D) C_4-carbazole identified in the Brazilian diesel sample.

higher carbazole homologues (for example, C_4-carbazole, molecular ion 223, also produces m/z 209), it was apparent that the C_3- and C_4-carbazoles were the major carbazole homologues and represented the majority of the neutral nitrogen compounds in this sample. Carbazole itself was not detected in this sample. The elution order generally was C_5- < C_4- < C_3- < C_2- < methyl carbazole < carbazole although some overlapping does occur. To confirm peak assignments, the UV spectrum (220–400 nm) of each peak was collected online using a photodiode-array detector. Two representative UV spectra (peak 4 and 7) are presented in Fig. 7A. (UV spectra for the authentic standards of carbazole and indole exhibited characteristic λ_{max} at 270 and 290 nm with little overlap.) Peak 4 was identified by LC–MS to be C_4-carbazole and peak 7 to be C_3-carbazole. The two UV spectra were very similar, indicating that alkyl groups had little effect on the UV absorption of carbazoles [12].

The analysis of the Brazilian light cycle oil revealed that the major neutral nitrogen compounds were indoles (indole, methyl indoles, and dimethyl indoles [13]) (Fig. 3B). Approximately 13 major peaks representing indoles and carbazoles were observed. Representative UV spectra of different alkyl indoles (peaks 2 and 6) are shown in Fig. 7B. Although indoles and carbazoles eluted at approximately the same retention time region (Fig. 3A and B), they can be distinguished by signal ratios at 290 and 270 nm. The signal ratio (290 nm/270 nm) is greater than 2 for carbazoles and less than 0.6 for indoles. LC–MS analysis of this sample, however, showed only carbazoles because of the low mass sensitivity of LC–MS for indoles. The LC–MS

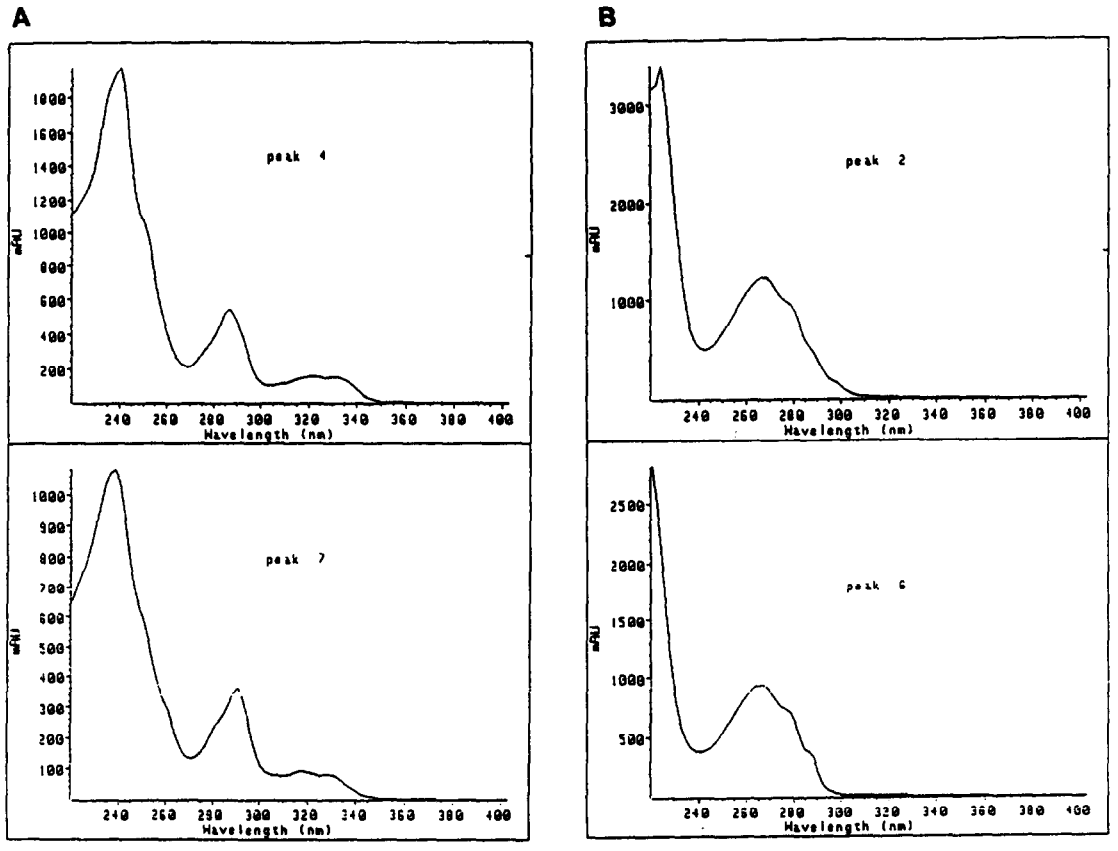

Fig. 7. UV spectra of (A) carbazoles in the Brazilian diesel sample and (B) indoles in the Brazilian light cycle oil.

sensitivity for indole was approximately three orders of magnitude less than for carbazole, presumably due to the relatively high volatility of indole. As a result, direct analysis of indoles by particle beam LC–MS was not possible. (Enrichment of indoles by extraction or column chromatography is needed for analysis by particle beam LC–MS.) Among the carbazoles detected in this light cycle oil sample (by LC–MS), carbazole (peak 13) and methyl carbazoles were the major homologues. The HPLC profile of the Arabian straight run diesel sample was very similar to that of the Brazilian diesel. As with the Brazilian diesel, carbazoles were determined to be the major neutral nitrogen compounds in the Arabian straight run diesel sample, but in much lower quantities.

The concentrations of total carbazoles and indoles in the three samples were estimated by HPLC–UV. The total carbazole concentrations were approximately 2440, 435 and 514 mg/l in the Brazilian diesel, the Brazilian light cycle oil and the Arabian straight run diesel, respectively. The total indole concentration was measured to be approximately 21 770 mg/l in the Brazilian light cycle oil. Indoles were not found in the other two oil samples. Due to the lack of reference standards, carbazole and indole were used to quantify their alkyl homologues at 290 and 270 nm, respectively. Thus, the concentrations reported can only serve as an estimation. Based on the UV detector sensitivity for standards of carbazole and indole, a method detection limit of ppm level can be readily achieved for analysis of both classes of compounds in diesel oils by normal-phase HPLC.

4. Conclusions

By using alumina normal-phase liquid chromatography, we have demonstrated the usefulness of a direct analysis method for determination of neutral nitrogen compounds in diesel oils. Combining MS and photodiode-array detection, we analyzed three diesel samples of different origins and illustrated the potential application of such a direct analysis method for petroleum products. Although particle beam LC–MS showed poor sensitivity for indoles, it displayed exceptionally good sensitivity and selectivity for carbazoles and therefore can be used to screen for carbazoles in petroleum products without labor-intensive sample preparations. This method, however, is not applicable to basic nitrogen compounds because of their high polarities.

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References

[1] L. Chan, J. Ellis and P.T. Crisp, *J. Chromatogr.*, 292 (1984) 355.
[2] H.V. Drushel and A.L. Sommers, *Anal. Chem.*, 38 (1966) 19.
[3] M. Dorbon and C. Bernasconi, *Fuel*, 68 (1989) 1067.
[4] J.F. McKay, J.H. Weber and D.R. Latham, *Anal. Chem.*, 48 (1976) 891.
[5] B.A. Tomkins and C.-H, Ho, *Anal. Chem.*, 54 (1982) 91.
[6] S.J. Marshman, *Fuel*, 70 (1991) 967.
[7] J.-M. Schmitter, H. Colin, J.L. Excoffier, P. Arpino and G. Guiochon, *Anal. Chem.*, 54 (1982) 769.
[8] G.K. Hartung and D.M. Jewell, *Anal. Chim. Acta*, 26 (1962) 514.
[9] G. Grimmer, J. Jacob and K.-W. Naujack, *Anal. Chem.*, 55 (1983) 2398.
[10] M. Dorbon, I. Ignatiadis, J.-M. Schmitter, P. Arpino, G. Guiochon, H. Toulhoat and A. Huc, *Fuel*, 63 (1983) 565.
[11] D.W. Later, T.G. Andros and M.L. Lee, *Anal. Chem.*, 55 (1983) 2126.
[12] J. Mao, C.R. Pacheco, D.D. Traficante and W. Rosen, *Fuel*, (1994) in press.
[13] J. Mao, C.R. Pacheco, D.D. Traficante and W. Rosen, *Anal. Chem.*, (1994) submitted for publication.