

Ion-exchange resins in the isolation of nitrogen compounds from petroleum residues

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Abstract

In this work, preparative liquid chromatography was used for the separation of the nitrogen compounds in a sample of heavy gas oil from a Brazilian petroleum. Initially it took place a pre-fractionation by neutral aluminium oxide and the compounds were separated in different classes such as: hydrocarbons, resins (compounds of low molecular mass and intermediate polarity) and asphaltenes (polar compounds with high molecular mass). A comparison of the fraction of resins was performed by re-fractionating with modified silica (with potassium hydroxide and hydrochloric acid), or with ion exchange resins (Amberlyst A-27 and A-15), being isolated the basic and neutral compounds, that were analyzed by GC–MS in the scan and selected ion monitoring modes. Quinolines, benzoquinolines, tetrahydroquinolines were found in the basic fraction and carbazoles derivatives were found in the neutral fraction.

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1. Introduction

The nitrogen compounds that occur in petroleum adversely affect many important catalytic and product stability. Nitrogen is a universal component of fossil fuels, generally associated with the organic portion of crude materials; its level is around 1–2% in shale oil and coal. With the possible exception of some petroleum products of commercial value, nitrogen compounds are regarded as undesirable due to the problems that they may pose in refining. A number of basic compounds are toxic; several of the aza heterocycles and aromatic primary amines are known, or suspected to be carcinogens [1,2]. Neutral nitrogen compounds appear, in general, to be less toxic than basic compounds, but several dibenzocarbazoles have been reported to show carcinogenic activity. A detailed knowledge of the types and concentration of nitrogen compounds present in petroleum products is clearly desirable to optimize methods for their removal and specify methods for the safe handling of such materials [3].

Several works are related to nitrogen compounds characterization in fuel which can be found in [4–16]. Some of those refer about atmospheric gas oil and light cycle oil [10,14,15,17]. Other papers are related to the presence of quinolines, indoles and carbazoles [9,12–16].

In a previous work [17], we have investigated the effects of extraction temperature, pressure and addition of water on the liquid yield and on the characteristics of extracts and residues from supercritical fluid extraction (SFE) of a high-ash Brazilian mineral coal using alcohol as primary solvent. Resins were found to be the major constituent fraction in all extracts, a study to better characterize this fraction has been conducted. It is well known that resins are the portion of the liquids derived from coal that contain polar compounds, such as pyridines, quinolines, phenols, etc. [18].

The resins are typically compounds with a highly polar terminal group that frequently contains an oxygen, sulfur or nitrogen, as well as of a long chain with alkyl groups. Due to the complexity of resins, it is impossible to characterize them without a good pre-fractionation step, such as liquid–liquid extraction, solvent extraction or preparative liquid chromatography (prep-LC) [17,19]. In the last years, prep-LC has been the most

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used technique, because of its well-known advantages [19].

Numerous separation and identification schemes using activated neutral oxide aluminum or modified silica to separate into neutral and basic nitrogen compounds [7,8,12,14]. There is a general consensus about the difficulty in removing the nitrogen compounds of complex matrices.

In this work, it was analyzed the basic and neutral nitrogen compounds in petroleum residue heavy gas oil (HGO). First, we developed a pre-separation scheme using neutral aluminum oxide to obtain the nitrogen compounds fraction. Acid and basic modified silica gel, acid (Amberlyst A15) and basic (Amberlyst A27) resins were used to separate basic and neutral nitrogen compounds.

2. Experimental

2.1. Reagents and samples

The residue (HGO) was produced by Petrobras, in Brazil. The ion-exchange resins, Amberlyst A15 (strongly acidic with sulfonic acid functionality, surface area: $50 \text{ m}^2 \text{ g}^{-1}$,

porosity volume: 32%, exchange capacity: $4.7 \text{ mequiv. g}^{-1}$ or $1.8 \text{ mequiv. ml}^{-1}$) and Amberlyst A27 (basic resin, with active group: $-\text{N}(\text{CH}_3)_2\text{H}^+\cdot\text{Cl}^-$, surface area: $65 \text{ m}^2 \text{ g}^{-1}$, porosity volume: 51%, exchange capacity: $2.6 \text{ mequiv. g}^{-1}$ or $0.7 \text{ mequiv. ml}^{-1}$) from Sigma were used in the study. The standard compounds, purchased from Aldrich, were quinoline, isoquinoline, benzo[*h*]quinoline, indole, phenanthridine, acridine, dodecane, biphenyl and fluorene.

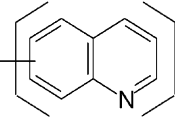
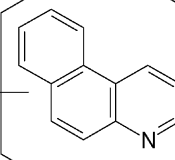
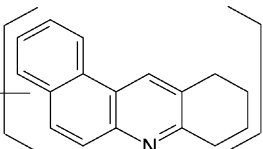
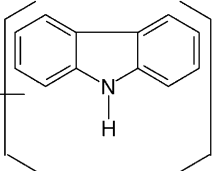
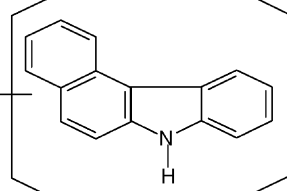
All the reagents and solvents were analytical-reagent grade, purchased from Merck (Darmstadt, Germany). The main solvents (*n*-hexane, methylene chloride, methanol and ethanol) were bi-distilled prior to use, to avoid some interference in the process.

Glassware was washed with detergent and then rinsed with distilled water, acetone and hexane, and placed in an oven at 300°C for 30 min. All glassware was covered with aluminum foil to prevent contamination.

2.2. Analytical procedures

The pre-separation was achieved by a slight modification of the method developed by Shiraiishi et al. [14]. Twenty

Table 1
Generic molecular structures of the monitored nitrogen compounds

Compounds	<i>M</i>	Molecular structures	Ions
Alkyl quinolines	129		143, 157, 171, 185, 199, 213, 227, 241, 255
Alkyl benzoquinolines	179		193, 207, 221, 235, 249, 263, 277, 291, 305
Alkyl tetrahydrobenzoquinolines	233		247, 261, 275, 289, 303, 317, 331, 345, 359
Alkyl carbazoles	167		181, 195, 209, 223, 237, 251, 265, 279, 293
Alkyl benzocarbazoles	217		231, 245, 259, 273, 287, 301, 315, 329, 343

M is the molecular ion of the non-alkylated compound and *n* represents the number of methylene groups added in the molecule.

grams of neutral aluminum oxide previously activated at 400 °C for 12 h in an oven, were slurry packed into a glass column (520 mm × 15 mm i.d.) with methylene chloride. The samples analyzed were a mixture of standards or 1.0 g of residue (HGO), dissolved in a minimum volume of methylene chloride and deposited on the top of column. The saturated hydrocarbons were first collected by elution with *n*-hexane (25 ml). The aromatics and sulfur compounds were displaced by elution with 25 ml of *n*-hexane-methylene chloride (60:40 (v/v)). The nitrogen compounds were eluted with methylene chloride (50 ml) and the most polar fraction with methanol (50 ml).

2.3. Fractionation of basic and neutral nitrogen compounds

2.3.1. Method A: resins Amberlyst A15 and A27

2.3.1.1. Resin A27 activation. Five grams of Amberlyst A27 were washed with 50 ml of NH₄OH solution in methanol (10% (v/v)) and shaken for 5 min. The following solvent sequence was used to wash the resin: 25 ml of ethanol, water until pH 7, 25 ml of acetone and 25 ml of *n*-hexane.

2.3.1.2. Resin A15 activation. Five grams of Amberlyst A15 were washed with 50 ml of hydrochloric acid in methanol (10% (v/v)) and shaken for 5 min. The same sequence of solvents was used to wash the resin.

2.3.1.3. Extraction of the neutral and basic compounds. Five grams of Amberlyst A27 were packed into a glass column (230 mm × 14 mm i.d.) with methylene chloride. The fraction of nitrogen compounds or standard compounds was diluted in a minimum volume of methylene chloride and deposited on the top of column. The basic and neutral fraction was eluted with 50 ml methylene chloride and concentrated until 1 ml. The acid fraction was retained in the resin and discharged.

Five grams of resin A15 were packed in another glass column, with the same dimensions. The basic and neutral fraction (from the first column) was deposited on the top of column. The neutral fraction was eluted with 50 ml of methylene chloride. The basic fraction was eluted with 50 ml of isopropylamine in hexane (10% (v/v)). The eluted fractions were collected and concentrated by rotary evaporation.

2.3.2. Method B: retention on silica modified with KOH and HCl

The method used was based on those developed by Caramão and co-workers [20,21] with slight modifications.

2.3.2.1. Preparation of silica modified with KOH. Ten grams of silica gel (70–230 mesh ASTM), previously activated at 140 °C for 4 h, were treated with a solution of 2.5 g of KOH in 40 ml of isopropanol and 40 ml of diethyl ether. The mixture was maintained under magnetic stir for 10 min.

2.3.2.2. Preparation of silica modified with HCl. Ten grams of silica gel previously activated were treated with

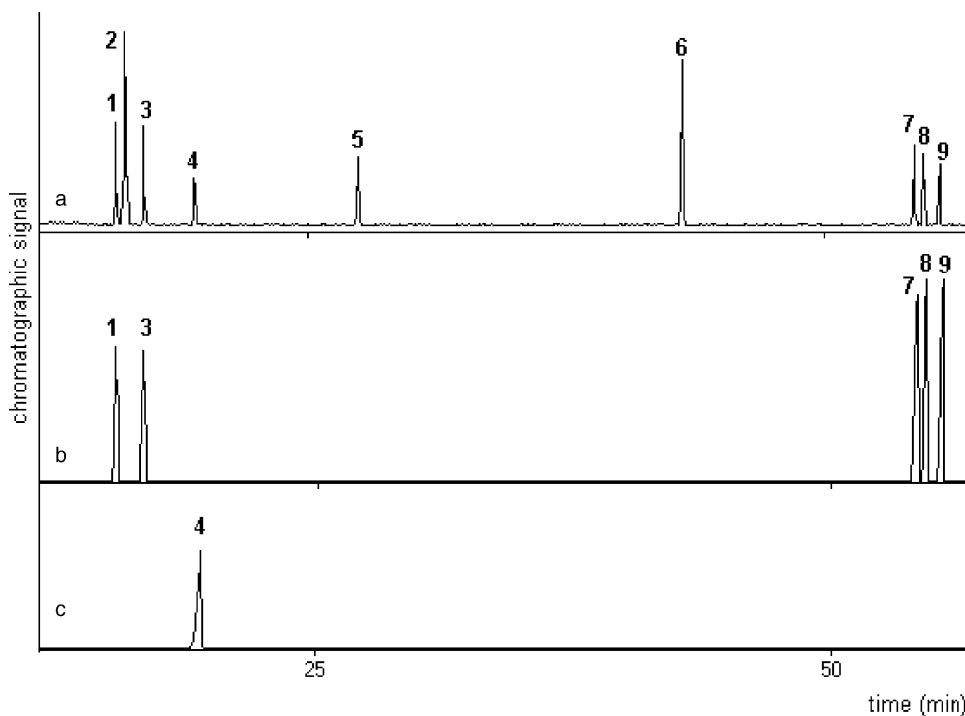


Fig. 1. Chromatogram (GC-MS) of standards mixture: (a) standard mixture; (b) basic fraction in modified silica; (c) neutral fraction in modified silica. Peak identification: 1—quinoline; 2—dodecane; 3—isoquinoline; 4—indole; 5—biphenyl; 6—fluorene; 7—benzo[*h*]quinoline; 8—acridine; 9—phenanthridine.

a solution of 5.5 ml of concentrated HCl in 40 ml of isopropanol alcohol and 40 ml of diethyl ether. The mixture was maintained under magnetic stir for 10 min.

2.3.2.3. Extraction of the neutral and basic compounds.

The SiO_2/KOH was packed in a glass column and washed with 80 ml of diethyl ether and 40 ml of methylene chloride. The fraction of nitrogen compounds or standards were diluted in minimum volume of methylene chloride and deposited on the top of column. The elution was carried out with 100 ml of methylene chloride. The acid fraction was retained in the column and discharged. The eluted fraction, composed by basic and neutral compounds, was concentrated in a rotary evaporator.

The SiO_2/HCl was packed in another glass column and washed with 80 ml of diethyl ether and 40 ml of methylene chloride. The basic and neutral fraction (from the first column) was deposited on the top of column. The neutral fraction was eluted with 100 ml of methylene chloride. The

basic fraction was eluted with 50 ml of isopropylamine in hexane (10% (v/v)). The elution fractions were collected and concentrated by rotary evaporation until the dryness. The samples were dissolved in a small amount of methylene chloride prior to analyze by GC–MS.

2.4. Chromatographic analysis

For gas chromatographic analysis, a GC–MS Shimadzu QP5050A instrument was used, using electron impact (EI) ionization at 70 eV and an OV-5 column (60 m \times 0.25 mm i.d.; 0.25 μm film thickness). Injector and interface were at 280 $^\circ\text{C}$. A split injector was used with a split ratio of 1:50. Chromatographic conditions:

- (a) Standard compounds analysis: 80 $^\circ\text{C}$ (5 min), 80–100 $^\circ\text{C}$ (2 $^\circ\text{C min}^{-1}$), 100–110 $^\circ\text{C}$ (1 $^\circ\text{C min}^{-1}$), 110–150 $^\circ\text{C}$ (2 $^\circ\text{C min}^{-1}$), 150–280 $^\circ\text{C}$ (5 $^\circ\text{C min}^{-1}$) and 5 min in rest.

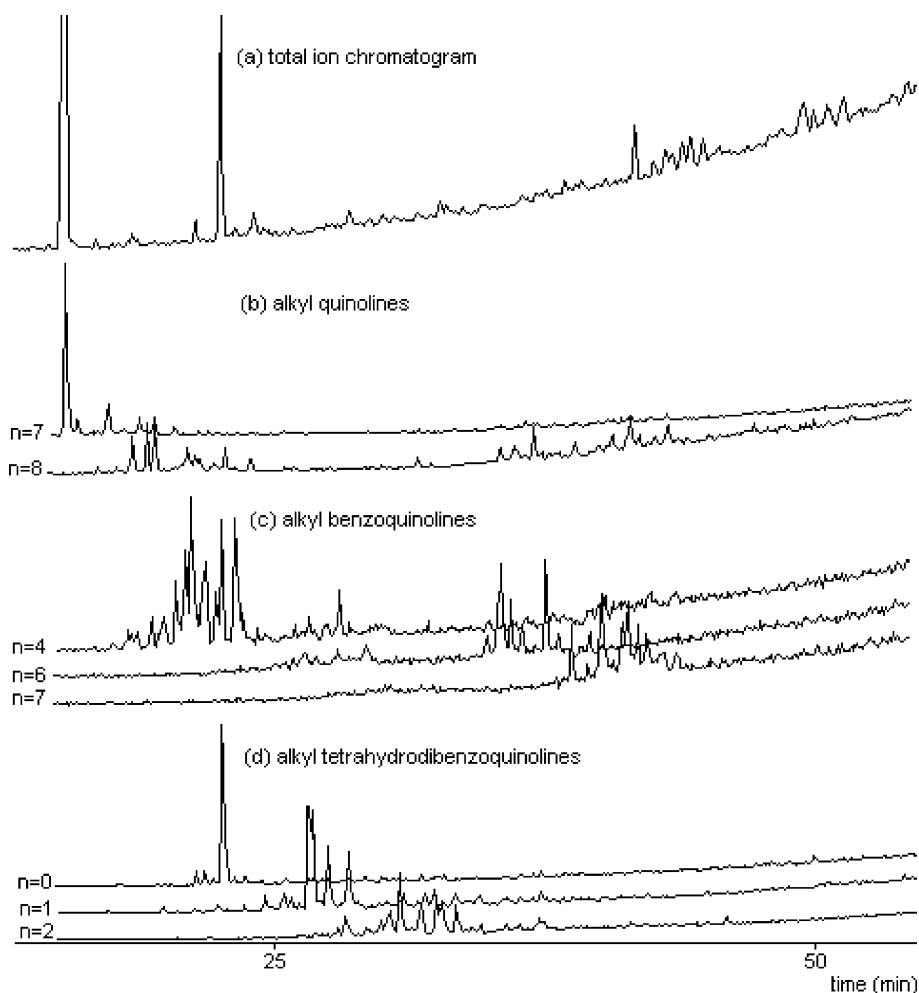


Fig. 2. Chromatogram (GC–MS) of the basic nitrogen compounds, extracted by modified silica chromatography: (a) total ion chromatogram; (b) selective ion chromatogram of alkyl quinolines (m/z 227 and 241); (c) selective ion chromatogram of alkyl benzoquinolines (m/z 235, 263 and 277); (d) selective ion chromatogram of alkyl tetrahydrodibenzoquinolines (m/z 233 and 247).

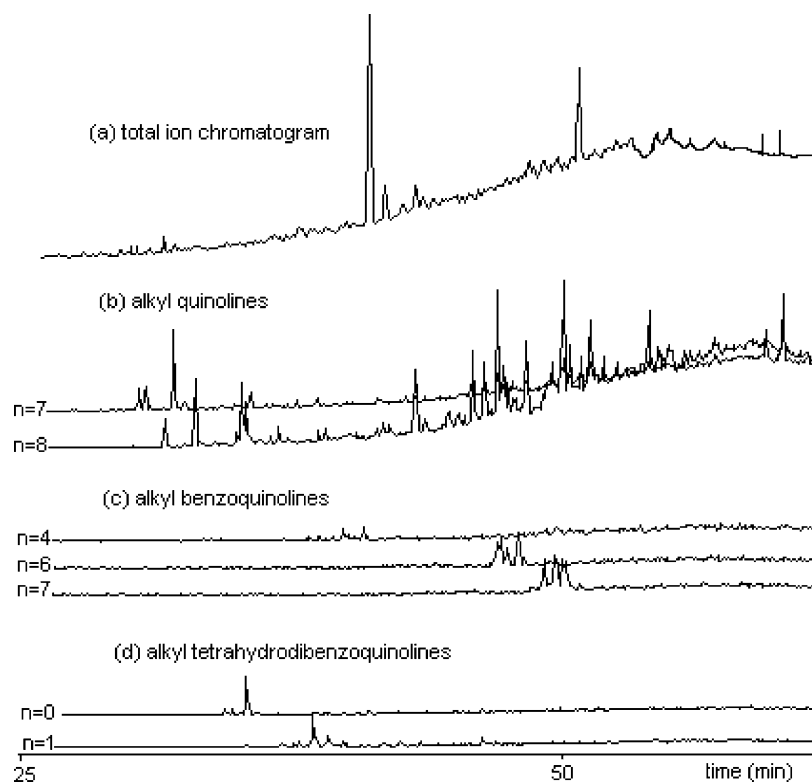


Fig. 3. Chromatogram (GC–MS) of the basic nitrogen compounds, extracted by ion-exchange chromatography: (a) total ion chromatogram; (b) selective ion chromatogram of alkylquinolines (m/z 241 and 255); (c) selective ion chromatogram of alkyl benzoquinolines (m/z 235, 263 and 277); (d) selective ion chromatogram of alkyl tetrahydrodibenzoquinolines (m/z 233, 247 and 261).

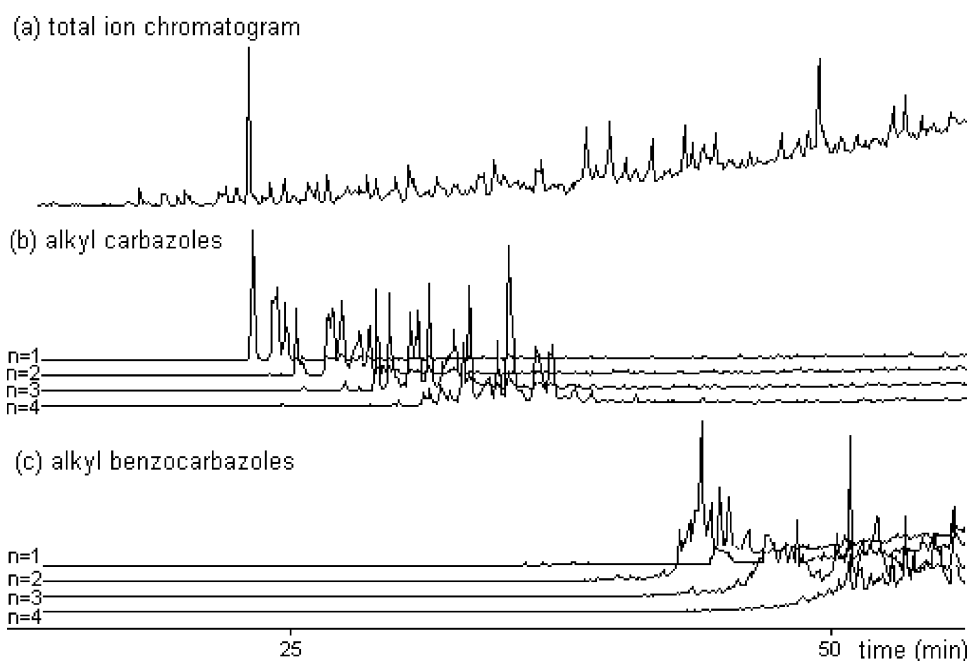


Fig. 4. Chromatogram (GC–MS) of the neutral nitrogen compounds, extracted by modified silica chromatography: (a) total ion chromatogram; (b) selective ion chromatogram of alkyl carbazoles (m/z 181, 195, 209, and 223); (c) selective ion chromatogram of alkyl benzocarbazoles (m/z 231, 245, 259 and 273).

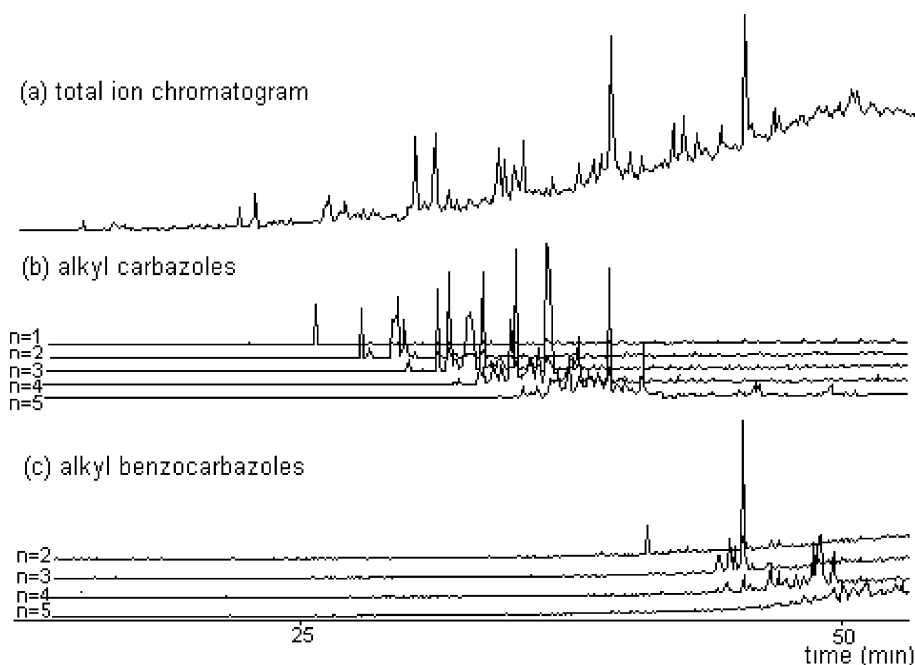


Fig. 5. Chromatogram (GC–MS) of the neutral nitrogen compounds, extracted by ion-exchange chromatography: (a) total ion chromatogram; (b) selective ion chromatogram of carbazoles (m/z 181, 195, 209, 223 and 237); (c) selective ion chromatogram of benzocarbazoles (m/z 245, 259, 273 and 287).

(b) Sample analysis: 170 °C (5 min), 170–280 °C (2 °C min⁻¹) and 20 min in rest.

Compound identification was based upon retention time comparison with standards and it was also confirmed by using the GC–MS computer library system.

All model compounds used in this work were injected individually into the GC–MS system to determine their retention times, purity and mass-fragmentation characteristics. Then the standard mixture (100 mg l⁻¹) was used to determine the optimum resolution conditions.

Mass spectrometry of organo-N compounds usually yields high molecular ions and no characteristic fragmentation, except for the loss of common alkyl groups (CH₃, C₂H₅) and NCH₂⁺ [10].

The identification of the classes of compounds in the sample were made by injection in the scan mode and re-injections in the selected ion monitoring (SIM) mode by monitoring of the ions of alkyl quinolines, alkyl benzoquinolines, alkyl tetrahydrodibenzoquinolines, alkyl carbazoles and alkyl benzocarbazoles. It used the ions $M + 14n$, where M is the molecular ion of the non-alkylated compound and n represents the number of methylene groups added in the molecule. It was monitored from $n = 1$ –9, for all the fractions. Table 1 shows the generic structures of the monitored compounds.

3. Results and discussion

3.1. Test with standards

The total ion chromatograms of a mixture of nine standards compounds, that were selected to test, in the con-

centration of 100 mg l⁻¹ are shown in Fig. 1a. The methods (silica modified and ion exchange resins) separated efficiently the basic compounds (quinoline, isoquinoline, benzo[*h*]quinoline, acridine, phenanthridine, Fig. 1b) and neutral compounds (indole, Fig. 1c) from the standard mixture. The non-nitrogenated compounds (dodecane, fluorene and biphenyl, Fig. 1a) were also satisfactorily separated in the initial pre-separation using neutral aluminium oxide, as was expected.

3.2. Basic nitrogen compounds in the HGO

The total ion chromatograms (TIC) of the basic nitrogen fraction of HGO are shown in Fig. 2a (silica modified extraction) and Fig. 3a (ion exchange resin extraction). These figures also show the selective ion chromatograms that were obtained by monitoring of the ions of alkyl quinolines, benzoquinolines and tetrahydrodibenzoquinolines. These figures show only the chromatograms that presented some peaks, that is, the injections that did not present peaks were discarded. In Figs. 2b and 3b it is possible to note the presence of C₇–C₈ alkyl quinolines. For benzoquinolines (179 + 14 n), the compounds achieved were C₄, C₆ and C₇ alkyl derivatives (Figs. 2c and 3c). The tetrahydrodibenzoquinolines (233 + 14 n) distribution shows of C₀–C₂ homologues for silica modified (Fig. 2d) and C₀–C₁ for ion-exchange resin (Fig. 3d).

3.3. Neutral nitrogen compounds in the HGO

The total ion chromatograms (TIC) of the neutral nitrogen fraction of HGO are shown in Fig. 4a (silica modified)

and Fig. 5a (ion-exchange resin). The neutral compounds monitored from HGO are alkyl carbazoles and alkyl benzocarbazoles. In Fig. 4b, it is possible to note the presence of C₁–C₄ alkyl carbazoles (167 + 14*n*) from silica modified. Fig. 5b presents C₁–C₅ alkyl carbazoles from ion exchange resin. From the benzocarbazole series (217 + 14*n*), C₁–C₄ was achieved in silica modified and C₂–C₅ in the ion-exchange resin fraction, as it is shown in Figs. 4c and 5c.

4. Conclusions

As can be seen, several aza-compounds are present in the basic and neutral nitrogen fractions, confirming the selectivity of the proposed method for separation of nitrogen containing compounds.

The petroleum-derived fuel contained two major classes of nitrogen compounds: the carbazoles (in neutral fraction) and the quinolines (in basic fraction).

In a general way, the two procedures used for the extraction of the nitrogen compounds (modified silica and ion-exchange resins) presented good results. According the chromatographic profiles, presented in the previous figures, it is noticed a better resolution for the nitrogen compounds extracted with modified silica, indicating to be this one more appropriate for this separation.

The methodology used still needs some improvements because, due to the complexity of the sample, the chromatograms present no-resolved peaks and low selectivity, once the compounds could only be identified when the technique of monitoring of ions was applied.

References

- [1] W. Cautreels, K.V. Cauwenberghe, *Atmos. Environ.* 10 (1976) 1447.
- [2] P.J. Doherty, R.M. Hoes, A. Robbat Jr, C.M. White, *Anal. Chem.* 56 (1984) 2697.
- [3] P. Burchilli, A.A. Herod, J.P. Mahon, E. Pritchard, *J. Chromatogr.* 281 (1983) 109.
- [4] D. Kendall Albert, *Anal. Chem.* 50 (1978) 1822.
- [5] M. Granda, R. Mendez, S.R. Moinelo, J. Bermejo, *Fuel* 72 (1993) 19.
- [6] F.M. Lanças, M.A. Barbirato, *Fuel Sci. Technol. Int.* 12 (1994) 493.
- [7] E. Ekinici, S. Türkay, M. Citiroglu, A. Akar, *Fuel Process. Technol.* 37 (1994) 175.
- [8] F.M. Lanças, M.A. Barbirato, *Fuel Sci. Technol. Int.* 12 (1994) 507.
- [9] J. Mao, C.R. Pacheco, D.D. Traficante, W. Rosen, *J. Chromatogr. A* 684 (1994) 103.
- [10] J. Mao, C.R. Pacheco, D.D. Traficante, W. Rossen, *Fuel* 74 (1995) 880.
- [11] Y. Martín, R. García, R.A. Solé, S.R. Moinelo, *Energy Fuels* 10 (1996) 436.
- [12] I. Merdrignac, F. Behar, P. Albrecht, P. Briot, M. Vandembroucke, *Energy Fuels* 12 (1998) 1342.
- [13] G.W. Mushrush, E.J. Beal, D.R. Hardy, J.M. Hughes, *Fuel Process. Technol.* 61 (1999) 197.
- [14] Y. Shiraishi, T. Hirai, I. Komasa, *Ind. Eng. Chem. Res.* 40 (2001) 293.
- [15] G.C. Laredo, S. Leyva, R. Alvarez, M.T. Mares, J. Castillo, J.L. Cano, *Fuel* 81 (2002) 1341.
- [16] B. Bennet, M. Chen, D. Brincat, F.J.P. Gelin, S.R. Lartes, *Org. Geochem.* 33 (2002) 545.
- [17] C. Dariva, J.V. Oliveira, M.G.R. Vale, E.B. Caramão, *Fuel* 76 (1997) 585.
- [18] B.A. Dew, S.C.F. Robinson, *Fuel* 64 (1985) 861.
- [19] S. Karan, H.M. McNair, F.M. Lanças, *LC GC* 5 (1987) 41.
- [20] E.B. Caramão, L.M.F. Gomes, M.D. Oliveira, A. Bristoti, F.M. Lanças, *Fuel Sci. Technol. Int.* 8 (1990) 881.
- [21] F.M. Lanças, E.B. Caramão, *Fuel Sci. Technol. Int.* 14 (1996) 417.