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Basic Nitrogen Compounds Identification in Rasco Crude Oil Blend and in its Distillates and Residue

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Abstract: The basic nitrogen content in Rasco crude oil and light gas oil (LGO), heavy gas oil (HGO) and in naphtha and kerosene produced from Rasco crude oil a 50% Sarir/50% Mesla crude blend; a feedstock for Ras Lanuf refinery was determined; Rasco crude oil, LGO and HGO contain 47, 13 and 88 ppm nitrogen respectively whilst naphtha and kerosene contain zero ppm basic nitrogen. Some of the physical and the chemical properties of Rasco crude oil and its LGO, HGO and residue were determined, followed by extraction of basic nitrogen compounds from Rasco crude oil and from its LGO, HGO and residue by hydrochloric acid extraction method. Separation and identification of these types of compounds was attained by a GC-MS technique and the identified basic nitrogen compounds are quinoline, isoquinoline and acridine derivatives and the identified non basic nitrogen compounds are the indole derivatives.

INTRODUCTION

Basic and non basic nitrogen compounds naturally occurring in petroleum and petroleum distillates influence different stages of petroleum refining[1, 2].

Nitrogen compounds reduce stability of petroleum distillates by colour, odour and sediment formation[2-4]. Similarly basic nitrogen compounds are strong inhibitors in cracking, hydrocraking reforming processes, hydrodenitrogenation and in hydrodesulfurization reactions by interacting with the acidic sites of the catalyst employed causing catalyst poisoning. In this reaction basic nitrogen compounds are electron pair donors (EPD) and the catalyst is electron pair acceptors (EPA)[2,4-7] Non basic nitrogen compounds inhibition in hydrodesulphurization reactions has been observed and described;hydrogenation reduction reaction of these compounds that take place in hydrodesulphurization reactions process leading to the formation of basic type[7-9], or by a strong adsorption of non basic nitrogen compounds over the support surface of the catalyst [7,10,11].

Methods of separation, identification and characterization as well as methods of quantitative determination of basic and non basic nitrogen compounds in petroleum distillates are available and can be found in references [1-8, 12-23].

Since no work is available related to basic nitrogen compounds in Rasco crude oil, the aim of this work is to determine quantitatively basic nitrogen content in Rasco crude oil and in its kerosene, naphtha, LGO and HGO as well as extraction, separation and identification of basic nitrogen compounds from this crude oil blend and from its LGO, HGO and residue; by following a slight modification of the Hartung and Jewel separation scheme[1] and subsequent separation and identification of basic nitrogen compounds by a GC-MS technique[2,7,20].

EXPERIMENTAL

The properties of Rasco crude oil blend and its LGO, HGO and residue were obtained following ASTM standard methods, whilst basic nitrogen content in Naphtha (IBP 40^0C), Kerosene (IBP 155^0C), LGO, HGO and Rasco crude oil blend was determined following, UOP-312, UOP-313 and UOP-269-70 standard methods[7,24-26]. All samples were taken from the Ras Lanuf refinery.

Before basic nitrogen compounds extraction the samples were diluted and dissolved in the proper solvent as follow, a raw Rasco crude oil blend sample was diluted with an n-heptane, HGO sample was dissolved and diluted with an n-heptane whilst residue sample was dissolved and diluted with a 1:1 toluene/

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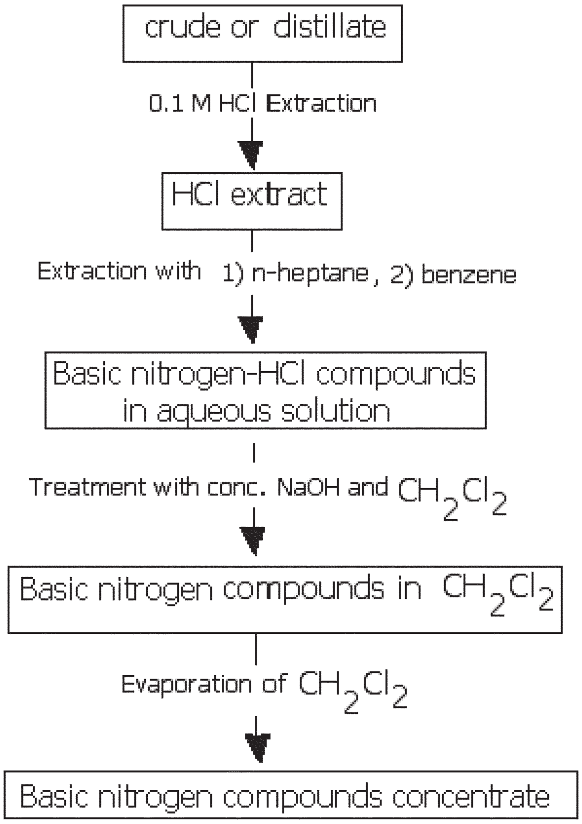

Fig. 1. Basic nitrogen compounds separation scheme.

xylene mixture. Figure 1 shows the separation scheme of basic nitrogen compounds from the samples; basic nitrogen compounds were extracted from each sample with 0.1M HCl acid solution; the acid extract of each sample was extracted with n-heptane followed by benzene and the resulting acidic aqueous solution was reacted with concentrated NaOH in the presence of dichloromethane to raise the pH to 12-13. The liberated basic nitrogen compounds were extracted from the NaOH solution with dichloromethane. The light-yellow dichloromethane layer was evaporated to about 1-2 ml for GC-MS separation and identification of basic nitrogen compounds. Samples, solvents and reagent volume are tabulated in Table 1.

Basic nitrogen compounds were separated and identified by GC-MS (Thermo Finnigan Trace GC and Trace DSQ). 2-4 µl of each basic nitrogen compounds concentrate from each sample was injected into the GC fitted with a 30 m, 0.25 mm id, 0.25 ìm df capillary column (5% diphenyl-95% dimethyl polysiloxane), coupled directly to MS spectrometer detector; operating in the electron impact mode at 70 eV, mass detector gain 1.00 KV, ionization current 100 ìA, full scan 40-300 µ. GC operating temperature was as follows initial temperature was 85^0C for 1 min, 5^0C / min to 200^0C, for 20 min and 5^0C / min to 270^0C, for 5 min, injector temperature was 280^0C at constant temperature split mode, carrier gas was helium flow rate 1.0 ml/min; at constant flow, MS transfer line and the ion source temperature were 250^0C. The nitrogen compounds in each sample were identified by a computer matching method, comparing their spectra with those of the NIST Library of Mass Spectral Data.

Table 1. Volume of samples, HCL and solvents.

Sample	Volume litre	Solvents	0.1M HCl	CH_2Cl_2
Rasco crude blend	2.4	n-Heptane 600 ml	6 x 500 ml	700 ml
LGO	2.0	-	5 x 500 ml	700 ml
HGO	2.0	n-Heptane 500 ml	5 x 500 ml	700 ml
Residue	1.0	1:1 toluene/xylene 2 L	6 x 250 ml	700 ml

RESULTS AND DISCUSSION

Basic nitrogen compounds were extracted by HCl according to the following basis; basic nitrogen compounds are electrons pair donor (EPD) and acids are electrons pair acceptor (EPA)[2,4-7]; in basic nitrogen compounds, the nitrogen atom has a pair of electrons out of the ring that is available for sharing with an acid forming a water soluble salt, this can be simplified by writing the equation for the reaction between a basic nitrogen compound as dimethylquinoline in crude or distillates $(C_{11}H_{11}N^{:})_{org}$ and aqueous hydrochloric acid solution $(HCl)_{aq}$ forming the water soluble dimethylquinoline hydrochloride salt[1,27-29].

$$(C_{11}H_{11}N^{:})_{org} + HCl_{aq} \rightarrow (C_{11}H_{11}NH^{+}Cl)_{aq}$$

dimethylquinoline hydrochloride

Dimethylquinoline can be regenerated from its water soluble salt dimethylquinoline hydrochloride by adding up a concentrated aqueous NaOH solution in the presence of organic solvent as dichloromethane, the regenerated dimethylquinoline dissolve in the organic solvent and can be separated from the aqueous layer by extraction with the added organic solvent[1,15,28-29].

$$(C_{11}H_{11}NH^{+}Cl^{-})_{aq} + NaOH \rightarrow (C_{11}H_{11}N^{:})_{org} + NaCl$$

In the other hand the extracted non basic nitrogen compounds as trimethylindole ($C_{11}H_{12}NH$); in this type of nitrogen compounds, the nitrogen's extra out of the ring pair of electrons is not available to share with acids. By the same token these nitrogen compounds have a high electron density in the ring and can accept an acid only at the expense of the aromatic ring character that is by strong adsorption to an acid[7, 27, and 28].

Table 1 shows that a large volume of samples and reagent were used to perform the separation of basic nitrogen compounds from the samples in order to acquire a quite concentrated basic nitrogen compounds mixture suitable for a GC-MS analysis.

The physical and some of the chemical properties of Rasco crude oil blend, LGO, HGO and residue are tabulated in Table 2, from Table 2 it is clear that basic nitrogen content in LGO is very low whilst HGO contains the highest basic nitrogen content, the percentage of total basic nitrogen to the total nitrogen content is 23.5%. UOP-312 control plant test results gave that basic nitrogen content is zero in both Naphtha and Kerosene; it is clear that basic nitrogen content increases as the boiling point of the distillation cut increases.

GC-MS technique revealed that the extracted basic nitrogen compounds contain some non basic nitrogen compounds (the indole derivatives); GC-MS was able to separate and identify both basic nitrogen compounds and the accompanied non basic nitrogen compounds effectively, all the identified basic nitrogen and non basic nitrogen compounds are tabulated in Table 3.

All the identified basic nitrogen compounds in a raw Rasco crude oil blend sample and in LGO, HGO and residue produced from this crude oil blend did not show any structure alteration or rearrangement.

Total ion chromatograms of the separated basic nitrogen compounds from Rasco crude oil blend, LGO, HGO and residue are shown in Figures 2, 3, 4, and 5 the numbers associated with the peaks refer to the retention time of the compounds in the samples.

The mass spectra of the identified basic nitrogen compounds in the samples are shown in Figures 6-15 whilst mass spectra of non basic nitrogen compounds are shown in Figures 16-19.

Figures 6-9 are reproduced mass spectra of dimethyl, ethyl-methyl, trimethyl quinoline, and 1,2-dimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline; molecular ion peaks of these compounds appear at m/z 157, 171, 171 and 185 whilst the base peaks appear at m/z 157, 170, 171 and 185 respectively.

Figures 10 – 13 are reproduced mass spectra of substituted alkyl hydroacridine and acridine and these are 7-ethyl-1,2,3,4-tetrahydroacridine, ethylacridine, 1,2,3,4,7,8,9,10-Octahydro-12-methylbenzoacridine, and 1,2,3,4,8,9,10,11- Octahydro-7-methylbenzoacridine; molecular ion peaks of these compounds appear at m/z 207, 211, 251 and 251 whilst the base peaks appear at m/z 196, 206, 251 and 251 respectively.

Figure 14 are reproduced the mass spectrum of 2,3,4-trimethylbenzoquinoline; the molecular ion peak of this compound appears at m/z 221 and the base peak appears at m/z 220, and the only identified alkyl substituted benzoisoquinoline compound is

Table 2. Properties of Rasco crude oil blend, LGO, HGO and residue.

Property	Method	RCOB	LGO	HGO	Residue
Specific gravity @15.6 °C	ASTM D-1298	0.8340	0.8192	0.8480	0.9104
Density @15.6 °C	ASTM D-1298	0.8336	0.8188	0.8476	0.9099
API° gravity	ASTM D-1298	38	41	35	24
Initial boiling point (IBP) °C	ASTM D-86	-	207	279	-
Final boiling point (°C)	ASTM D-86	-	338	-	-
Flash point (°C)	ASTM D-93	-	89	-	124
Pour point (°C)	ASTM D-97	18	-9	27	41
Cloud point (°C)	ASTM D-2500	-	-3	-	-
Aniline point (°C)	ASTM D-611	-	81	94	-
Total Aromatic (wt %)		-	9.27	9.30	-
Cetane index	ASTM D-976	-	59	-	-
Total sulfur (wt %)	ASTM D-4294	0.1393	0.0414	0.1372	0.2532
Total nitrogen (wppm)	ASTM D-3228	200	-	-	-
Basic nitrogen (wppm)	UOP-269 and 313	47	13	88	-

RCOB = Rasco crude oil blend

Table 3. Basic and non basic nitrogen compounds identified in Rasco crude oil blend, LGO, HGO and residue.

m/z	Identified compounds	RT. Min	Fraction
157	2,7-dimethylquinoline	12.09	RCOB, LGO
171	ethyl-methylquinoline	13.57	RCOB, LGO
171	Trimethylquinoline	14.61	RCOB, LGO, HGO
159	Trimethylindole	16.44	RCOB, HGO
173	Tetramethylindole	17.07	RCOB, HGO, R
185	1,2-Dimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline	17.56	RCOB, LGO, HGO
187	Pentamethyl indole	18.52	RCOB, LGO, HGO
211	7-ethyl-1,2,3,4-tetrahydroacridine	21.45	RCOB, LGO
213	6-methyl-2-(2-thienyl)-1H-indole	24.83	RCOB, LGO
207	Ethylacridine	26.35	all
221	Trimethylbenzoisoquinoline	30.01	all
251	1,2,3,4,7,8,9,10-octahydro-12-methylbenzoacridine	31.49	RCOB, HGO
251	1,2,3,4,8,9,10,11-octahydro-7-methylbenzoacridine	34.17	RCOB, HGO
221	2,3,4-trimethylbenzoquinoline	34.83	RCOB, HGO

R = Residue

trimethylbenzoisoquinoline the mass spectrum of this compound is shown in Figure 15 the molecular ion peak of this compound appears at m/z 221 and the base peak appears at m/z 220.

Non basic nitrogen compounds are shown in Figures 16-19; these are tri, tetra and penta methylindole and 6-methyl-2-(2-thienyl)-1H-indole (a non basic nitrogen compound containing sulfur), the molecular ion peaks of these compounds appear at m/z 159, 173, 187 and 213 and the base peaks appear at m/z 158, 173, 186 and 213 respectively. The mass spectrum of 6-methyl-2-(2-thienyl)-1H-indole shows an M + 2 ion peak of about 4% of the abundance of the main molecular ion peak that is a typical of ^{32}S containing compound.

The base peaks of all the identified basic and non basic nitrogen compounds show a 100% relative abundance this is due to the high stability of the cation radical through the aromatic ring of the nitrogen compounds as well mass spectra of these compounds show a loss of the stable HCN neutral molecule; a typical fragmentation pattern of nitrogen compounds.

The identified basic nitrogen compounds in Rasco crude oil blend and in its LGO, HGO and residue are quinoline, isoquinoline and acridine derivatives whilst the non-basic nitrogen compounds come with the separated basic nitrogen compounds are only the indole derivatives.

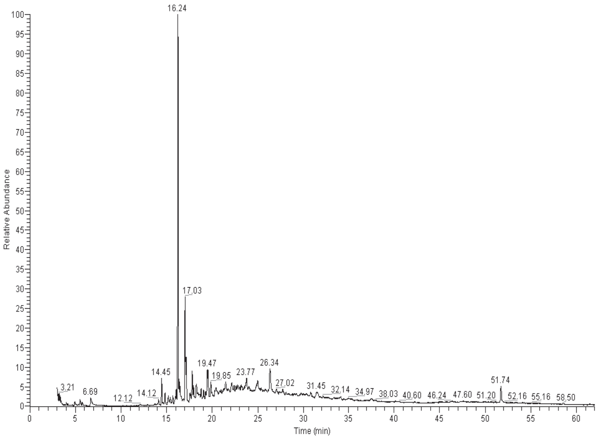

Fig. 2. Total ion chromatogram of nitrogen compounds in Rasco crude oil.

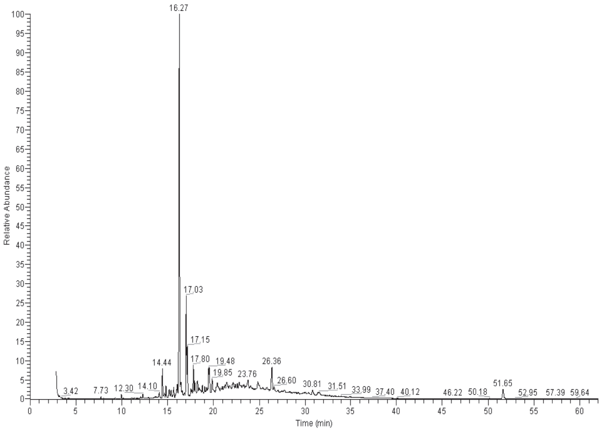

Fig. 3. Total ion chromatogram of nitrogen compounds in LGO.

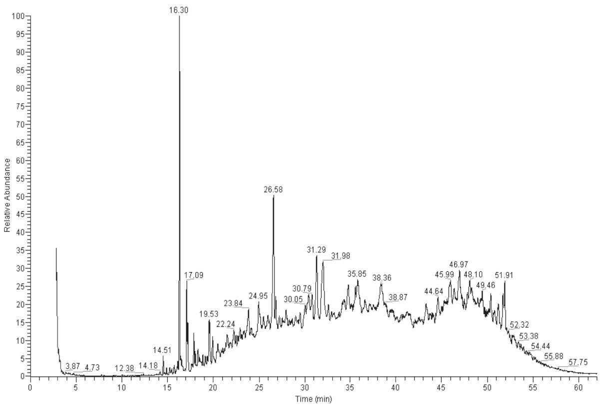

Fig. 4. Total ion chromatogram of nitrogen compounds in HGO.

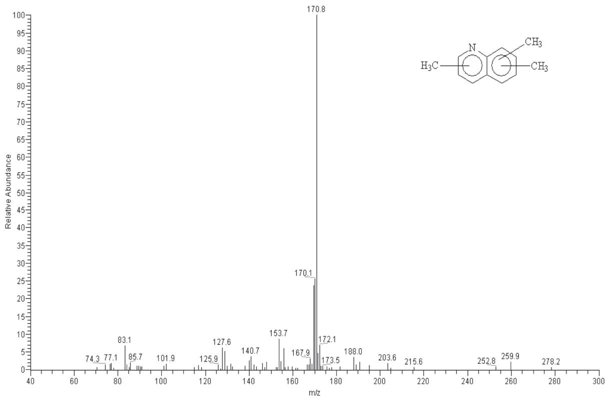

Fig. 8. Trimethylquinoline mass spectrum.

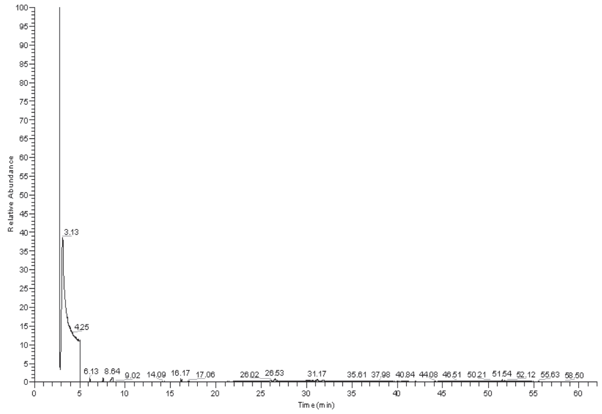

Fig. 5. Total ion chromatogram of nitrogen compounds in residue.

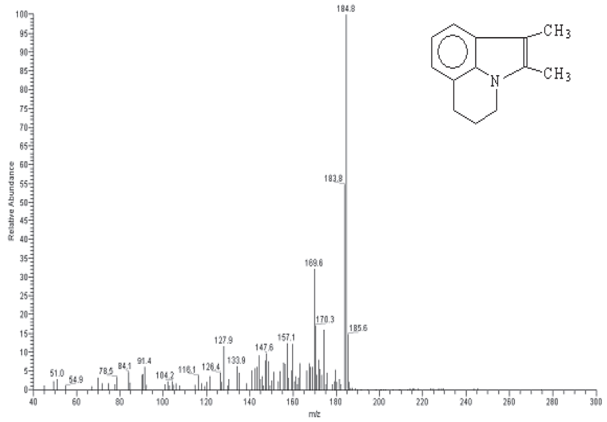

Fig. 9. 1,2-dimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline mass spectrum.

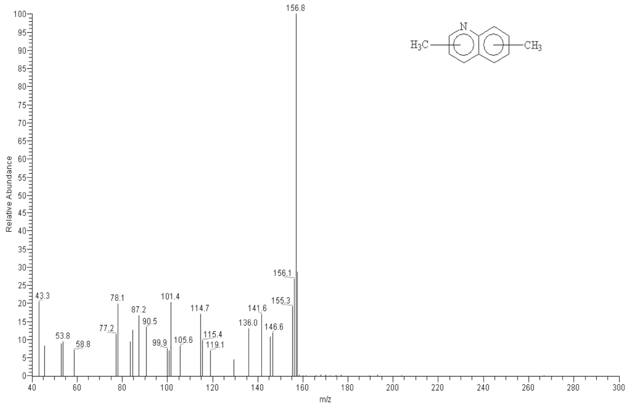

Fig. 6. Dimethylquinoline mass spectrum.

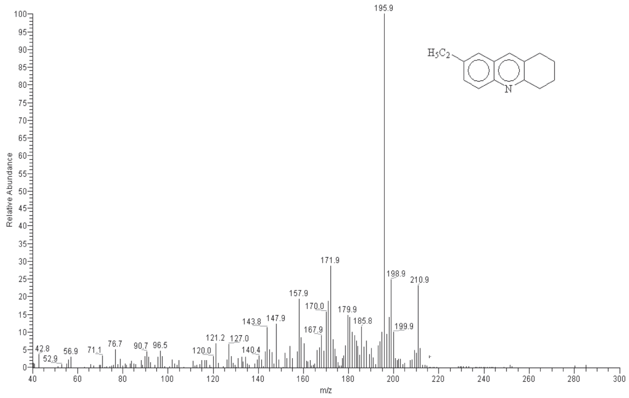

Fig. 10. 7- ethyl-1,2,3,4-tetrahydroacridine mass spectrum.

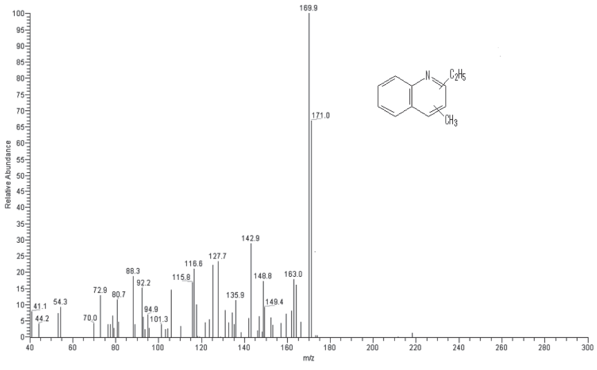

Fig. 7. Ethyl-methylquinoline mass spectrum.

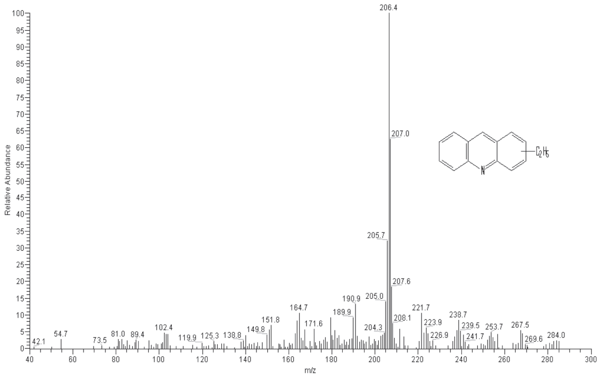

Fig. 11. Ethylacridine mass spectrum.

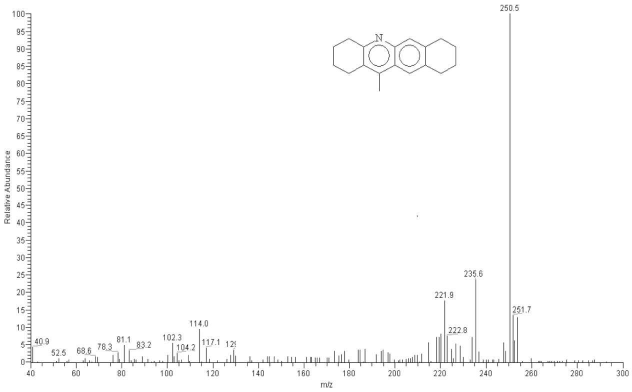

Fig. 12. 1,2,3,4,7,8,9,10-Octahydro-12-methylbenzoacridine mass spectrum.

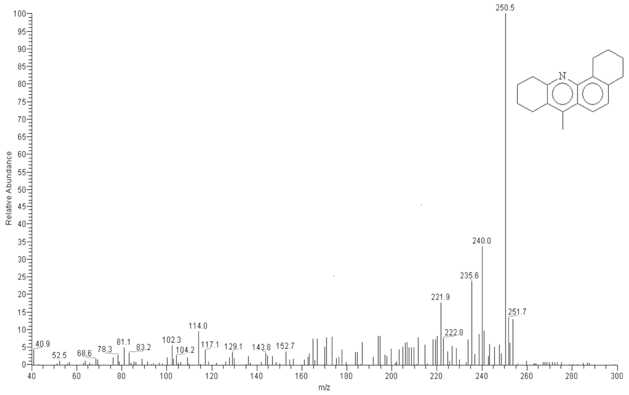

Fig. 13. 1,2,3,4,8,9,10,11-Octahydro-7-methylbenzoacridine mass spectrum.

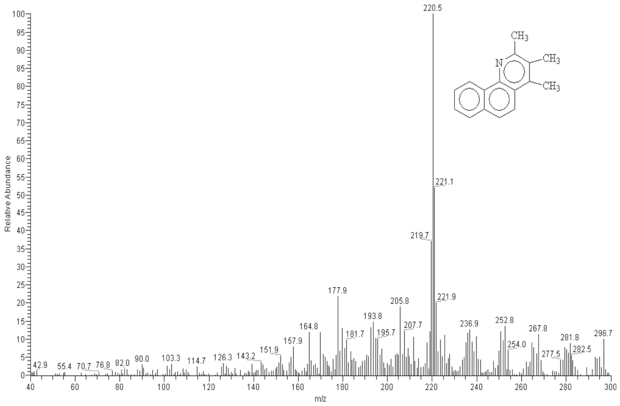

Fig. 14. 2,3,4-trimethylbenzoquinoline mass spectrum.

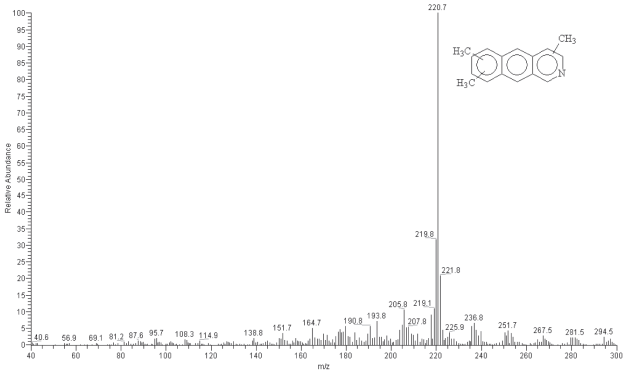

Fig. 15. Trimethylbenzoisoqionoline mass spectrum.

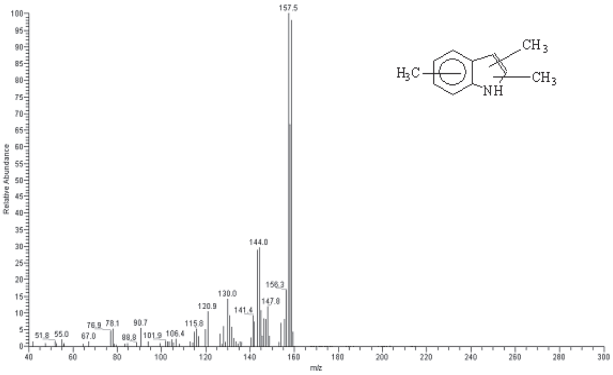

Fig. 16. Trimethylindole mass spectrum.

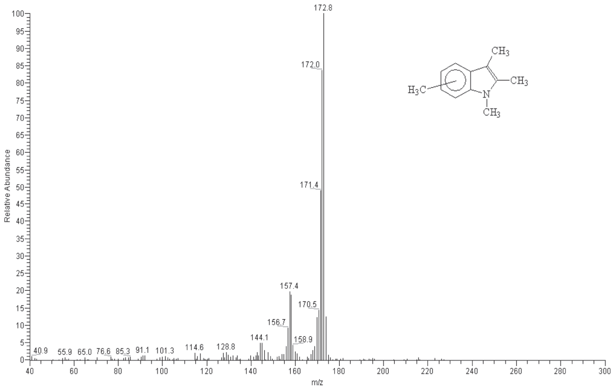

Fig. 17. Tetramethylindole mass spectrum.

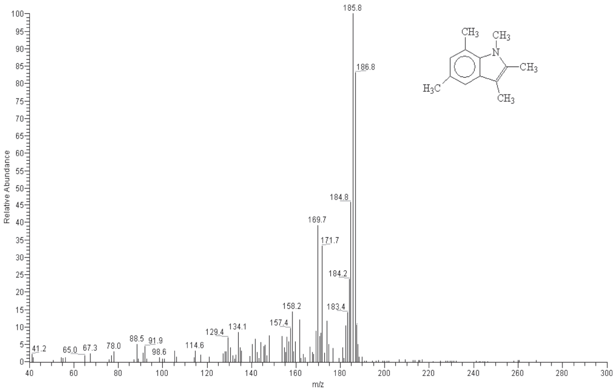

Fig. 18. Pentamethylindole mass spectrum.

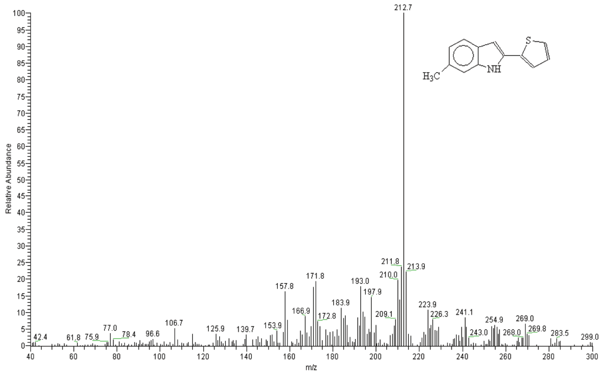

Fig. 19. 6-methyl-2-(2-thienyl)-1H-indole mass spectrum.

CONCLUSION

Basic nitrogen content was quantitatively determined in Rasco crude oil and in its naphtha, kerosene, LGO and HGO. Although the basic nitrogen compounds present in low concentration, these compounds were successfully extracted, concentrated, separated and identified in Rasco crudes oil in its LGO, HGO and residue accompanied with some basic nitrogen compounds.

The identified basic nitrogen compounds are quinoline, isoquinoline and acridine derivatives and the identified non basic nitrogen compounds are the indole derivatives.

The identified basic and non basic nitrogen compounds in Rasco crudes oil are thermally stable through the refining processes parameters of this crude oil.

The identified basic nitrogen compounds in residue are only trapped basic nitrogen compounds molecules.

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