

## Combining NMR and GC-MS to Characterize Olefin Rich Fractions of Automotive Gasolines

A. C. O. Silva, R. A. S. San Gil\*, C. R. Kaiser, D. A. Azevedo

Departamento de Química Orgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, CT, Bl. A Cidade Universitária, Ilha do Fundão, 21941-972, C.P. 068556 – RJ, Brazil (rsangil@iq.ufrj.br)

L. A. D'Avila

Departamento de Processos Orgânicos, Escola de Química, Universidade Federal do Rio de Janeiro – RJ, Brazil

**Keywords:**  $^1\text{H}$  NMR; FCC gasolines; conjugated dienes; column chromatography.

**Abstract:** Gasolines obtained during FCC process (Fluid Catalytic Cracking) have better antiknocking properties, but tend to form gum, which results from olefin polymerization of conjugated dienes. Considering the low concentration of these compounds in this kind of fuel, olefin rich fractions were obtained by eluting FCC gasoline samples through packed silica gel columns impregnated with silver nitrate. Unsaturated rich fractions were obtained, and selectivity towards olefin-type hydrocarbons was the following: internal olefins (linear or branched) were first eluted and then terminal and conjugated dienes. These fractions were analyzed by  $^1\text{H}$  NMR and GC-MS.

**Resumo:** Durante o processo FCC (Craqueamento Catalítico Fluido) são geradas gasolinas de maior octanagem, porém mais instáveis em relação à formação de goma – processo de polimerização de olefinas, iniciado pelos dienos conjugados. Considerando a baixa concentração destes compostos neste tipo de combustível, foram obtidas frações ricas em compostos insaturados, a partir do fracionamento de amostras de gasolina de FCC, por percolação através de colunas de sílica impregnada com sal de prata. Essas frações foram analisadas por RMN  $^1\text{H}$  e CG-EM. As colunas utilizadas permitiram obter frações ricas em compostos insaturados e apresentaram seletividade para os diferentes tipos de olefinas: eluíram primeiro as olefinas internas – ramificadas ou lineares, sendo preferencialmente retidas as do tipo terminal linear e os dienos conjugados.

### Introduction

Fluid Catalytic Cracking – FCC process – is an extremely important process for gasoline production. It converts heavy fractions obtained from atmospheric distillation of petroleum into lighter hydrocarbons in the gasoline range ( $\text{C}_5$  to  $\text{C}_{12}$ ). FCC gasoline obtained by this process is perfectly useful, since its appreciable content of aromatic-, branched paraffin- and olefin-type hydrocarbons is responsible for its high octane number – a value that expresses the antiknocking properties of a fuel.<sup>1</sup> However, this product shows a certain degree of instability and the tendency to

gum formation. Gum is the resultant residue of polymerization reactions of olefins in which conjugated dienes could act as precursor agents at the beginning of this polymerization process.<sup>2,3</sup>

Identifying basic aspects of FCC gasolines generated from Brazilian petroleums that lead to the formation of gum precursors is extremely important. It can help to devise new strategies towards the development of catalysts or any alternative process to reduce gum formation, even when processing worse quality fuels. Identification has been usually made at bench scale in pilot riser units, generating FCC gasoline and varying both

bulk and operational conditions, according to the gum content that is formed.<sup>4</sup> Since FCC gasoline volumes obtained by this process are incompatible with some routine methods of measuring gasoline instability is a limiting factor in the simulation step. In addition, such methods are time consuming and unprecise.

The most accurate method to measure gasoline instability against gum formation is known as Potential Gum ASTM D873. It consists in an accelerated aging process of a certain quantity of gasoline and lasts 240 minutes, showing appreciable deviations with gum content observed for samples naturally aged. Another commonly used method is the Diene Number UOP 326, based on the Diels Alder reaction between conjugated dienes present in the sample and maleic anhydride. The major flaw in this method is that about 100 mL of gasoline and up to 10 hours are required to obtain satisfactory results. Besides, it cannot be applied directly to commercial gasolines, because of the presence of anhydrous ethanol.

The chromatographic method known as PIANIO (Paraffins, Isoparaffins, Aromatics, Naphtenics, Isoolefinics and Olefinics) requires sample volumes of about 0.2 mL and over 3 hours of total analysis, and it allows characterization of several gasoline chemical compounds.<sup>5</sup> However, it is not an effective tool for the quantification of conjugated dienes that lead to gum formation, due to low concentration in the fuel. The determination of hydrocarbon types in naphthas and gasolines can also be performed by fluorescent indicator adsorption (FIA). An ASTM method

notwithstanding, a large amount of samples is necessary, and it fails to quantify the amount of different types of olefins.<sup>6-8</sup>

Chromatographic separation using silica gel with silver nitrate ( $\text{AgNO}_3$ ) is also used in the identification of unsaturated compounds. The retention mechanism is based on  $\text{Ag}^+$  ions capability, forming stable adducts with olefins and reducing elution time when compared with other kinds of compounds also present in samples. Some applications can be found in the separation of terpenoids from vegetable extracts using gas chromatography (GC)<sup>9,10</sup> and of methyl esters from vegetable oils, employing thin layer chromatography (TLC).<sup>11</sup> This method has been used in the petroleum and derivatives industry for separation of paraffin-type compounds, aiming at fuel characterization.<sup>12</sup>

NMR spectroscopy has been used for some time as a technique for determination of gasoline composition, and some authors report on short analysis time per sample. Nevertheless, no chemical pretreatment qualifies the technique as a powerful tool to identify and quantify different hydrocarbon types from the cracking process and straight run gasolines, including aromatics and oxygenates in commercial gasoline samples.<sup>13-23</sup> The usual approach consists of subdividing NMR spectra into regions, where each region is associated with a specific hydrocarbon structure. Further, more accurate subdivisions are possible.<sup>13,15,16,18,19,21</sup> However, it is known that most regions are not structurally pure<sup>14,20,21</sup>, since demarcations are not precise and cutoff points might change, depending on the nature of the sample.

A method based on the combination of Diels-Alder derivatization of dienes and  $^{13}\text{C}$  NMR analysis of the resulting adducts was developed, using a high field magnet.<sup>22</sup> That made it possible for us to identify a number of  $\text{C}_5$  and  $\text{C}_6$  dienes as well as to make a qualitative assessment of the relative amounts of cyclic and acyclic diolefins. Also, in high resolution conditions, two-dimensional (2D)  $^1\text{H}$  NMR experiments were performed, providing clear identification of some conjugated diolefin isomers.<sup>23</sup> Quantification was performed by 1D  $^1\text{H}$  NMR and the applicability of the methodology was noted/observed/possible for samples in which concentration of conjugated dienes was not so low. On the other hand, 1D  $^1\text{H}$  NMR homodecoupling experiments were more appropriate for these dienes identification.

In a previous work in our laboratory, we observed the efficient application of 2D NMR to the analysis of synthetic mixtures, though it was limited when used for Brazilian gasolines and their fractions.<sup>24</sup> Thus, the aim of the present work is the development of an analytical methodology to characterize olefins in FCC gasolines without derivatization, as performed by Alemany and Brown.<sup>22</sup> Here, columns with modified stationary phases were used, and the eluted fractions were analyzed by  $^1\text{H}$  NMR. Results were compared with those obtained by gas chromatography – mass spectrometry (GC-MS).

## Experimental

### *FCC gasoline samples*

FCC gasoline samples were used as received, obtained from Reduc and Manguinhos refineries, both located in Rio de Janeiro; some naphtha samples were provided by Departamento de Química Inorgânica, Instituto de Química, UFRJ (proceeding from Cenpes - Petrobras, Rio de Janeiro). Table 1 shows specifications from the gasoline samples studied, as well as commercial standard dienes employed to optimize elution experiments and analysis.

The stationary phases and columns were prepared as follows: silica gel (previously washed with ethyl acetate) was mixed with an  $\text{AgNO}_3$  solution, at a 5:1 ratio  $\text{SiO}_2:\text{AgNO}_3$ . The suspensions obtained were heated at  $120^\circ\text{C}$  for one hour. The resulting material consisted of the modified stationary phase (MSP).  $\text{AgNO}_3$  was stored in aluminum-covered flasks in the dark chamber. Samples (standard dienes and FCC gasolines) were eluted through the columns under two different conditions: in conventional adsorption chromatography, a suspension was obtained mixing MSP with hexane. After the material was packed, the samples were eluted using polarity gradual increasing of the solvents; a method called dried column was used, by which the samples were injected into the columns containing dried MSP, using first hexane and then ethyl acetate for elution, with no polarity gradual increasing.

### *NMR and GC-MS experiments*

$^1\text{H}$  NMR analyses were carried out on a Bruker DRX 300 and DPX 200 spectrometers. Spectra were obtained by using 5 mm tubes,  $\text{CDCl}_3$  (solvent and lock

signal), TMS (reference), at room temperature (20°C). Samples were diluted in TMS/CDCl<sub>3</sub> (0.5% v/v), obtaining solutions of 30% v/v final concentration.

Acquisition conditions: pulse duration: 9.2 μs (90°), with 5 dB attenuation; acquisition time: 2.8 s; interval between pulses: 1.5 s; number of scans: 16.

**Table 1.** Gasoline samples specifications and commercial standard dienes employed to optimize elution experiments and analysis.

Name	Origin	Olefins amount (%)
Gasoline FCC_M/ 2002	Manguinhos Refinery	7.2 (m/m)
Gasoline FCC_R/ 2002	REDUC	17.9 (v/v)
Gasoline FCC_M/ 2003	Manguinhos Refinery	10.6 (v/v)
Gasoline FCC_R/ 2003	REDUC	26.1 (v/v)
Naphtha A5/ 2003	CENPES	Not given
Naphtha A4/ 2003	CENPES	Not given
Naphtha A7/ 2003	CENPES	Not given
Naphtha 012/ 2003	CENPES	Not given
Gasoline FCC_M/ 2003-2	Manguinhos Refinery	20.8 (v/v)
1,3-cycloheptadiene	Aldrich	> 95
2,5-dimethyl-2,4-hexadiene	Aldrich	> 95
Dicyclopentadiene	Aldrich	> 95
<i>E</i> -2-methyl-1,3-pentadiene	Merck	> 95

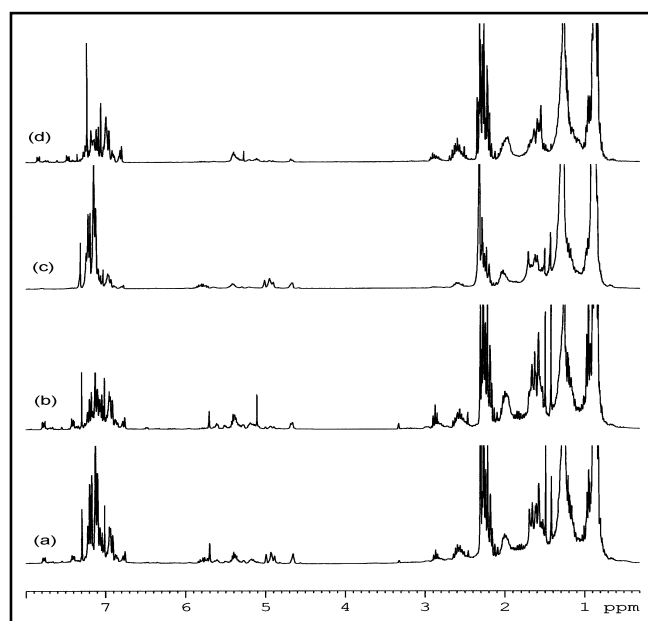
GC analyses were carried out on an HP 5890 chromatograph coupled to an HP 5972 mass spectrometer. A capillary column coated with DB-5 (30 m x 0.25 mm id, 0.25 μm thickness; J & W Scientific, Folsom, CA, USA) was used, and He was the carrier gas. The GC oven was heated using the following temperature program: 30°C to 220°C at 4°C min<sup>-1</sup> with an initial isothermal period of 15 min. Injections were as follows: 2 μL, split 1:20 (gasoline

fractions) or 1 μL, split 1:50 (raw gasolines). Detector and injector temperatures were held at 270°C. MS results were obtained in both SCAN and SIM (selective ion monitoring) modes.<sup>25</sup> Mass spectral analyses were performed using comparison of fragmentation patterns from Wiley 275 library spectra.

## Results and Discussion

$^1\text{H}$  NMR spectra of gasoline samples are shown in Figure 1, in which similarity in terms of the distribution of parafinic (between 0 and 3 ppm) and aromatic (region 6.7 to 7.6 ppm) compounds can be observed. The octane number (expressed as RON, 'Research Octane Number') was

determined for the samples studied, according to Mühl et al.<sup>26-28</sup>, based on chemical shift ranges indicated in Table 2. The results are listed in Table 3. As can be seen, all the samples have high octane number, and the highest value observed is 100.



**Figure 1.**  $^1\text{H}$  NMR spectra of gasoline samples. (a) FCC\_M/2003-2; (b) A5/2003; (c) FCC\_M/2002; (d) A7/2003.

**Table 2.** Chemical shift  $^1\text{H}$  range for determination of RON by NMR.<sup>26-28</sup>

Type of hydrogen	Chemical shift range ( $\delta$ , ppm)
(A) aromatic ring	8.0 - 6.6
(B) insaturation	6.0 - 4.5
(C) $\text{CH}_3$ linked to aromatic ring	3.0 - 2.0
(D) CH aliphatic	2.0 - 1.5
(E) $\text{CH}_2$ aliphatic	1.5 - 1.0
(F) $\text{CH}_3$ aliphatic	1.0 - 0.6

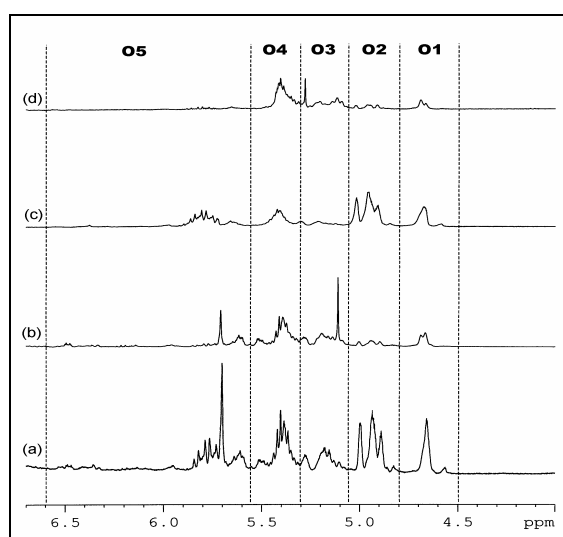
$$\begin{aligned}
 S &= A + B + C + D + E + F \\
 \%H_{\text{ar}} &= 100 (A/ S) \\
 \%H_{\text{olef}} &= 100(B/ S) \\
 \text{RON (NMR)} &= 83.14 + 0.48 (\%H_{\text{ar}}) + 1.02 (\%H_{\text{olef}})
 \end{aligned}$$

**Table 3.** Research octane number (RON) obtained for the samples studied.

Gasoline sample	% H <sub>ar</sub>	% H <sub>olef</sub>	RON
FCC_M/ 2002	12.61	2.81	92.06
FCC_R/ 2002	8.90	2.76	90.23
FCC_R/ 2003	5.37	2.63	88.40
A4/ 2003	21.45	1.93	95.40
A5/ 2003	10.26	3.78	91.92
A7/ 2003	10.86	2.04	90.43
O12/ 2003	12.75	3.48	92.82
FCC_M/ 2003-2	12.96	3.52	92.95

The chemical shift range between 4.50 and 6.60 ppm, characteristic of olefinic hydrogens, was divided into 5 sub regions (Figure 2): O1 (4.50 – 4.80 ppm) due to CH<sub>2</sub>- from branched terminal olefins; O2 (4.80 – 5.05 ppm) due to CH<sub>2</sub>- from linear terminal olefins; O3 (5.05 – 5.30 ppm) due to CH- from branched internal olefins; O4 (5.30 – 5.55 ppm) due to CH- from *Z/E*

olefins and O5 (5.55 – 6.60 ppm) due to CH- from conjugated double bonds, together with CH- from linear terminal olefins. These sub regions were previously defined in the literature.<sup>16</sup> Table 4 lists the relative distributions of the different types of olefinic hydrogens present in the samples studied.



**Figure 2.** <sup>1</sup>H NMR spectra (expanded olefinic region) of gasoline samples. (a) FCC\_M/2003-2; (b) A5/2003; (c) FCC\_M/2002; (d) A7/2003.

**Table 4.** Relative distribution (%) of olefinic hydrogens present in the gasoline samples.

gasoline	Olefinic regions ( $\delta$ , ppm)				
	O5 6.60 – 5.55	O4 5.55 – 5.30	O3 5.30 – 5.05	O2 5.05 – 4.80	O1 4.80 – 4.50
FCC_M/ 2002	26.79	17.87	8.74	34.28	12.32
FCC_R/ 2002	15.45	35.77	22.08	12.08	14.62
FCC_R/ 2003	10.63	36.11	23.68	13.21	16.37
A4/ 2003	20.15	32.32	32.70	7.60	7.22
A5/ 2003	23.98	33.18	27.18	7.44	8.22
A7/ 2003	7.28	46.30	30.65	8.21	7.55
012/ 2003	15.24	32.24	27.92	9.83	14.78
FCC_M/ 2003-2	39.84	20.00	12.40	18.76	9.00

It should be noted that Sarpal et al.<sup>16</sup> considered only open chain linear internal conjugated dienes, which is not in agreement with the present study: several diene standards, conjugated or not, were used. As a consequence, for those that did not show this structural pattern, olefinic hydrogens signals were found in other sub regions, different from expected. For example, the chemical shifts of hydrogens from non conjugated and terminal branched conjugated dienes were found in sub regions of mono olefins. On the other hand, open chain internal conjugated dienes (branched or not) and non branched cyclic dienes (conjugated or not) showed signals in sub region O5, between 5.55 and 6.15 ppm.<sup>25</sup> Signals due to diene hydrogens were detected by NMR, but some structural patterns were not predicted in the literature<sup>16</sup>, resulting in different chemical shift sub regions. This fact also interferes with quantification of different kinds of olefins in FCC gasolines by NMR. If diene standards that showed chemical shift deviation for olefinic hydrogens were present in these samples, it would cause a misinterpretation of the <sup>1</sup>H NMR spectrum; some regions would be underestimated,

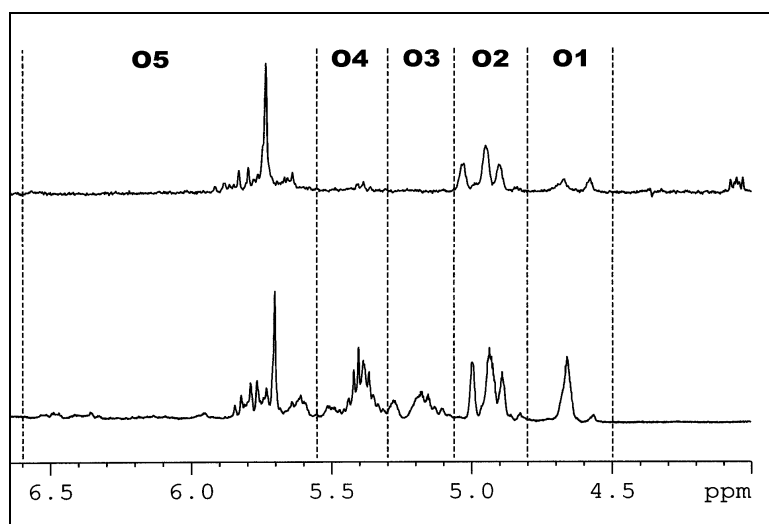
whereas others would be overestimated, generating a false molar composition of that kind of structure.

Experiments on the fractionation of FCC gasoline samples were aimed at the retention of olefinic compounds, obtaining paraffin- and aromatic-free samples. The determination of olefin structures present would be more efficient in principle, without overlapping from signals due to other kinds of hydrocarbons, mostly in the paraffinic region of the spectrum. Polar solvents used were chosen *would reduce detection bias and provide clear identification of olefinic hydrogen signals in NMR spectra.*

In the experiments where 1 mL of sample was injected into the column, total elution of O3 olefin type hydrogens with apolar solvent was observed. Small fractions of O1, O2, O4 and O5 hydrogens were also detected in the spectra from hexane extraction. For experiments in which 0.5 mL of sample was injected into the column, a different behavior was observed: the five olefin types were eluted with an apolar solvent, at a small ratio, and with a polar solvent at a great ratio. In these experiments, most of the O3 type compounds were eluted with the first solvent, being detected in trace quantities in

the fractions obtained after AcOEt. The results observed in this series of experiments suggest that when a large amount of sample was injected into the column, unsaturated compounds that showed previously larger affinity with the columns were preferentially retained: O2 and O5. When decreasing that amount, it was possible to retain all olefin types simultaneously, except O3, whose weak interaction has already been observed. Also, the intensity of the signal assigned to  $-\text{O}-\text{CH}_2-\text{CH}_3$  from AcOEt ( $\sim 4.12$  ppm) increased, when the spectra of the fractions were obtained with that solvent, situated in

the O1 region, due to  $^1J_{\text{C-13/H-1}}$ . The other solvent signals in the paraffin region of the spectra overlapped with the signals from hydrogens present in the sample, as well as those from hexane. The ideal amount of sample to be injected into the columns was then considered to be 0.25 mL/g  $\text{SiO}_2$ . Figure 3 shows that this choice was appropriate, considering the analyses of sample FCC\_M/ 2003-2 before and after elution. It can be noticed that a terminal linear olefin fraction was obtained.

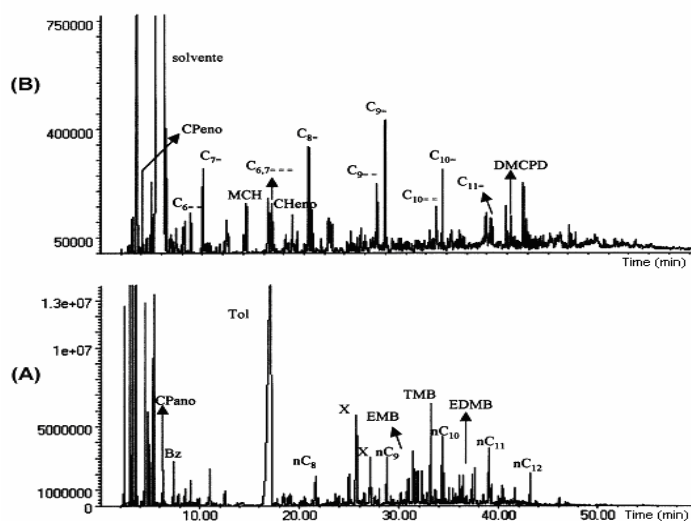


**Figure 3.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) of sample FCC\_M/ 2003-2: Bottom, raw gasoline; Top, terminal linear olefin fraction.

Some fractions were analyzed by GC-MS, in order to identify diene compounds (Figure 4). By fractioning one of the samples (gasoline A5/2003) it was found that a great fraction of olefins containing O3 and O4 type hydrogens was eluted with the

apolar solvent – hexane. Mass spectra analysis of one of these fractions indicated the presence of 2,4-dimethyl-1,3-pentadiene, which shows hydrogen signals in O1, O2 and O5 regions from the  $^1\text{H}$  NMR spectrum.





**Figure 4.** Total ion chromatograms: (A) – FCC\_M/ 2002 gasoline sample; (B) – olefin-rich fraction. (A): CPano = cyclopentane, Bz = benzene, Tol = toluene, X = xilenes, EMB = ethyl-methylbenzene, TMB = trimethylbenzene, EDMB = ethyl-dimethylbenzene. (B): solvente = AcOEt, CPeno = cyclopentene, MCH = methyl-cyclohexane, CHeno = cyclohexene.

Most olefinic content of the sample was eluted with a polar solvent (AcOEt), including all olefin sub-types. In these fractions, some standard dienes were detected: 2-methyl-1,3-pentadiene (O2 and O5), 2,4-dimethyl-1,3-pentadiene (O1, O2 and O5), 2,5-dimethyl-2,4-hexadiene (O5) and 2,4-hexadiene (O5). They were also observed by  $^1\text{H}$  NMR analysis. The fractionation of sample A4/2003 was similar, where compounds 2,4-dimethyl-1,3-pentadiene and 2,5-dimethyl-2,4-hexadiene were observed by both  $^1\text{H}$  NMR and GC-MS techniques. During division of FCC\_M/2003-2 sample, it seemed that selectivity was higher when considering retention of compounds containing O2 and O5 hydrogens (besides O1). Moreover, the presence of 1,7-octadiene (O2 and O5) and

2,4-dimethyl-1,3-pentadiene along the elution was detected.

Almost all the olefinic content of the samples was eluted with the apolar solvent - cyclohexane. Dienes such as 2,4-hexadiene, 2,4-dimethyl-1,3-pentadiene and 1,7-octadiene were also observed.  $^1\text{H}$  NMR spectra allowed the visualization of several kinds of olefinic hydrogens in the samples, whereas in GC-MS fragments characteristic of dienes were obtained. Thus, the information extracted from NMR spectra, in which some standard dienes presented chemical shift deviations for the olefinic hydrogens is not thoroughly consistent with GC-MS data, since various olefin-type standards, dienes or not, should have been analyzed by both techniques, which did not occur. Indeed, the correlation between NMR and GC-MS data can allow us to infer the presence or absence of

dienes in the samples analyzed, but nothing can be said about other types of unsaturated compounds present in these samples.

### Conclusions

Column selectivity, both in conventional and dry column adsorption chromatography, lead to faster elution of internal olefins (linear or branched, sub regions O3 and O4 respectively) and preferential retention of those showing O2- and O5-type hydrogens. Using SiO<sub>2</sub>/AgNO<sub>3</sub> columns as MSP was a good alternative for resolution of olefins present at low concentration in FCC gasoline samples. The columns used were able to retain selectively such compounds, generating fractions in which aromatic and paraffin content was strongly decreased or eliminated.

The combination of <sup>1</sup>H NMR and GC-MS techniques has shown to be a faster method for evaluation of olefins in gasolines. Reproducibility tests to validate these analyses is underway. As only standard dienes were analyzed by GC-MS, only this kind of olefins could be analyzed by both techniques. As for the other olefins present in the samples, correlation between NMR and GC-MS results was not feasible.

### Acknowledgements

The authors would like to thank Prof. Eliane D'Elia for naphtha samples, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Conselho Nacional de Desenvolvimento

Científico (CNPq, process 460230/01-8 NV) for financial support.

### References

1. A.A. Lappas, D.K. Latridis, I.A. Vasalos, *Catal. Today* **50** (1999) 73.
2. J.M. Nagpal, G.C. Joshi, I.D. Singh, K. Kumar, *Oxidation Commun.* **21** (1998) 468.
3. G. Puente, U. Sedran, *Energy Fuels* **18** (2004) 460.
4. W. G. Gilbert, *Stud. Surf. Sci. Catal.* **149** (2004) 247.
5. L. A. Silva, V. M. M. Costa, *Ciencia-Tecnica-Petroleo* **1** (1997) 43.
6. B.N. Barman, *Fuel* **74** (1995) 401.
7. B.J. Feuerhelm, H. Thomas, J.C. Froehling, J. Watt, G. Schaatsbergen, *J. Chromat. Sci.* **41** (2003) 564.
8. N. Kosal, A. Bhairi, M. A. Ali, *Fuel* **69** (1990) 1012.
9. R.A. Bernhard, *Anal. Chem.* **34** (1962) 1576.
10. M.H. Klouwen, R.J.I. Heide, *J. Chromatography A* **7** (1962) 297.
11. H.C. Collins, G.L. Braga, P.S. Bonato, *Introdução a Métodos Cromatográficos*, 4<sup>th</sup> ed.; UNICAMP: Campinas, 1990.
12. F. M Lanças, *Cromatografia em Fase Gasosa*, 1<sup>st</sup> ed.; Acta: São Carlos, 1993.
13. R. Meusinger, *Fuel* **75** (1996) 1235.
14. D.J. Cookson, B.E. Smith, *Energy Fuels* **1** (1987) 111.
15. G.S. Kapur, A.P. Singh, A.S. Sarpal, *Fuel* **79** (2000) 1023.
16. A.S. Sarpal, G.S. Kapur, S. Mukherjee, A.K. Tiwari, *Fuel* **80** (2001) 521.
17. R. Meusinger, *Anal. Chim. Acta* **391** (1999) 277.

18. D. J. Cookson, B. E. Smith, *Fuel* **68** (1989) 776.
19. A.P. Singh, S. Mukherjee, A.K. Tiwari, W.R. Kalsi, A.S. Sarpal, *Fuel* **82** (2003) 23.
20. G. S. Kapur, S. Berger, *Fuel* **81** (2002) 883.
21. J. Burri, R. Crockett, R. Hany, D. Rentsch, *Fuel* **83** (2004) 187.
22. L.B. Alemany, S. H. Brown, *Energy Fuels* **9** (1995) 257.
23. M.I. Altbach, C.P. Fitzpatrick, *Fuel* **73** (1994) 223.
24. A.C.O. Silva, C.R. Kaiser, D.A. Azevedo, L.A. D'Avila, R.A.S. San Gil, *Abstracts of the IX Encontro de Usuários de RMN*, Angra dos Reis, Brazil, 2003.
25. A.C.O. Silva, *MSc. Thesis*, Universidade Federal do Rio de Janeiro, Brazil, 2004.
26. J. Mühl, V. Srića, *Fuel* **66** (1987) 1146.
27. J. Mühl, V. Srića, M. Jednačak, *Fuel* **72** (1993) 987.
28. J. Mühl, V. Srića, M. Jednačak, *Fuel* **68** (1989) 201.