STUDY OF THE NAPHTHENIC ACIDS RECOVERY FROM PETROLEUM USING AN IONIC MATERIAL AS STATIONARY PHASE IN THE SOLID PHASE EXTRACTION (SPE) PROCESS

J. F. De Conto[1]; M. R. Oliveira[1]; A. S. Carvalho[1]; L. S. Freitas[2], E. V. Benvenutti[3], E. Menezes[3], C.C. Santana[1] and S.M. Egues[1].

1-Intituto de Tecnologia e Pesquisa – ITP – Laboratório de Síntese de Materiais e Cromatografia – LSINCROM – Universidade Tiradentes – UNIT. Av Murilo Dantas, 300 – CEP: 49032-490 – Aracaju-SE – Brasil. Telefone: (79) 3218-2190 – Email: jfconto@gmail.com
2-Departamento de Química – Universidade Federal de Sergipe – UFS. Cidade Universitária Prof. José Aloísio de Campos – CEP 49100-000 – São Cristóvão – SE – Brasil.Telefone: (79) 2105-6654 – Email: lisiane_santos_freitas@yahoo.com.br
3-Instituto de Química – Universidade Federal do Rio Grande do Sul – UFRGS. Av Bento Gonçalves, 9500 – CEP 91501-970 – Porto Alegre – RS – Brasil. Telefone: (51) 3316 – 7176 – Email: benvenutti@iq.ufrgs.br

ABSTRACT: Naphthenic acids cause corrosion in the equipment used in the petroleum processing. Considering difficulties in the identification of these compounds present in the petroleum sample is necessary to study new methodologies to identify the acid compounds. Solid phase extraction (SPE) with ionic phases has been widely used for this purpose, because it promotes greater selectivity, lower consumption of solvents and small amount of the stationary phase. The proposed study is the acid compounds recovery using SPE method. A new stationary phase was synthesised and called pyridiniunpropylsilica (*SiPy*). Linear and monocycles acids were used as model system in the SPE for calculation of recovery. Further tests were performed with Brazilian petroleum. The stationary phase synthesised showed satisfactory results for the recovery and identification of the acidic compounds presented in the model system as well in the resin fraction from petroleum.

KEYWORDS: Solid phase extraction, naphthenic acids, petroleum.

1. INTRODUCTION

The petroleum is constituted basically by an organic chemical compounds mixture with hydrogen and carbon and other minorities compounds as nitrogen, sulfur, oxygen and some metals. The percentage in weight of each chemical element present in the petroleum is 11-14 % of hydrogen, 83-87 % of carbon, 0.06-8 % of sulfur, 0.11-1.7% of nitrogen, 0.1-2% of oxygen and up to 0.3% of metals (Thomas *et al.*, 2004).

The small amount of oxygenated compounds found in the petroleum is a problem in the refine process, main the carboxylic acids knew in the industry as naphthenic acids. These compounds are corrosion agents in petroleum refining equipment (Wu *et al.,* 2004). The naphthenic corrosion occurs in the refine equipment where the temperature is between 220 and 400 ºC. In temperatures higher than 400 ºC the naphthenic acids break and form a protective pellicle in the refinery equipment (Clemente e Fedorak, 2005).

Therefore the naphthenic corrosion depends on the presence and nature of a determined acid group (Campos, 2005) and size and structure of the naphthenic acid (Campos *et al.,* 2009). Due to the corrosion in the refinery equipment be caused by specific naphthenic acids, whose are present in low concentration in the crude oil some analytic techniques to determination of these acids have been studied (Purcell *et al*., 2007; Nielsen *et al*., 2008).

The solid phase extraction (SPE) is a technique that has been used to concentrate and separate naphthenic acids from petroleum. One
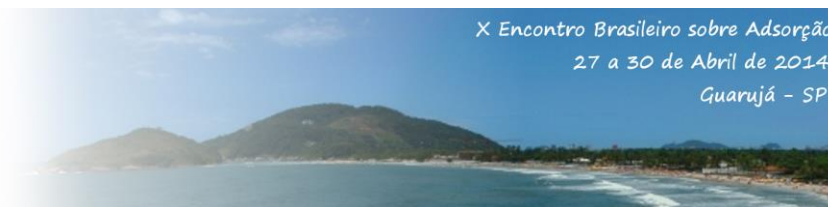
can verify that the SPE methodology using the ionic exchangers has been studied by several researchers. Some commercial anionic exchange or ionic exchange resins are applied as stationary phase in the SPE process to this finality.

Jones *et al*., (2001) used a quaternary amine (SAX) to isolate the aliphatic and naphthenic acids from the crude oil samples. According to the authors this methodology is effective to separation of acid compounds from light and heavy oils. Campos *et al.,*. (2006) performed the isolation of acids fraction through of the SPE technique with an ionic exchange resin (Amberlyst 27). Using this stationary phase was possible to obtain a pure acid fraction, allowing the analysis and identification of the acids compounds present in the petroleum.

The liquid-liquid extraction (LLE) and SPE using Amberlyst 25 were applied by Borgund *et al.* (2007) to extract acids compounds from petroleum. According to the authors when the SPE technique was applied the amount of acids extracted was three times greater than those obtained by LLE.

Moraes and collaborators (2009) obtained a fraction rich in acid compounds from Brazilian petroleum using the SAX as stationary phase in the SPE process. The capacity of extraction of the stationary phase and SPE technique were confirmed by the authors after the naphthenic acids identification by gas chromatography analysis. De Conto *et al*. (2012) proposed the synthesis of a new stationary phase (Dab-Al$_3$O$_2$) to use in the acid compound removal from Brazilian petroleum through SPE methodology. The authors tested the Dab-Al$_3$O$_2$ using, firstly, a model system composed by standards acid compounds and after with a petroleum fraction. The efficiency of the Dab-Al$_3$O$_2$ in the acid compounds removal was compared with the two commercial anionic exchanges (SAX and NH$_2$). According to the authors, the Dab-Al$_3$O$_2$ shows the greater extraction of acid compounds from petroleum matrix than the two commercial stationary phases.

So, the proposal of this work is synthetize a new stationary phase combining silica and ionic group, i.e., silica modified with ionic group to optimize and improve the acid naphthenic removal from petroleum matrix using the SPE technique.

2. METHODOLOGY

2.1. Synthesis of the pyridinium-propylsilica ionic material

The synthesis procedure of the ionic material was adapted of Menezes *et al.*, 2012. The ionic adsorbent synthesis was prepared by the sol-gel synthesis method. The tetraethylorthosilicate (TEOS) and 3-chloropropyltrimethoxysilane (CPTMS) were used as precursor reagents, both from Aldrich. It was used 90% (molar) of TEOS and 10% (molar) of CPTMS. The HF (Merck) was used as catalyst. Firstly, the TEOS was pre-hydrolyzed by adding 80 mL of ethanol and 8.0 mL of distilled water with constant stirring for 2 h at room temperature. Subsequently, it was added CPTMS, 8.0 mL HF solution (1 mol L^{-1}). The mixture was stirred for 40 min at room temperature, followed by temperature increasing to 40 °C for gelation. Afterward, the material was dried in over at 110 °C. The second step was performed the grafting reaction of pyridine: 6.5 g of the material obtained in the first step was immersed in 70 ml of pyridine in toluene solution (2.5 mol L^{-1}) and heated at reflux temperature for 24 h. The solid was separated, washed with toluene, ethanol, ethyl ether, and heated at 50 °C under vacuum.

2.2 Characterization of pyridinium propylsilica (SiPy)

The N$_2$ adsorption isotherm was determined at the boiling point of liquid nitrogen, using Micromeritics 3020 Krypton equipment. The adsorbent materials were previously degassed at 130 °C under vacuum for 4 h. The specific surface was determined by the BET (Brunauer, Emmett, and Teller) multipoint technique (Brunauer *et al.,* 1938) and the pore size distribution curve was estimated using the obtained using BJH (Barret, Joyner, and Halenda) method (Barret *et al*., 1951).

The ionic material was submitted to transmission FTIR analysis using an IR cell that allows obtaining spectra of sample after heat treatment in vacuum, without air exposition. The IR cell was described elsewhere in detail (Pavan *et al*., 2002). Self-supporting disk of the material, with a diameter of 2.5 cm, weighing ca. 100 mg was prepared. The disk was heated at 200 °C, under vacuum (10^{-2} Torr) for 1 h. The spectrum of the sample was obtained at room temperature, using a Varian 640 FT-IR Spectrometer, with a resolution of 4 cm^{-1} and 150 cumulative scans.
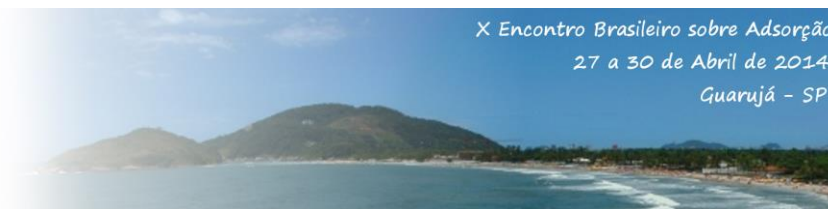
The carbon elemental analysis on *SiPy* sample, previously treated at 180 ^{o}C for 1 h, was carried out in a Perkin-Elmer analyzer, model 2400. The analysis was made in duplicate. To determine the amount of exchangeable chloride ions in ionic material, 100.0 mg of the solid was immersed in 30 mL of 0.1 mol L^{-1} HNO$_3$ solution and the displaced chloride ions in the solution phase were titrated with standard 0.0250 mol L^{-1} AgNO$_3$ solution, using the potentiometric method. The amount of exchangeable chloride ions found is equivalent to the amount of pyridinium groups available in the ionic material sample. The determination was carried out in duplicate.

2.3 System model and petroleum sample preparation

The removal of acids was performed through of the SPE process according to De Conto *et al.*, 2012. The stationary phase used was *SiPy*. The seven acids standards from Aldrich were used. Where four acyclic acid (Z = 0) with chain of C$_{12}$, C$_{14}$, C$_{20}$, C$_{22}$ and three cyclic acid (Z = −2) with C$_6$, C$_7$, C$_8$ (Figure 1) A mixture of acids was prepared at concentrations of 10 mg L^{-1} for acyclic acids and cyclic ones. The solution containing the mixture of acids was placed on top of the SPE cartridge and aspirated in a low vacuum and was performed in triplicate.
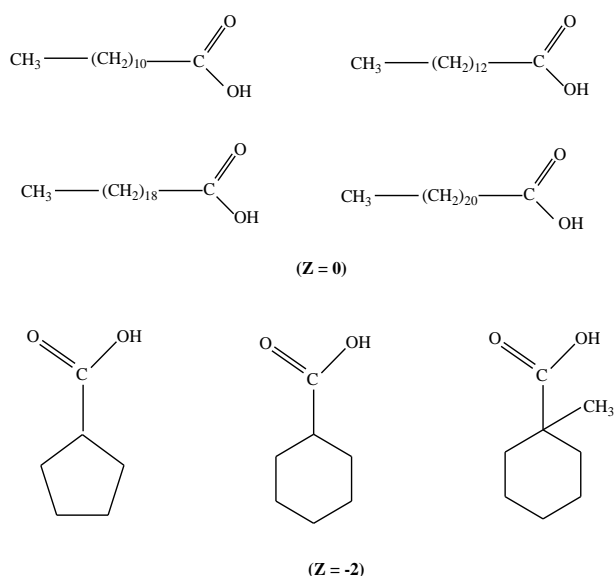

Figure 1- Chemical structure of the naphthenic acids.

The sample petroleum used in the SPE process was called B1 (24.6 ^{o}API and total acid number 0.5 mg KOH/g). Firstly the petroleum was fractionated in saturates, aromatics, resins, and asphaltenes (SARA fractionation method). SARA fractionation was performed according to the procedure described in a previous study (Karam and Lanças, 2004). The resin fraction (RF) was separated to verify the removal efficiency of petroleum acid compounds by the new stationary phase. This FR was fortified with standard acid to verify the matrix effect. The acids were identified by comparison with the reference ions table presented by Clemente and Fedorak, 2004.

2.4 SPE procedure

The SPE procedure was performed according to De Conto *et al.*, 2012. In SPE, the new stationary phase pyridinium-propylsilica (*SiPy*) was used. The SPE cartridge, with 500 mg stationary phase, was conditioned with 5 mL of hexane. After this, 10 mL of the standard sample was eluted through the column and the interferences were removed by elution with 10 mL of hexane. The recovery of the acid fraction of the sample was carried through of the elution with 20 mL of ethyl ether containing 10% (v/v) formic acid. Following this, 10 mL of methanol were allowed to flow through the cartridge for recovery of polar compounds that could still be adsorbed on the stationary phase. Subsequently, the acidic fraction was dried under flowing N$_2$ and solubilized with 1 mL of dichloromethane (DCM) for later analysis.

2.5 Chromatography analysis

The acidic fraction was derivatized before chromatography analysis with N-tert-butyldimethylsilyl-N-methyl-trifluoro aceta-mide (MTBDSTFA) (De Conto *et al.*, 2012). To the chromatographic analyses the samples were dissolved in 900 µL of DCM and 100 µL of ethyl laurate solution 500 mg L^{-1} (internal standard). Chromatographic analyses were performed on a Shimadzu model QP – 2010 Plus gas chromatograph coupled to a mass spectrometry detector (GC/MS). The capillary column used was OV-5 (methyl silicone 5% phenyl groups) with a 0.25-mm internal diameter, 0.25-mm thickness film of the stationary phase, and 30 m length. The chromatographic conditions were injection mode splitless, injector and interface temperature 280 ^{o}C and 300 ^{o}C, respectively, injected volume 1 µL. The mobile phase was helium gas with flow rate

of 1 mL min^{-1}. The temperature program was started at 85 ^{o}C for 1 min, heated at 2 ^{o}C min^{-1} to 280 ^{o}C, and left at this temperature for 10 min.

3. RESULTS AND DICUSSION

3.1. *SiPy* characterization

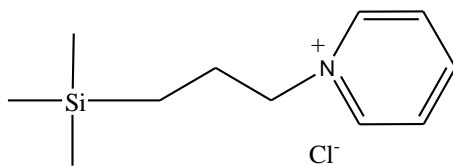The Figure 2 shows the chemical structure of the material *SiPy*.

Figure 2 – *SiPy* ionic material structure.

The material with ionic character was characterized regarding to the textural analysis, infra-red (FTIR) and elemental analysis. These characterizations will be discussed subsequently. Through of the results of the textural analysis one can observe that the adsorption desorption isoterm of the SiPy material is type IV, a tipical isoterm of mesoporous material (Figure 3A).

The BET area of the SiPy was 187 m^2 g^{-1} and pore volume was 0.47 cm^3 g^{-1}. The pore size distribution curve is shown in the Figure 3B. In this Figure one can verify that SiPy material has a pore diameter between 4 and 12 nm, the result confirms the mesoporosity of the material.

The infrared spectrum (Figure 4) shows the organic fraction of the SiPy sample indicated by adsorption bands at 1634 e 1487 cm^{-1}, these vibrations are attributed to the vibration modes of the ion pyridium ring (Benvenutti, 1992).

The inorganic component of the *SiPy* material can be identified by silica bands at 1980 and 1865 cm^{-1} (Maniar *et al*., 1990) and by silanol bands between 3700 and 3500 cm^{-1} (Costa *et al*., 1997). The presence of ion pyridium in the treated sample at 200 ^{o}C, under vacuum, is an evidence of the high thermal stability of the organic group. This result indicates that the organic group is covalently bonding on the surface (Menezes *et al.*, 2012).
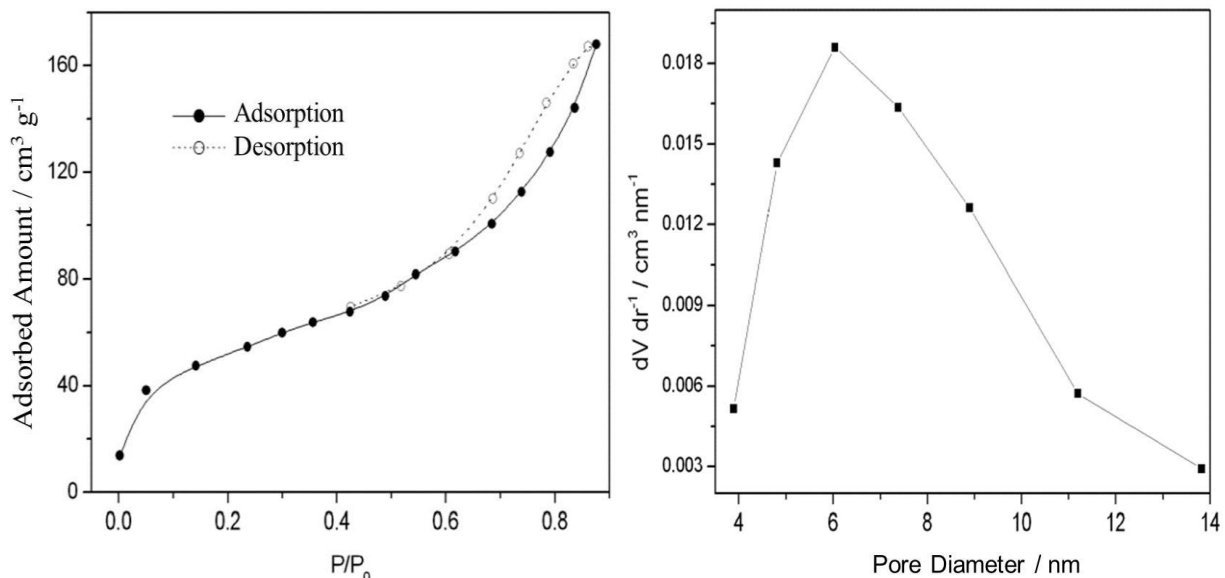

Figure 3 – A) Adsorption and desorption isoterm of the SiPy material and B) pore size distribution curve of *SiPy* material.
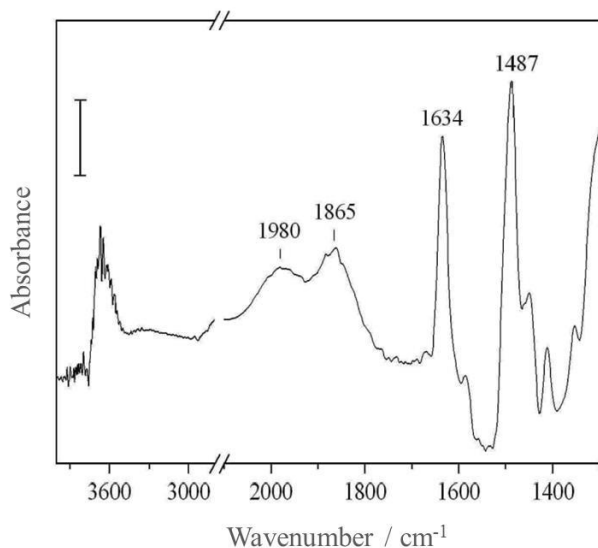
Figure 4 - Absorption infrared spectra of the *SiPy* material obtained at room temperature, after heat treatment at 200 °C in vacuum. The bar value is 0.2.

In the elemental analysis (Table 1) one can verify the amount of Carbon and Nitrogen present in the sample, confirming the silica modification with organic group. It can be observed that the ionic material (SiPy) shows about 1 mmol of organic group in 1 g of the material.

Tabela 1. Elemental Analysis

Sample	Elemental Analysis (mmol g^{-1})		
	% C [a]	% N [a]	% Cl^{-} [b]
SiPy	1.14	0.94	0.95

a Obtained by elemental analysis, mmol of pyridinium group per gram of adsorbent.
b Obtained by potentiometric analysis, mmol of pyridinium group per gram of adsorbent.

3.2. Acid compounds recuperation of the model system

The results obtained through of the acid mixture standard eluation by the stationary phase *SiPy* are show in the Figure 5.

As seen in the Figure 5, the acyclic acid recovery was better than the cyclic acid. These results were expected because the cyclic acid has more interaction with the stationary phase due to it lower pKa compared with the acyclic acids (De Conto *et al.*, 2012). According to (Allinger *et al.*, 1978) cyclic acids have lower pKa when compared with acyclic acids with the same carbon number, so the adsorption of the cyclic acid in the ionic exchange stationary phases have higher interaction force than the acyclic acid. This fact decreases the cyclic acid recovery.
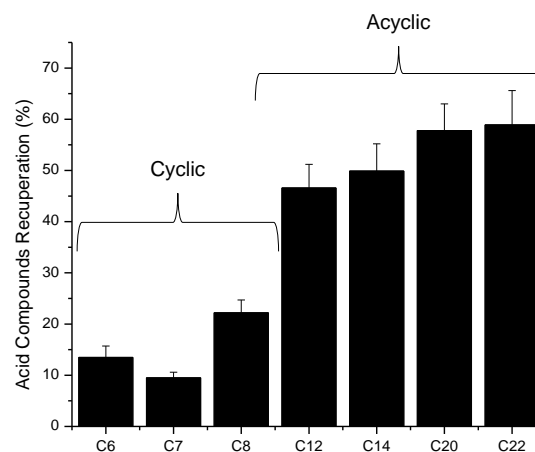

Figure 5 – Percentage of the acid compounds recovery from the model system.

The acyclic acids recovery was close to 50 % for acid compounds with carbon number C_{12}, C_{14} and close to 60 % for acid compounds C_{20} and C_{22}. In the work of Jones et al. (2001) the authors shows the recuperation of acid compounds through of the SPE using SAX (commercial phase) as stationary phase of 98 ± 10.2% for C_{14} and 81 ± 12.2% for C_{22}. One can verify that the percentage of the acids recuperation in the Jones's work was bigger than in this work. However is important to emphasize that in this work only 0.5 g of stationary phase and 20 mL of solvent were used while in the Jones's work 10 g and 55 mL were used, respectively. These results showed the great efficiency of the synthesized material in the acid compounds recovery.

De Conto *et al*., 2012 used three different stationary phase (SAX, NH_2 and $Dab-Al_3O_2$) to the acid compounds recovery. The stationary phase and solvent amount were the same used in this work. However the cyclic acid recovery using the stationary phases synthesized in this work showed bigger recuperation, almost twice of the C_6, C_7, C_8 when compare with the stationary phases tested by De Conto *et.al.*, 2012. This fact should be emphasized, because the cyclic naphthenic acids recovery is a challenge of the analytic chemistry due to the strong adsorption in the stationary phase

and consequently, difficulty of elution these compounds.

Regarding to the acyclic acids, the percentage of recovery was similar to the results found by De Conto *et al.*, 2012. However, the surface area of the materials SAX, NH_2 and Dab-Al_3O_2 were bigger than surface area of *SiPy*. Thus, the percentage of recovery per unit area of stationary phase is higher for the phase synthesized in this work.

3.3. Acid compounds recuperation from petroleum

The extraction of acid compounds in the petroleum matrix was performed by SPE, using the resins fraction (RF) obtained from the pre-fractionation (SARA). The extraction of acid compounds was performed with pure RF and RF spiked with a mixture of standard acids, so the matrix effect could be evaluated. Figure 7 shows the chromatograms obtained by GC/MS analysis of the extracts from both samples FR and spiked FR, using the stationary phase *SiPy*.

The chromatogram of Fig. 7A shows that through of the SPE process using *SiPy* stationary phase was possible extracted seven acyclic acids (C_{11} à C_{18} except the C_{15}) and only one monocyclic acid (C_{18}). In the Fig. 7B, can be noted that the standard acid added in the sample was identified.

The recovery of the acids standard added in the petroleum sample was of 25–48% of the cyclic acids, and 55–83% of the acyclic acids. These results show that the others compounds present in the petroleum matrix does not influence the recovery of acidic compounds in this fraction of petroleum.
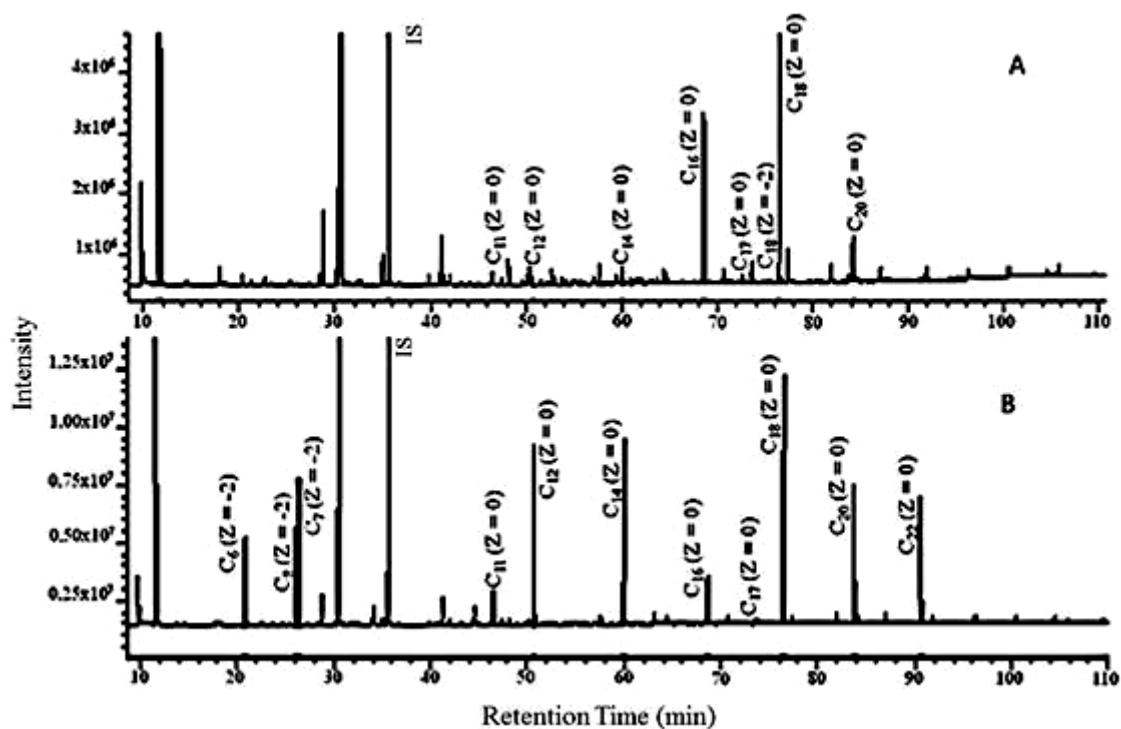

Figure 7 - Chromatograms obtained by GC/MS of the petroleum resins samples (A) RF and (B) RF spiked with standard acid compounds, eluted by *SiPy* stationary phase.

4. CONCLUSION

The synthesized mesoporous materials, *SiPy*, showed adequate characteristics to be used as stationary phase in SPE for acidic compounds recovery from a petroleum resins fraction. It was observed that the percentage of cyclic acids recovery using the *SiPy* was better than the results found in the literature. This result is promising because the recovery of cyclic acid, main short chain and high polarity, from complex matrixes is a challenge to the analytical chemistry. The *SiPy* showed a percentage of recovery of the acid
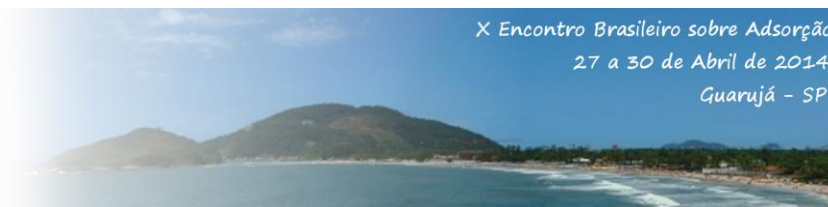
compounds per unit area of the stationary phase greater than commercial stationary phases. The SPE process using *SiPy* as stationary phase to recovery cyclic and acyclic acid compounds showed satisfactory results for the recovery, characterization, and quantification of the acidic compounds presented in the model system as well as in the resin fraction from petroleum.

5. REFERENCE

ALLINGER, N. L., CAVA, M. P., JONGH, D. C., JOHNSON, C. R., LEBEL, N. A., STEVENS, C. L. *Química orgânica*, Guanabara, Rio de Janeiro 1978.

BARRETT, E.P.; JOYNER, L.G.; HALENDA P.P. *The determination of pore volume and area distributions in porous substance. I. computations from nitrogen isotherms*. J. Am. Chem. Soc., v 73, p. 373-380, 1951.

BENVENUTTI E.V. *Antimônio (V) Disperso na Superfície de Sílica Gel. Síntese, Caracterização e Propriedades*. Tese de Doutorado, Unicamp, Campinas, SP, Brasil, 1992.

BORGUND, A.E.; ERSTAD, K.; BARTH, T. *Fractionation of Crude Oil Acids by HPLC and Characterization of Their Properties and Effects on Gas Hydrate Surfaces*. Energy Fuels, v 21, p. 2816-2826, 2007.

BRUNAUER S.; EMMETT P.H.; TELLER E. *Adsorption of gases in multimolecular layers*. J. Am. Chem. Soc., v 60, p. 309-319, 1938.

CAMPOS, M.C.V. *Estudos dos ácidos naftênicos do gasóleo pesado derivado do petróleo Marlin.* Tese de Doutorado, UFRGS, Porto Alegre, RS, Brasil, 2005.

CAMPOS, M.C.V.; OLIVEIRA, E.C.; FILHO, P.J.S.; PIATNICKI, C.M.S.; CARAMÃO, E.B. *Analysis of tert-butyldimethylsilyl derivatives in heavy gas oil from brazilian naphthenic acids by gas chromatography coupled to mass spectrometry with electron impact ionization.* J. Chromatogr. A, v 1105, p. 95-105, 2006.

CLEMENTE, J.S.; FEDORAK, P.M. *A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids.* Chemosphere, v 60, p. 585–600, 2005.

CLEMENTE, J.S.; FEDORAK, P.M. *Evaluation of the analyses of tert-butyldimethylsilyl derivatives of naphthenic acids by gas chromatography – electron impact mass spectrometry.* J. Chromatogr. A, v 1047, p. 117-128, 2004.

COSTA, T.M.H.; GALLAS, M.R.; BENVENUTTI, E.V.; JORNADA, J.A.H. *Infrared and thermogravimetric study of high pressure consolidation in alkoxide silica gel powders.* J. Non-Cryst. Solids, v 220, p. 195 -201, 1997.

DE CONTO, J.F.; NASCIMENTO, J.S.; DE SOUZA, D.M.B.; COSTA, L.P., EGUES, S.M.S.; FREITAS, L.S.; BENVENUTTI, E.V. *Solid phase extraction of petroleum carboxylic acids using a functionalized alumina as stationary phase.* J. Sep. Sci., v 35, p 1044–1049, 2012.

JONES, D.M.; WATSON, J.S.; MEREDITH, W.; CHEN, M.; BENNETT, B. *Determination of Naphthenic Acids in Crude Oils Using Nonaqueous Ion Exchange Solid-Phase Extraction.* Anal. Chem., v 73 (3), p. 703-707, 2001.

KARAM, H. S. M. H. M., LANÇAS, F. M., Liq. Chromatogr.Gas Chromatogr. Mag., v 5, p 41–48, 2004.

MANIAR, P.D.; NAVROTSKY, A.; RABINOVICH, E.M.; YING J.Y.; BENZIGER, J.B. *Energetics and structure of sol-gel silicas.* J. Non-Cryst. Solids, v 124, p. 101-111, 1990.

MENEZES, E.W.; LIMA, E.C.; ROYER, B.; DE SOUZA F.E.; DOS SANTOS, B.D.; GREGÓRIO, J.R.; COSTA, T.M.H.; GUSHIKEM, Y.; BENVENUTTI, E.V. *Ionic silica based hybrid material containing the pyridinium group used as an adsorbent for textile dye.* J. Colloid Interface Sci, v 378, p 10–20, 2012.

MORAES, M.S.A., GRUBER, L.D.A., MACHADO, M.E., GELLER, A.M., BORTOLUZZI, J.H., GOMES, A.O., GUIMARÃES, R.C.L., ZINI, C.A.; CARAMÃO, E.B. *Análise de Ácidos Naftênicos em Petróleo Brasileiro utilizando SPE e Cromatografia Gasosa (mono e bidimensional).* 32ª Reunião Anual da Sociedade Brasileira de Química, Fortaleza, CE, 2009.

NIELSEN, K.E.; DITTMER, J.; MALMENDAL, A.; NIELSEN, N.C. *Quantitative Analysis of Constituents in Heavy Fuel Oil by 1H Nuclear Magnetic Resonance (NMR) Spectroscopy and Multivariate Data Analysis.* Energy Fuels, v 22, p. 4070–4076, 2008.

PAVAN, F.A.; GOBBI, S.A.; COSTA, T.M.H.; BENVENUTTI, E.V. *FTIR thermal analysis on anilinepropylsilica xerogel.* J. Therm. Anal. Calorim., v 68, p 199–206, 2002.

PURCELL, J.M.; JUYAL, P.; KIM, D.G.; RODGERS, R.P.; HENDRICKSON, C.L.;

MARSHALL, A.G. *Sulfur Speciation in Petroleum: Atmospheric Pressure Photoionization or Chemical Derivatization and Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry.* Energy Fuels, v 21, p. 2869-2874, 2007.

THOMAS, J. E. A. P.; TRIGGIA, A. A.; CORREIA, C. A.; VEROTTI, C.; XAVIER, J. A. D.; MACHADO, J. A. D.; SOUZA, J. E. S.; PAULA, J. L.; ROSSI, N. C. M.; PITOMBO, N. E. S.; GOUVÊA, P. C. V. M.; CARVALHO, R. S.; BARRAGAN, R. V. *Fundamentos de Engenharia de Petróleo*, Rio de Janeiro, Editora Interciência, 2004.

WU, X.; JING, H.; ZHENG, Y.; YAO, Z.; KE, W. *Erosion–corrosion of various oil-refining materials in naphthenic acid.* Wear, v 256, p. 133–144, 2004.

6. ACKNOWLEGMENT