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Basic Nitrogen Compounds in Crude Oils: Effect on Mineral Dissolution During Acid Stimulation Processes

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Abstract

Several papers have reported the potential formation damage as a result of the adverse interactions among acids, formation fluids and minerals during acid stimulations operations. However, few studies have focused on the effect of the acid consumption capability of crude oils upon the efficiency of matrix acidification, particularly that capability arisen from the nitrogen compounds content. This paper ascertains: 1) the release of basic nitrogen compounds from crude oils, due to reactions with HF (3%), HCl, citric and acetic acids (all of them 10%), 2) the effect of these nitrogen compounds released into the aqueous phase upon the dissolution of silicate and alumino-silicate minerals.

Eight Venezuelans crude oils were brought into contact with acidic solutions for 10 days at 70°C in batch experiments. The resulting aqueous solutions were analyzed by coupled gas chromatography-mass spectroscopy (GC/MS) and used to dissolve quartz, kaolinite and K-feldspar at 70°C, during 5 days. The initial and final concentrations of Al, K and Si in solution were determined by inductively coupled plasma, atomic emission spectroscopy (ICP-AES).

GC/MS analyses showed that a complex mixture of cationic nitrogen compounds, such as R-Quinolines, R-Pyridines and Carbazoles, are released into solution when crude oils are treated with acid. The type of acid lead the amount and kind of nitrogen-organic compounds (N.O.C) extracted during crude oil - acid interactions.

The analysis by ICP-AES indicated that the presence of small amounts of the N.O.C. in the aqueous phase (0.002%

to 0.04%) inhibits up to 72 % the elements released by mineral dissolution. This is probably due to the shielding of the mineral surface active sites and should be the reason for efficiency decrease of matrix acidification. The presence of these compound reduced the oil recovery up to 20%, in laboratory displacement experiments.

Introduction

The main purpose in any acidification treatment is the dissolution of minerals from the formation or precipitated solid material in the near wellbore areas. All of these in order to increase permeability^{1, 2}. This is usually achieved by employing HF and HCl or their mixtures, as well as acetic, formic and citric acids, among others³.

The mechanisms and effects causing damages to the formation during stimulation processes have been well documented⁴. Some of the inconvenients reported are secondary phase precipitation^{4,5}, formation of organic deposits^{6,7}, and fine migration^{4,8}. Nevertheless, the basic properties of crudes have been poorly considered when designing a stimulation process⁹, just as acid properties (acid number) of crudes are considered in recovery processes with alkaline additives¹⁰.

Nitrogen compounds are well known constituents of crude oil, with an average content of 0.094% by weight and as high as 0.75% in some California oils. These compounds are believed to conform a major fraction of the basic compounds in crude oils¹¹. Pyridines, Quinolines and some substituted Pyrroles, such as 2,4-Dimethylpyrroles, particularly alkylated Benzoquinolines, have been recognized as major classes of basic compounds, whereas Indoles, some Pyrroles, and Carbazoles are regarded as non-basic compounds⁹.

The significance of knowing the basic properties of a particular crude is due to the fact that basic compounds can interact with the acids injected in the formation, generating in-solution species that can affect mineral dissolution and precipitation processes in the porous medium. Moreover, understanding these neutralization reactions of a crude's basic compounds with a given acid solution, can contribute to the knowledge of the formation of sludges and asphaltenes

precipitation in stimulation processes. Thus, this paper is mainly aimed at studying the interactions of different crudes with acid solutions, and how these latter can affect the dissolution of quartz, kaolinite, and K-feldspar, as well as crude recovery.

Experimental Part

Experiments at static conditions

60-ml Teflon closed acid-mineral reaction systems, in static conditions at 70°C, were used to evaluate the dissolution of Ottawa sand (98% SiO₂), kaolinite (El Pao, Bolívar State, Venezuela) and K-feldspar (microcline, NIST 70-A) in 3%-HF solutions, HCl, acetic (CH₃COOH) and citric acids (C(CH₂)₂OH(COOH)₃) at 10%. The solid-liquid ratio employed in this experiments was 1 g of mineral in 50 ml of acid solution (1:50).

The mineral-acid interactions were studied both with unreacting acids and after-reacting acids with crudes having different °API gravities and basic properties: El Furrial, Barúa, Motatán and Mene Grande (Table 1).

The reactions of crudes with each of the above mentioned acids were evaluated in 500-ml Teflon vessels, with a crude-acid ratio of 100 g of crude to 300 g, for 10 days at 70°C. For one crude e.g. El Furrial the extraction process of compounds nitrogenated with HCl (10%) was evaluated with time, in order to determine that 10 days are enough to extract the maximum quantity of nitrogenated compounds under these reaction conditions.

Once the crude-acid reactions had finished, the mixture was separated through Teflon funnels and further filtered by gravity using equipments made up with the same material.

Once separated and filtered the acids which reacted with crudes were used to evaluate the effect of the presence of organic compounds soluble in aqueous phase on the mineral-acid interactions under the same reaction conditions as those employed in the mineral-acid systems.

After taking an aliquot of 50 ml of solution reacted with the different crudes for the study of the effect of the presence of organic compounds in solution on the dissolution of minerals, the remaining solution was taken to a pH of 10 with a NaOH (0.1 M) solution, evidencing solids precipitation (NCppt.), which were separated for their quantification and characterization. Organic compounds were then extracted from the aqueous solution with 100 ml of benzene. This latter was rotoevaporated in a nitrogen flow, at 70°C, and the extract obtained (NCsol.) was characterized by infrared spectroscopy (IR) and gas chromatography coupled with mass spectrometry (GC/MS).

The concentration of nitrogenated organic compounds extracted by the acids of each crude was calculated through the following equation:

$$CNCE = \frac{NC_{sol.} + NC_{ppt.}}{VA} = \frac{NCE(mg)}{VA(l)} \dots\dots\dots(1)$$

The concentration of Si, Al and K were determined in acid solutions before and after reacting with the different minerals, by ICP-AES.

The main purpose of this paper is to evaluate the effect of the presence of organic compounds in aqueous phase, as a product of the neutralization of the organic bases naturally present in crudes, on the dissolution of quartz, kaolinite and potassium feldspar. Therefore, no characterization was performed in the crudes after interacting with the different acids employed.

Experiments at dynamic conditions

In order to evaluate the effect of the interactions that can take place during acid stimulation processes on crude recovery, 4 displacement tests of El Furrial crude with NaCl (1%) were performed. A water-pretreated Berea core along with 3 Berea cores pretreated with different solutions in HCl (10%) were employed.

The pretreatment consisted in vacuum saturation of the samples for 2 hours, in Teflon beakers. One of the cores with HCl (10%), another one with HCl (10%) after reacting with El Furrial crude for 10 days at 70°C, and the third one with a 200-ppm solution of 2-methyl-quinoline in HCl (10%). This nitrogenated organic compound was previously identified in the interaction experiments of El Furrial crude with HCl at 10%. Once the pretreatment had finished, the displacement tests were performed in a triaxial cell, at 70°C, and a confinement pressure of 3000 psi, according to the following procedure:

- The solution occupying the porous volume (PV) of the core was displaced with an aqueous solution of NaCl (1%), at a rate of 1 ml/min. until the output solution pH reached a value, within the ± 10% error, equal to that of the input solution. This occurred typically after displacing about ≈ 35 PV.
- The core was saturated with El Furrial crude at the same injection rate until a water irreducible saturation (Swi) was reached.

El Furrial crude was displaced with a NaCl solution until the oil irreducible saturation (Sor) was reached.

Results and Discussion

Results obtained are shown in Tables 1 through 8 and in Figures 1 through 5. The discussion is divided into three sections: in the first place, the interactions between acids and crudes are analyzed. Secondly, the effect of the released organic compounds, in solution, on the dissolution of the three minerals: quartz, kaolinite and K-feldspar is discussed. As a reference, the dissolution of the three minerals by the four acids studied in the absence of organics in solution is

presented. Finally, the influence of the transfer of organics into solution on the recovery of crude in displacement tests is shown.

Table 1 shows the basic properties of crudes from different Venezuelan reservoirs, selected as the starting point for this study. It can be observed that these crudes show a relatively wide range of °API, basic number and Nitrogen (N) content.

Figure 1 shows that there is a good correlation of the basic properties with the nitrogen content and °API gravities of these crudes. This correlation has been explained by the accumulation of biodegrading bacteria (rich in N) in the crude's heavy fractions: resins and asphaltenes. However, very little is known about the distribution of the N compounds^{9,11}. The correlation is important since it makes it possible to analyze the effects of organic compounds transfer in terms of a widely known parameter, such as °API gravity.

Crude oil-acid interactions

This section evaluates the effect of time, type of crude and type of acid on the organic compounds transfer from crude to solution. The types of organic compounds transferred are identified and the total mass is characterized.

Effect of time on the extraction of nitrogen compounds.

A very important aspect to be considered is the time required for the nitrogenated compounds transfer to occur from the crude towards the aqueous acid phase. The evaluation of this aspect was carried out through a study on El Furrial crude-HCl (10%) interaction in terms of time at 70°C. El Furrial crude was selected due to its °API, which is typical in acid-stimulated reservoirs. Besides, this crude is obtained from one of the most productive fields in Venezuela (295 MBOPD). Figure 2 evidences that for this particular system the organics-in-solution maximum concentration, measured by eq. 1, is reached approximately 5 hours after the reaction. This shows that they should occur during stimulation processes which generally involve contact times of at least 12 hours.

As a consequence of the results shown above reaction times higher than 5 days were selected. This allows to obtain the maximum in-solution concentrations and also to estimate the effects of matrix acidizing treatments with retarding acids, that may provide deeper acids penetration requiring longer acid - formation contact times.

Usually, it is believed that stimulation processes can be very effective in sandstones where significant acid penetration are reached¹². For that reason, lot of research has been conducted to finding ways to extend the action of acid deeper into the formation^{13,14}.

Effect of the type of crude. Despite the fact that acid stimulation processes are usually carried out in light and medium crude reservoirs, in this paper the effect of the type of

crude (basic nitrogen content) on the neutralization process of organic bases and/or natural cationic surfactant during their interaction with a HCl (10%) solution is studied.

In order to demonstrate this effect the following crudes, having different basic properties and °API, were selected: Barúa, Hamaca, Mene Grande and Furrial. The results of these interactions are presented in Table 2. It is evidenced that the crude having the highest °API (Furrial) and thus less basic nitrogenates content, produces the highest concentration of these compounds in solution. No correlation between basic nitrogen and the extraction percentage of nitrogenated species from the different crudes, when interacting with this acid, was observed.

The above suggests that it is easier to extract nitrogenated compounds from some light crudes than from medium and heavy crudes.

The GC/MS characterization of the extracts obtained from the HF interaction with the Mene Grande crude (16 °API) and El Furrial crude (26 °API) showed a predominance of nitrogenated compounds, with a typical characteristic of these compounds for each crude (Fig. 3). It is worth noticing that some of the species identified in these extracts were mainly R-Quinolines, Indoles, Pyrroles and Carbazoles, which have also been reported in other studies⁹. Nonetheless, the presence of similar nitrogenated species in both extracts suggests that these kind of compounds are more likely to react. This could explain the low capacity of crudes, having high basic numbers, to transfer nitrogenated compounds to the aqueous phase, since these reactions depend on the properties of the nitrogenated species, such as molecular weight.

Effect of the type of acid. An evaluation of the interactions of El Furrial crude (Table 1) with acetic and citric acids at 10% and inorganic acids i.e. HF (3%) and HCl (10%) was performed in order to ascertain the effect of the acid type upon the extraction of nitrogenated compounds.

It is important to mention that the acid concentrations employed in this study are similar to those used for acid stimulation processes of wells⁵, except in the case of citric acid, which can also be employed in these acid formulations as chelating agent of iron in solution^{1,3}.

Table 3 shows that the quantities of nitrogenated compounds transferred from the crude to the aqueous phase are higher with HF (3%) than with the rest of the evaluated acids. This trend was also observed with Barúa, Urdaneta and Mene Grande crudes (Manrique and Mogollón, non-published results).

For El Furrial crude oil the GC/MS molecular characterization (Fig. 4) showed that fluorhydric (3%) and citric (10%) acids extract compounds with lower molecular weight than those obtained with El Furrial crude-HCl (10%) reaction system. Some of the compounds identified in the extracts are Indoles and Pyridines and specially Methyl-

Quinilones with more than 90% reliability (Fig. 5). Other organic compounds possibly present are sulphur compounds and esters.

Based on the above evidence it is possible to state that the attack of acids on crudes is mainly concentrated on nitrogenated compounds. Those compounds having lower molecular weight are more easily released towards the solution.

Mineral-acid interactions

The effect of the HF (3%), HCl (10%), acetic (10%) and citric (10%) acids on the dissolution of quartz, kaolinite and K-feldspar (microcline) was studied. This was achieved by determining the concentrations of Si, Al and K in solution resulting from the interaction of acids with minerals, under static conditions, at 70°C for 5 days (Table 4). In order to determine the effect of the presence, in acid aqueous phase, of nitrogenated organic compounds (extracted from the crudes by interaction with four acids) additional experiments with the acid aqueous phase and minerals were performed. The percentage ($\Delta\%$) of dissolution inhibition of minerals (Table 6) was established by comparing these results with those obtained from the experiments performed in absence of nitrogenated organic compounds.

The main reasons for selecting those three minerals were their abundance in oil bearing and their contrasting reaction rates. Actually, their average life time at 25 °C and pH = 5.0 is 34,000,000 years for quartz; 6,000,000 years for kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$); and 921,000 years for microcline (KAlSi_3O_8)¹⁵.

Effect of the type of acid. Table 4 shows that the quantity of Si extracted by HF (3%) is 4.3 to 680 times higher than that extracted by chlorhydric, acetic and citric acids at 10%. Likewise, the quantity of Si extracted from quartz by HF (3%) is higher than those extracted from kaolinite and K-feldspar.

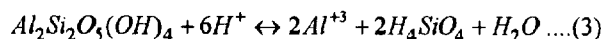
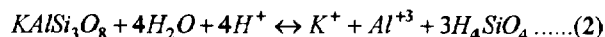
Another interesting aspect (Table 4), is that the quantity of Al extracted by HF from kaolinite and K-feldspar is 8.5 to 60 times higher than that extracted by the other three acids.

The above statements clearly demonstrate the catalytic power of HF, which can be due to the following reasons: on one hand, the known capability of F^- to complex Si in solution, keeping a saturation degree of the solution far from equilibrium, and, thus, the reaction rate in its maximum value. On the other hand, the F^- could be participating in the attack to the mineral surface, accelerating the rupture of the Si-O bonds, and, consequently, the collapse of the crystalline structure.

Inversely to what was observed in the experiments with HF, the quantity of Si extracted from quartz, by hydrochloric, acetic and citric acids, is lower than those extracted from kaolinite and K-feldspar, according to the relative reactivities of the three minerals¹⁵. The significance of this behavior is that it makes possible the selective attack of the mineral

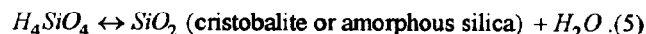
matrix, this is, the selection of the acid will determine the attack to one mineral or the other.

It is to be expected that, according to the following reactions:



for instance, in the case of K-feldspar dissolution (2), the resulting in-solution concentrations of Si and Al have a ratio or stoichiometric index of 3.

The Si/Al stoichiometric indexes, for kaolinite and K-feldspar, are much lower than expected (Table 5). This kind of situations are usually due to the precipitation of secondary mineral phases. The Al phase precipitation is discarded since it would cause higher Si/Al indexes than expected. Thus, precipitations as the one shown in the following reaction should be occurring:



It is also possible that kaolinite be precipitating in the experiments with K-feldspar.

According to the reaction rates of the minerals studied, the resulting Si concentrations should be in the order of *K-feldspar* > *kaolinite* > *quartz*; and those of Al: *K-feldspar* > *kaolinite*. Nevertheless, this does not occur for any acid. This can be explained by the above mentioned precipitation of secondary phase, even if the possibility that the reaction rates change when concentrated acids are used should also be considered. As regards this last statement, the lack of kinetic data avoided to be conclusive.

Effect of the organic nitrogen compounds. The effect of the presence, in acid aqueous phase, of nitrogenated organic compounds (extracted from crudes by interaction with four acids) is discussed. Table 6 shows the percentages of dissolution inhibition of minerals ($\%\Delta$), which were estimated with the Si, Al and K resulting concentrations in solution, using formulas such as the following:

$$\% \Delta \psi = \frac{[\psi]_{\text{acid}} - [\psi]_{\text{acid/N-comp}}}{[\psi]_{\text{acid}}} \times 100 \dots\dots\dots(6)$$

where: $[\psi]_{\text{acid}}$ is the specific element resulting concentration, in solution, from the interaction of the acids with the minerals, and $[\psi]_{\text{acid/N-comp}}$ is the resulting concentration, in solution, from the interaction of the minerals with acids, which previously interacted with crude oils. Due to the errors associated with the Si, Al and K determinations in solution,

only those $\% \Delta \psi > 10$ should be considered significant.

It can be observed in Table 6 that the presence of nitrogenated organic compounds (N.O.C.) have a significant dissolution inhibition effect of the three minerals on the inorganic acids: HF and HCl. These results suggest that the N.O.C. can be interacting (sorbing) with the surface of minerals, producing a screening effect before the attack of H^+ .

For the organic acids - acetic and citric - no inhibition of the minerals dissolution was observed. Apparently, the N.O.C. prefer to interact with the acids' anions than with the surface of minerals. However, further investigation have to be made to evaluate how these nitrogen compounds (N.O.C.) interacts with carbonate minerals. Specially with HCl, HCOOH (formic acid) and CH_3COOH , acids used in the matrix acidizing of carbonates¹³.

The presence of N.O.C. in HF produces a particularly significant e.g. 72% inhibition of the Si release, by dissolution of kaolinite. Nonetheless, the dissolution power of HF is still slightly higher than that of the other acids. Additional experiments were carried out in order to verify if the N.O.C. extracted from different crudes could induce variable magnitudes of dissolution inhibition of minerals. Kaolinite was employed in these experiments since, according to the above discussion, its dissolution is inhibited by the N.O.C. from El Furrial crude. Crudes having higher contents of N than El Furrial were selected, and an attempt was done to induce the effect in HCl.

Table 7 shows that dissolution inhibition of kaolinite, calculated with the Si released into solution, remains essentially constant, despite the use of crudes having °API gravities between 9.1 and 26, which release up to 57% less of N.O.C. than El Furrial crude. Assuming that our hypothesis about the screening of minerals by sorption of the N.O.C. is correct, the inhibition constancy is explained by "saturation" of the mineral surface active sites.

A unique fact, evidenced in Table 7, is the increase of the Al release from kaolinite in the presence of N.O.C.. Table 6 makes it possible to corroborate that actually no other element in no other mineral, is released into solution in significantly higher quantities when the N.O.C. are present. The result of this fact should be the relative enrichment of Si minerals in the rock, making it more inert to acid attacks. As a consequence, successive stimulations should have lower efficiency, unless Si complexing agents are added.

Laboratory oil recovery experiments (preliminary results). The displacement tests of El Furrial crude, with NaCl (1%) aqueous solution, were designed in order to obtain evidences about the influence of the acid-crude interaction on the recovery.

Table 8 shows that initial porosities (ϕ) and permeabilities in air (k) of the four Berea cores employed are similar. Nonetheless, the oil residual saturations to crude (Sor) differ

significantly according to the pretreatment used.

Pretreatments including HCl (10%) (tests 2, 3 and 4) produce increases of permeability to crude (k_o) of 44% to 75% compared to water pretreatment (test 1). This is the expected result since the acid, by dissolution of the most reactive minerals, increase pore connectivity. Nevertheless, only the HCl (10%) pretreatment (test 2) without additives produced an increase of the recovery or decrease of the crude's residual saturation (Sor). The similarity between the results obtained in tests 3 and 4 indicates that the N.O.C. are actually playing a significant role among the different organic compounds extracted by the acids of the crudes.

The above results indicate that the presence of N.O.C. (tests 3 and 4) counteracts the HCl beneficial effect on the recovery (test 2), causing almost its neutralization.

It has been reported, that the adsorption of cationic surfactants increase the oil wettability of reservoir rocks. However, under low pH conditions ($pH < pzc$ or point of zero charge) mineral surfaces tend to become positively charged and cationic surfactants adsorption is significantly reduced¹³. Thus, the possibility that these organic compounds (N.O.C.) significantly modify the wettability under the studied conditions is discarded.

Additionally, in the pretreated samples (tests 2,3 and 4) an increase of the pressure (plugging) after reaching a 35% water saturation was evidenced. This effect was corrected by a reflux, making it possible to produce a lower mobility of water with respect to oil due to this effect.

Finally, the above results evidence that the chemistry of acid-crude oil interactions and its influence on the recovery are extremely complex. Thus, additional studies are required to determine and understand, with further details, how the N.O.C. can affect the mineral dissolution and the efficiency of stimulation processes.

Conclusions

1. The N content and the crude's basic properties have a good linear correlation with API gravity, which can be due to the genesis of crudes. Nevertheless, the quantity of N organic compounds extracted by the acids does not have any relation with the crude's N content. It could be said that the molecular weight of N compounds is determinant.

2. The order of extraction capacity of nitrogenated organic compounds of crudes is : $HF > HCl > acetic > citric$. In static systems the maximum N.O.C. extraction is reached after 5 hours, which is a relatively short period of time if compared to those of acid stimulation.

3. Despite the observed precipitation of secondary phases and that the dissolution mechanisms of the minerals studied are still poorly known, our results corroborate that the HF presents more capability than chlorhydric, acetic and citric acids to dissolve K-feldspar, kaolinite and quartz. It is to be expected that this statement be extensive to other aluminosilicate minerals.

4. Hydrochloric, acetic and citric acids dissolve aluminosilicates preferably: K-feldspar and kaolinite, while their ability to dissolve quartz, a silicate, is much lower. Presumably, the attack to the mineral structure occurs, preferentially, in the O-Al-O bonds. This makes possible the selective attack of the rocks' mineral matrix.

5. There is a synergy between inorganic acids and nitrogenated organic compound, released from crude, which inhibits the dissolution of K-feldspar, kaolinite and quartz. This does not occur with organic acids. The acid-nitrogenated organic compounds mixture produces decreases of up to 20% of the recovery of crude.

6. Finally, we would like to stress that it is not pretended to generalize the conclusions raised from this work to other conditions. However, we believe our criteria could be useful for future well acid treatments studies.

Nomenclature

CNCE = Concentration of nitrogen compounds extracted (mg/kg).

NCE = Weight of nitrogen compounds extracted (mg).

NCsol. = Weight of nitrogen compounds extracted from the solution (mg).

NCppt. = Weight of nitrogen compounds precipitated during the basification of the solution with NaOH (mg).

VA = Volume of acid used for the extraction (l).

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TABLE 1. Basic properties of different Venezuelan crude oils.

Crude oil	° API ⁽¹⁾	Basic number ⁽²⁾ (mg KOH/g of crude oil) ^(a)	Total Nitrogen ⁽³⁾ (mg/kg)	Basic Nitrogen ⁽⁴⁾ (mg/kg)	Basic Nitrogen ⁽⁵⁾ (%)
Boscán	8,6	5,16	11700	1260	11
Hamaca	9,1	6,14	9000	1490	17
Tía Juana	10,4	4,12	8900	960	11
Mene Grande	16	3,99	7110	920	13
Urdaneta	18	3,82	7500	910	12
Barúa	19	3,97	5280	960	18
El Furrial	26	0,98	4050	670	16
Lago Centro	40	0,38	930	77	8

Determined following: (1) ASTM D-287; (2) ASTM D-2896 / D-4739; (3) ASTM D-4629; (4) SHELL 1468 and (5) Basic N. (%) = (Basic N/ Total N) x 100.
(a) Quantity of perchloric acid expressed in terms of equivalent number of mg of KOH that are required to titrate 1 g of the sample (ASTM D 2896 - 92).

TABLE 2. Final concentrations, in aqueous solutions, of nitrogen compound extracted during the interactions of different crude oils with HCl (10%) at 70°C for 10 days (Effect of the type of crude).

Crude oil	°API	Basic Nitrogen (mg/kg)	Nitrogen compounds extracted (mg/kg)
Hamaca	9,1	1490	240
Mene Grande	16	920	200
Barúa	19	960	160
El Furrial	26	670	380

Initial concentration = 0

TABLE 3. Nitrogen compounds extracted during the interaction of El Furrial crude oil with different acids at 70°C for 10 days (Effect of the type of acid).

Acid	Nitrogen compounds extracted (mg/kg)
HF (3%)	450
HCl (10%)	380
Acetic (10%)	350
Citric (10%)	330

TABLE 4. Effect of the type of acid upon the Si, Al and K concentrations (μmol/l) resulting from mineral dissolution, at 70°C, after 5 days (Mineral-acid interactions).

Acid	Si			Al		K
	Quartz	Kaolinite	K-Feldspar	Kaolinite	K-Feldspar	K-Feldspar
HF (3%)	204	34	172	262	216	7.9
HCl (10%)	0.6	7.7	4.7	33	12	5.8
Acetic (10%)	0.3	n.s	3.0	n.s	3.6	3.4
Citric (10%)	0.4	7.9	n.s	13	n.s	n.s

Minerals / solution ratio = 1 g / 50 ml (1:50).
n.s = not studied

TABLE 5. Effect of the acids upon the stoichiometric index, in solution, resulting from the dissolution of different minerals at 70 C, after 5 days (*Mineral-acid interactions*).

Acid	Si/Al		K/Al
	Kaolinite	K-Feldspar	K-Feldspar
HF (3%)	0.12	0.80	0.04
HCl (10%)	0.23	0.39	0.48
Acetic (10%)	n.s	0.80	0.94
Citric (10%)	0.61	n.s	n.s

Expected Si/Al ratio for Kaolinite = 1 (eq. 3).

Expected Si/Al ratio for K-Feldspar = 3 (eq. 2).

Expected K/Al ratio for K-Feldspar = 1 (eq. 2).

TABLE 6. Porcentual decrease (%Δ) of the amount of Si, Al and K liberated from minerals, at 70°C, after 5 days, due to the presence, in the acid solution, of compounds extracted from El Furrial crude oil (*Effect of the organic nitrogen compounds*).

Acid	%ΔSi			%ΔAl		%ΔK
	Quartz	Kaolinite	K-Feldspar	Kaolinite	K-Feldspar	K-Feldspar
HF (3%)	11	72	12	29	13	10
HCl (10%)	33	16	3	-25	26	2.2
Acetic (10%)	-13	n.s	8	n.s	8	1.5
Citric (10%)	8	2	n.s	-14	n.s	n.s

Minerals / solutions ratio = 1 g / 50 ml (1:50).

Negative numbers mean increase.

TABLE 7. Effects of the compounds extracted from different crude oils on the porcentual decrease of Si (%ΔSi) and Al (%ΔAl) released from kaolinite in HCl (10%), at 70°C, after 5 days (*Effect of the organic nitrogen compounds*).

Crude oil	%API	Basic Nitrogen	%ΔSi	%ΔAl
Furrial	26	670	16	-20
Mene Grande	16	920	22	-24
Barúa	19	960	18	-15
Hamaca	9.1	1490	16	-29

TABLE 8. Comparative results from the displacement test of El Furrial crude oil with NaCl (1%) in Berea cores, at 70°C and confinement pressure of 3000 psi (*Laboratory oil recovery experiments*).

Test	φ (%)	k (mD)	Pretreatment	k _o (mD)	Swi (%)	Sor (%)
1	16.6	100	Water	16	28	54
2	16.5	105	HCl	23	23	32
3	16.6	119	HCl + Furrial	28	24	57
4	16.5	106	2-MQ (a)	24	26	49

φ = initial porosity; k = initial air permeability; k_o = oil permeability; Swi = irreducible water saturation and Sor = irreducible oil saturation.

(a) 200 mg/kg of 2- Methyl-Quinoline in HCl 10%

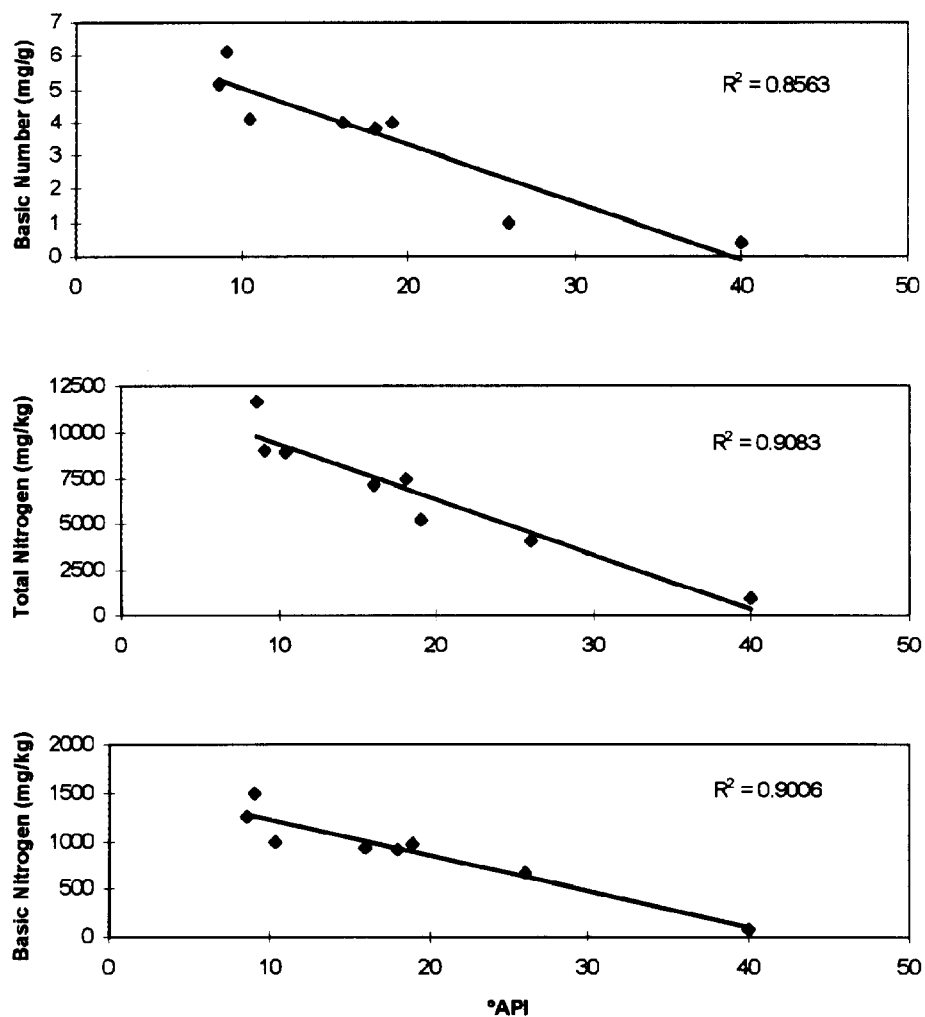


Fig. 1. Correlation between the °API and basic properties of different Venezuelan crude oils.

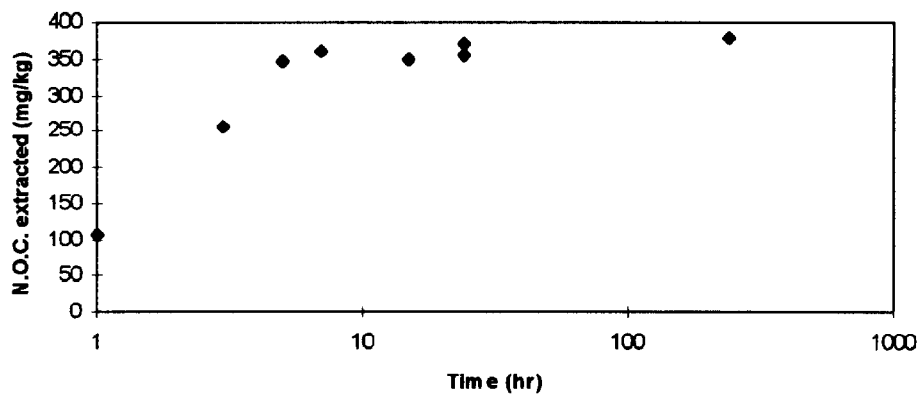


Fig. 2. Effect of time on the extraction of nitrogen compounds (N.O.C.) in the system HCl (10%) - El Furrial crude oil at 70°C.

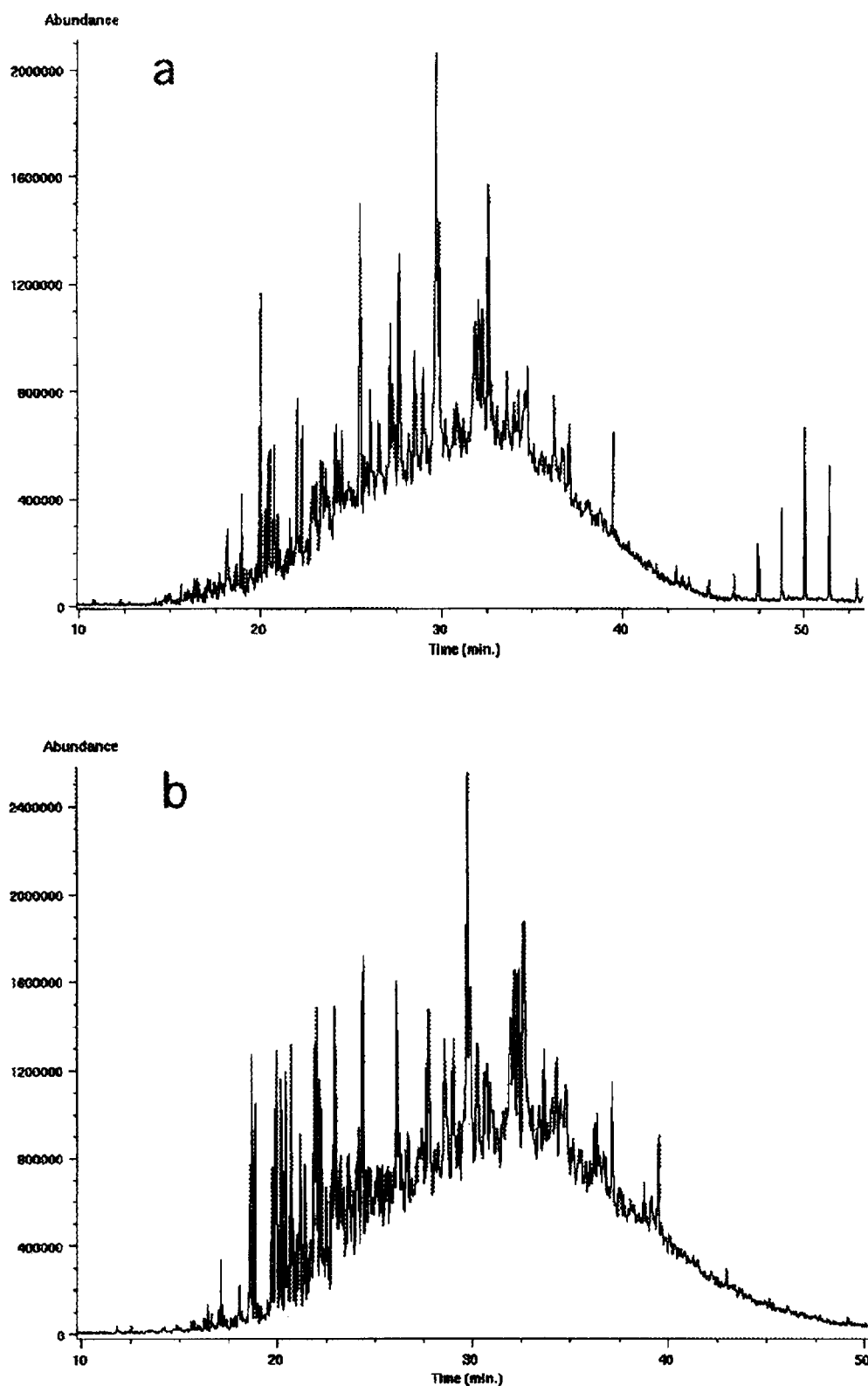


Fig. 3. GC/MS thermogram of the organic compounds present in the aqueous extracts obtained by interactions, at 70°C during 10 days, of HF with Mene Grande (Fig. 3a) and Furrial (Fig. 3b) crude oils.

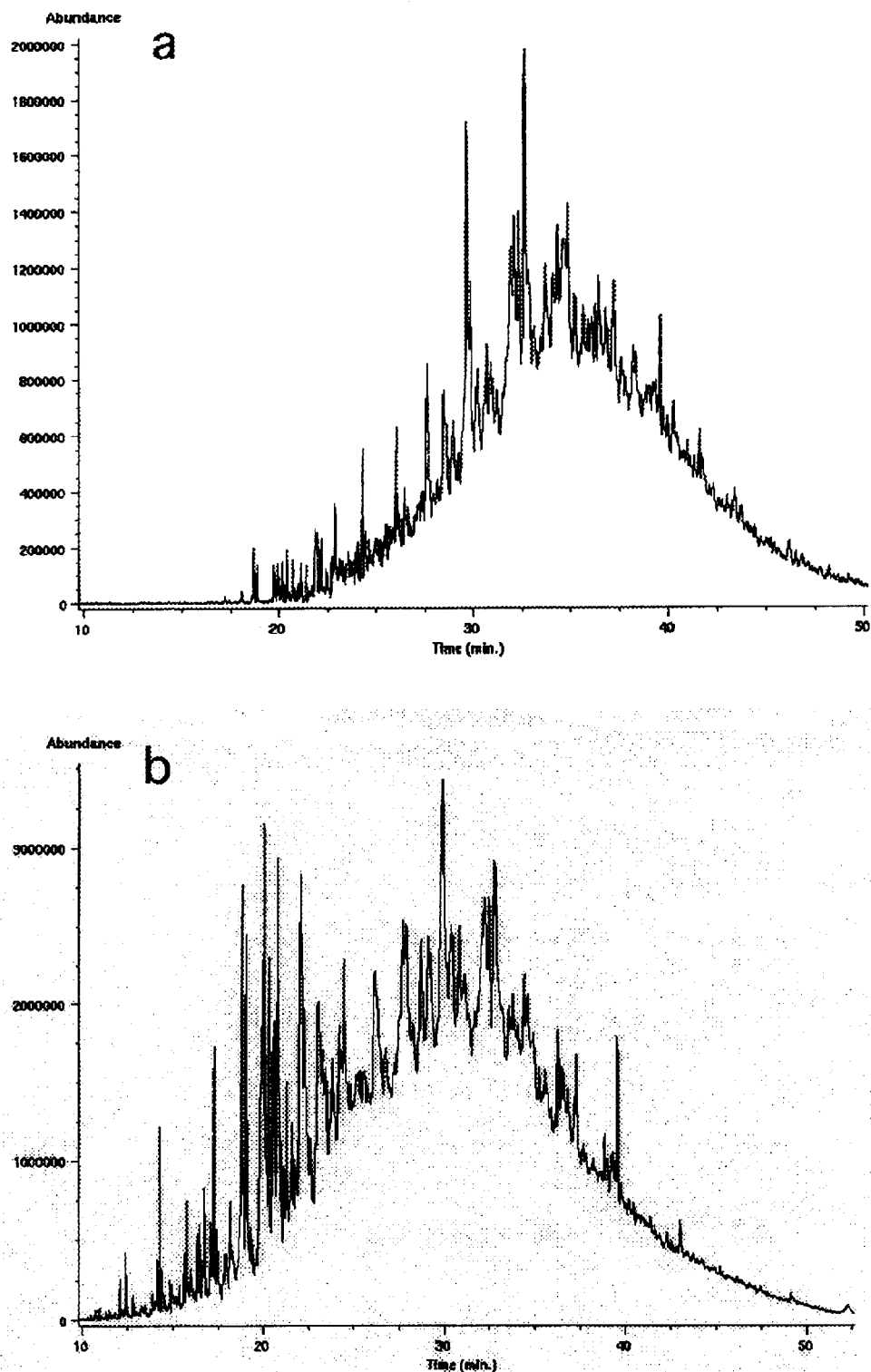


Fig. 4. GC/MS thermogram of the organic compounds present in the aqueous extracts obtained by interactions, at 70°C during 10 days, of Furiel crude oils with HCl (Fig. 4a) and Citric acid (Fig. 4b).

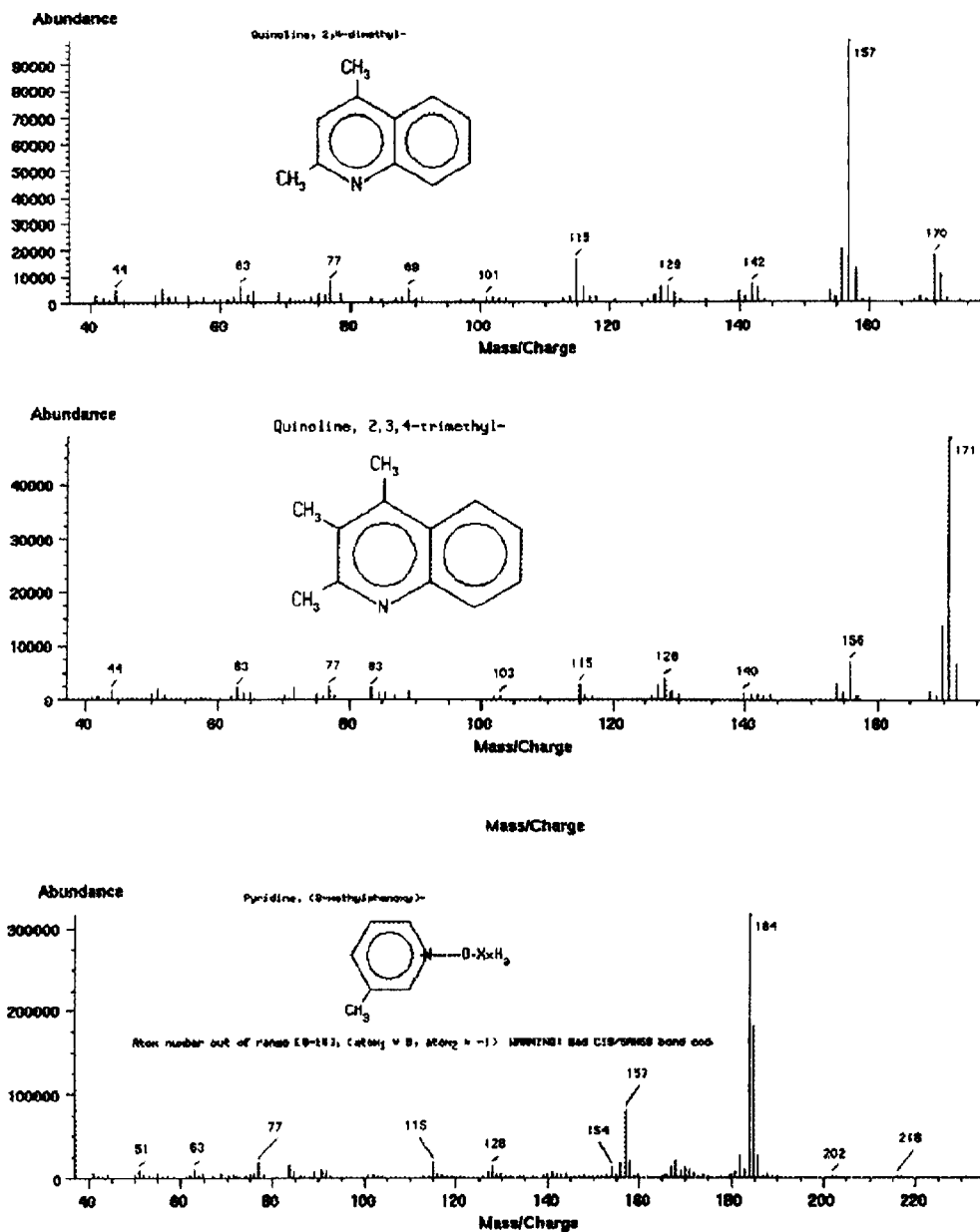


Fig. 5. Examples of nitrogenated compounds present in the aqueous extracts. The figure also shows the corresponding mass/charge (m/z) ratio of each compound.