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MOLECULAR MONITORING OF RESIDUAL CORROSION INHIBITOR ACTIVES IN OILFIELD FLUIDS: IMPLICATIONS FOR INHIBITOR PERFORMANCE

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ABSTRACT

In recent years a number of significant advances in the molecular monitoring of residual corrosion inhibitors in oilfield fluids have been reported. The techniques used, chromatography and mass spectroscopy, provide molecular specificity with high sensitivity, and allow individual molecules to be tracked at low levels (sub ppm) throughout oil production systems.

These analyses have demonstrated for the first time how individual corrosion inhibitor molecules behave in real systems, and the results obtained have shown some interesting phenomena. For example, for a series of quaternary ammonium compounds, the concentrations of residual inhibitor molecules remaining in the fluid is dependant not only on the length of the alkyl chain, but also the degree of methyl branching.

In an attempt to explain these field observations, a number of laboratory partition and surface adsorption experiments have been performed on pure synthetic and industrial grade quaternary ammonium corrosion inhibitor compounds. By relating the results of these laboratory studies with data obtained from the field, a more complete understanding of oilfield corrosion inhibitor behaviour has begun to evolve.

Keywords: corrosion inhibitors, residuals, quats, chromatography, mass spectrometry, partitioning, surface adsorption, performance

INTRODUCTION

In recent years, a number of new developments in the monitoring of residual corrosion inhibitors in oil field fluids have been reported. [1-6] The techniques employed include those based on UV and fluorescence spectrophotometry, [1,2] HPLC [3] and chromatographic and mass spectroscopic techniques such as gas chromatography - mass spectrometry (GC-MS) and electrospray - mass spectrometry (ES-MS). [4-6] Mass spectrometry has particular advantages over other methods of analysis in it's ability to provide high resolution molecular detail with high sensitivity. This has allowed individual corrosion inhibitor actives to be tracked through production systems with particular effect. [4-6]

With these advances, we are now able to monitor changes in the molecular composition of inhibitor formulations as the product is distributed throughout oilfield systems. Active corrosion inhibitor molecules analysed in this way have included quats and imidazolines, and for the former, uptake in the system appears to be dependant not only on chain length, but also on whether the alkyl chain is branched or linear.

This paper will review these field observations, and will describe our attempts at explaining these results through simple laboratory partition and surface adsorption experiments. The possible implications of these studies with regards to performance of the active chemistries will then be discussed.

EXPERIMENTAL PROCEDURE

Pure synthetic quat standards (C12, C14, C16 and C18) were obtained from Aldrich Chemical Co, and a mixed standard prepared with each component present at 10,000 ppm in methanol. Commercially available generic quat actives studied included linear even chain length "Coco" quats derived from a natural palm oil source, and odd chain length (C13/C15) methyl branched and linear quats of synthetic origin. Stock standards were prepared at 10,000 ppm concentrations in methanol.

Oil field brines were analysed following documented procedures. [4-6] Briefly, internal standard (a C18 quat) was added to the sample, and an aliquot passed through a C18 solid phase extraction cartridge. The cartridge was then dried, and the actives of interest eluted off with methanol. This extract was then analysed by gas chromatography - mass spectrometry (GC-MS), or electrospray-mass spectrometry (ES-MS).

Partition experiments were performed by spiking solutions of a model hydrocarbon (decane)/synthetic brine mixture (3% NaCl) with 100ppm equivalent of quat actives. The solutions were mixed well, allowed to settle, and the layers separated by centrifugation. The layers were then isolated, and the molecules of interest analysed directly by GC-MS.

Surface adsorption experiments were performed in sweet or sour CO_2 saturated 3% NaCl solutions, to which was added 500mg of iron powder. The inhibitor was added at an effective concentration of

100ppm, and the species in solution allowed to adsorb for 2 hours. The solid was then isolated by filtration, and extracted with an acidified methanol solution to wash off the adsorbed species. The bulk solution and the solid extract were then analysed by GC-MS.

QUATS ANALYSIS

Quats by GC-MS

Thermolytic fragmentation of quaternary ammonium corrosion inhibitor actives at high temperatures in a GC injection port produces mainly dimethyl alkyl tertiary amines which are readily amenable to analysis by GC-MS (Figure 1). Thus for a typical Coco quat formulation, the dimethyl alkyl amines produced by this process are usually C12, C14 and C16 in length, although carbon chain lengths in the range C8 to C18 have also been observed, dependant on the source of the material. An example GC-MS analysis of a Coco quat containing inhibitor formulation is shown in Figure 2. Clearly evident are the C12, C14 and C16 dimethylalkyl amines, their corresponding benzylmethylalkyl amines, and benzyl chloride.

An example analysis of a synthetic quat formulation is shown in Figure 3. Here two pairs of peaks are observed, the first pair representing linear and methyl branched C13 alkyl chains, the second representing C15 linear and methyl branched alkyl chains. Co - injection of synthetic standards has revealed that the methyl branched isomer is the first compound to elute, which is consistent with the known chromatographic behaviour of methyl branched hydrocarbons. Thus GC-MS is able to differentiate not only between the length of carbon chains in the molecule, but also the degree of branching.

One additional advantage of the GC-MS analysis of quat actives is their fragmentation behaviour in the mass spectrometer. This results in the formation of abundant and diagnostic m/z 58 ions for each of the quat derived alkyl amines (Figure 4). By selectively monitoring this diagnostic ion, a highly selective and sensitive analysis for quats is possible .[4,5]

Quats by Electrospray-Mass Spectrometry (ES-MS)

Recently, the technique of Electrospray - Mass Spectrometry (ES-MS) has been applied with success to the analysis of oilfield chemicals, and in particular , corrosion inhibitor actives. [6] Quats are very responsive to the electrospray ionisation process as they are permanently charged molecules, and as a result ES-MS is a sensitive tool for monitoring these species. As an example, the ES-MS mass spectrum of a Coco quat formulation is shown in Figure 5. Each peak represents the molecular ion of the intact quat molecule with little or no fragmentation being observed. This "soft" ionisation mechanism is an important advantage of ES-MS, and this allows the determination of the active molecules of multi component corrosion inhibitor formulations in a single analysis .[6]

QUAT RESIDUALS

Since the development of GC-MS and ES-MS procedures for quats, a number of production fluids from oilfield locations around the World have been analysed, and some interesting observations have been made. For example, the molecular compositions of the inhibitor formulations are almost always altered following injection of the chemical into the system. In particular, higher molecular weight quats are often shown to become depleted relative to their lower molecular weight counterparts in the residual fluid samples studied.

This effect was particularly pronounced in the case of a gas condensate system that had been treated with a quat containing product . ES-MS analysis of the injected product showed a series of quat actives in the range C8 - C18, with the C12, C14 and C16 components predominating (Figure 6A).

Following chemical injection into the production system however, ES-MS analysis of residual inhibitor in the brine showed a greater predominance of the lower molecular weight C8 and C10 components relative to the longer chain C12 - C18 quats (Figure 6). Such a change in the relative distributions of quat actives has been observed in many other examples of residual analyses performed in our laboratories.

As well as selective uptake of higher molecular weight quats within production systems following chemical treatment, isomeric discrimination has also been observed for synthetic quat actives applied to a Northern European sour gas production system. Analysis of the product injected showed the characteristic pairs of C13 and C15 linear and methyl branched quats, as described previously (Figure 7A). After treatment however, analysis of residual inhibitor associated with the brine solution showed major differences in the relative proportions of these molecules. Whilst the higher molecular weight components were depleted relative to the C13 components, as observed for even chain length compounds, it was also apparent that in this sour system, selective uptake of the methyl branched isomer (C13A and C15A) in preference to the linear isomer had occurred (Figure 7B).

Selective adsorption of higher molecular weight quaternary ammonium compounds onto solid surfaces has been previously reported, [7] and this mechanism could account for the field observations made. However, preferential partitioning of the longer chain components into the hydrocarbon phase could not be discounted. A series of simple laboratory partition and surface adsorption experiments were therefore performed in an attempt to provide an explanation.

QUAT PARTITION EXPERIMENTS

Quaternary ammonium compounds are well known to partition favourably into aqueous oilfield brines and hence are commonly used as components of water soluble corrosion inhibitors . To quantify this in relation to their observed behaviour in production systems, a simple partition test was performed between a model hydrocarbon solution (decane) and a synthetic 3% NaCl brine. This partition test was performed at ambient temperature with a loading of 100ppm quat (as actives).

In the case of the synthetic quat mixture, the quat active molecules were observed to partition almost exclusively into the aqueous phase (> 98%). Only the C18 compound was observed to partition to any extent into the oil (ca. 1%). Little if any change in the relative proportions of individual molecules was observed in comparison with the standard (Figure 8). Similar partition results were obtained for the synthetic C13/C15 quat mixture, and in particular, no discrimination between linear and methyl branched alkyl chain quats was apparent.

QUAT SURFACE ADSORPTION STUDY

The surface adsorption characteristics of a variety of quat actives were studied by dosing inhibitor molecules into CO_2 saturated brine containing finely suspended iron filings. After a two hour period, the solid was isolated by filtration, and the adsorbed actives washed off with acidified methanol. The extract was then analysed alongside a sample of the bulk solution. For the even chain quat mixture adsorbed under sweet conditions, a marked increase in the amount of inhibitor adsorbed to the surface was observed with an increase in molecular weight (Figure 9). Such an observation has been previously reported for C13/C15 quats analysed by TOF-SIMS, [7] and is consistent with the data obtained from residual analysis of quat inhibitors in the field.

For the C13/C15 quat mixture, a similar preferential adsorption of the higher molecular weight C15 quats was observed (Figure 10), with elevated levels relative to the standard associated with the solid, and depleted levels in the brine. For the isomeric components under sweet conditions, the linear isomer appeared to be adsorbed in preference to the methyl branched isomer. This appears to contradict the observations made in a real field system, where the residual in the brine was dominated by the linear molecule, and depleted in the branched molecule. As this production system was sour, this could account for these differences, although the exact reasons why this occurs are not clear at this stage. An attempt was made to perform the adsorption experiments under sour conditions by the addition of sodium sulphide to the CO_2 saturated brine, but we were unable to reproduce the field observations. Interestingly however, significantly less residual was observed in the bulk fluid after treatment, a fact which could account for the enhanced performance of quaternary ammonium compounds under sour conditions. Further work is in progress to understand the fundamental mechanisms of surface adsorption in relation to quats, and to correlate their laboratory and field behaviour with electrochemical performance measurements.

CONCLUSIONS

1. The monitoring of residual corrosion inhibitor actives in oilfield brines with high resolution molecular specific techniques such as GC-MS and ES-MS has revealed some interesting insights into how inhibitor molecules behave in real systems.

2. For a series of quaternary ammonium compounds, the concentrations of residual inhibitor molecules remaining in the field fluids is dependant not only on the length of the alkyl chain, but also the degree of methyl branching.

3. By use of simple laboratory surface adsorption and partitioning experiments, the dominant mechanism that controls the redistribution of quaternary ammonium actives in field systems would appear to be surface adsorption.

4. Further work is in progress to try and understand the fundamentals of this adsorption process in relation to inhibitor performance, and system conditions.

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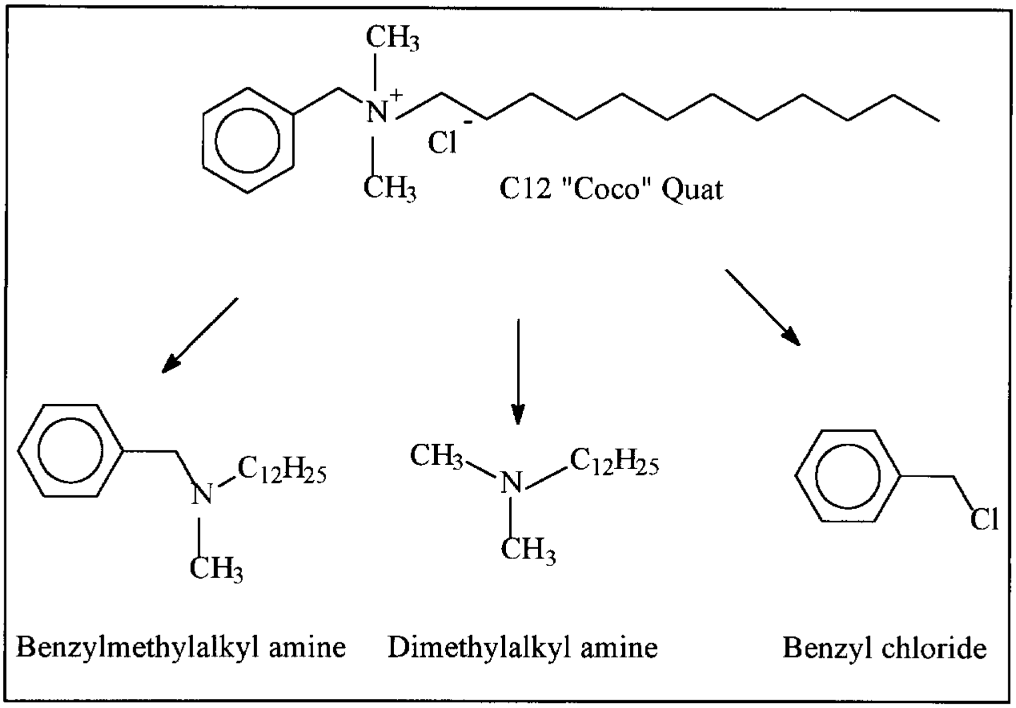

FIGURE 1 - Thermolytic fragmentation of Quat actives by GC-MS

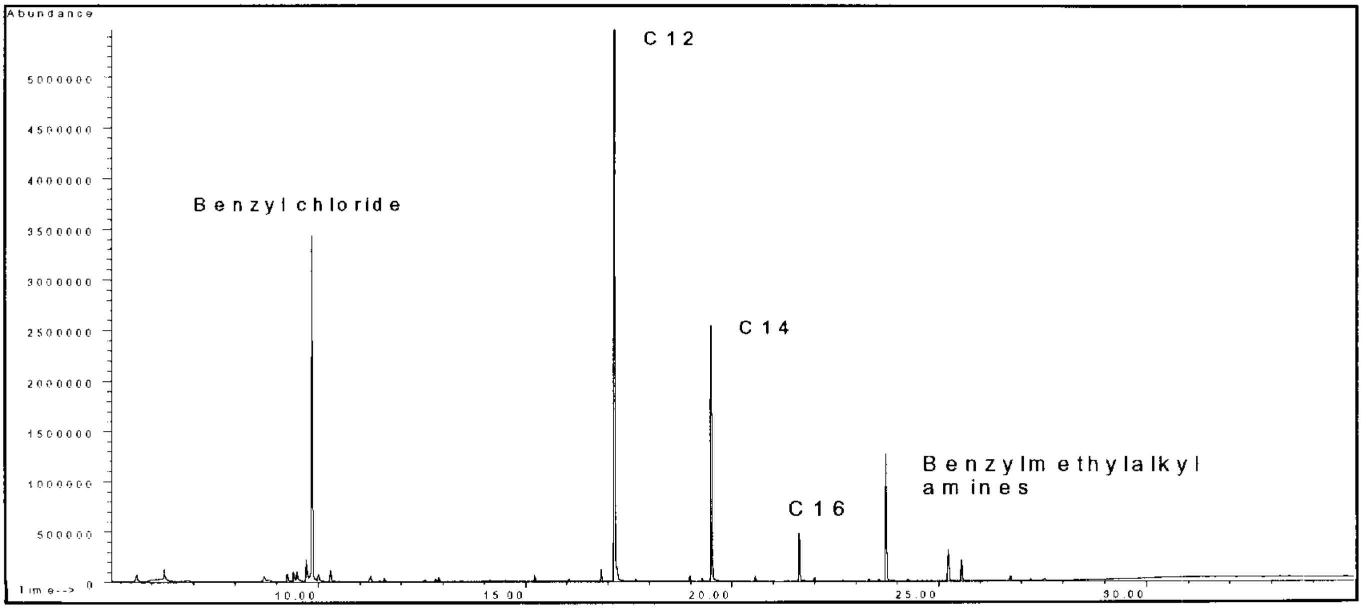

FIGURE 2 - GC-MS of a typical "Coco" quat (C12, C14, C16) formulation

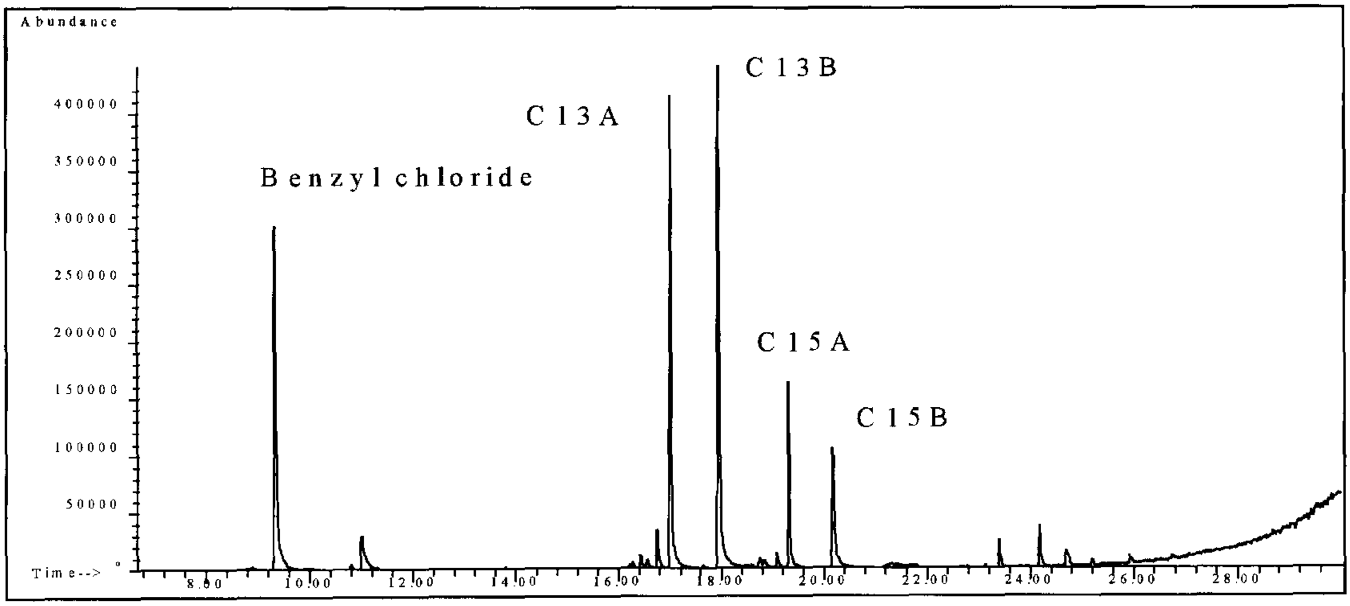

FIGURE 3 - GC-MS Analysis of a synthetic C13/C15 quat mixture (A: methyl branched alkyl chain and B: linear alkyl chain)

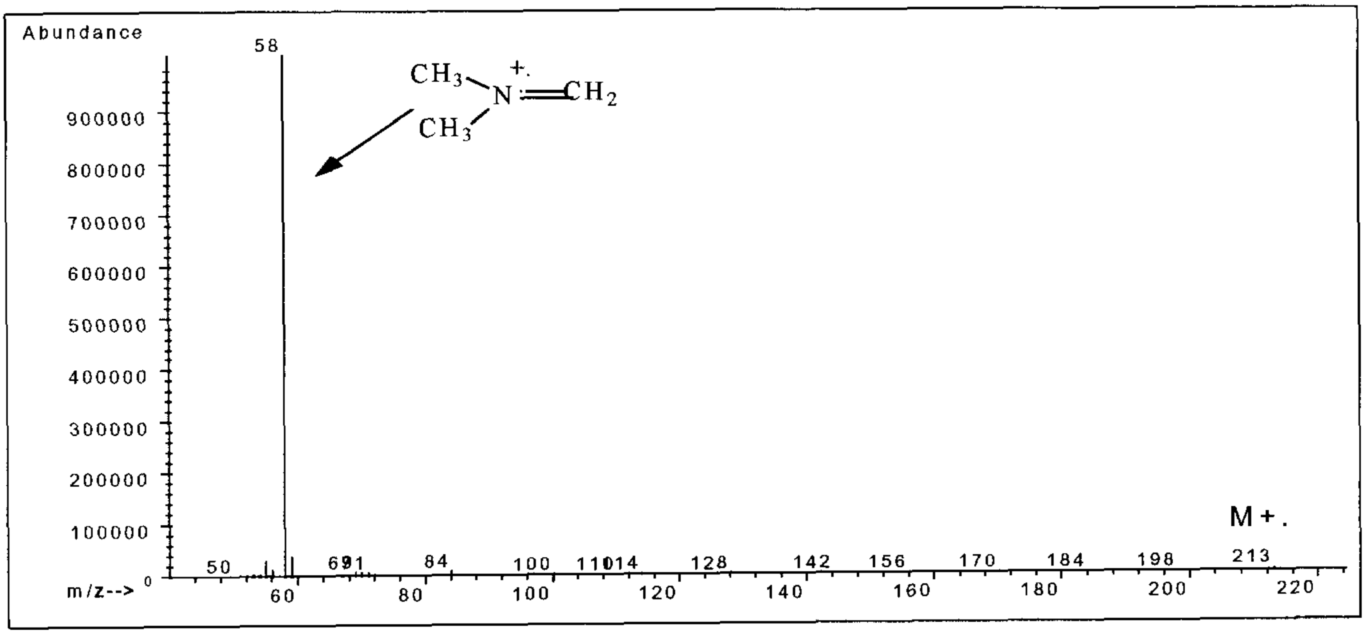

FIGURE 4 - Electron impact mass spectrum of a C12 dimethyl alkyl amine

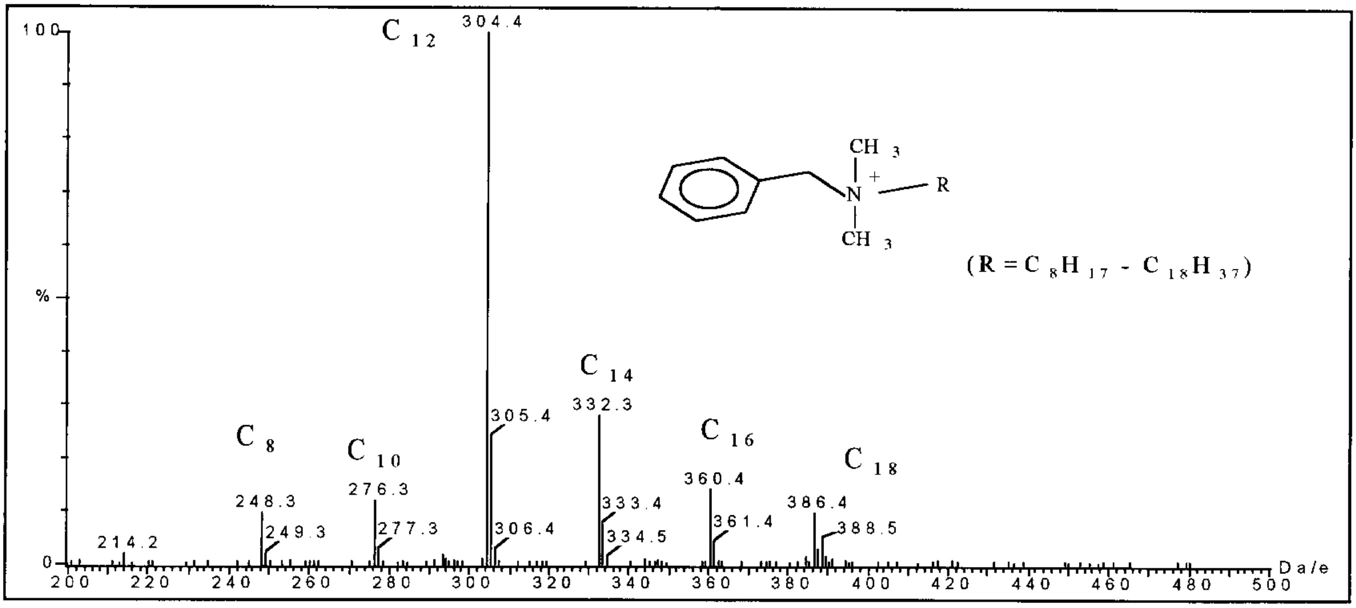

FIGURE 5 - Positive ion ES-MS mass spectrum of a benzalkonium chloride type Coco quat

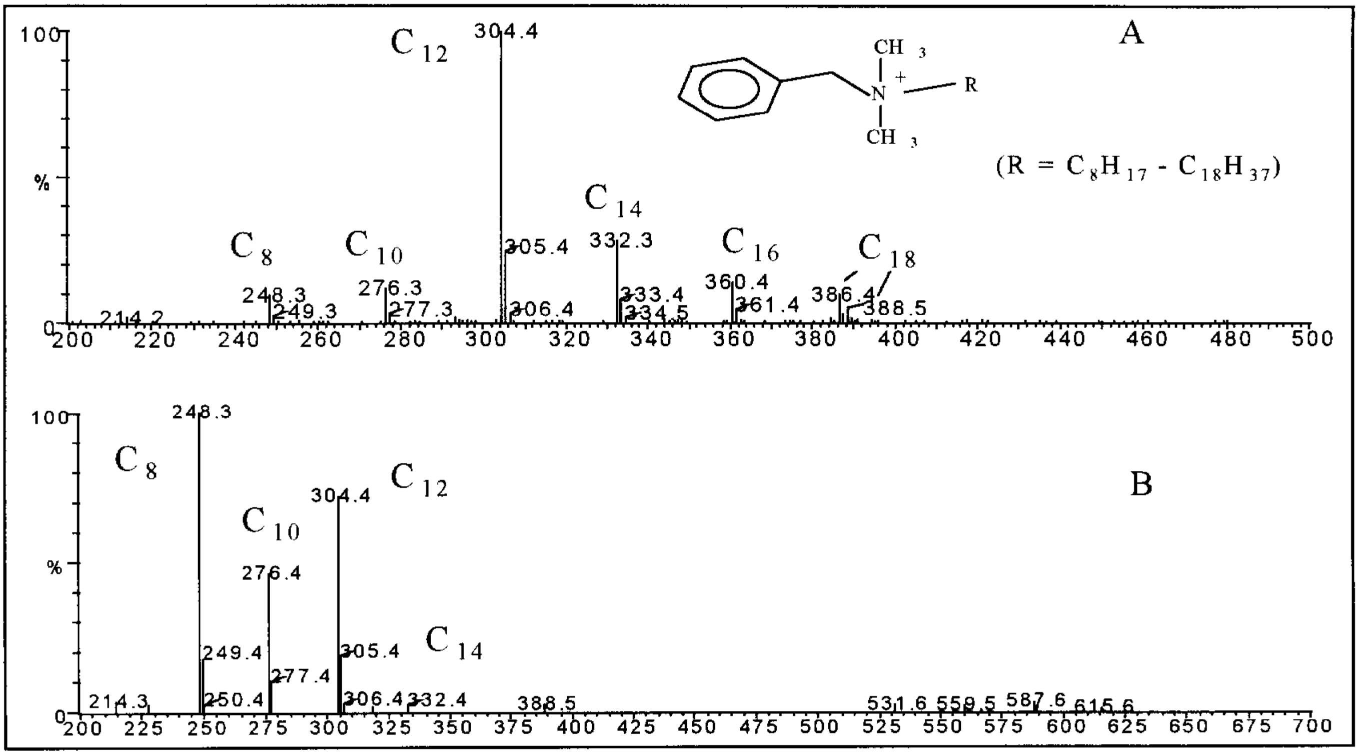

FIGURE 6 - ES-MS analysis of a quat containing product (A) before chemical injection and (B) the residual profile obtained by ES-MS analysis of the treated brine

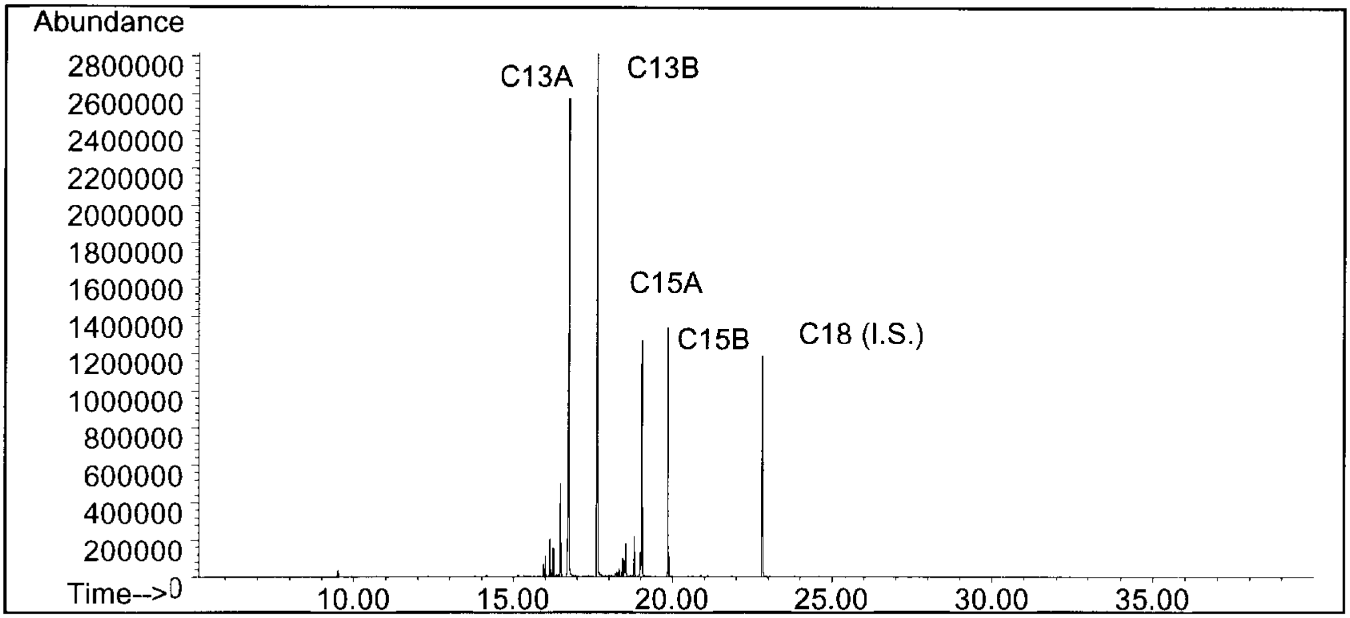

FIGURE 7A - GC-MS of a synthetic C13/C15 quat product before chemical injection

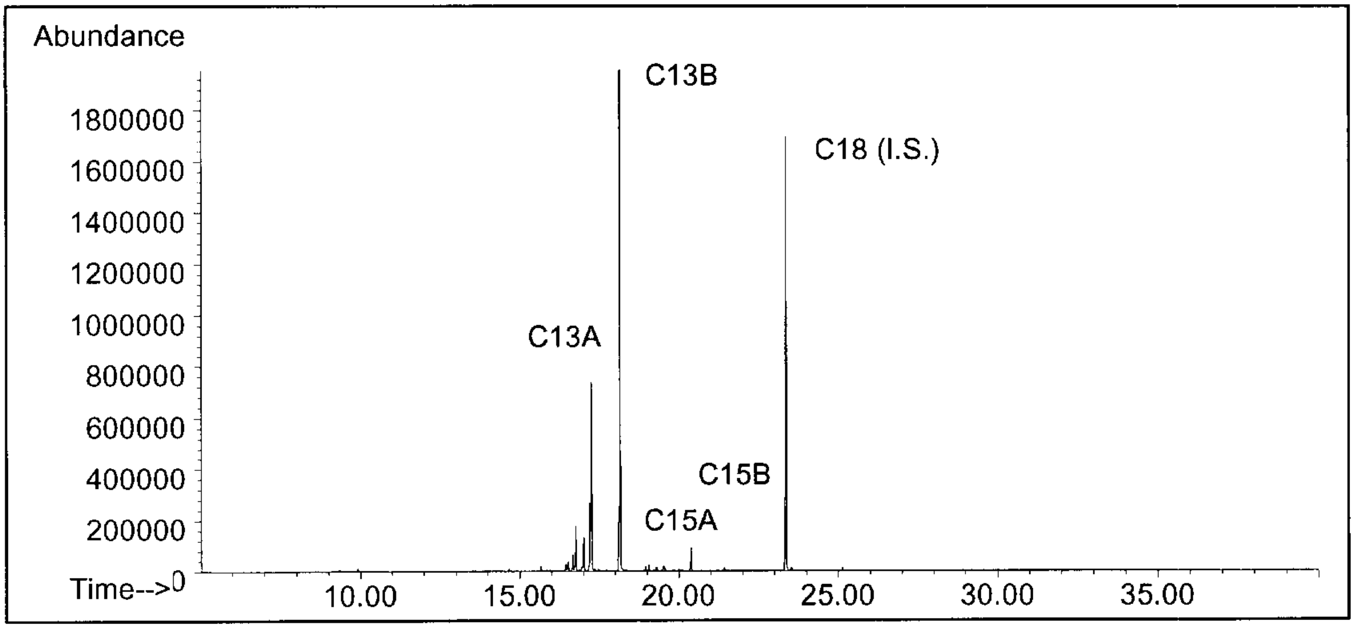

FIGURE 7B - GC-MS of residual C13/C15 synthetic quat actives isolated from a produced water sample

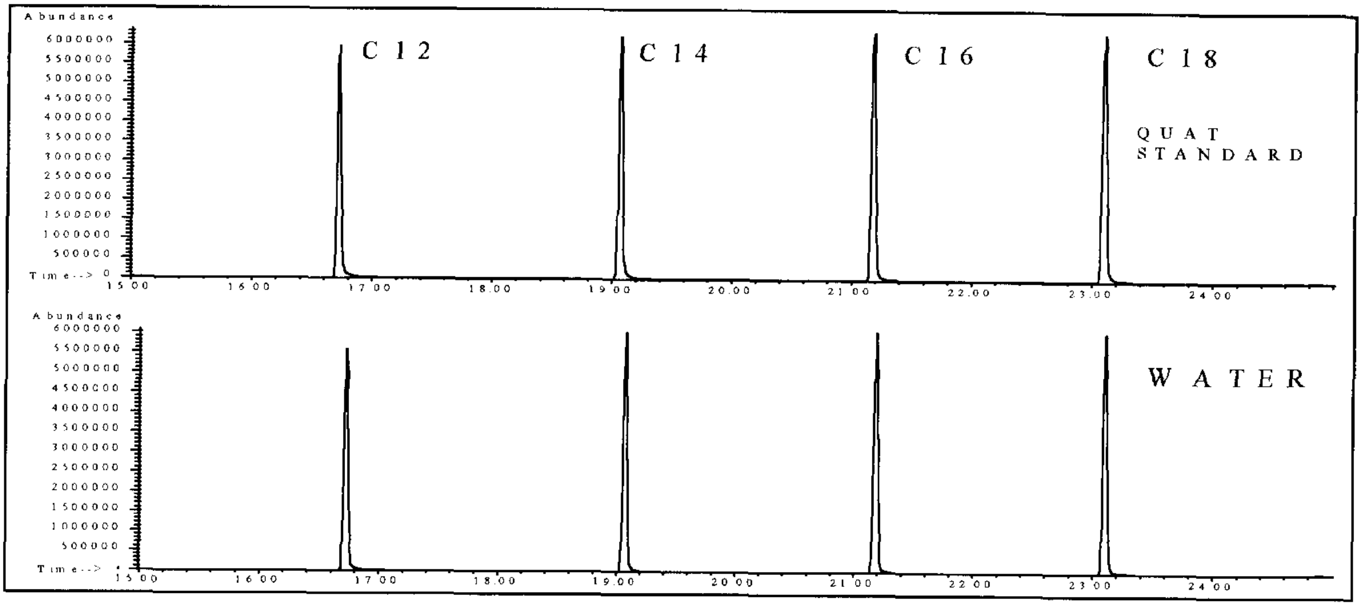

FIGURE 8 - GC-MS of aqueous phase associated C12, C14, C16 and C18 quats after partitioning, and the corresponding quat standard

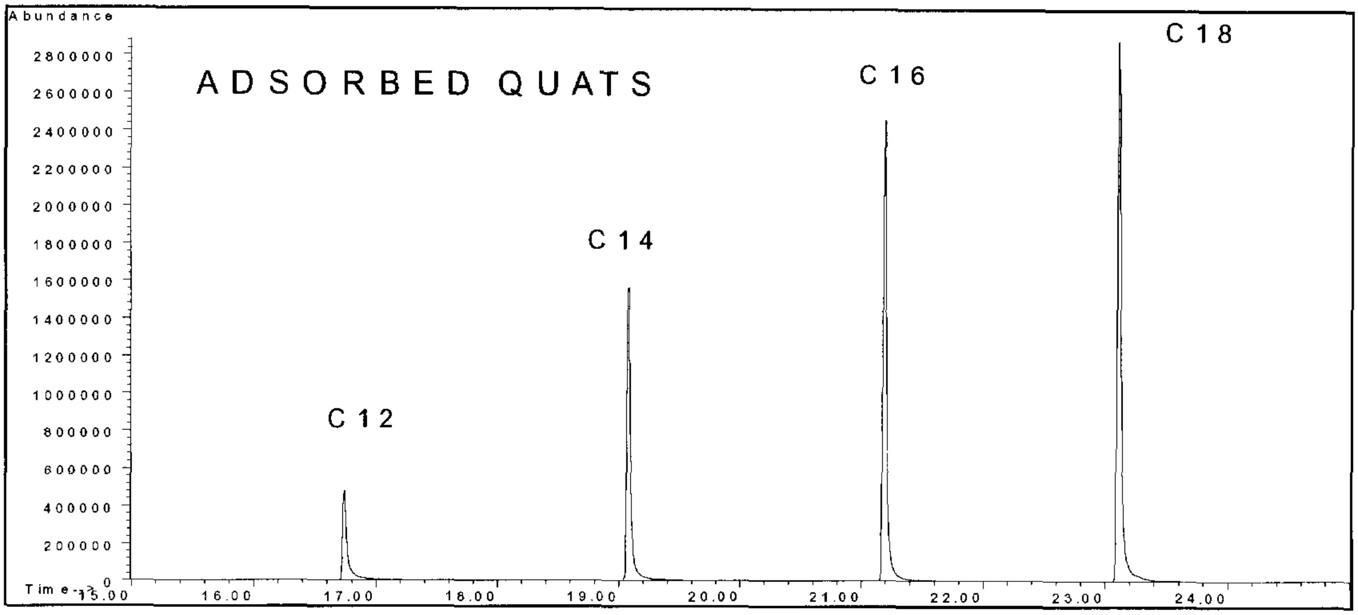

FIGURE 9 - Surface adsorption characteristics of C12, C14, C16 and C18 quats analysed by GC-MS

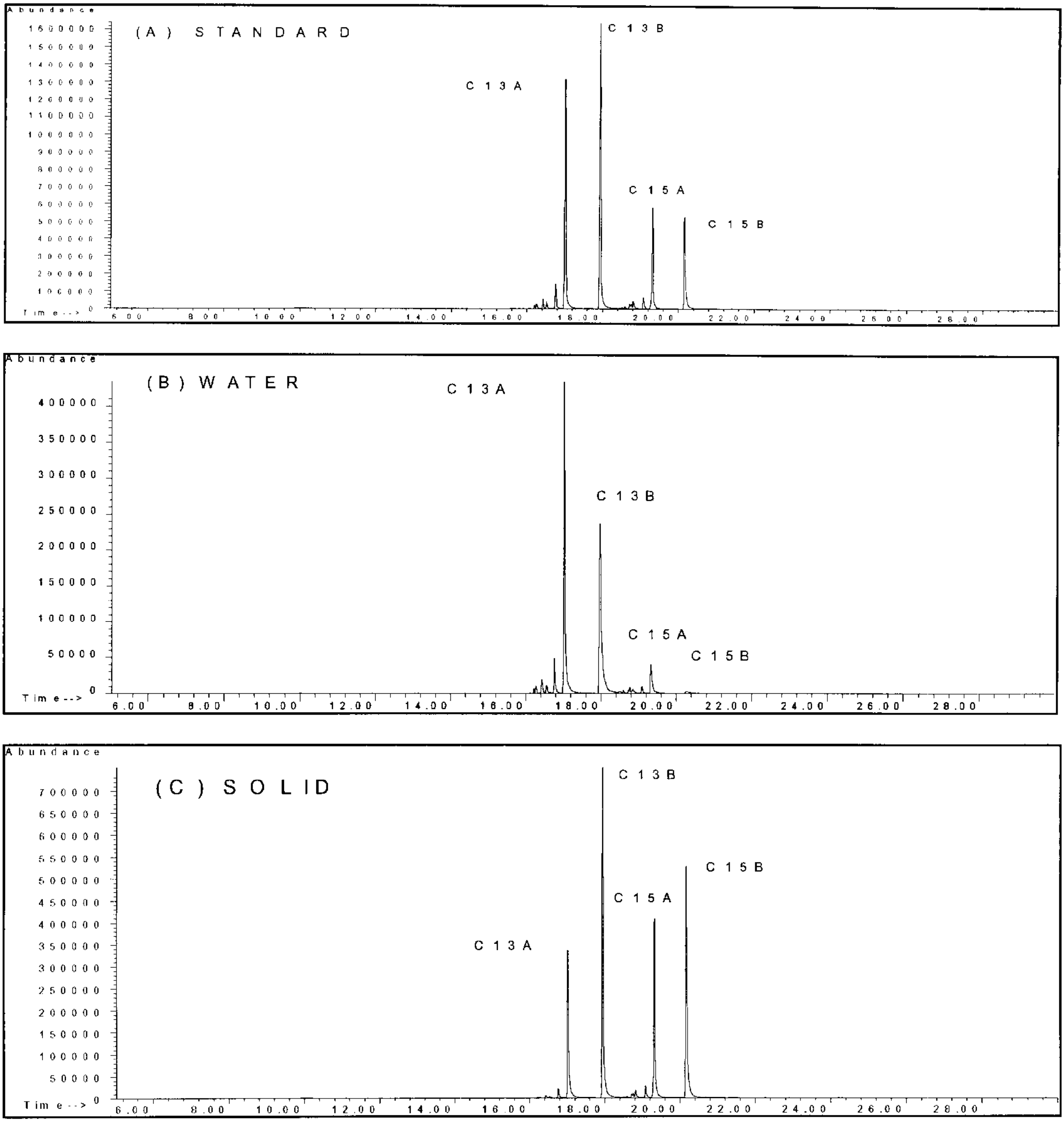

FIGURE 10 - Surface adsorption of C13/C15 quat actives: a) standard quats, b) Quat residual in the aqueous phase and c) quats associated with the solid phase.