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STUDY OF TWO CHROMATOGRAPHIC TECHNIQUES (GPC AND TLC) FOR THE SEPARATION AND SPECIATION OF S, V AND Ni IN PETROLEUM PRODUCTS

by

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LIST OF ABBREVIATIONS

DCM: Dichloromethane

GPC: Gel Permeation Chromatography

HMW: High Molecular Weight compounds

HPLC: High Performance Liquid Chromatography

HR-ICP MS: High Resolution-Inductively Coupled Plasma Mass Spectrometry

ICP MS: Inductively Coupled Plasma Mass Spectrometry

IE: Ion Exchange

LA: Laser Ablation

LC: Liquid Chromatography

LMW: Low Molecular Weight

LOD: Limits Of Detection

LR: Low Resolution

MMW: Medium Molecular Weight

MR: Medium Resolution

NP: Normal Phase

ppm: parts per million

RP: Reversed Phase

SARA: Saturate, Aromatic, Resin and Asphaltene

SEC: Size Exclusion Chromatography

SEM: Scanning Electron Microscope

THF: Tetrahydrofuran

TLC: Thin Layer Chromatography

UHPLC: Ultra High Performance Liquid Chromatography

UV: Ultra Violet

VD: Vacuum Distillates

VR: Vacuum Residues

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1. INTRODUCTION

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1.1. CONTEXT

There is a need for alternative sources of carbonaceous fuels as the demand for transportation energies increases and the availability of classic crude oil sources decreases. Oil companies must therefore make better use of lower quality resources to produce fuels such as heavy crude feedstocks (such as Venezuelan oils) and refinery residues (Vacuum Residues, VR), which are transformed into light products for being used as energy sources and converted into transportation fuels [1], [2].

Heavy oils are contaminated with metals, present in crude oils at concentration levels of hundreds of ppm, or heteroelements such as sulfur present at several percents [2]. Nickel and vanadium are the most abundant metals in petroleum and occur partly as organometallic compounds (metalloporphyrins) [3]. The problems that can be caused by these elements include the deactivation of refining catalysts, corrosion of the equipment and environmental pollution [2], [3]. Thus, metals and non-metals are generally undesirable and must be extracted or reduced to very low levels from the heavy fractions of crude oils before processing them into fuels.

Demetallation to remove nickel and vanadium and desulphurization of the feed are involved in the hydroconversion processing of heavy fractions prior to their catalytic cracking processes in order to protect the catalysts [1]. Their treatment is therefore more complicated compared with the processing of conventional oils as the concentration of metals and non-metals are generally higher, which also raises the overall refining costs [4], [5].

The most suitable methods to achieve metal and non-metal speciation in petroleum samples, in order to optimize their removal, are based on the combination of chromatographic separation with element specific detection [6].

Inductively Coupled Plasma Mass Spectrometry (ICP MS) was found to be the best choice for trace element determination in oil and derivatives because it offers several advantages, such as:
- High sensitivity.
- Simultaneous multi elemental analysis.
- Low Limits Of Detection (LOD).

However, the introduction of organic matrices into ICP MS is a difficult task due to:
- Polyatomic interferences by the formation of polyatomic ions with carbon, oxygen, argon and nitrogen.
- Carbon deposits at the interface and on the ion lenses.
- Decrease of the sensitivity and ion transmission.
- Matrix effects due to the introduction of organic solvents.
- Perturbation or extinction of the plasma.

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Therefore, the oxygen/argon ratio and the use of nebulizers and High-Resolution ICP-MS systems should be considered [3], [5], [7].

One of the most widely used separation technique for the analysis of petroleum products ,the Gel Permeation Chromatography (GPC), separates molecules according to their molecular sizes (hydrodynamic volumes) using mobile phases consisting of organic solvents, the same solvents are used to dissolve or dilute crude oil. The most commonly used solvents are xylene or tetrahydrofuran (THF), with porous gels for the molecular separation. This separation method provides useful information for a better understanding of the diffusion of metal and non-metal species within the pores of petroleum processing catalysts [5], [6].

1.2. INTEREST

The interest of the oil industry to increase processing of ever more heavy crude oils into lighter products (gasoline, diesel, etc.) is spurred by the increasing energetic demand and the large negative impact of vanadium, nickel and sulfur (catalyst poisoning, corrosion and environmental pollution), so the extraction of these elements from heavy fractions is required. Information on the size and chemical form in which these species are present (speciation) is important for the choice and optimization of the porosity of hydrodemetallation and hydrodesulfurization catalysts necessary to allow their effective removal during petroleum refining [2], [5], [6], [8], [9].

The presence of vanadium and nickel metalloporphyrins in crude oil is important not only from the economic and environmental point of views but also because they are often used as tracers in geochemical prospecting. The nickel/vanadium ratio has an important role in the classification of petroleum sources by their geochemical origins [2]–[6], [8]–[10]. However, metals complexed in these porphyrins are only a small amount of the total metal content in the oil. The rest of the metal is bonded to unidentified high molecular weight complexes (non-porphyrins) whose existence is only hypothetical [11].

1.3. OBJECTIVES

The goal of this work is to study the speciation of metals (nickel and vanadium) and sulfur in solutions of heavy oil fractions and crude oils. Separation by size of sulfur, vanadium and nickel containing compounds using GPC columns and multi elemental analysis of these species by ICP High Resolution MS will be achieved.

1.4. BIBLIOGRAPHIC STUDY

1.4.1. Definition and composition of oil

Crude oil, also called petroleum ("rock oil"), is the most profitable and practical source of energy.

It comes from the chemical and microbiological decomposition of plants and animals organic matter, under high pressure and high temperature.

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Crude oil is a complex hydrocarbon mixture, therefore not ideal for analysis, containing a low percentage of sulfur, nitrogen and oxygen compounds along with trace amounts of heavy metals (mainly vanadium and nickel) and other elements. The composition of crude oil varies depending on its geological origin [2], [4], [5].

The main families of petroleum compounds are known to be:
- nParaffines and isoparaffines (alkanes).
- Naphthenes (cycloalkanes).
- Aromatic and polyaromatic structures.
- Heteroatomic structures.
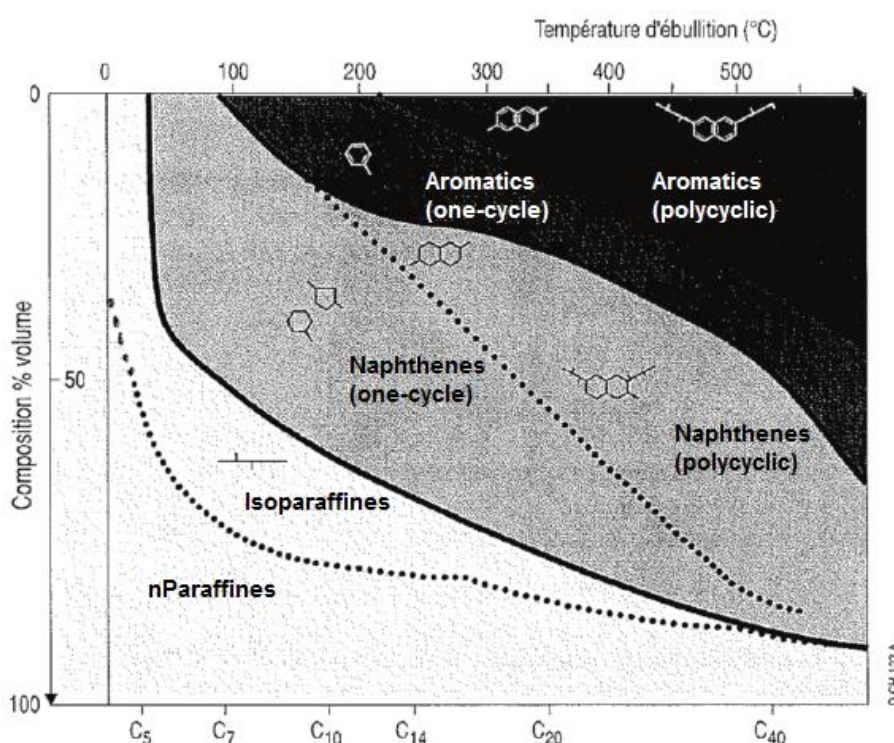
Figure 1. Composition of a crude oil [12].

A crude oil can be separated by distillation according to the boiling points in the following cuts, which are then treated according to their uses:
- Gas: gaseous at room temperature methane (CH_4), butane (C_4H_{10}).
- Gasoline: distilled at 180 ° C.
- Kerosene: distilled between 150 and 240 ° C.
- Diesel: distilled between 210 and 350 ° C.
- Residues: non-distillable fraction at atmospheric pressure, > 390 ° C.
- Vacuum Distillates (VD): vacuum distilled fraction 350-550 ° C.
- Vacuum Residues (VR): no vacuum distilled fraction> 550 ° C.

Light cuts (gas, gasoline and kerosene) consist mainly of simple and branched alkanes from 1 to 20 carbons, cycloalkanes and rarely one-cycle aromatics. Diesel can contain

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compounds up to four cycles, some containing nitrogen or sulfur. Heavy fractions (VD or VR) consist principally of cycloalkanes and polycyclic aromatics and heteroatomics [12].
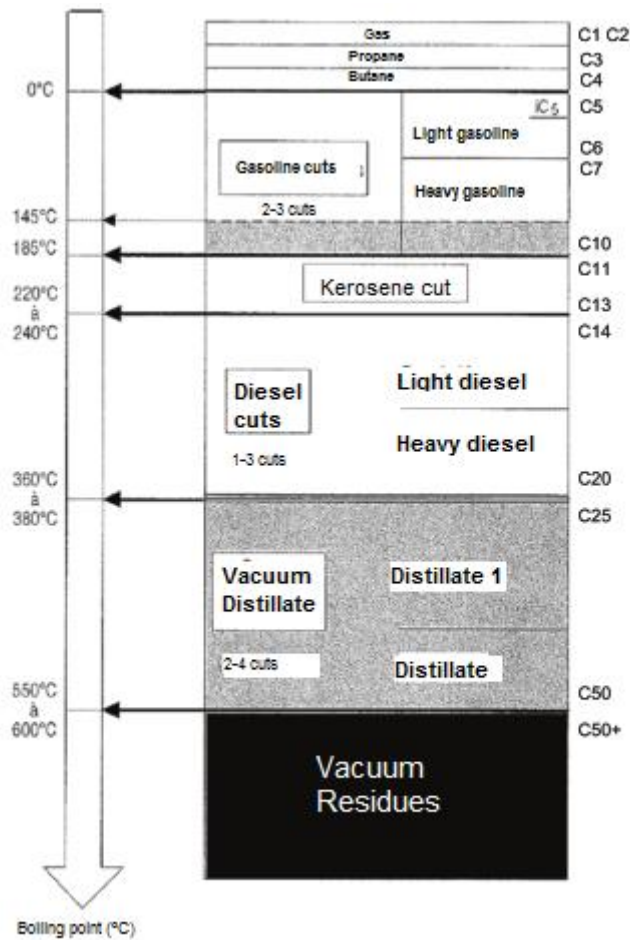
Figure 2. Illustration of the different distillation cuts of a crude oil [12]*.*

Heavy oil fractions:

Crude oil is composed of "light" or "heavy" fractions. Heavy fractions are defined as molecules containing more than 25 carbon atoms and presenting a structural complexity which increases with the boiling point (*Figure 3*) [1].
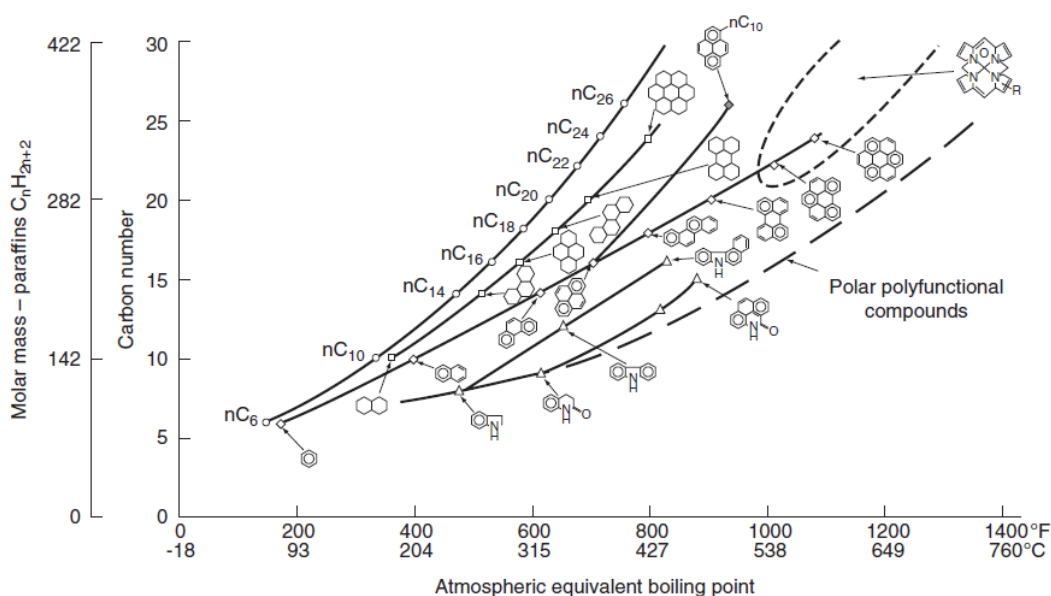
Figure 3. Increase of molecular structures with the boiling point [1]*.*

As conventional oil reserves are decreasing, an increasing focus is made on unconventional reserves. These consist of heavy oils and are more difficult to treat compared to the light ones since their refining and conversion to light products requires expensive hydrotreatment steps, demetallation and desulfurization. To improve the efficiency of such processes, it is necessary to improve the characterization of these heavy oils, but they are of a very high complexity and fractionations by polarity have to be carried out in order to simplify these matrices.

The main characteristics of heavy oils (high viscosity and significant content of heteroatoms) are directly related to the significant presence of highly polar compounds, such as resins and asphaltenes [1]. Asphaltenes, the fraction of petroleum insoluble in alkanes (pentane or heptane) and soluble in toluene, contain high amounts of molecules of variable aromaticity with different contents of heteroatoms, such as sulfur, and complexed metals, such as nickel and vanadium, which are harmful compounds to the conversion processes and to the environment [2].

1.4.2. Metals in crude oils

Crude oil is a naturally occurring complex matrix composed predominantly of saturated and aromatic hydrocarbon mixture, but also containing sulfur, nitrogen, oxygen compounds, metals (mainly Ni and V), emulsified water and minerals [4], [5].

Metals are more concentrated in heavy crude oils, specifically in the heaviest polar fractions, at relatively high concentrations [4], [6], [9]. The most abundant metals in petroleum are nickel and vanadium, except when contaminated with co-produced salts (chlorides of sodium, magnesium, calcium etc.) or corrosion products introduced during transportation (e.g. iron) [5]. Nickel and vanadium are thought to exist as porphyrin complexes in a range between 10 and 1000 ppm [2], [6], [9], [11].

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The existence of nickel and vanadium complex in crude oils is important for both economy and environment since they are responsible for the deactivation by pore clogging of hydrocracking catalysts for petroleum desulfurization treatments, which results in an increase in the formation of gas and coke and a reduction in the amount of gasoline produced [5]. A better understanding of the nature of these metals in petroleum is of relevance. These metals are extracted from crude oil by demetalling units, prior to refining [4], [9], [10], [13].

The composition of crude oil is known to vary depending on several characteristics including type of geological formation, location, age of the rocks and depth. These factors can cause the metal concentration to change considerably. Both the absolute concentration of metals and the nickel/vanadium ratio, constant in crude oils of common source rocks, are useful for oil geochemical classification. The nickel/vanadium ratio also provides valuable geological information, such as the maturation and the environmental conditions present during sedimentation [4], [5], [9]–[11].

Nickel and vanadium occur mainly in petroleum samples in the following forms:
- Non-polar metalloporhyrin compounds which complex principally nickel, vanadium, iron or copper.
- Poorly characterized and hypothetic (not confirmed) high molecular weight polar non-porphyrinic species.
- Naphthenic acid salts which bind principally Ca, Mg, Zn and Ti [2], [9], [14].

There are no nickel and vanadium species in saturated fractions of crude oils but the nickel and vanadium porphyrins are predominantly present in the heavy polar fractions of crude oil (about 95% of total concentration in VR), meaning that they are not highly volatile compounds [15]. Porphyrins are strongly associated with asphaltenic components by π-π bonding or can be trapped in the asphaltene aggregates or macromolecular networks and often cannot be identified [2], [4], [5], [9], [11].

Porphyrins were described in the beginning of the 20th century as tetrapyrrolic complexes of vanadyl (VO^{2+}), iron (II) and nickel (II) with structures similar to chlorophyll pigments, which predominate in plants, and the heme pigments, which occur are most significantly in animals (*Figure 4*). The wider distribution and higher concentrations of chlorophyll pigment reported suggest that chlorophyll is the most common precursor of metalloporphyrins, after their degradation, replacing the Mg^{2+} at the sediment-water interface by Ni^{2+} and VO^{2+} under the prevailing Eh (redox potential) and pH conditions. The high chelating constant resulted in high stability of these compounds [4], [16].

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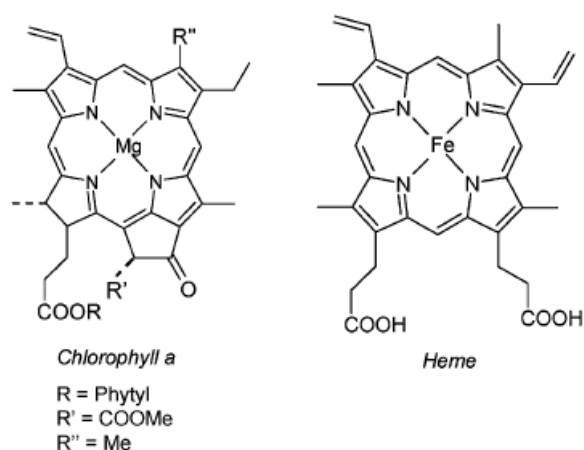
*Figure 4. Possible biological precursors of petroporphyrins* [2]*.*

Porphyrins are present in petroleum predominantly as vanadyl and nickel chelated compounds. Six main types of these porphyrins have been identified: etio porphyrins (ETIO) and deoxophylloerythroetio porphyrins (DPEP), dicyclic-deoxophylloerythroetio porphyrins (di-DPEP), rhodo-etio porphyrins (rhodo-ETIO), rhodo-deoxophylloery- throetio porphyrins (rhodo-DPEP), and rhodo-dicyclic-deox- ophylloerythroetio (rhodo-di-DPEP). The most abundant were reported to be ETIO and DPEP. Regarding the nickel porphyrins, ETIO homologues are largely predominant; vanadium is usually complexed by either etio porphyrins or DPEP [2], [10], [17]. In addition, three new species of vanadyl porphyrins corresponding to molecules of $C_nH_mN_4VO_2$, $C_nH_mN_4VO_3$, and $C_nH_mN_4VO_4$ have been recently discovered in crude oil. *Figure 5* shows their possible structures [17].

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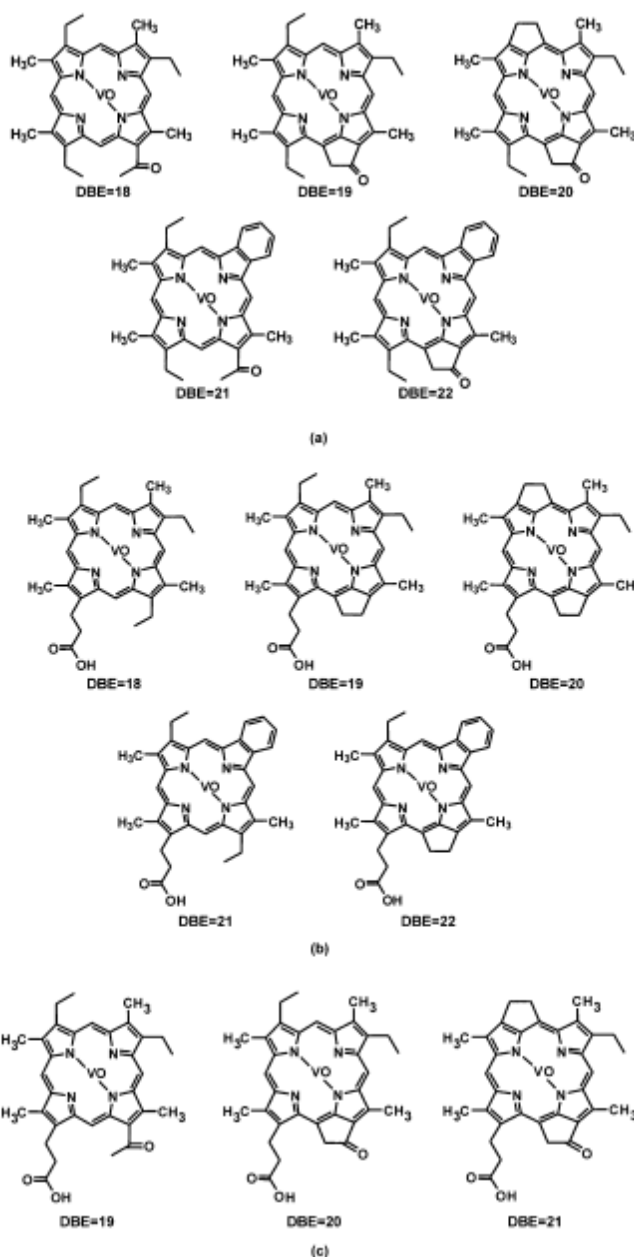
Figure 5. Proposed structures of new class species of vanadium compounds in Venezuela Orinoco crude oil subfractions: (a) for $N_4V_1O_2$, (b) for $N_4V_1O_3$, and (c) for $N_4V_1O_4$. DBE is the number of rings plus double bonds to carbon [17].

1.4.3. Sulfur in crude oils

Sulfur concentration may reach a range between 0.04 and 5 %,making it one of the most abundant heteroelements in crude oils [2], [5].

Sulfur is generally found in the form of thiols, sulfides, disulfides, thiophene, dibenzothiophene and alkyl derivatives of these molecules; H_2S can also be present, depending on the crude oil source [5].

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The content of sulfur is problematic for petroleum industries and needs to be removed by efficient desulfurization processes, such as hydrodesulfurization, before refining processes. Some problems with the refining process can be related to the presence of sulfur containing compounds, which is frequently the main contaminant of crude oil. These problems include corrosion, instability of the final products and catalyst poisoning [5].

The presence of sulfur in fuels is also responsible for the emission of toxic sulfur dioxide into the atmosphere after the combustion of petroleum products, leading to environmental contamination and health problems. That is why many countries have approved environmental regulations that require a reduction in sulfur levels in fuels; therefore, producers are searching for effective sulfur-removal processes [5], [9]. According to the European legislation, the sulfur concentration in gasoline and diesel should be less than 10 ppm from 2009 what makes the knowledge about the sulfur speciation at low detection limits important for oil industries in order to improve its extraction from the crude oil and the production of the demanded very low sulfur content fuels [2], [18].

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2. EXPERIMENTAL

2.1. MATERIALS

2.1.1. Solvents

Tetrahydrofuran (THF) Multisolvent® GPC grade ACS, stabilized with 250ppm of 2,6-Di-tert-butyl-4-methylphenol (BHT) from Scharlau.

2.1.2. Samples

A crude oil provided by Total.

A VR provided by IFP Energies nouvelles.

2.1.3. Dilutions

The oil samples were analyzed diluted in stabilized THF with dilution factors of 100 for the Total crude oil and 160 for the IFP VR. Dilutions were made by weight, using a precision scale.

Figure 6. Picture of the precision scale used.

2.2. EXPERIMENTAL TECHNIQUES AND METHODOLOGY

2.2.1. ICP MS

An ICP-MS (Inductively Coupled Plasma Mass Spectrometry) device detects and quantifies the isotopes of the elements present in a sample. The molecules introduced are atomized and ionized by an argon plasma at 8000 °C. The different isotopes are then detected according to their m/z ratio and the intensity of each isotope is measured. ICP MS is applied for trace element determination in oil and derivatives because of its known advantages, such as low LOD, multielemental measurement capability and high sensitivity. The instrument used in this project is an ELEMENT XR HR ICP MS from Thermo Scientific.

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The most important parts of an ICP-MS are:

- Sample introduction:

Samples are introduced by a nebulizer which creates an aerosol from the liquid solution. This aerosol is driven by an argon carrier gas into the plasma. Normally, only a small homogeneous part of the aerosol created by the nebulizer is injected, the rest is removed through a drain. In this case, there is no drain as a total consumption nebulizer is used. The nebulization chamber used for total sample injection is heated to enhance the introduction of organic matrices.

- ICP plasma source:

The plasma used in an ICP-MS is made by a quartz torch and consists of ionized argon atoms at 8000 ° C. This high temperature desolvates, volatizes, atomizes and ionizes the molecules of the sample introduced. The ions formed should be elementary and monocharged.

- Interface:

Before mass separation, the beam of ions formed in the plasma is focused into the mass-analyzer by two cones (sampling cone and skimmer cone) and an ion lens. The cones used are made of platinum instead of nickel, for the analysis of organic matrices as they are more resistant to the corrosion in the presence of oxygen used during organic analysis.

- Mass filter / detector:

The mass filter separates the ions introduced by means of their m/z ratio. On the ELEMENT XR HR ICP MS, separation occurs first in a magnetic sector and then in an electrostatic sector (double focusing magnetic sector field ICP-MS) and the detection system combines a dual mode Scanning Electron Microscope (SEM) with a Faraday detector for a linear response over 12 orders of magnitude.
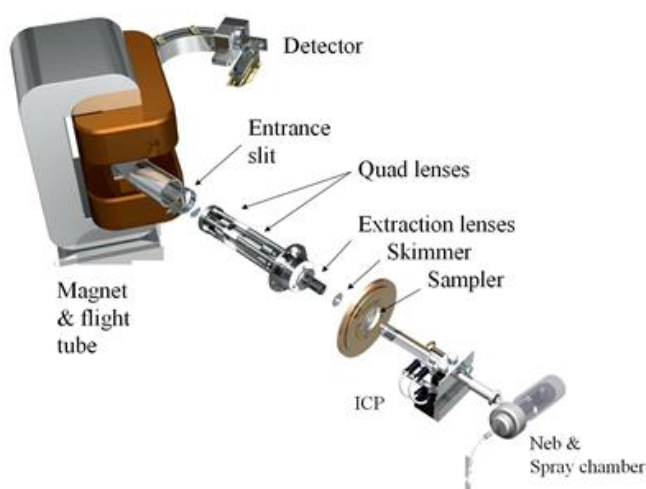

Figure 7. HR-ICP MS schematic diagram [19].

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However, ICP MS has several limitations and interferences. The formation of polyatomic or multicharged or polyatomic ions may happen, creating isobaric or polyatomic interferences on the m/z measured values. To overcome these problems a collision cell or correction equations can be used. It is also possible to solve these interferences by the analysis of the non-interfered isotope of the element or the use of high-resolution ICP-MS systems.

Analyte	Interference
$^{56}Fe = 55.93494$	$^{40}Ar^{16}O = 55.95729$
$^{75}As = 74.92160$	$^{40}Ar^{35}Cl = 74.93123$
$^{52}Cr = 52.94065$	$^{37}Cl^{16}O = 52.96081$
$^{40}Ca = 39.96259$	$^{40}Ar = 39.96238$
$^{87}Sr = 86.90889$	$^{87}Rb = 86.90918$

Table 1. Examples of polyatomic interferences in ICP MS.

In this case, the introduction of organic samples may also cause carbon deposition on the sampler and skimmer cones and on the ion lenses. Oxygen has to be added and the oxygen/argon ratio in the plasma has to be high enough to enable complete carbon combustion.

2.2.2. LC

Liquid Chromatography (LC) is a separation technique in which the separation of the different compounds present in a sample is based on their physical and/or chemical properties.

Of the different types of LC that exist, the techniques used in this project are:

- Size-exclusion chromatography (SEC):

SEC or gel permeation chromatography (GPC) when an organic solvent is used as mobile phase is described below.

- Normal-phase chromatography (NP):

In NP chromatography separation of the sample components is performed in terms of polarity by interactions between these compounds and the stationary phase of the column, but also between these compounds and the mobile phase used as eluent. In this case, the stationary phase is polar. The less polar components will be eluted faster than polar ones with the apolar mobile phase. Thin Layer Chromatography (TLC), a NP chromatographic mode, is described in section 5 named "Future studies".

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Other LC techniques are:

- Reversed-phase chromatography (RP):

Opposite to NP, RP chromatography is carried out with non-polar stationary phases and polar solvents.

- Ion-exchange chromatography (IE):

IE separate charged compounds by the exchange between the ions in the sample and the ions fixed to the charged stationary phase.

2.2.2.1. GPC

GPC is used to separate molecules according to their molecular size or more accurately, according to their hydrodynamic volume. The separation is carried out on liquid chromatography columns made of porous gels. In this type of chromatography there are no interactions between the analyte and the stationary phase but the molecules with higher hydrodynamic volume than the average pore size are excluded and first eluted because they explore only a portion of the porosity. In contrast, smaller molecules are eluted last as they are able to explore a larger part of the porosity. This technique enables to obtain molecular weight distributions.

The popularity of GPC in petroleum analysis is due to the importance of the size of the metal complexes for the adaptation of the size of catalyst pores for the hydrodemetallation process [2].

2.2.3. GPC-HR ICP MS

Chromatographic separations were achieved using a High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP MS) instrument (ELEMENT XR, Thermo Scientific) on-line coupled to three Gel Permeation Chromatography (GPC) Columns (PLgel 5 µm MIXED-D, Agilent) provided by IFP.

The working parameters given in Table 1 were optimized performing mass calibration at low resolution (LR) and medium resolution (MR) and controlling mass offset values daily. The mass calibration is made each time the ICP plasma is turned on using a tune solution containing Li, B, K, Na, Sc, Co, Fe, Ga, Y, Rh, In, Ba, Lu, Tl and U in THF at a concentration of 1 µg/L. The columns are equilibrated at flow rate of 1 mL/min for a least 12 hours before the start of the analyses.

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Thermo Scientific ELEMENT XR HR-ICP-MS	
Power (W)	1500
Plasma Ar gas flow rate (L/min)	16
Auxiliary gas flow rate (L/min)	0.9
Nebulizer gas flow rate (L/min)	0.6
O2 gas flow rate (L/min)	0.08
Mobile phase flow rate, splitted from 1L/min (μL/min)	38
Extraction lens (V)	-2000
Focus lens (V)	-1235
X-deflection lens (V)	-0.25
Y-deflection lens (V)	-0.25
Shape lens (V)	125
Measured isotopes	32S, 51V and 58Ni
Search and integration window (%)	150, 60
Sampling time (ms)	100
Number of sample per peak	10
Detection mode	Triple
Scan type	Escan
Integration type	Average
Mass resolution	Medium (4000)
Agilent PLgel GPC Columns x 3	
Solvent (stabilized THF) flow rate (mL / min)	1
Injected sample volume (μL)	20
ID (mm)	7.5
Length (mm)	300
Stationary phase	MIXED-D
Porosity (Å)	100
Particle size (μm)	5
Column temperature (°C)	21-22

Table 2. GPC-(HR)-ICP-MS operating parameters.

The HR ICP MS was equipped with a quartz injector (1.0 mm inner diameter) and Pt sampler cone, and skimmer cone. GPC columns were coupled to the ICP-MS for the speciation of sulfur and metals by size of the molecules, after a certain equilibration time. However, a splitter is needed at the column outlet to introduce a lower flow of 40 μL/min into the ICP MS by a Dionex™ UltiMate™ 3000 Basic Automated System, which includes a pump and an autosampler. Solutions are delivered into a total consumption nebulizer fitted on a thermostated nebulization chamber at 60 °C by a water/glycol mixture using a RTE–111 thermostat (Neslab, Thermo Fisher Scientific).

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Figure 8. Instrumentation: pump and autosampler (1), GPC columns (2), splitter (3), nebulizer (4), ICP-MS (5) and temperature controler (6).

Methodology:

- The first day of analysis a solution of each sample in stabilized THF was prepared. These two solutions were injected every day of the study several times, up to 13 injections.

- Fresh solutions of each sample in stabilized THF were prepared every day and injected once on the same day of preparation.

- One solution of each sample in stabilized THF prepared on the 24th of February 2014, prior to this study, and conserved at room temperature during three months, were injected once every day of analysis.

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3. RESULTS AND DISCUSSION

3.1. SIX-DAY REPEATABILITY STUDY IN STABILIZED THF

THF is potentially dangerous because of its tendency to form highly explosive peroxides when stored in air and exposed to light. Stabilization of THF with BHT is required to minimize this problem during waste disposal.

The signals obtained for nickel, vanadium and sulfur in a crude oil and a VR by GPC-HR ICP MS after 6 days of analysis were discussed to study their stability over time and the effect of the THF stabilizer in the aggregation of the present molecules.

3.1.1. Evolution of the size distribution of S, V and Ni compounds of the solutions prepared the first day of analysis

The profiles obtained by GPC-HR ICP MS for the solutions prepared on the first day of analysis are presented in *Figure 9* as normalized graphs with respect to the total area of the chromatogram in order to make direct comparisons easier. The distribution profiles of the three elements analyzed in the two different heavy oil fractions differ from one injection to another during the six days of work. This evolution is very difficult to see except for the change observed for the signal corresponding to the first injection of each solution, which may indicate that the column was not yet stabilized. Another problem is that an evolution in the retention times is observed, which would be solved by analysing a solution of polystyrene standards at the beginning and the end of the week.

The profiles obtained for vanadium show three different sections: a first one (fraction 1) between 17 and 23 minutes corresponding to High Molecular Weight compounds (HMW), the fraction 2 corresponding to complexes of Medium Molecular Weight (MMW) from 23 to 28 minutes and finally the Low Molecular Weight (LMW) compounds (fraction 3) between 28 and 58 minutes.

The distributions of sulfur, vanadium and nickel were calculated as a percentage of the total area by measuring the area of the three fractions from the GPC-HR ICP MS chromatograms, following the well-defined cutting times given by the profiles for vanadium. Changes on the distribution of the elements in these fractions 1, 2 and 3 are seen in *Figure 10* more clearly than directly on the chromatograms described before. The results obtained show that the aggregation of sulfur compounds remains stable, but vanadium and nickel distribution percentages for LMW experience a decrease during the week, while an increase of HMW percentages is observed. This means that LMW compounds are aggregated over time, leading to HMW compounds. A comparison of the two samples analyzed can be made and shows that the aggregation trend for the VR is more pronounced. A little difference may be reported between the distribution of the first solutions and the ones prepared three months earlier.

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Figure 9. Normalized GPC-HR ICP-MS profiles of sulfur, vanadium and nickel of the solutions prepared on the first day of analysis of the VR from IFP (a) and the crude oil from Total (b).

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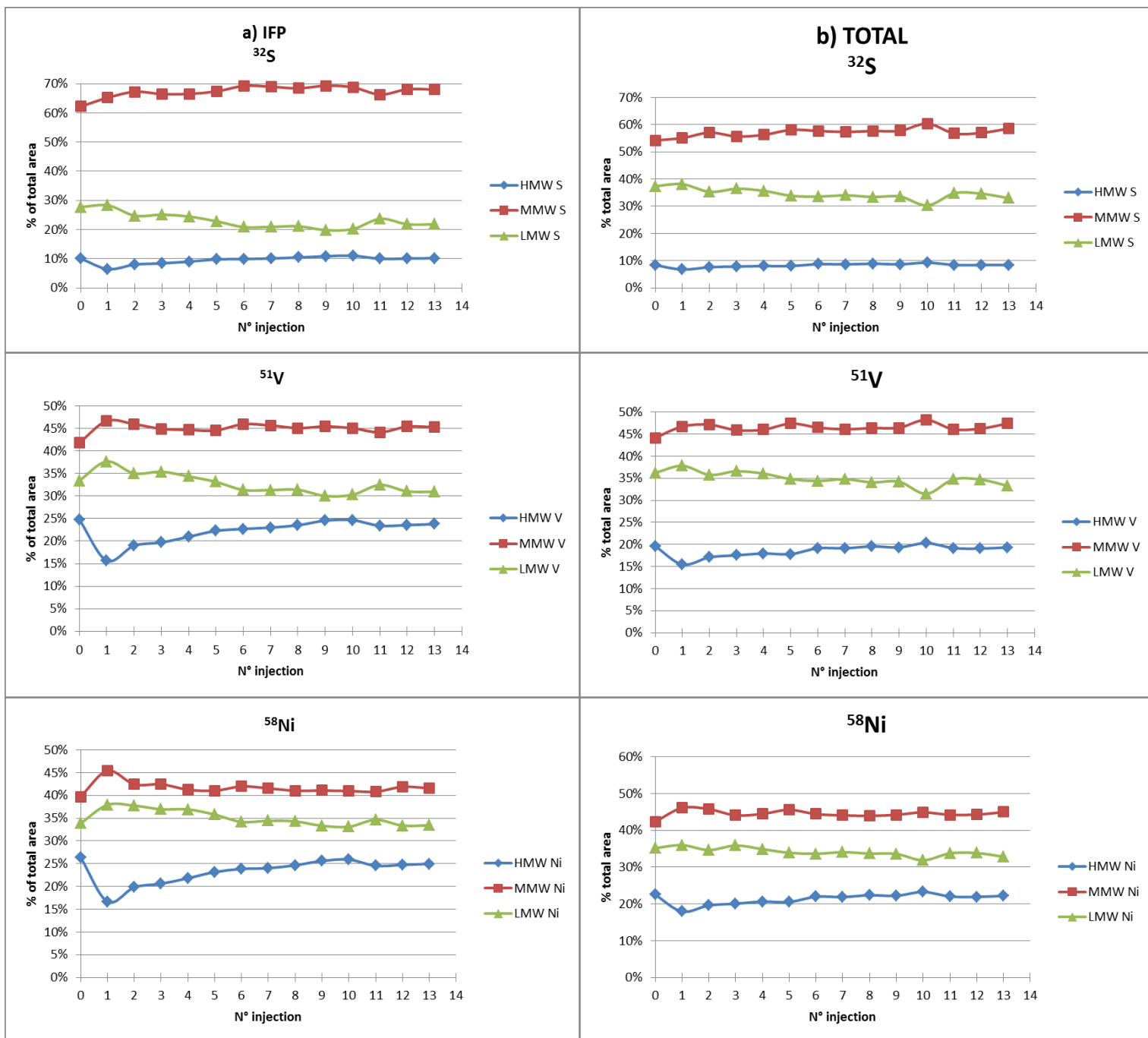
Figure 10. Distribution of elements analyzed in the solutions prepared the first day of analysis (injections 1-13) and one injection of the solutions prepared in February (injection 0) by GPC-HR ICP MS.

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3.1.2. Size distribution of S, V and Ni compounds of the fresh solutions

The aggregation of LMW compounds over time to form HMW ones is confirmed, as seen in the following graph (*Figure 11*) where the chromatograms obtained by GPC-HR ICP MS for the daily prepared solutions are presented. The peak corresponding to the HMW compounds of the February control samples is much more intense than for the fresh solutions prepared on the same day of the analysis, and lower LMWs can be remarked for both VR and crude oil.

On the contrary, the percentage distributions of sulfur, vanadium and nickel of the daily prepared solutions remain stable as exemplified in *Figure 12*. As the profiles of the fresh solutions are identical, solutions prepared on the day of the analysis could be used as controls in subsequent studies.

To check if the aggregation observed for samples of February continues, they are injected every day during the week of analysis. The results are discussed in the following section.

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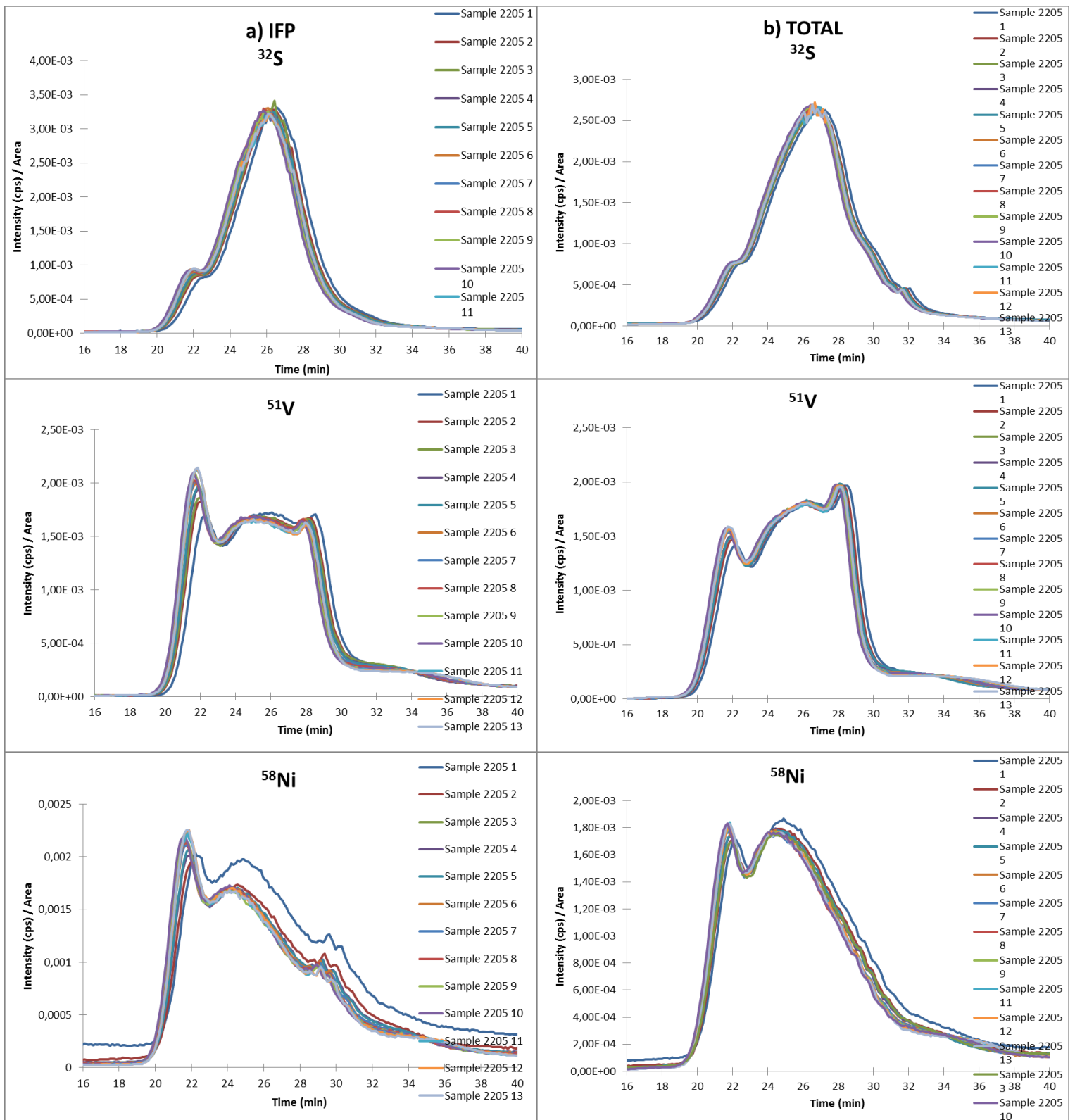
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Figure 11. Normalized GPC-ICP-MS profiles of sulfur, vanadium and nickel of the fresh solutions of the VR from IFP (a) and the crude oil from Total (b).

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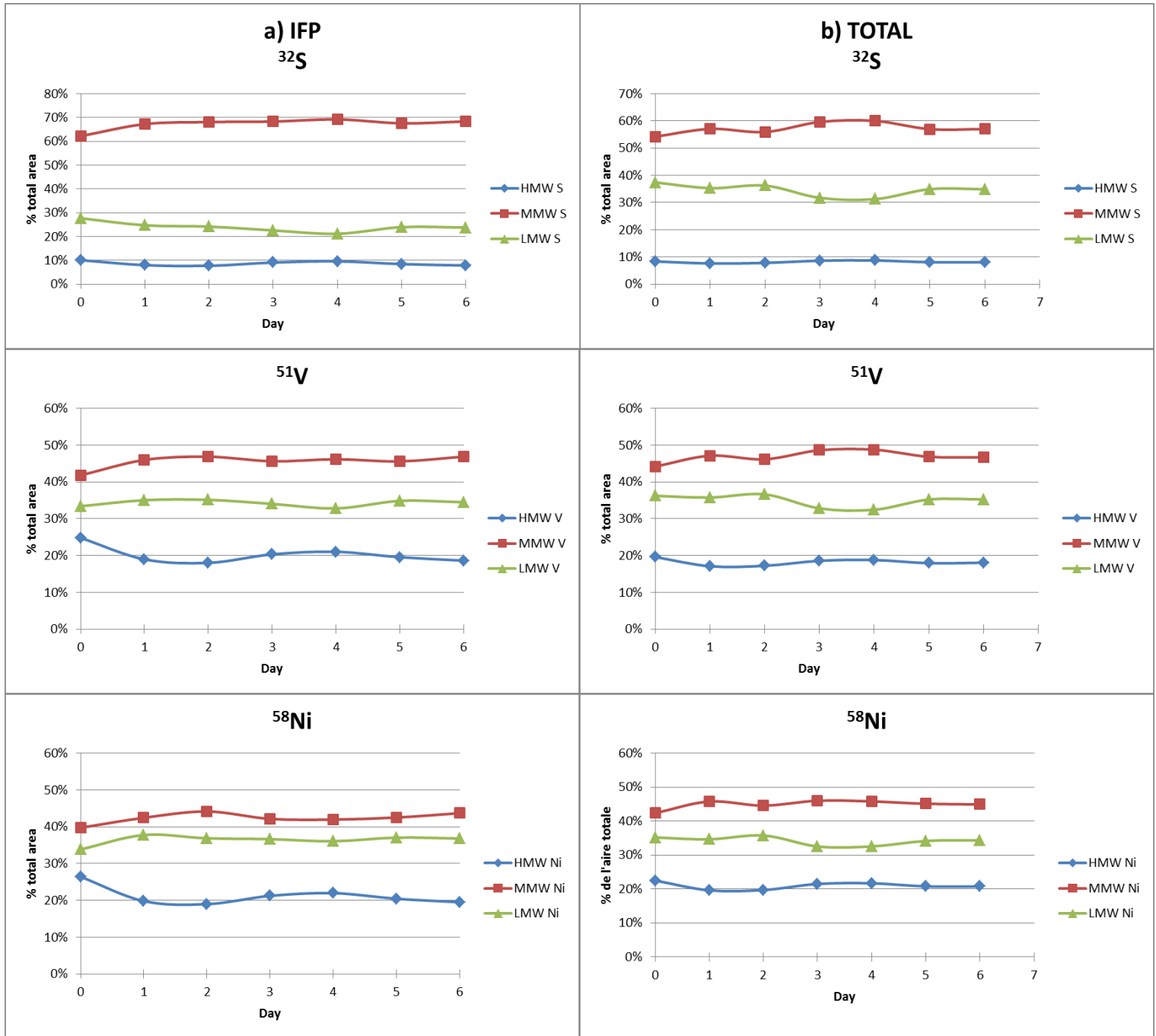
Figure 12. Distribution of elements analyzed in the fresh solutions (day 1-6) and one injection of the solutions prepared in February (day 0) by GPC-ICP MS.

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3.1.3. Evolution of the size distribution of S, V and Ni compounds of the solutions prepared on February

Figure 13 and *Figure 14* show that aggregation does not continue after three months as the size distribution profiles for the solutions prepared on February do not change during the week of experiments, as happened for those of the fresh samples. HMW, MMW and LMW distribution percentages of sulfur, vanadium and nickel remain stable too for both samples prepared on February. Thus, solutions prepared 3 months in advance could be used as controls. However, this would require to confirm that evolution has been fully completed and not just a slow kinetic aggregation, which can distort the results. It is very hard to prepare solutions and to plan the experiences three months in advance, therefore, it is preferred to work with fresh solutions to prevent sample evolution when the sequences are long.

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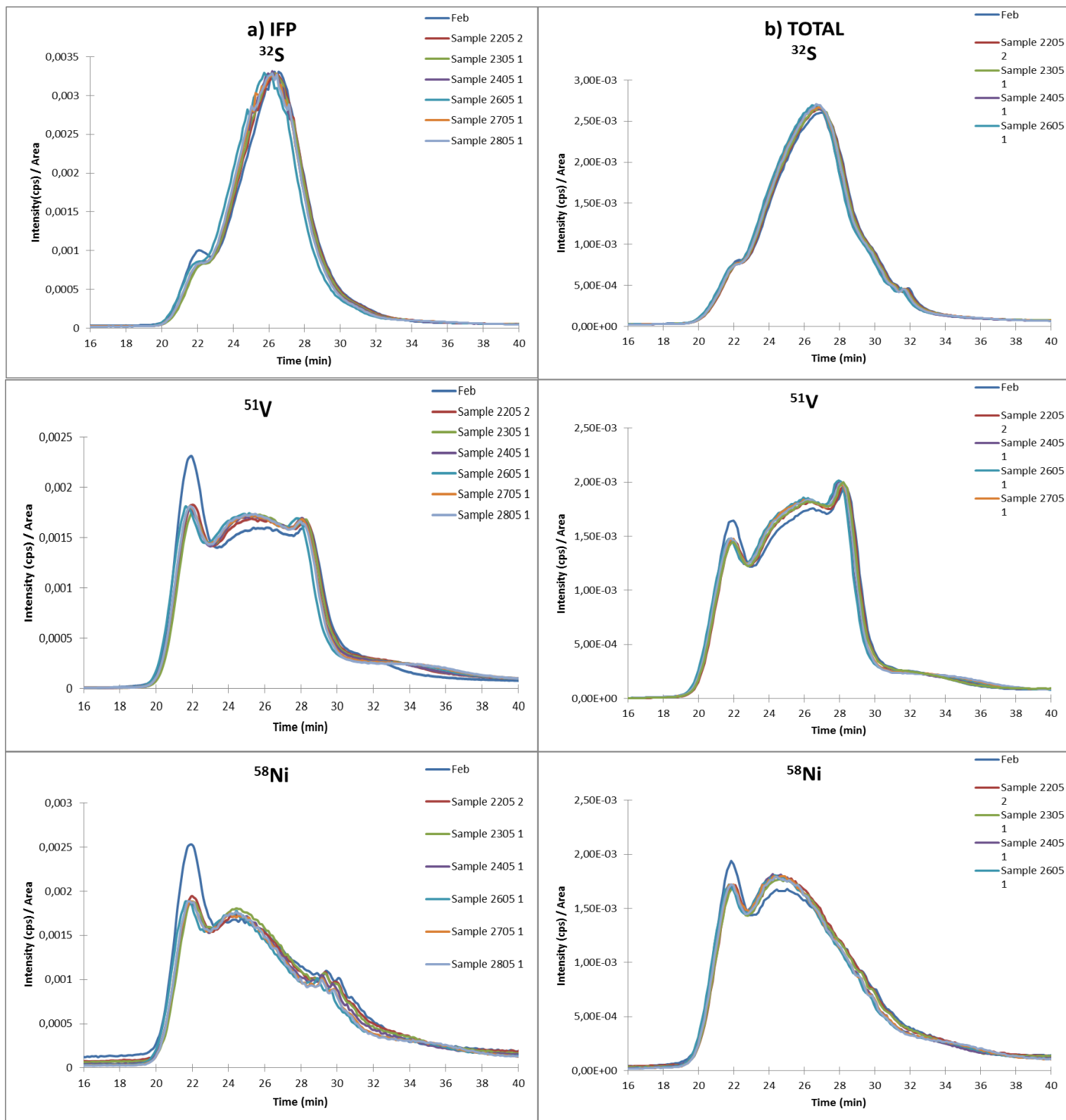
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Figure 13. Normalized GPC-ICP-MS profiles of sulfur, vanadium and nickel of the solutions prepared in February of the VR from IFP (a) and the crude oil from Total (b).

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Figure 14. Distribution of elements analyzed in the solutions prepared in February by GPC-ICP MS.

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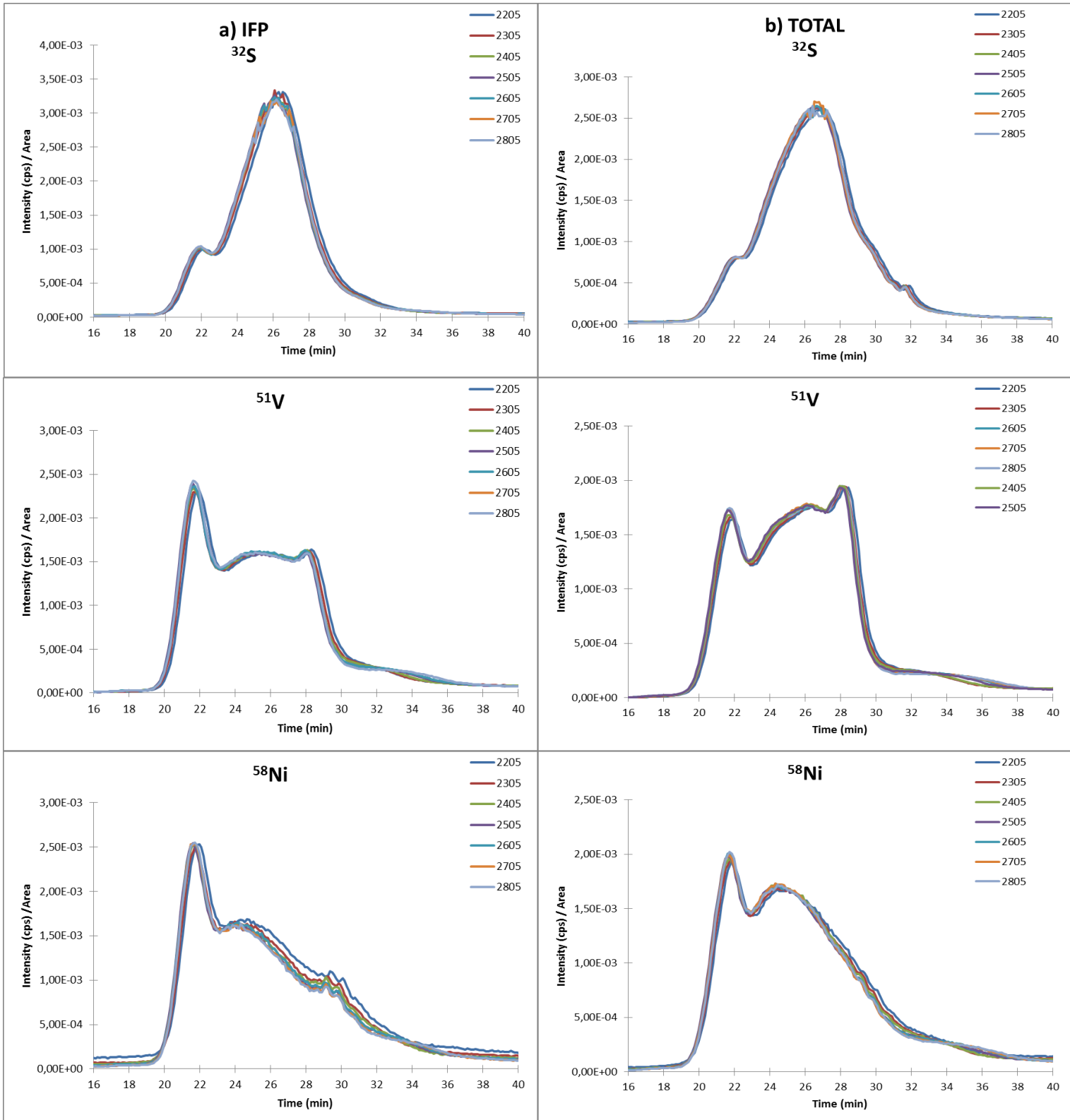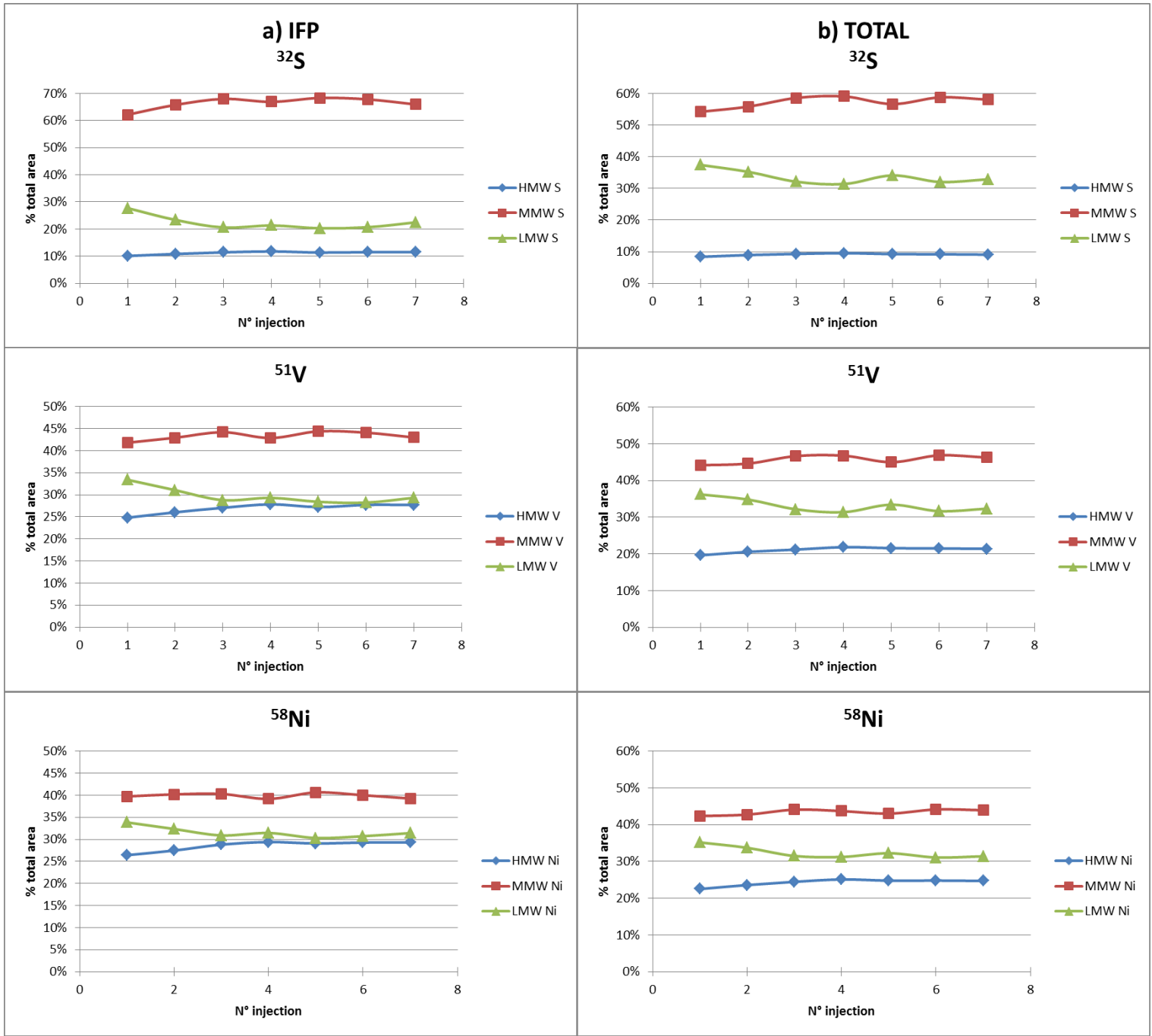
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4. CONCLUSIONS

The size distributions of sulfur, vanadium, and nickel compounds in the Total crude oil and the IFP VR solutions in stabilized THF have been determined using GPC-ICP HR MS. The most important conclusions drawn from the results are:

- Aggregation of LMW compounds of vanadium and nickel into HMW compounds is observed for both solutions over 6 days of analysis and the aggregation trend for the VR provided by IFP is more pronounced.

- A remarkable aggregation is reported over three months. It does not continue over one week of analysis after this time for the two solutions prepared on February, which could mean an aggregation of slow kinetics.

- Fresh solutions, prepared on the day of the analysis, can be used as reliable controls for long sequences as their size distribution profiles are the same during the week of analysis.

Size distributions of sulfur, vanadium, and nickel compounds in crude oils and their distillation cuts have been determined previously by Alain Desprez injecting the same solutions in THF without stabilizer over one week by GPC-ICP HR MS. It was observed that the HMW compounds proportion increased because of the aggregation of MMW or LMW metallic compounds, depending on the sulfur content of the samples analyzed.

Controlling the aggregation of these compounds is important for the optimization of the different hydrotreatment and hydrocraking processes, so the work in stabilized THF described in this report was proposed to confirm and to complete the results obtained in THF without stabilizer.

It may be concluded from the comparison between the two studies that the addition of little amounts of BHT as stabilizer changes the size distribution profiles of the different compounds as in not stabilized THF there is higher content of HMW compounds (*Figure 15*), the most difficult to remove.

Furthermore, the stability of the samples is higher in stabilized THF since they suffer less aggregation for vanadium and nickel than in the not stabilized solvent. As seen in *Figure 16*, LMW compounds have a great tendency to aggregate to form HMW compounds.

However, conclusions on the stability of products between stabilized and not stabilized THF need to be verified, as the first manipulations in THF without stabilizer were made using different GPC columns. To ensure that the evolution of the aggregation of the product depends only on one parameter, the differences between two solvents, the columns used in the first study will be passed from THF without stabilizer to stabilized THF.

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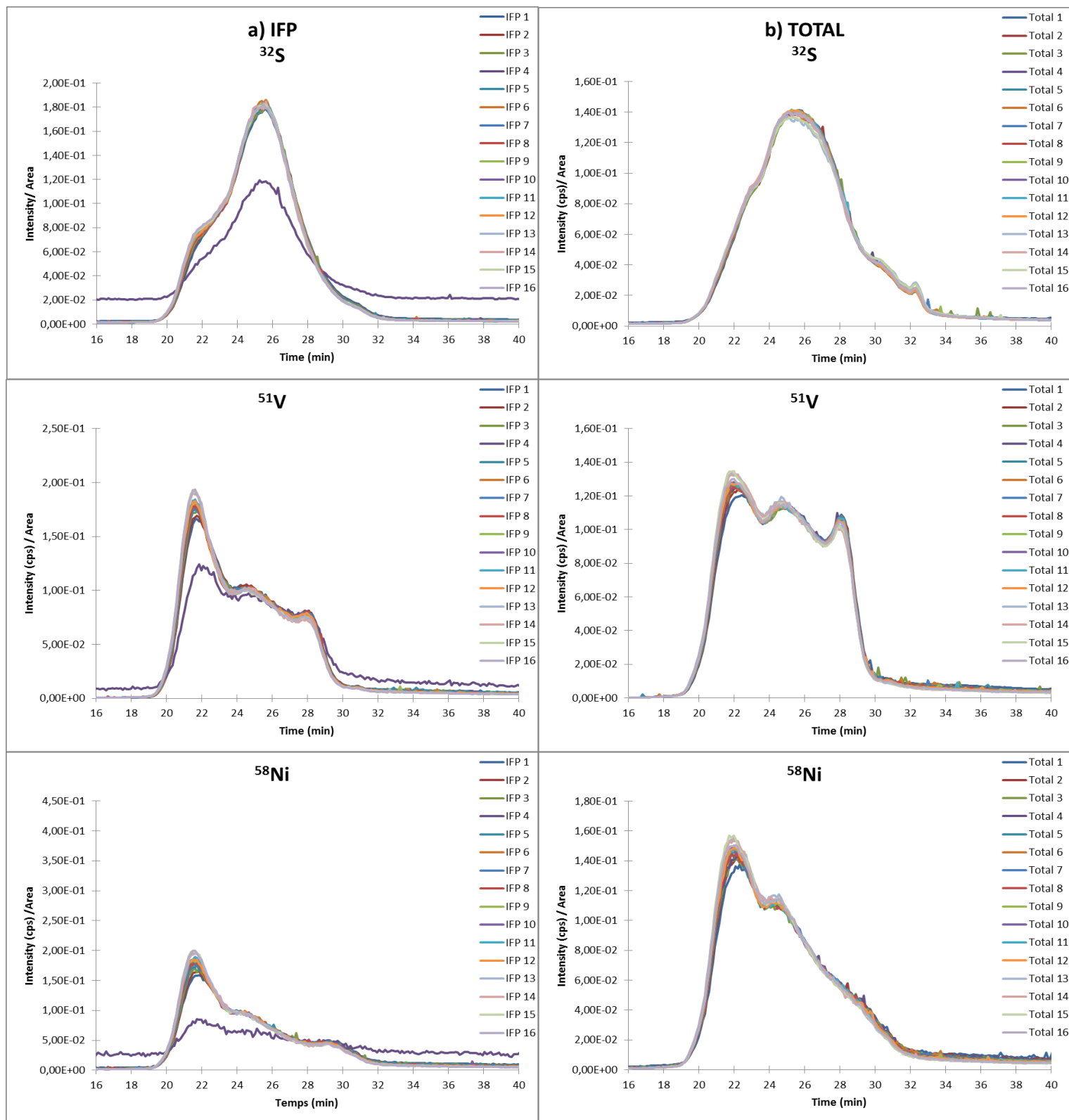*Figure 15. Normalized GPC-HR ICP-MS profiles of sulfur, vanadium and nickel of VR from IFP (a) and crude oil from Total (b) solutions in not stabilized THF.*

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Figure 16. Distribution of elements analyzed in not stabilized THF by GPC-HR ICP MS.

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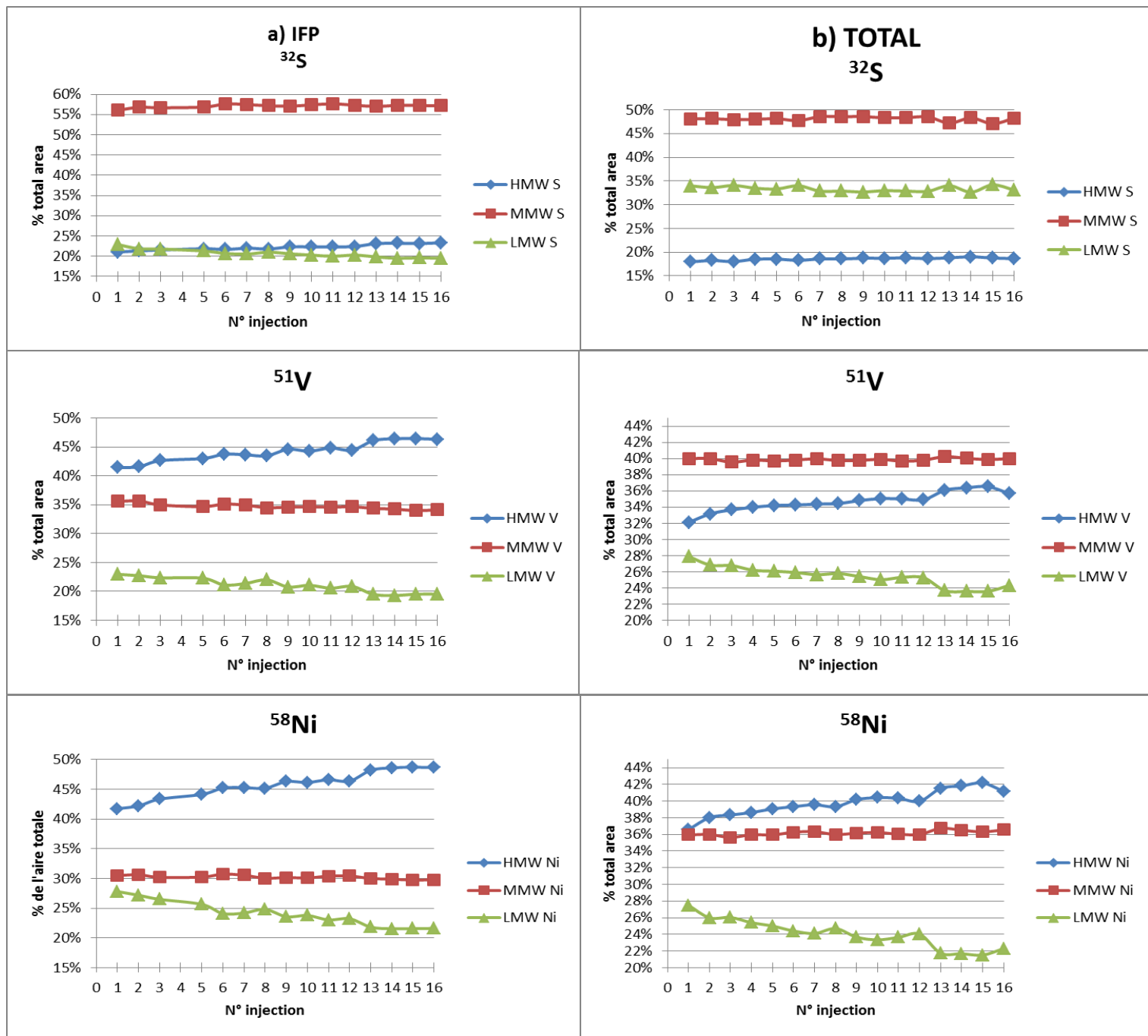
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5. FUTURE STUDIES

5.1. SIX-DAY REPEATABILITY STUDY IN XYLENE

The same study by GPC-HR ICP MS of sulfur, vanadium and nickel size distributions over time will be carried out in xylene in order to understand the effect of the solvent in the aggregation of molecules and the stability of the samples analyzed.

The xylene is one of the most widely used solvents in GPC, with THF and stabilized THF, so comparing the results obtained with each of them is of great importance. Furthermore, xylene has two valuable advantages: it is more economic and involves less risk while working, being unnecessary to add stabilizers.

An old set of GPC columns will be passed from THF to xylene and the separation will be checked with injections of polystyrene standards and a crude oil.

5.2. DEVELOPMENT OF A THREE STEP TLC SEPARATION

The aim is the determination of sulfur, vanadium and nickel distribution in two crude oils and the two porphyrinic standard controls given in *Figure 17* according to their polarity by TLC and X-ray fluorescence or laser ablation (LA) HR ICP MS.
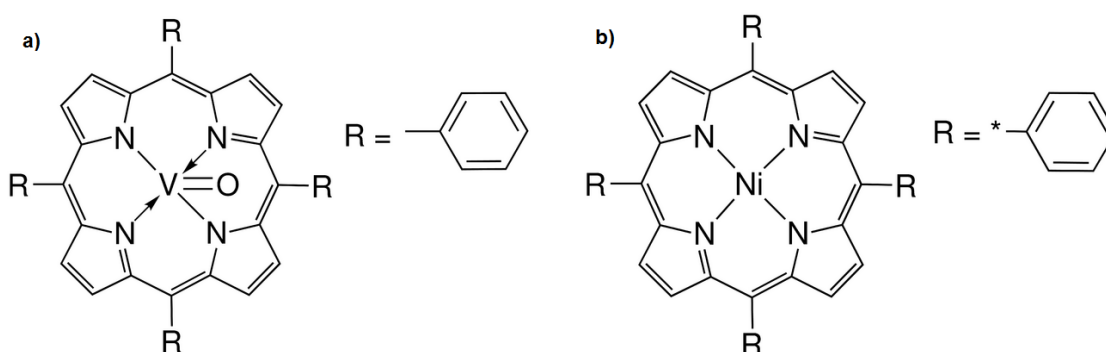

Figure 17. Porphyrinic standards: (a) 5,10,15,20-tetraphenyl-21H,23H-porphine vanadium (IV) oxide and (b) 5,10,15,20-tetraphenyl-21H,23H-porphine nickel (II).

To characterize heavy oils, which are of a very high complexity, a preliminary step of matrix simplification is recommended, in order to improve demetallation and desulfurization steps during refining processes of heavy petroleums to obtain fuel. Fractionation by polarity of crude oil into saturate, aromatic, resin and asphaltene (SARA) fractions by column liquid chromatography is one of the most common methods for crude oil fractionation. Thin layer chromatography (TLC) has been applied to the analysis of crude oil and its related products in order to avoid the precipitation of asphaltenes on the columns. Other TLC advantages are: low cost, simple instrument requirement, high sample throughput and simultaneous fractionation of crude oil into SARA [1], [9], [20], [21].

The edge of the TLC plates, sheets of coated stationary phases such as silica, are immersed the edge of the plate in the mobile phase, which is developed through capillary force. The separation is due to the differences of affinity of the molecules between the mobile phase

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and the stationary phase, which cause different compounds to move at different rates on the TLC plate [20].

Methodology:

Solutions of two crude oils in chloroform were prepared (CHROMASOLV® Plus, for HPLC, ≥99.9%, contains amylenes as stabilizer, Sigma-Aldrich). Solutions were deposited using a micropipette at 0.5 cm above the edge of the TLC plate. The plates used were of silica gel on TLC Al foils (Fluka, Sigma-Aldrich) with 50Å medium pore diameter. They were immersed in TLC developing tanks, which prevent solvent evaporation (*Figure 18*), filled with the following solvents of increasing polarity:

A. Hexane (95% n-hexane, for use in Liquid Chromatography (HPLC & UHPLC) & Spectrophotometry, J.T.Baker).

B. Hexane : dichloromethane (DCM) (CHROMASOLV®, for HPLC, ≥99.8%, contains amylene as stabilizer, Sigma-Aldrich) 55:45

C. DCM : methanol (LC-MS Ultra CHROMASOLV®, tested for UHPLC-MS, Fluka, Sigma-Aldrich) 99.5:0.5

This elution system was developed by Vicmary Vargas to provide the best separation between crude oil subfractions at different concentrations and allowing their clear observation at 254 and 366nm UV wavelengths.

Figure 18. Picture of the TLC developing tank used.

In order to optimize TLC elution conditions, several migrations (1,2 and 3) of crude oil solutions in chloroform of dilutions factors 4 (D4) and 5 (D5) and one of 50000 ppm (50) were performed by varying the eluent fronts and the number of application of each solvent.

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System	Eluent	Nº applications	Eluent front
	A	5	10
	B	2	8,5
1	C	1	4
	A	1	10
	B	1	8,5
2	C	1	3,5
	A	1	10
	B	1	10
3	C	1	5,2

Table 3. TLC migrations.

The best separation of the components appears to be achieved for the number of applications done in the first experience and for the 50000 ppm solution.

A fourth TLC separation with the two porphyrinic standard controls dissolved in xylene to achieve a 200 ppm concentration, was carried out under those conditions. As expected, VO porphyrin migration distance (4.3 cm) is small compared to the distance of the Ni porphyrin (5.2 cm), which cannot be seen in the picture, on a polar adsorbent like silica gel as a result from the dipole-dipole interaction and/ or hydrogen-bonding between the polar site of the adsorbent or solvent and the oxygen of vanadyl (VO) in the complex [22]. It could be concluded that this type of vanadium and nickel porphyrins are present in the resin and aromatic fractions respectively.
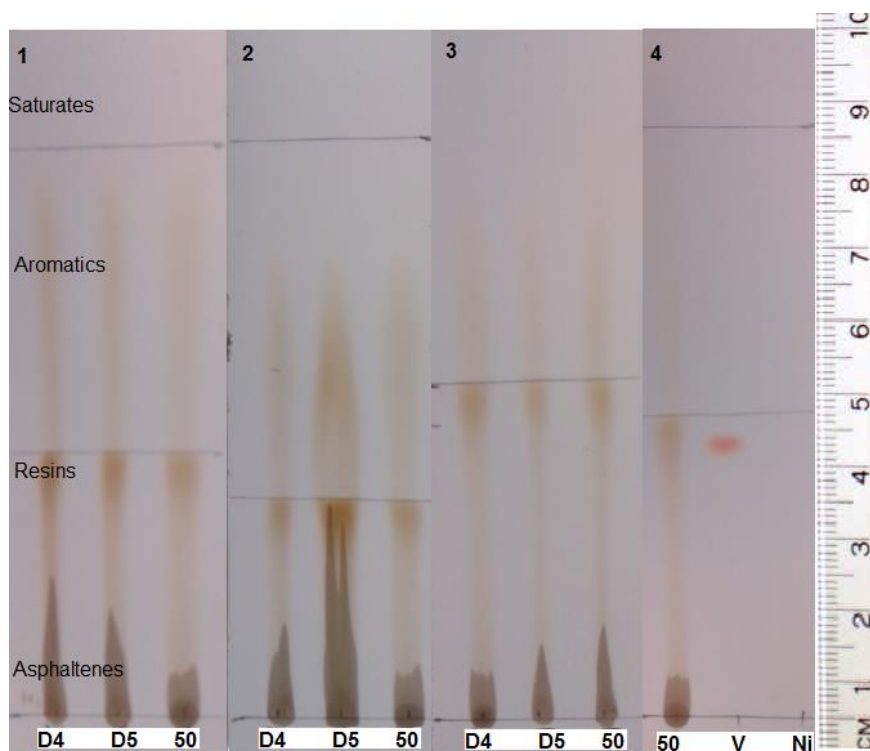

Figure 19. Comparison of the TLC separations carried out.

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X-ray fluorescence or laser ablation (LA) HR ICP MS measurements on TLC plates will be performed to study the distribution of the different sulfur, vanadium and nickel species present in the different fractions of crude oils and chose the best eluent front, concentration of the solutions and number of applications of each solvent for the migration.

The knowledge of these key parameters determined through our experiments will be used for High-performance thin-layer chromatography (HPTLC) migration which will improve resolution and reproducibility compared to TLC.

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