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Abstract

The capability of inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) to achieve total concentration and speciation using direct injection of petroleum products after solvent dilution for severely interfered isotopes was demonstrated here with different applications cases. For the direct determination of heavy elements (Z>70) in organic matrices, the ICP-MS/MS was less sensitive than the ICP-HRMS. For light elements (Z<40), the sensitivity was similar or better using ICP-MS/MS and for interfered elements (Si, S, Ca, Fe), the use of the two quadrupoles combined to the octopole reaction/collision cell (ORC) with He, O_2 or H_2 gave similar or better detection limits (LOD) than the ICP-HRMS in medium resolution. Comparable or better sensitivity were obtained replacing the 1.5 mm by the 1 mm injector diameter and especially for lighter elements (Z<30) using the ICP-MS/MS. LOD in xylene were ranging from 0.004 µg/kg (V) to 0.9 µg/kg (Al) and appeared in the lowest values published in the literature using ICP-MS/MS in hydrocarbons. To demonstrate the performance of the ICP-MS/MS using direct injection of petroleum products after dilution in hydrocarbon solvent, three application cases were presented.

Sulfur at very low levels in reformates was successfully monitored in oxygen mode using the oxide ion ($^{32}S \rightarrow {}^{48}SO$). The background equivalent concentration (BEC) origin was attributed to solvent contamination by sulfur and was confirmed by ultra-violet fluorescence (UVF) method. Using H_2 for Ni ($^{58}Ni \rightarrow {}^{58}Ni$) and O_2 for V ($^{51}V \rightarrow {}^{67}VO$) as reactant gas, the direct injection ICP-

MS/MS method easily confirmed Ni and V concentrations measured using wavelength dispersive X-rays fluorescence (WDXRF) and allowed the determination of 14 elements in the asphaltene fraction, with concentrations ranging from 0.3 mg/kg (Al and Pb) to 37.4 mg/kg for Fe.
For speciation of Ni, V and S, gel permeation chromatography (GPC) hyphenated to ICP-MS/MS is particularly powerful using O_2 (2.5 mL/min) both for vacuum residue and hydrotreated (HDT) vacuum residue. Contrary to GPC-ICP-HRMS where two injections of sample were required (medium resolution for S and V and low resolution for Ni), GPC-ICP-MS/MS easily allowed the acquisition of the 3 elements in one mode during the same run and considerably reduce the analysis cost and time. Both for total and speciation analysis, the direct injection after solvent dilution ICP-MS/MS method is a significant advantage and appealing in high-volume petroleum laboratories.

Keywords : trace analysis; detection limits; speciation; petroleum products; polyatomic interferences; ICP-MS/MS; ICP-HRMS; GPC; vacuum residue

1 Introduction

Intensive studies have been dedicated to trace and ultra trace metals determination in petroleum products in the recent years [1–4]. The need of the petroleum industry in this field is related to exploitation activities and exploration : contamination during oil production and refining (e.g. prevention of catalyst poisoning, corrosion and pollution control [5]), and geochemical characterization of source rocks and basins in order to identify geochemical biomarkers [6] in oil-oil or oil-source rock correlation. The existence of metals in fossil fuels was firstly established by Alfred Treibs in the 1930s [7]. Trace metals are also incorporated into petroleum fractions as organometallic compounds (*e.g.* geoporphyrins) initially present in the crude oil [8] or added during the various processes of refining [9]. Their concentration are always ranged between µg/kg and mg/kg levels but low amount of certain metals can have drastic effects as a contaminant. The determination of a particular metal is mainly driven by their poisoning effect on catalysts during refining processes [10]. It is then important to better characterise their distribution in the petroleum fractions as this can improve oil refining strategies. Thus, several characterization of metal complexes in petroleum products exist and if we focus on heavy fractions and oils that are more and more used in the petrochemical industry, vanadium (V), nickel (Ni), and sulfur (S) present in these oils plays a critical role during oil-refining processes. These elements could lead to corrosion of the equipment, environmental pollution, and contamination of the final petroleum products. In order to treat them efficiently, information on the size and chemical form (speciation) of these elements are of major importance to choose the porosity of refining catalysts.

Many techniques have been used for the determination of metals in petroleum fractions including X-rays fluoresence (XRF) [11,12] or microwave induce plasma atomic emission spectrometry (MIP-AES) [13] or even laser induced breakdown spectroscopy (LIBS) analysis [14]. For total trace determination, inductively coupled plasma (ICP) techniques are generally used [3,4,15,16] and allow sufficient detection limits for most of the cases in the petroleum industry and are also conventionnaly hyphenated to separation techniques to reach speciation analyses [17,18]. The inherent high sensitivity of ICP-MS detection together with isotopic ratio capabilities opens new fields of applications in petrochemistry or geochemistry, but the introduction of organic substances is not that easy as this technique was not initially designed for organic samples analysis [4]. Specific configurations of sample introduction systems are required in order to

97 minimize organic solvent load into the ICP plasma [19]. Moreover, specific polyatomic
98 interferences are disturbing the spectra due to the massive presence of carbon, oxygen and sulfur
99 within the plasma, originating from the petroleum cuts. For this reason, various approaches have
100 been adopted within the last years in order to minimize the presence of carbon within the plasma:
101 emulsification, decomposition of the sample matrix, but also laser ablation and analysis through
102 electrothermal vaporization. Most of these approaches were already reviewed in [3] and the
103 advantages and drawbacks of the introduction of organic/hydro-organic matrices in ICP was
104 deeply reviewed by [4,20].
105 The determination of light or interfered elements done in the specific case of direct injection of
106 the organic substances within the plasma torch of the ICP-MS was mainly done with the help of
107 high resolution ICP-HRMS [21,22], essentially when difficult isotopic interferences are present
108 [23,24]. Such an instrument is quite expensive and not available in most of the lab of the
109 petroleum industry for routine organic analyses. The recent commercialisation of an inductively
110 coupled plasma tandem mass spectrometry (ICP-MS/MS) by Agilent [25–28] and Thermo
111 Fischer Scientific [29], is specifically dedicated to solve polyatomic interferences in organic
112 solvents and attain lower detection limit. It will be then interesting for the petroleum industry to
113 investigate this instrument in order to have a specific idea of the capabilities of such system for
114 difficult elements (for example S, Si, Fe) and especially for heavy matrices. In 2017, a complete
115 review about ICP-MS/MS applications for total and speciation analyses was published [28].
116 However, to our knowledge, a very few number of papers [26,30] are reported in the literature
117 about the application of the ICP-MS/MS to organic products with direct injection, and the most
118 difficult solvent used was ethanol. Ethanol is anyway not a sufficient “good solvent” to solubilize
119 most of the petroleum fractions and harsher solvent (difficult to introduce in the plasma) like
120 xylene or even THF are commonly used to dissolve hydrocarbons. In order to avoid difficult
121 organic solvent introduction into the plasma, two recents papers reported acid digestion of
122 petroleum products followed by ICP-MS/MS for multi elements analysis at trace levels, allowing
123 external calibration by means of aqueous standards but this preparation step is time consuming
124 compared to direct injection [31,32].
125 Also for the speciation of heavy crude oils a few number of papers is existing in the literature.
126 One of the main approches proposed actually in the litterature is based on the use of gel

permeation chromatography (GPC) coupled to ICP-HRMS [23,24] and very recently ICP-MS/MS [33].

This work is based on the direct injection of hydrocarbons after solvent dilution within the plasma torch of the ICP-MS in order to minimize the preparation steps, but also to support organic solvent issued from separation techniques. This article will present the two approaches for total direct determination of organic substances and speciation with GPC obtained with an ICP-MS/MS compared to ICP-HRMS for various elements and matrices. The interferences due to the presence of carbon, oxygen and sulfur within the plasma are solved with the use of a collision/reaction chamber [18] or the use of high resolution ICP-MS [21,34]. Optimization parameters for these two configurations are optimized and the different figures of merit are discussed concerning linearity, background equivalent concentration (BEC) and detection limits. Three cases of application in the petroleum industry (Ultra trace sulfur in solvents, Asphaltene elemental composition and Speciation in heavy matrices) are then presented to give an overview of the capabilities of the ICP-MS/MS compared to the ICP-HRMS.

2 Materials and methods

2.1 Solutions and samples

Different lots of the same solvent grades of toluene and xylene (mixture of o, m, p-xylene) AnalaR Normapur were obtained from VWR Chemicals (Fontenay s/s Bois, France) and used for most of the preparation and sulfur detection. For the GPC experiments, American Chemical Society-grade THF with 250 ppm of butylated hydroxytoluene (BHT) as stabilizer (Scharlau, Spain) was used for the solutions, sample dilutions and as the mobile phase. A Premisolv solvent was provided by SCP Science (Courtaboeuf, France) and used as a sulfur free solvent.

A Conostan (SCP Science, Courtabouef, France) multi-element oil-based standards (S-21+CoK) containing 500 mg/kg of Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V and Zn was used. A specific mono-elemental oil-based standard was used for S, Hg and As calibration. Multi-element working standard solutions at 0.10, 0.20, 0.50, 1.0, 2.0, 5.0, 10, 20 and 50 µg/kg, were prepared by the appropriate dilution of these solutions in xylene. Calibration solutions were prepared by weighing and the exact added concentrations were recalculated afterwards.

Different petroleum cuts are provided by IFP Energies nouvelles (IFPEN) (Solaize, France) and their main characteristics are described in Table 1. Straight Run Naphtha samples directly issued from different refineries were used as sulfur free solvent. Vacuum residue (VR) from Middle East already used in [24] and its hydrotreated (HDT) vacuum residue issued from a deep hydrodemetallation pilot plant experiment (E) were used for GPC analyses. Asphaltenes fraction (A) was recovered from the partial Vacuum residue flocculation in contact with the n-heptane as already described in [35].

Table 1: Characteristics of the petroleum cuts provided for the various experiments.

Samples	Simulated distillation IFPEN 1202			XRF		
	T5	T50	T95	Ni [mg/kg]	V [mg/kg]	S [%w/w]
Asphaltene A	na	na	na	350	655	na
Naphtha 16J	15	88.7	158	na	na	na
Naphtha 16F	49	100	185	na	na	na
Naphtha 16A	24	71	145	na	na	na
Vacuum Residue VR	482	625	725	58	183	5.7
HDT vacuum residue E	na	na	na	3	6	0.49

na: not available

2.2 Instrumentation

2.2.1 ICP-MS and GPC-ICP-MS

ICP-MS and GPC-ICP-MS analyses were achieved using an ICP-MS/MS and a ICP-HRMS. The most important instrumental parameters are presented in Table 2. The first one is an ICP-MS/MS 8800 instrument from Agilent (Agilent Technologies, Japan). In this instrument, the collision-reaction cell (CRC) is an octopole located in-between two quadrupole analyzers, this cell can be filled with a collision or a reactive gas in order to reduce interferences on the ions of interest. All monitored isotopes are detailed in Table 2 in function of the resolution (low, medium, high) for the ICP-HRMS and gas mode (no gas, He, H_2 and O_2 mode) for the ICP-MS/MS. In No gas mode, the width of the bandpass of the first quadrupole analyzer is fully open or used as an ion guide and the second quadrupole analyzer is set at the chosen mass. In He gas mode, the width of the bandpass of the first quadrupole analyzer is fully open and the second quadrupole analyzer is set at the chosen mass. In H_2 gas mode, the width of the bandpass of the first quadrupole analyzer is set to single mass width and the second quadrupole analyzer is set to the same single mass width because H_2 did not react with the chosen elements. Finally for the O_2 gas mode, the width of the bandpass of the first quadrupole analyzer is set to the element of interest mass width and the second quadrupole analyzer is set to the element of interest mass width + 16 to let the monoxide of the element going through the second quadrupole: For some elements in the oxygen

mode, the mass of the second quadrupole is let to the same single mass width in order to verify the reactivity of the element and how much has not reacted within the collision/reaction chamber. This was the case for : $^{48\rightarrow48}$Ti, $^{51\rightarrow51}$V, $^{56\rightarrow56}$Fe, $^{59\rightarrow59}$Co, $^{60\rightarrow60}$Ni, $^{62\rightarrow62}$Ni, $^{75\rightarrow75}$As.

The second ICP-MS is an Element XR double focusing sector field inductively coupled plasma mass spectrometer (Thermo Fisher, Germany). A micro-flow total consumption nebulizer (DS-1, Cetac) without drain [36] was tested. Samples were delivered using an ASX-520 (CETAC, Omaha, NE) autosampler. Some elements were monitored with low resolution (R=300), medium resolution (R=4000) and high resolution mode (R=10000). Samples were delivered using an ASX-500 (CETAC, Omaha, NE). For total experiments, the reduction of the amount of organic vapor entering the plasma was obtained using a Peltier-cooled spray chamber cooled down at -5 °C.

For both instruments, the sampler and skimmer cones covered with Pt were used due to organic injection and the necessity of adding oxygen within the plasma.

For the GPC experiment, the mobile phase was delivered by a Dionex HPLC system with an UltiMate 3000 microflow pump, an UltiMate 3000 autosampler, and a low port-to-port dead-volume microinjection valve. Chromatographic separation was performed by three polystyrene-divinylbenzene GPC columns connected in series (porosity of 100 Å, 1000 Å and 10,000 Å). The GPC eluted fractions were splited to introduce the same flow of 0.03 ml/min as total analysis (Table 2) into the high resolution ICP-MS *via* a modified DS-5 microflow total consumption nebulizer (CETAC, Omaha, NE) fitted with a laboratory-made single-pass glass spray chamber thermostated at 60 °C by a water/glycol mixture using a temperature controlled bath circulator (Neslab RTE-111, Thermo Fisher Scientific, Waltham, MA).

The same set of columns was used with the Agilent 8800 ICP-MS instrument. An Agilent 1290 Infinity liquid chromatographic device was used. The elution system was equipped by specific THF resistant parts. In this case, the total GPC eluted fractions was introduced within the Scott spray chamber by the means of a Burgener T2002 nebulizer using Pharmed tubing.

To minimize carbon-buildup on the sampler cone, O_2 was added within a mixture of Argon/oxygen (Ar/O_2:80/20) between the spray chamber and the torch for the ICP-MS/MS, a typical flow between 230 and 270 mL/min of the Ar/O_2 mixture is used depending on the application. Pure oxygen was added to the sample Ar flow using a mass flow controller with the ICP-HRMS, a flow of 80 mL/min was used.

221 **Table 2: Operating conditions for total analysis using ICP-MS apparatus**

	Thermofisher Element HRMS with DS-1	Agilent ICP-MS/MS 8800
RF power [W]	1500	1550
Plasma gas flow [L/min]	16	18
Optional gas flow [L/min]	O_2: 0.08	Ar+O_2: 0.23-0.27*
Carrier gas flow [L/min]	0.565	0.50
Auxiliary gas flow rate [L/min]	0.9	
Number of replicates	3	3
Liquid flow rate [ml/min]	0.03	0.50-0.70*
Nebulizer	Modified DS-5	Burgener T2002
Nebulization chamber	Low dead volume (8 cm^3) spray chamber without drain [36]	Scott type – double pass
Spray chamber temperature [^oC]	60	-5
Torch Z-position [mm]	-3	5
Injector	1.0 mm ID quartz injector	1.0 or 1.5 mm ID quartz injector
Detection mode	Triple	
Resolution (HRMS) and gas mode (ICP-MS/MS) for monitored elements	-low resolution (R=3000) $^{10\text{ and }11}B$, ^{23}Na, ^{27}Al, ^{29}Si, ^{31}P, ^{34}S, ^{44}Ca, $^{46\text{ and }47}Ti$, ^{51}V, ^{53}Cr, ^{54}Fe, ^{59}Co, ^{60}Ni, $^{63\text{ and }65}Cu$, $^{66\text{ and }68}Zn$, ^{75}As, $^{95\text{ and }98}Mo$, $^{107\text{ and }109}Ag$, $^{118\text{ and }120}Sn$, $^{137\text{ and }138}Ba$, $^{200\text{ and }202}Hg$, $^{206,\ 207\text{ and }208}Pb$ -medium resolution (R=4000) $^{10\text{ and }11}B$, ^{23}Na, ^{27}Al, ^{28} and ^{29}Si, ^{31}P, ^{32} and ^{34}S, ^{39}K, ^{44}Ca, ^{46} and ^{48}Ti, ^{51}V, ^{52} and ^{53}Cr, ^{54} and ^{56}Fe, ^{59}Co, ^{58} and ^{60}Ni, ^{63} and ^{65}Cu, ^{75}As, ^{95} and ^{98}Mo, ^{107} and ^{109}Ag, ^{118} and ^{120}Sn, ^{137} and ^{138}Ba, ^{200} and ^{202}Hg, $^{206,\ 207}$ and ^{208}Pb -high resolution (R=10000) ^{28}Si, ^{39}K and ^{75}As	-No gas ^{10}B, ^{11}B, ^{23}Na, ^{34}S, ^{51}V, ^{58}Ni, ^{59}Co, ^{60}Ni, ^{62}Ni, ^{63}Cu, ^{65}Cu, ^{66}Zn, ^{75}As, ^{95}Mo, ^{97}Mo, ^{107}Ag, ^{109}Ag, ^{118}Sn, ^{120}Sn, ^{135}Ba, ^{137}Ba, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{206}Pb, ^{207}Pb, ^{208}Pb -He mode ^{23}Na, ^{27}Al, ^{31}P, ^{47}Ti, ^{49}Ti, ^{51}V, ^{52}Cr, ^{53}Cr, ^{56}Fe, ^{57}Fe, ^{58}Ni, ^{59}Co, ^{60}Ni, ^{62}Ni, ^{63}Cu, ^{65}Cu, ^{66}Zn, ^{68}Zn, ^{75}As -H_2 mode ^{27} -> ^{27}Al, ^{28} -> ^{28}Si, ^{51} -> ^{51}V, ^{52} -> ^{52}Cr, ^{53} -> ^{53}Cr, ^{56} -> ^{56}Fe, ^{57} -> ^{57}Fe, ^{58} -> ^{58}Ni, ^{59} -> ^{59}Co, ^{60} -> ^{60}Ni, ^{62} -> ^{62}Ni, ^{63} -> ^{63}Cu, ^{65} -> ^{65}Cu, ^{66} -> ^{66}Zn, ^{68} -> ^{68}Zn -O_2 mode ^{31} -> ^{47}P, ^{32} -> ^{48}S, ^{33} -> ^{49}S, ^{34} -> ^{50}S, ^{48} -> ^{64}Ti, ^{51} -> ^{67}V, ^{56} -> ^{72}Fe, ^{58} -> ^{74}Ni, ^{60} -> ^{76}Ni, ^{62} -> ^{78}Ni, ^{75} -> ^{91}As ^{48} -> ^{48}Ti, ^{51} -> ^{51}V, ^{56} -> ^{56}Fe, ^{59} -> ^{59}Co, ^{60} -> ^{60}Ni, ^{62} -> ^{62}Ni, ^{75} -> ^{75}As, ^{58} -> ^{58}Ni
Extract [V]	-2000	1: 0 - 2: -160
Omega bias [V]		-80
Cell gas		no gas/ O_2 (0.23-0.32 mL/min)/ He (2-3 mL/min)/ H_2 (2-3.1 mL/min)

222 *For GPC, different liquid and Ar+O_2 flow rates are used after optimization

2.2.2 UVF and XRF apparatus

UVF analysis following ISO 20486 was performed using an Antek Multitek (PAC-Alytech, Juvisy sur Orge, France) with syringe injection. The instrument was calibrated between 0.2 and 2 mg/kg with DiButylSulfide and a volume of 20 µL was injected.

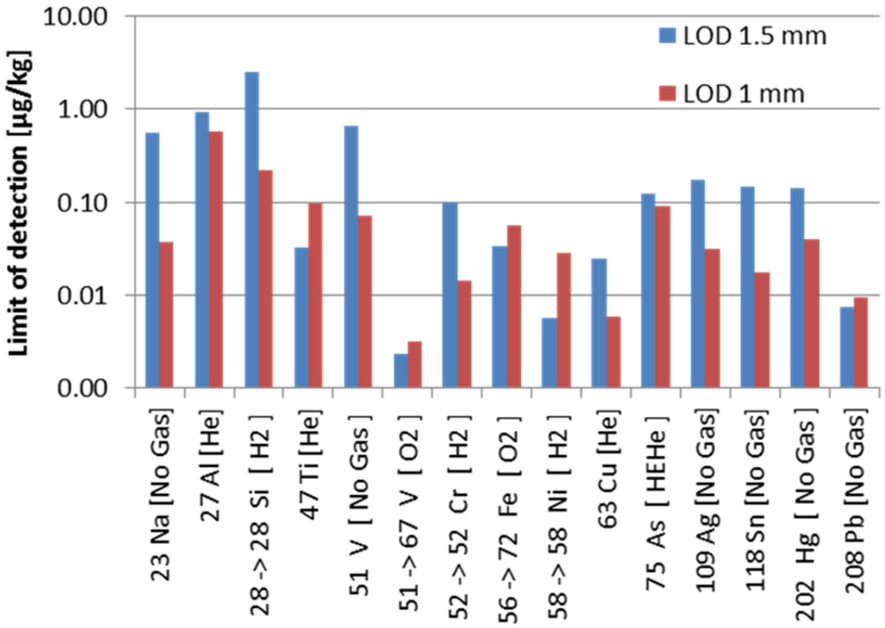
For wavelength dispersive X-rays fluorescence (WDXRF) analysis, a Panalytical Axios (Almelo, Netherlands) 4 kW equipped with a Cr anode was used. 6 ml of the solution was introduced within a cup with a Mylar 6µm film. The Ni and V K_α were followed and the C/H and S matrix effect were compensated using the Cr Compton line according to an internal IFPEN method.

3 Results and discussion

3.1 Optimization of the ICP operating parameters

The configuration of the ICP-MS/MS and the ICP-HRMS was tested by calibrating the instruments between 0 to 50 or 100 µg/kg in xylene. Polyatomic interferences were solved by the use of medium resolution (R=4000) with the HRMS or with the use of the a collision/reaction cell using the ICP-MS/MS. For the different gas modes used with the ICP-MS/MS, the carrier gas was firstly optimized and then the various lenses were adjusted. The gas flow in the collision/reaction was finally optimized according to each application tested in order to reach the best signal to noise ratio.

Most of the optimized parameters both for the ICP-MS/MS and the ICP-HRMS are reported in Table 2. According to Agilent recommendations for organic introduction, the standard injector tube (2.5 mm internal diameter) was replaced by a 1.5 mm i.d. injector. Two types of injector were tested with the 1.5 and 1.0 mm internal diameter. The two configurations tested shows that for most of the elements the 1.0 mm injector allowed similar detection limit or increase of the sensitivity by a factor up to 10 times. This increase of sensitivity was more effective for lighter elements with atomic mass lower than 30 (Figure 1). The 1.0 mm injector was then kept for each application, as previously reported by Poirier *et al.*, [15] for the total analysis of Ni, V, Fe and Ca in petroleum crude oil *via* direct dilution using ICP-MS.



252

253 **Figure 1: Comparison of detection limits obtained using diameters 1.0 and 1.5 mm for two injectors**
254 **proposed for the ICP-MS/MS.**

255 ***3.2 Analytical figures of merit***

256 For each element, the calibration curve was built acquiring the signal for various isotopes and
257 using the diversity of the modes offered by each instrument. Low, medium and high resolutions
258 were followed with the ICP-HRMS and the no gas, helium, hydrogen and oxygen modes were
259 used and optimized with the ICP-MS/MS. Typical curves for heavy interfered elements (S, Si,
260 Fe) are respectively shown Figure 2 to Figure 4 for the most sensible mode retained for each
261 element. From each calibration curve, the limit of detection (LOD) and the background
262 equivalent concentration (BEC) are calculated according to the following equation:

263

264 $y = ax + b$ with $BEC = {}^{b}/_{a}$ and $LOD = 3xBECxRSD_{blk}$ [37]

265 The relative standard deviation of the blank (RSD_{blk}) was calculated according to 3 replicates of
266 xylene.

267

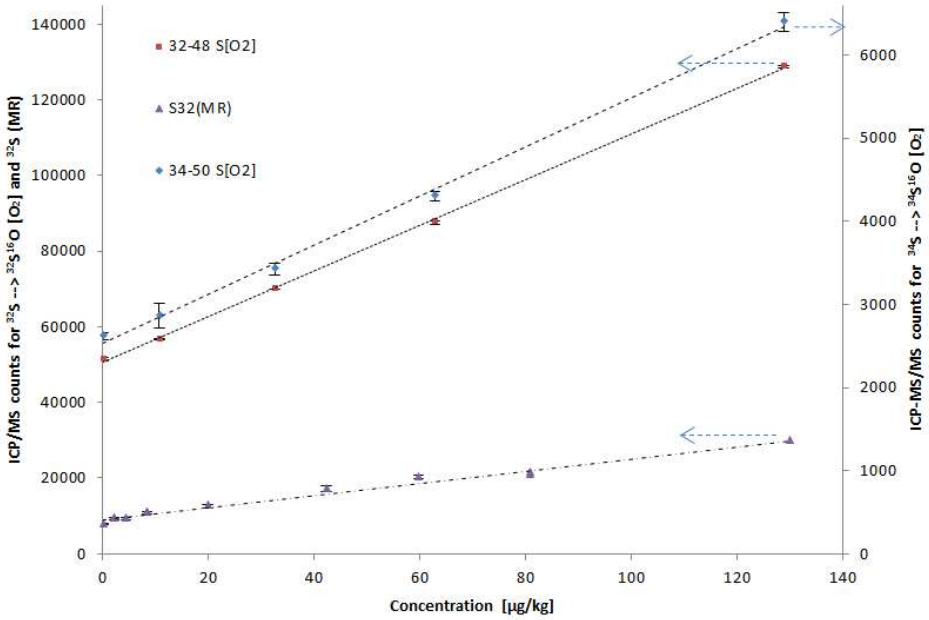


Figure 2: Calibration curves for S using ICP-HRMS or ICP-MS/MS (Arrows indicate the correct axis for all calibration curves)

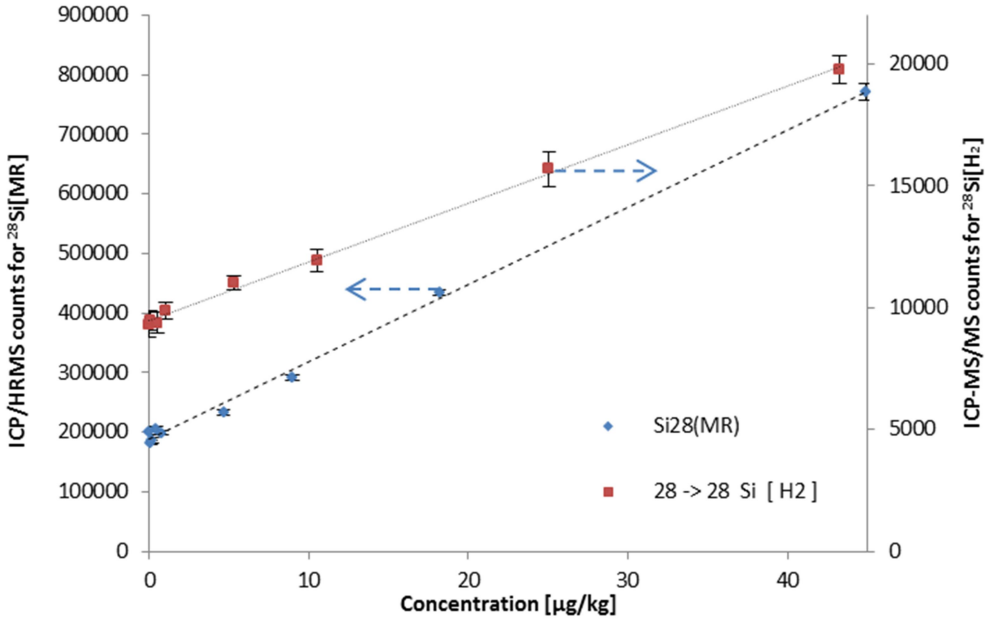


Figure 3: Calibration curves for Si using ICP-HRMS or ICP-MS/MS (Arrows indicate the correct axis for all calibration curves)

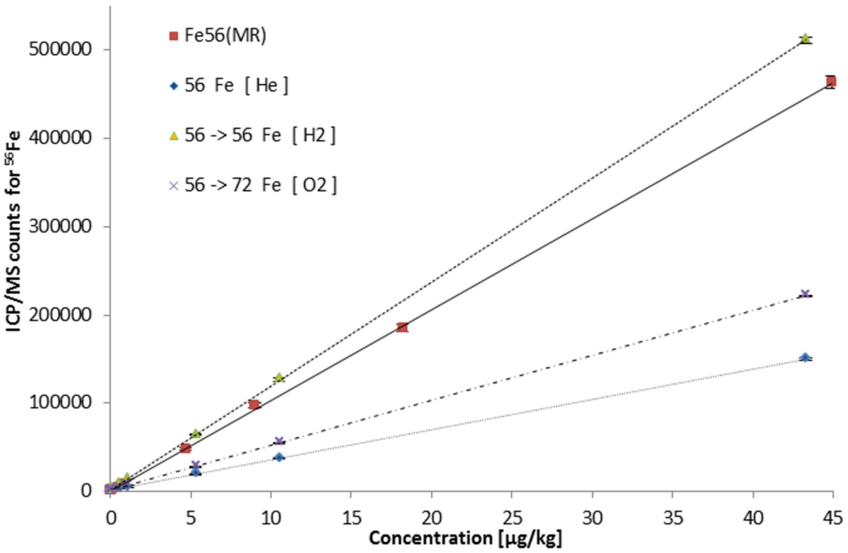


Figure 4: Calibration curves for Fe using ICP-HRMS or ICP-MS/MS

For S, Si, and Fe, respectively presented in Figure 2, Figure 3 and Figure 4, a nice sensitivity is obtained allowing trace elemental analysis in organic products. Anyhow, the BEC for S and Si is rather high compared to Fe. This high BEC might be due to contamination of the solvent or background emission not resolved by the high resolution or configuration of the ICP-MS/MS. For S, the origin of this BEC will be discussed later in 3.3.1, but for Si this phenomenon was already observed in Chainet *et al.* [18] and was attributed to the use of an injector and torch made of quartz that provoke a Si background signal.

The results obtained for most of the elements for both the ICP-HRMS and the ICP-MS/MS are represented in Figure 5. For light elements ($Z<40$) having no specific interferences, the new ICP-MS/MS has better or similar performances than the ICP-HRMS. For heavy elements ($Z>70$), the ICP-MS/MS is a little bit less sensible than the ICP-HRMS due to a better transmission of ions through the magnetic and electrostatic sectors in the low resolution mode. This is also due to the fact that these elements do not suffer from interferences and that the low-resolution mode is

294 sufficient to transmit these isotopes to the detector. For more difficult elements having
295 interferences, the potential of the ICP-MS/MS with different gases (H_2, He, O_2) and the use of the
296 initial quad to limit the analyte entering the reaction chamber allows similar or better
297 performances than the ICP-HRMS using medium resolution. Important elements for the
298 petroleum industry (S, Si, Fe), but also for new biofuels specifications (P, Ca) have excellent
299 performances compared to conventional system using traditional single quadrupole ICP-MS.
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301
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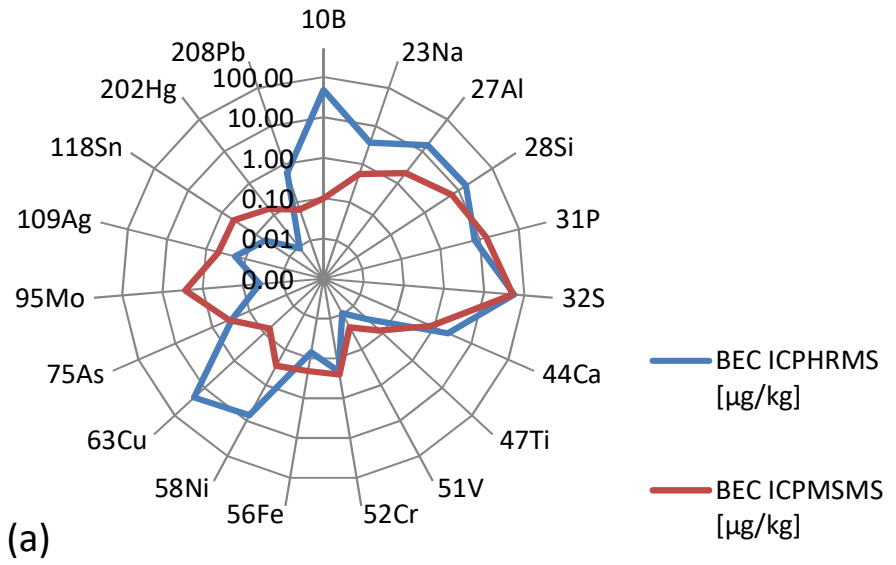

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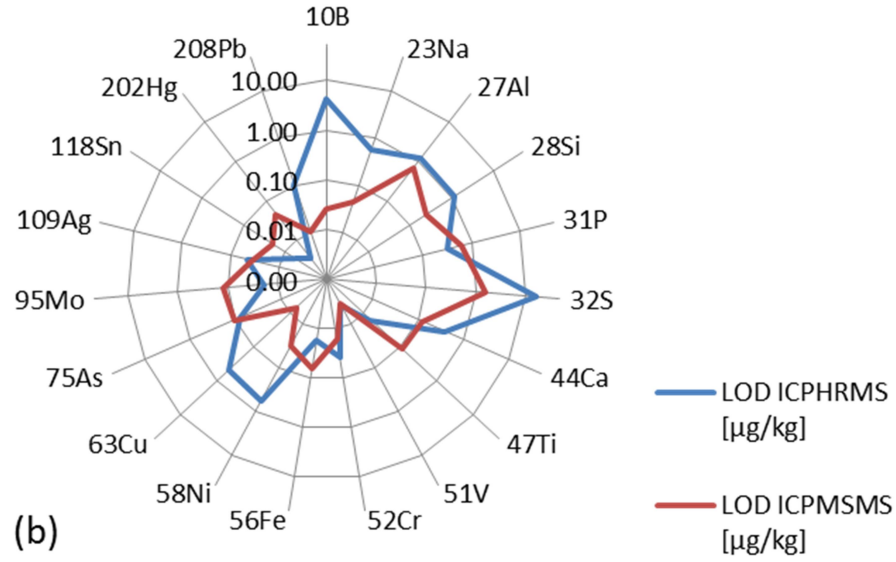


304

305 **Figure 5: Comparison of Background Equivalent Concentration (a) and Limit of Detection (b) for**
306 **various elements between ICP-HRMS and ICP-MS/MS detection.**

307

3.3 Application cases :

3.3.1 Ultra trace sulfur determination in solvents using ICP-MS/MS

The sulfur determination in petroleum products is not a real challenge as most of products are containing more than traces level of sulfur. There is however some cases where the sulfur concentration might be challenging, typically for naphtha used in reforming application where the concentration of sulfur might be as low as possible. When the calibration for sulfur is done at low level (Figure 2), the BEC is important compared to the LOD obtained for such element (Figure 5) and this was already pointed by preceding work [26]. Anyhow, most of the work done until now for S in organic matrices with ICP-MS/MS are using isotopic dilution after digestion procedure [27,30–32] and measure S levels between 4 mg/kg and 2.7%.

For very low levels of S, it was then important to determine the origin of this BEC, considering that different sources of BEC can be attributed. Typically, the BEC can be due to solvent contamination ($BEC_{solvent}$) or noise due to the instrumentation contamination or electronic noise of the detection. ($BEC_{instrumental}$). It should be noted that using digestion procedures, Yang *et al.* [32] observe a very low BEC in aqueous matrices.

Four different solvents (toluene, xylene, naphtha, Premisolv) were then tested to determine the various contributions of the BEC with different lot numbers and volatility. For this experiment, a calibration curve was prepared with adding of S using a sulfur mono-elemental oil-based standard between 5 and 300 µg/kg in the four selected solvents. These mixtures were introduced into the ICP-MS/MS and the settings of the plasma were adjusted in order to have the best signal to noise ratio of the instrument depending on the volatility of the solvent injected. One condition per solvent were retained and the $^{32 \rightarrow 48}S$ and $^{34 \rightarrow 50}S$ transition were kept to measure the S signal within each solvent. The $^{34}S/^{32}S$ isotope ratio of the S signal within the different solvents is interesting with a value of 21.20±0.83. This value is very similar to the theoretical value of 22.5 for the relative abundance of naturally S occurring isotope and this concordance might confirm that the BEC of the instrument is mainly driven by the S signal and not due to electronic noise.

The BEC obtained for each solvent and conditions is given in Table 3. The BEC is not equivalent when different lots of the same solvent are analyzed. As the conditions of the plasma was linked to the use of specific solvent and different BEC were obtained with an unique condition of the plasma, this difference of the BEC can then be attributed to the lot number of the solvent and then

directly to its residual S concentration. This indicates that the residual S concentration present in the solvent might be the only contributor to the BEC and that the $BEC_{instrumental}$ might be negligible. The Premisolv was also analyzed by UVF following ISO 20846 due to its high level of sulfur. A comparative value of 233 µg/kg was obtained with this technique, showing that the level of the BEC with the ICP-MS/MS (251 µg/kg) is mainly due to the S contamination. The BEC obtained for each new solvent can then be assigned to the level of concentration of sulfur in the solvent as it is conventionally done when standard addition are used. It is then possible to measure ppb level of S in various solvents by spiking the solvent with increasing concentrations of S and determining the S content by standard addition. It is interesting to note that pollution between 30 to 250 µg/kg of S were observed in the various solvents used in this work. Such information might be crucial for selecting feed used in reforming application.

Table 3: BEC [µg/kg] of $^{32\rightarrow48}$S obtained for each solvent and plasma conditions.

Lot number \ Solvents:	Naphtha	Toluene	Xylene	Premisolv
16J	75		78	
16F	86	80	32	
15G			54	
16A	68	98		
others				251

3.3.2 Trace elemental composition of Asphaltenes by ICP-MS/MS

Asphaltenes fraction are known to contain an important concentration of Ni, V and S that are easily measured due to their high level, but the minor traces are barely investigated and it might be interesting to evaluate if others metals are present in the asphaltenes fractions of some crude oil. In order to evaluate the feasibility of such determination, a multi-element oil-based standard (S-21+CoK) was used to calibrate the instrument in THF between 0 to 100 µg/kg. The conditions of nebulization and each mode of gas (H_2, He and O_2) were optimized due to the fact that the volatility of THF is different than xylene previously used in section 2.2.1. Higher flow of oxygen (0.27 compared to 0.20 mL/min), hydrogen (3.1 compared to 2.0 mL/min) and He (3.5 compared to 2.5 mL/min) was observed for the optimum signals in the gas cell, as it was the case for the

optional gas (0.31 compared to 0.20 L/min). The asphaltenes fraction was diluted between 700 to 85000 times in THF and measured subsequently. Yttrium was added to all solutions to verify the potential impact of the viscosity of the solution and controlling the efficiency of the nebulizer with the asphaltene solution. The sulfur concentration was not measured due to the presence of sulfonates in the initial multi-element standard solution, but also the high concentration of such element that is not needing trace analysis instrument. The same fraction of asphaltene was diluted in toluene and measured by WDXRF using an internal method to measure S, Ni and V concentrations of the prepared solution. The results obtained for many elements are given in Table 4. Concentrations obtained for Ni (380 mg/kg) and V (630 mg/kg) by ICP-MS/MS are quite comparable to the conventional WDXRF IFPEN method (322 mg/kg for Ni and 655 mg/kg for V) and allow to validate the analysis of the asphaltene. As already described in the literature [38], iron is the fourth element present in the asphaltene fraction in terms of concentration. The value obtained for Mo is also very similar to others values available in the literature [16,39]. The others elements are in the same order of magnitude with value observed in the literature between sub ppm level to tenth of ppm [16,39]. Amongst them, the value for tin is quite high and might be due to container contamination.

Table 4: Concentration obtained by WDXRF and ICP-MS/MS for the asphaltene fraction

Elements	Concentration [mg/kg]	
	WDXRF	ICP-MS/MS
V	655	630
Ni	322	380
S (%)	6.87	nm
Fe	nm	37.4
Sn	nm	25
Mo	nm	8.8
Zn	nm	6.4
K	nm	4.2
Si	nm	3.9
Cr	nm	3.3
Ag	nm	1.7
Co	nm	1.6
Ba	nm	1.3
Cu	nm	1.2
Ti	nm	0.8
Pb	nm	0.3
Al	nm	0.3

nm : not measured

3.3.3 Speciation of Ni, V and S in heavy petroleum cuts by GPC-ICP-MS

Based on the excellent performance of the ICP-MS/MS for the sensitivity obtained for the calibration curve (Section 3.2), it was then interesting to investigate the response of the instrument when it was coupled to liquid chromatography and more specifically to GPC. Such technique is used since years to investigate the size of Ni, V and S in various petroleum cuts, but all of these publications are based on the use of GPC coupled to ICP-HRMS [23,24]. The challenge to follow transient signal is the need of numerous points per peak in order to avoid loss of resolution in the chromatogram. A very recent article mentioned the use of ICP-MS/MS to

monitor elemental signature on liquid chromatography [33]. Previous assay done in this work (section 3.1) have shown that different gas modes might be necessary to have the best sensitivity and previous work done with the ICP-HRMS have shown the use of different resolution according to the measured element. Switching between two gas mode require 10 seconds at least with the ICP-MS/MS and such switch is not feasible when the instrument is coupled to a separation technique. The change of mode between high and medium resolution for ICP-HRMS is also not described in the literature but require at least few seconds of stabilization. Consequently, it is not compatible with the monitoring of chromatograms. It was then important to investigate which mode of gas was the most adequate to monitor Ni, V and S during the same acquisition. For the ICP-HRMS, previous work have shown that S is detected using medium resolution only in order to solve the interference on the mass 32. Such higher resolution is also reducing the intensity of the final signal due to a lower slit in front of the magnetic sector and might be a limitation for trace element analysis. This is illustrated by the 10 times difference of signal for Ni between low and medium resolution in Figure 6. Then for low concentration (< 5 mg/kg Ni_{total}), two injections are necessary in order to acquire V and S with the medium resolution and Ni and V with low resolution. Such choice has an important impact on the sample throughput due to the time of the analysis (120 minutes of run for GPC [24]).

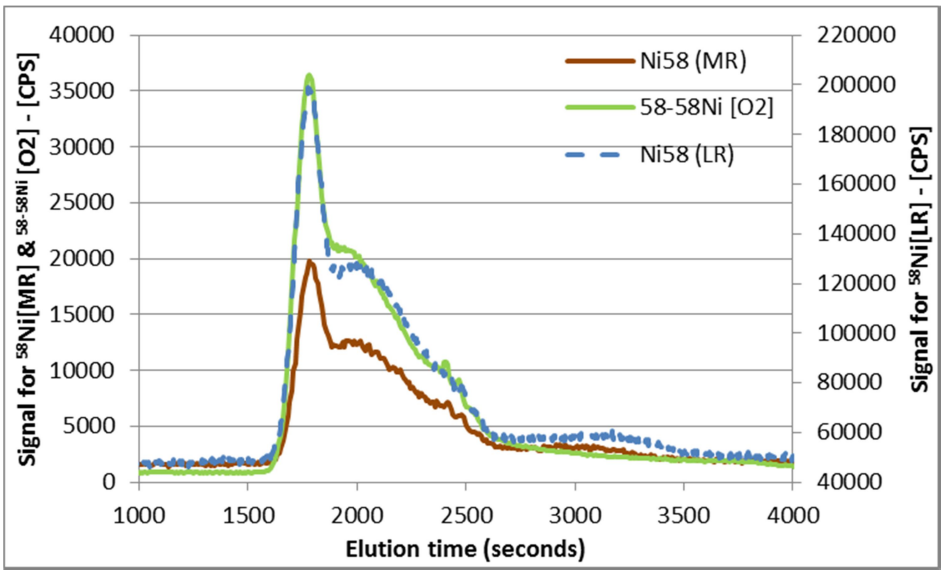
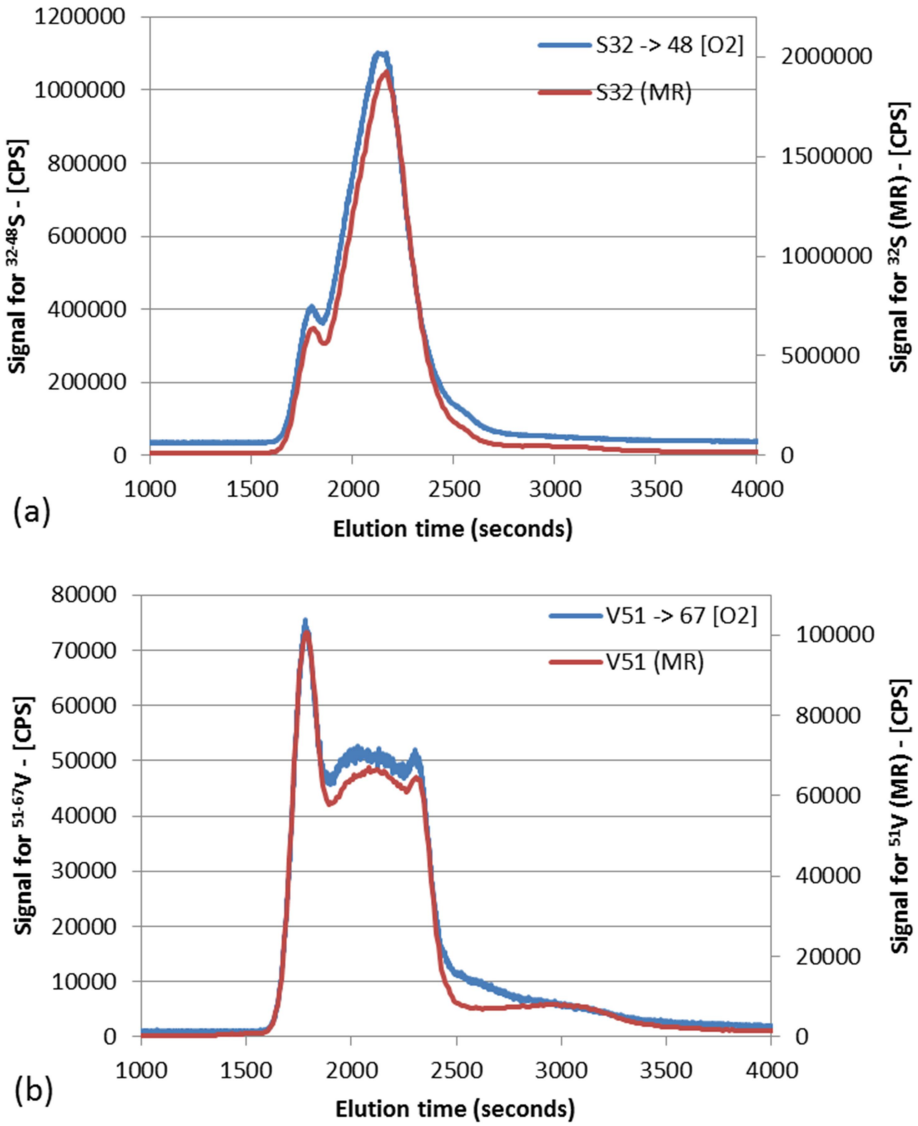


Figure 6: Comparison of GPC-ICP-MS/MS and GPC-ICP-HRMS chromatograms for Ni, injecting a VR with Ni content around 60 mg/kg

For the ICP-MS/MS, the O_2 mode was quite efficient for S (Figure 2) and V (Figure 1 and Figure S 1), but less effective for Ni due to the high enthalpy of reaction of Ni with oxygen. The He or H_2 mode was quite sensitive and was initially retained in the total injection (Figure 1) leading to lower sample throughput as in the case of ICP-HRMS for low concentration. Another way to observe an element with the ICP-MS/MS is to provoke a reaction within the reaction/collision cell and selecting the isotope that has not reacted at the end of the chamber. This is an interesting way to understand what has happened between the two quadrupole and is useful to understand and optimize the various instrumental conditions. Interestingly, the amount of Ni going through the reaction/collision chamber without reacting with oxygen was quite important and sufficient signal was obtained by looking at the $^{58}\rightarrow^{58}$Ni [O_2] mode.

A vacuum residue (VR) and its hydrotreated fraction (E) were eluted on the GPC column and the chromatogram obtained with the different modes are presented Figure 7 and Figure 8. The use of O_2 (2.5 mL/min) with Ni, V, S is particularly interesting for transient signal and allow the monitoring of the 3 elements in one mode only for the vacuum residue. For S and V (Figure 7), the signal is pretty similar for both instrument using the oxygen mode and the medium resolution but the signal to background ratio is slightly (+10%) better for the ICP-HRMS. For the Ni detection, the situation is different depending on the concentration observed on the GPC chromatogram. The profile obtained for the VR (Figure 6) is sufficient for all the mode tested. The signal to noise ratio is multiplied by a factor of two between the low and medium resolution mode of the ICP-HRMS, but the oxygen mode is even better for the ICP-MS/MS detection. When the hydrotreated feed is observed (Figure 8), the medium resolution is not sensible enough to obtain a clear distribution of the Ni entities and the use of a low resolution mode is then compulsory. This imply the use of both the medium resolution for S and V and the low resolution for Ni in order to obtain the information for all elements, reducing the sample throughput. The use of the ICP-MS/MS in the oxygen mode is sensitive enough to get a nice profile of the Ni entities on the hydrotreated feed. Such mode is then adequate to have Ni, V and S information during the same run allowing to reduce the analysis cost and time.



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450 **Figure 7: Comparison of GPC-ICP-MS/MS and GPC-ICP-HRMS chromatograms for S (a) and V**
451 **(b)**

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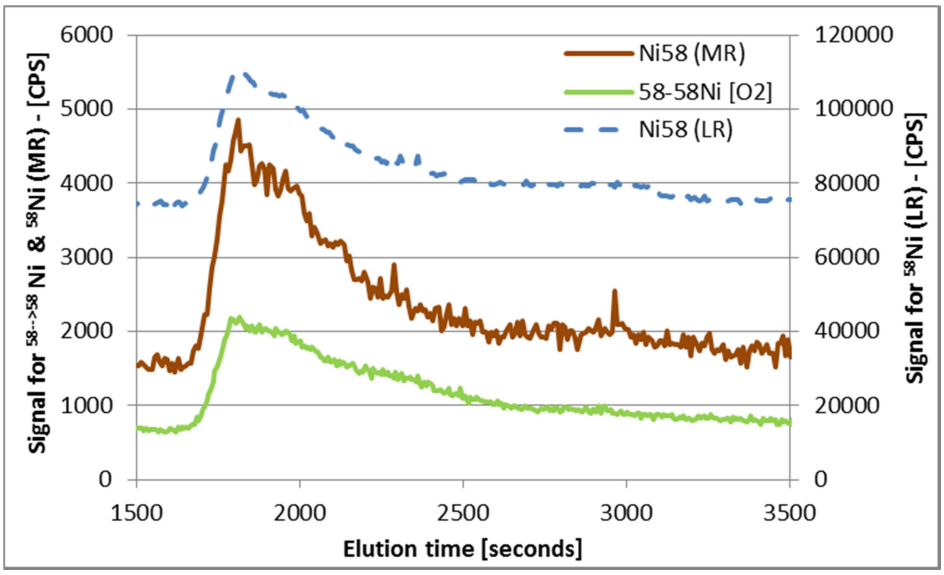

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454 **Figure 8: Comparison of GPC-ICP-MS/MS and GPC-ICP--HRMS chromatograms for Ni, injecting**
455 **the HDT VR with Ni content around 3 mg/kg**

456

4 Conclusions

The recent inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) was tested using direct injection of hydrocarbons after solvent dilution in order to investigate its use for the petroleum industry. Based on the fact that many previous authors have used ICP-HRMS for the monitoring of difficult elements in organic matrices, the results obtained for both ICP-MS/MS and ICP-HRMS were compared for both total concentration and speciation of severely interfered isotopes in petroleum products. The capability of ICP-MS/MS to achieve such performance using direct injection of petroleum products after dilution in hydrocarbon solvent was demonstrated here with different applications cases.

For the direct determination of heavy elements (Z>70) in hydrocarbon matrices, the ICP-MS/MS was less sensitive than the ICP-HRMS when the direct introduction of organic substances was used. For light elements (Z<40), the sensitivity was similar or better using ICP-MS/MS and for interfered elements (Si, S, Ca, Fe), the use of the two quadrupoles combined to the octopole reaction/collision cell (ORC) with He, O_2 or H_2 gave similar or better detection limits (LOD) than the ICP-HRMS in medium resolution. The results obtained with the ICP-MS/MS gave good performance with detection limit within the range of 0.004 µg/kg (V) to 0.9 µg/kg (Al) and appeared in the lowest values published in the literature using ICP-MS/MS in organic solvents.

Sulfur at very low levels in reformates was successfully monitored in the oxygen mode using the oxide ion ($^{32}S \rightarrow {}^{48}SO$). The background equivalent concentration (BEC) origin was attributed to solvent contamination by sulfur and was confirmed by UVF method. Using He, O_2 or H_2 as reactant gas, the ICP-MS/MS method easily confirmed Ni and V concentrations measured using wavelength dispersive X-rays fluorescence (WDXRF) and allowed the determination of 14 elements in the asphaltene fraction, with concentrations ranging from 0.3 mg/kg (Al and Pb) to 37.4 mg/kg for Fe.

For speciation of Ni, V and S, GPC-ICP-MS/MS is particularly powerful using O_2 both for high (vacuum residue) and low (HDT vacuum residue) contaminated heavy products. Contrary to GPC-ICP-HRMS where two injections of sample were required (medium resolution for S and V and low resolution for Ni), GPC-ICP-MS/MS easily allowed the acquisition of the 3 elements in one mode during the same run and considerably enhancing the sample throughput. This paper clearly demonstrates new opportunities of the ICP-MS/MS in the oil industry using direct

injection of petroleum feedstock's and products after dilution in hydrocarbon solvent for total determination of metals but also for advanced speciation in non-distillable fractions.

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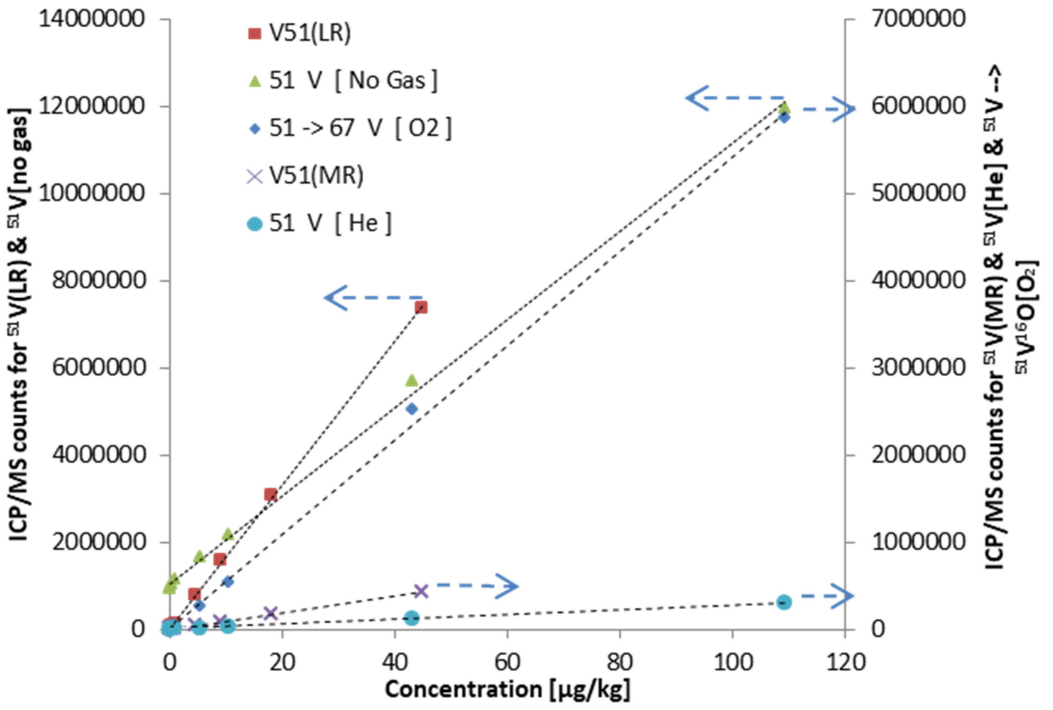
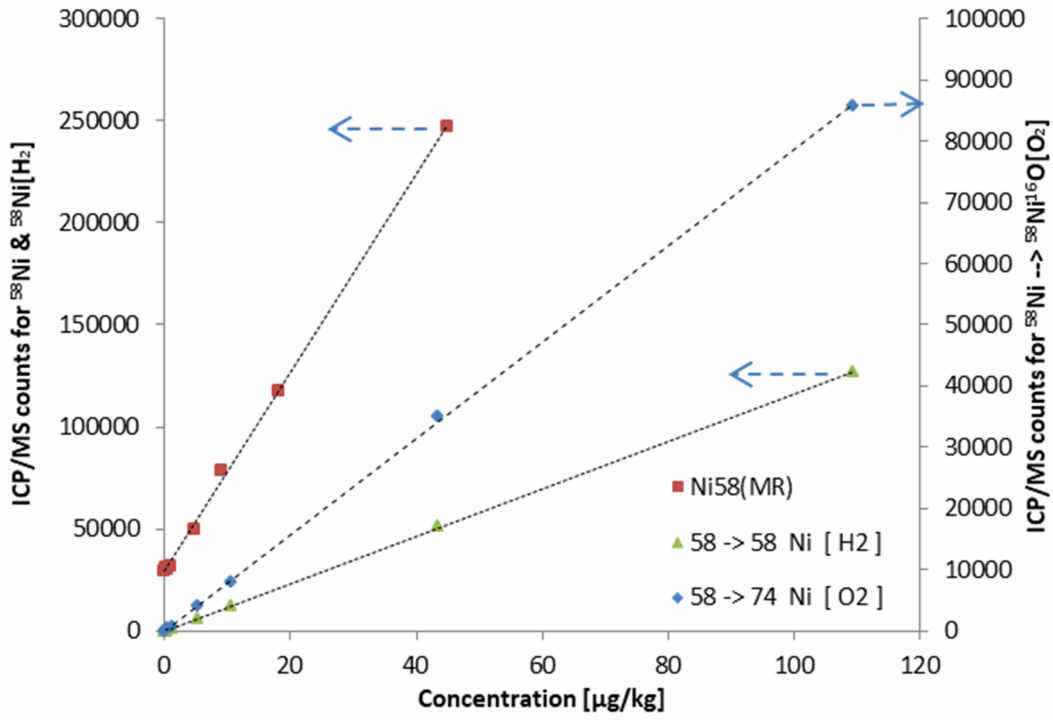
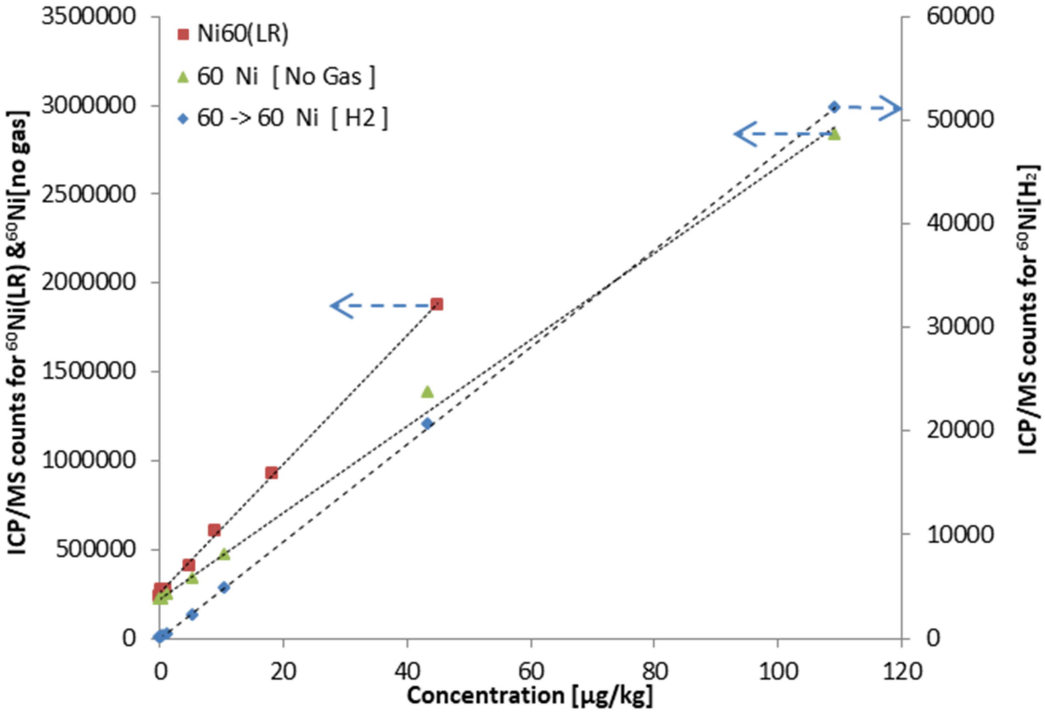
7 Tables and Figures

8 Supplementary material







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669 **Figure S 1: Calibration curves for Ni ($^{58\rightarrow58}$Ni and $^{60\rightarrow60}$Ni) and V using ICP-HRMS or ICP-MS/MS**
670 **(Arrows indicate the correct axis for all calibration curves)**