



HAL
open science

Development of a chromatographic methodology for the separation and quantification of V, Ni and S compounds in petroleum products

Vicmary Vargas, Jimmy Castillo, Ruben Ocampo Torres, Brice Bouyssi re,
Charles-Philippe Lienemann

► To cite this version:

Vicmary Vargas, Jimmy Castillo, Ruben Ocampo Torres, Brice Bouyssi re, Charles-Philippe Lienemann. Development of a chromatographic methodology for the separation and quantification of V, Ni and S compounds in petroleum products. *Fuel Processing Technology*, 2017, 162, pp.37 - 44. 10.1016/j.fuproc.2017.03.027 . hal-01566222

HAL Id: hal-01566222

<https://ifp.hal.science/hal-01566222>

Submitted on 20 Jul 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destin e au d p t et   la diffusion de documents scientifiques de niveau recherche, publi s ou non,  manant des  tablissements d'enseignement et de recherche fran ais ou  trangers, des laboratoires publics ou priv s.

Development of a chromatographic methodology for the separation and quantification of V, Ni and S compounds in petroleum products.

Vicmary Vargas^{a,b}, Jimmy Castillo^a, Ruben Ocampo Torres^d, Brice Bouyssiere^b and Charles-Philippe Lienemann^c

^aUCV, Facultad de Ciencias, Escuela de Química, Caracas, 1053, Venezuela

^bCNRS/UPPA, UMR 5254, IPREM/LCABIE, Hélioparc, 2 Avenue de Président Angot, 64053 Pau, France

^cIFP Energies Nouvelles-Lyon, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

^dGroupe de Physico-Chimie de l'Atmosphère Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé ICPEES UMR 7515 Université de Strasbourg/CNRS, 1 rue Blessig, 67000 Strasbourg

Corresponding author:

Brice Bouyssiere: brice.bouyssiere@univ-pau.fr

Tel: +33 559 407 752

Fax: +33 559 407 674

Abstract

The separation, quantification and identification of V, Ni and S and their compounds in crude oils or their refining fractions is a subject of great interest for the oil industry. Such elements and hetero compounds are harmful to industry catalysts and might be toxic to living organisms. This work presents a methodology based on the following two-step approach: (1) A chromatographic column separation is first performed on a silica gel column to produce six fractions from the initial crude oils or petroleum products, such as vacuum residues (VRs). This separation is achieved by varying the polarity of the elution solvent systems used. (2) These separated fractions are then studied using gel permeation chromatography (GPC) coupled to an inductively coupled plasma high-resolution mass spectrometry (ICP-HRMS).

Additionally, the use of ultraviolet (UV)-visible spectroscopy allows the identification of fractions containing porphyrinic-type compounds by detecting the Soret band at 405 nm. The correlation between this two-step approach is to deduce both the distribution and nature of Ni and V complexes within the sample. This method reduces the complexity of petroleum matrices and produces simpler fractions that can be used for further studies.

Keywords: Crude oil Analysis, Metallo compounds, Porphyrin extraction, Speciation, GPC ICP MS, Fractionation

1. Introduction

Petroleum is a complex mixture of compounds that are usually grouped into the following four chemical classes based on their polarity and solubility: saturates, aromatics, resins, and asphaltenes (SARA). Metals, particularly Ni and V, which can be present in crude oils at concentrations up to thousands of parts per million, are predominantly associated (~80%) with the asphaltene fraction of crude oils [1]. The presence of heavy metals in crude oils as free metals and/or associated oxide metals or complexed to organic compounds has been described in the literature. However, the molecular forms of these metallo compounds remains hotly debated. Acevedo et al. [2] indicated that the separation of metallo compounds using common separation techniques is very difficult. According to these authors, the metallo compounds in asphaltenes undergo an aggregate rearrangement after penetration, which leads to an aggregate structure in which the metallo compounds are trapped.

Several works have reported that the vanadium and nickel organo compounds present in crude oils exist predominantly as vanadyl- and nickel-chelated compounds (porphyrins) [3–7] and could be trapped in the asphaltene fraction during precipitation. However, they can also be linked or trapped in other types of macromolecular networks [2]. Several groups have isolated [8-10] and determined the structure of free porphyrins from geological sources (e.g., crude oils, oil shales, and coal) [11-15]. Those porphyrins were free bases or metal complexes, particularly involving Ni and V as $V=O$.

The separation of metalloporphyrins in crude oils is based on solubility class and polarity separation, Soxhlet extraction, vacuum sublimation, and chromatographic techniques, such as high-performance liquid chromatography (HPLC),

column chromatography and thin-layer chromatography (TLC)[3]. Solubility parameters have been demonstrated to have great potential to characterize the solubility and other properties of petroleum and fossil solids and liquids both experimentally and theoretically[16-19]. Several authors have reported that the metallocompounds of V and Ni become separated from each other during the process of isolation with pyridine/water extracts [8]. Therefore, examining these compounds without interference from each other has been impossible. To separate the different classes of compounds, HPLC has been coupled with graphite furnace atomic absorption spectroscopy [8,9], inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP mass spectrometry (ICP-MS) [3].

The association of metal porphyrins with asphaltenes likely explains the great difficulties encountered when extracting or separating these compounds from crude oils or residues. Although the association of metal porphyrins with asphaltenes is well documented, no general agreement on the mechanisms underlying these associations exists [2]. One reason for the strong interactions between these metallocompounds and the asphaltenes subfraction is that asphaltenes can trap these compounds in the inner structures of their aggregates.

Caumette et al.[20,21] developed a methodology to separate and speciate Ni and V compounds in crude oils. The resolution achieved using their technique allowed the discrimination of at least three classes of Ni and V species containing varying proportions of the metals as a function of the origin of the crude oil, the crude oil fraction (asphaltene vs. maltenes) and the dilution factor. **Even more recently, another group Wandekoken et al [22] developed a** methodology for separation of organic vanadyl

compounds in crude oil using fractionation by preparative liquid chromatography using as eluent different mobile phases, in their results all the V is linked to porphyrin structure, discarding the existence of non porphyrinics Vanadium compounds and a similar distribution of the vanadyl porphyrins between polar and non polar fractions. That work revealed that 60-110% of the V present was associated with porphyrinic structures.

Using Fourier transform ion cyclotron resonance (FTICR)-MS and a pre-separation method to simplify the petroleum matrices, many groups[23-25] have found evidence of porphyrinic structures. However, previously, no spectroscopic evidence of non-porphyrin metal complexes (Ni and V=O) has been found[10].

In this work, we present a procedure in which chromatographic separation is used to simplify the complex matrices of petroleum products, which are represented here with a vacuum residue (VR). The quality of the separation is determined by TLC. This first step allows fractionating the VR and simplifying the matrix. The second step then allows those fractions to be studied by GPC-ICP-HRMS in a simplified manner by quantifying and studying the size distributions of the V, Ni and S compounds within the oil VR. Better understanding the molecular structures of compounds in crude oils and petroleum products is important for developing innovative solutions for industry treatments. By analyzing the ultraviolet (UV) absorbance, the presence of metalloporphyrins in different fractions was detected. This methodology generates a clear separation of the V=O and Ni compounds and the direct extraction of trapped

porphyrins from the asphaltene fraction. Using the proposed methodology, 55% of the V and Ni compounds were separated preferentially in a middle-polarity solvent.

2. Experimental

2.1 Samples, materials and solutions

VR from Safaniya (Middle East) was obtained from IFP (Solaize, France) and contained 4.95% S, 149-mg/kg V and 47-mg/kg Ni. Its initial boiling point was 365°C, and 50% of the distribution was obtained at 611°C. The final boiling point was measured at 750°C.

Hexane, dichloromethane (DCM), methanol, acetone, chloroform, tetrahydrofuran (THF), silica gel plates, silica gel and complexes of Ni and V=O tetraphenyl porphyrins (TPPs) were obtained from Aldrich (Germany). All reagents and chemicals were of analytical or chromatographic grade.

2.2 Procedures

2.2.1 Chromatography column

The chromatography column was prepared using the wet method by pouring dry inactivated silica gel in a mixture of hexane:DCM(9:1) so that the separation could start with a low-polarity solvent. The resulting slurry was added into the glass column to efficiently pack it with silica. The sample was dissolved in the minimum amount of DCM required, and then, hexane was added until a ratio of 9:1 was reached. Then, this

solution was seeded into the column. The separation was performed by eluting the column with the following systems with varying solvent polarities, as shown in Figure 1: hexane:DCM (9:1), hexane:DCM (3:1), hexane:DCM (1:1), DCM:acetone (1:1), DCM:methanol (4:1) and chloroform:methanol:water (65:25:4). Using these mixtures, six fractions with solubility parameters ranging from 16 to 21 according to Hansen solubility parameters were collected [26].

2.2.2 GPC and ICP-HRMS Detection

Solutions of the collected fractions and the initial VR sample were prepared in THF and diluted one hundred-fold. The same dilution and solvent were applied to V (as V=O) and Ni TPP standards at concentrations of 10, 50, 100 and 200 mg/kg. For each sample, 20 μL was injected and eluted isocratically at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$ of THF for 120 min using a Dionex (Amsterdam, The Netherlands) HPLC system consisting of an UltiMate 3000 microflow pump, an UltiMate 3000 autosampler, and a low port-to-port dead-volume microinjection valve. A post-column splitter was used to divide the flow (20:1). The low-flow outlet (50 $\mu\text{L}/\text{min}$) led to the ICP-HRMS using a DS-5 microflow, and the high-flow outlet (950 $\mu\text{L}/\text{min}$) was sent to waste. A similar system was previously described by Desprez et al. (2014) [27]. Cummenet et al. work in a separation scheme using HPLC with Xilene–THF gradient and GPC, finding that part of metal-complexes is retained on the column according to non-specific retention mechanism. In our separation scheme the eluent for GPC separation is pure THF in order to maximize the solubility of all the components in crude oil and avoid any adsorption onto GPC packing minimizing in this way any non-specific retention mechanism.

The detailed conditions used for ICP-HRMS detection have been previously reported [27–29], and a summarized description is given below. A Thermo Scientific Element XR sector field ICP-HRMS instrument operated at a resolution of 4000 (medium resolution) was used to access spectrally interfered isotopes of ^{60}Ni , ^{32}S , and ^{51}V . The spectrometer was equipped with a Fassel-type quartz torch shielded with a grounded Pt electrode and a quartz injector (1.0 mm i.d.). A Pt sampler (1.1-mm orifice diameter) and a Pt skimmer (0.8 mm orifice diameter) were used. O_2 flow was continuously supplied to the nebulizer Ar gas flow. The MS was fitted with a modified DS-5 microflow total consumption nebulizer (CETAC, Omaha, NE) mounted on a laboratory-made, low-volume (8-mL), single-pass jacketed glass spray chamber without a drain, as described elsewhere [27].

The spray chamber was thermostated to 60°C with water using a Neslab RTE-111 (Thermo Fisher Scientific, Waltham, MA) temperature-controlled bath circulator.

Separations were conducted using three Styragel styrene-divinylbenzene gel permeation columns connected in series (7.8 × 300 mm). These columns were HR4 (particle size, 5 μm; exclusion limit, 600,000 Da of polystyrene [PS] equivalent), HR2 (particle size, 5 μm; exclusion limit, 20,000 Da), and HR0.5 (particle size, 5 μm; exclusion limit, 1,000 Da). A Styragel guard column (4.6 × 30 mm) was included before these three columns to protect them and prolong their lifetimes. The separation achieved by the columns was evaluated using a mixture of PS standards ranging from 2630 kDa to 381 Da with an hyphenation between GPC and a refraction index detector.

The ICP-HRMS conditions were controlled and optimized daily using a 1.0-ng g⁻¹ multi-element (V, Ni, S and Fe) tuning solution in THF delivered via a syringe pump. The

peaks of the isotopes chosen at these conditions were baseline resolved from the interferences.

A built-in software application was used to integrate the recorded signal. The data acquisition method was updated with a mass offset determined for each isotope to compensate for the mass drift resulting from the magnet sector.

2.2.3 Absorbance

Solutions of the collected fractions were prepared in THF, and absorbance spectra were measured with a UV spectrophotometer Shimadzu (UV-1800) using a 10-mm cell.

2.2.4 TLC

Solutions of the collected fractions were diluted in THF and applied (2 μ l) at the bottom of an SiO₂(10x6 cm)TLC plate, and the chromatographs was developed with the following solvent systems: hexane four times, hexane:DCM (55:45) twice, and DCM:methanol(99.5:0.5) once; the solvent front was varied in each case. This methodology allowed the fast separation of the mixture into the SARA classes, similar to the well-known SARA separation.

3. Results and discussion

The first sample separation resulted in six fractions, which were dried under argon atmosphere and then weighed to determine the percentages of recovery after separation. Table 1 lists the weight of each fraction and the total recovery, clearly

showing the efficiency and reproducibility of this method fractionating the Safaniya VR analyzed.

Each fraction of RV corresponds to a solubility class, each class is extracted by their solubility in solvents with polarity ranging from low polarity to high polarity in the following order *hexane:DCM (9:1)* < *hexane:DCM (3:1)* < *hexane:DCM (1:1)* < *DCM:acetone (1:1)* < *DCM:methanol (4:1)* < *chloroform:methanol:water (65:25:4)* according to the order shown in the table 1, Where the elution is started with a solvent mixture of little polar until reaching a polar mixture. The last solvent mixture have a very low water content to extract the remnant molecules adsorbed to silica and clean it. The variation in the polarity of the samples can be easily understood based on the Hansen solubility parameter [26]. **Figure 2** presents the solubility parameters of the solvent mixtures used calculated as the volume-weighted average and those of the fractions obtained from Safaniya VR.

Interestingly, the distribution of fractions from Safaniya 1 are notably different from those of Safaniya 2. This difference will be discussed further when a complete characterization of the Ni, V and S distributions is obtained.

Using TLC, we analyzed each fraction and achieved a separation based on polarity. Figure 3 shows the TLC and its appearance under UV light. The solvent front system and points of application can be clearly observed. Fractions 1, 2 and 3 elute with the solvent mixture, showing that the molecules in those fractions have low interactions with the silica surface. Some of the molecules present in fractions 4, 5 and 6 are retained at the application point, demonstrating the high interactions of these molecules with the silica. The retained fractions can be considered to be more polar fractions

present in the sample and are likely associated with asphaltenes. From the TLC results, we can conclude that most of the molecules constituting the asphaltene fraction in the VR are distributed in fractions 4-6, and thus, some of the V and Ni present in fraction 4 may be associated with asphaltenes.

Fractions 1-6 were dissolved in THF and injected into the GPC-ICP-HRMS. ICP-HRMS is used as a specific detector for the determination of V, Ni and S, and the signal intensity for each compound as a function of the retention time is obtained. According to Desprez et al.[27], the integration intervals corresponding to high-, medium-, and low-molecular weight compounds (HMW, MMW, and LMW, respectively) were determined to be as follows: 1100-1400 seconds for HMW compounds, 1400-1600 seconds for MMW compounds and >1600 seconds for LMW compounds. In the rest of this work, we discuss the compounds in terms of their molecular weights; however, the compounds are sorted according to their hydrodynamic volumes and that what we call molecules' include noncovalent aggregates.

To validate this two-step approach in which column chromatography is used to prepare six fractions that are then subjected to gel permeation separation, the chromatogram obtained from the VR was compared to the reconstructed Ni, V and S profiles obtained by combining all of the chromatograms obtained for each fraction for each analyte (S, Ni and V). This comparison is given in supplementary Figure B. The good match between the two approaches indicates that the separation method does not change the characteristics of the molecules constituting the VR matrix. Additionally, the errors arising from separation using these two methods (i.e., polarity and size exclusion) are low.

The intensity profiles of the mass distributions of vanadium and nickel in the six fractions obtained from Safaniya VR and Safaniya 2VR and of vanadium (as vanadyl) and nickel TPP standard solutions are shown in Figures 4 and 6, respectively. For the standard solutions, a relatively sharp peak with a maximum intensity at the retention time (1,700 seconds) is obtained for both porphyrins. This retention time corresponds to molecules of approximately 600 Da, which is typically the mass of free “alkyl” porphyrins.

As shown in Figure 4, the distributions of the amounts of vanadium in the six fractions obtained from Safaniya and its duplicate. **Figure 5** show clearly that vanadium is primarily concentrated in fractions 3, 4 and 5, with a major contribution from fraction 4. Fraction 3 presents a size distribution ranging from HMW to LMW compounds, with the highest proportion corresponding to MMW species. In contrast, for fraction 4, a trimodal distribution is observed, which is very similar to the result found for the original VR. Finally, fraction 5 exhibits a unimodal distribution that is concentrated in HMW species.

As shown in Table 1, the vanadium in fraction 3 corresponds mostly (80%) to MMW and HMW molecules. In contrast, that in fraction 4 contains approximately 50% HMW molecules, and this percentage increases to 70% in fraction 5. In fractions 1, 2 and 6, the amount of vanadium is not significant. These results point to the proposed separation methodology allows to extract an important percentage of the V associated with asphaltenes.

Table 1. Distributions of vanadium in the separated fractions and its repartition to HMW, MMW and LMW species in Safaniya and Safaniya 2.

Fraction	Percentage distribution of total V	Percentage of V in HMW species	Percentage of V in MMW species	Percentage of V in LMW species
1	0.3	34.2%	41.1%	24.7%
2	0.5	61.5%	29.4%	9.1%
3	17.5	33.1%	57.1%	9.8%
4	46.3	53.9%	26.7%	19.4%
5	34.6	71.5%	11.2%	17.3%
6	0.8	89.3%	9.1%	1.6%
Safaniya	100	56.7%	25.4%	17.9%
1	0.1	21.7%	36.1%	42.2%
2	1.2	49.8%	49.1%	1.1%
3	27.8	13.6%	51.1%	35.3%
4	43.6	55.5%	30.3%	14.2%
5	23.9	67.2%	9.7%	23.0%
6	3.4	70.0%	10.0%	20.0%
Safaniya 2	100	56.3%	25.2%	18.5%

Figure 6 shows the intensity profiles for the mass distributions of nickel in VR and its six fractions. The profile for Ni contained in the petroleum products is plotted and exhibits a wide molecular size distribution in three zones. The Ni is distributed in fractions 1-5 as show in [Figure 7](#). The size distributions of fractions 1 and 2 mostly consist of MMW and LMW compounds, and fractions 3 and 6 contain the remaining Ni present in the sample, exhibiting distributions similar to those of fraction 4 and 5 (i.e., concentrated in HMW compounds).

As shown in Figure 7, the distributions of the amounts of Ni in each fraction of Safaniya and its duplicate clearly indicate that the major contributions of nickel correspond to fractions 4 and 5, which containing nearly 70% of the total Ni in the sample. As previously observed for vanadium, fractions 1 and 2 (i.e., the low-polarity

fractions)are mainly composed of LMW and MMW compounds as show in **Table 2**. In contrast,fractions 4 and 5 are mainly distributed in the HMWregion

Well documented studies concluded that most of the metal compounds in crude oils are associate to asphaltenic fraction of the crude oil forming aggregates of high molecular weight. Results for V and Ni demonstrate that after the separation the fractions with medium and low molecular weight are those with higher metal content. The result shown that proposed separation methodology allows to extract an important percentage of the V and Ni associated with asphaltenes [1,2].,

Table 2. Distribution of nickel in the separated fractions obtained from Safaniya and Safaniya 2.

Safaniya Fraction	Percentage distribution of total Ni	Percentage of Ni in HMW species	Percentageof Ni in MMW species	Percentage of Ni in LMW species
1	15.6	18.3%	57.3%	24.4%
2	9.6	39.5%	44.1%	16.4%
3	3.1	57.6%	25.8%	16.5%
4	27.1	67.3%	14.2%	18.6%
5	43.1	73.0%	8.7%	18.3%
6	1.4	91.4%	7.1%	1.5%
	100	62.9%	19.4%	17.8%
<hr/>				
Safaniya 2				
1	8.9	14.7%	15.4%	69.9%
2	14.3	18.2%	46.2%	35.6%
3	4.6	54.9%	37.1%	8.0%
4	37.7	71.2%	21.5%	7.3%
5	30.0	66.5%	8.7%	24.8%
6	4.4	71.2%	9.5%	19.3%
	100	63.8%	19.6%	16.6%

Standard solutions of Ni and V=OTPPs in THF were used to collect the absorbance spectra. The Soret band characteristic of these compounds was observed at 412 and 420 nm, respectively, as shown in complementary Figure A. The extinction coefficient of Ni TPPs is 5 times lower than that of V=OTPPs because UV absorbance spectroscopy is more sensitive to the latter than to the former.

Figure 8 presents the absorbance spectra obtained for all fractions. For all fractions except fraction 3, the curve is a typical absorbance curve for crude oil compounds, with a decay band spanning from the UV region to 600 nm. In contrast, the absorption spectra of fraction 3 present a wide peak at approximately 405 nm, which is associated with the vanadylporphyrins present in these fractions. This fraction contains 20% of the V (Table 1) and 4% of the Ni (Table 2), and the V=O porphyrin response is 5 times higher than that of the Ni porphyrin. Additionally, fraction 3 (for V) is mainly distributed in the MMW and LMW zones according to size-exclusion chromatography, and free porphyrins are normally eluted in this range (Figure 4). Thus, this separation method liberates the V compounds from their aggregate forms or elutes a portion of the Ni and V present in the resins.

Figure 9 presents the intensity profiles for the mass distributions of sulfur in the six fractions. The profile of S contained in the VR is plotted as a continuous line and exhibits a wide molecular size distribution consisting of three zones: HMW, MMW and the tail. Fraction 4 shows a bimodal distribution of HMW and MMW. The remaining fractions exhibit monomodal profiles.

As shown in Figure 10, the distributions of the amounts of S in each fraction of SafaniyaVR and its duplicate clearly demonstrate that S is divided among fractions 1-5, with major contributions contained in fractions 1 and 4. As show in Table 3, fractions 1, 2 and 3 mostly correspond to the MMW compounds (60% for fractions 1 and 2 and 50% for fraction 3). Fractions 5 and 6 fall in the HMW compounds, whereas fraction 4 contains 48% HMW and 43% MMW and exhibits a bimodal profile (Figure 7).

Table 3. Distribution of sulfur in the separated fractions of Safaniya and Safaniya 2.

Safaniya Fraction	Percentage distribution of total S	Percentage of S in HMW species	Percentage of S in MMW species	Percentage of S in LMW species
1	34.4	7.7%	63.5%	28.8%
2	13.2	27.4%	58.2%	14.5%
3	6.1	43.7%	47.7%	8.7%
4	33.2	47.7%	43.3%	8.9%
5	12.7	63.8%	19.3%	16.9%
6	0.4	81.0%	15.6%	3.4%
	100	33.6%	49.5%	16.9%
<hr/>				
Safaniya 2				
1	50.8	8.5%	60.2%	31.3%
2	7.9	24.2%	60.6%	15.3%
3	3.6	38.6%	50.4%	10.9%
4	29.6	48.7%	43.0%	8.3%
5	7.2	64.3%	15.9%	19.8%
6	1.0	66.0%	16.3%	17.6%
	100	30.9%	48.4%	20.6%

The initial distributions of each fraction from Safaniya 1 differ substantially from those obtained for Safaniya 2 in terms of the initial masses (Figure 2). However, similar differences are not observed among the distributions of Ni, V and S compounds (Figures 4, 6 and 9) when considering the specific response of each element. Therefore, the

initial chromatographic separation is particularly well suited for the characterization of Ni, V and S compounds. Thus, when the information obtained on the polarity, size and Soret band detection is coupled to the specific detection by ICP-HRMS, the molecules present in the VR can be better characterized.

4. Conclusions

The proposed method is based on a combination of two separation techniques: an initial elution based on polarity and a second separation based on size exclusion. This method allows the separation of 55% of the metal compounds from the crude oil and generates a fraction that is rich in free metal porphyrins. Because these compounds are extracted from aggregates, the amount of metal compounds associated with aggregates decreases.

This chromatographic separation methodology allows the collection of fractions that are rich in V (fractions 4 and 5), Ni (fractions 4 and 5) and sulfur (fractions 1 and 4), and the distributions were found to remain constant when duplicate experiments were performed.

UV-visible analysis was also conducted to detect the Ni and V=O porphyrins and obtain a better understanding of their distributions and natures in the collected fractions.

The separations achieved good recovery of the starting material. Combining the information obtained on the polarity and size and the detection of the Soret bands contributes to obtaining a better characterization of the molecules present in the VR.

Conflict of interest:

The authors have no conflicts of interest to declare.

Funding:

This work was supported by the “Programme de Coopération Postgraduée (PCP) Pays andins”

The financial support of the Conseil Régional d’Aquitaine (20071303002PFM) and FEDER (31486/08011464) is acknowledged.

References

- [1] J. Chirinos, D. Oropeza, J. González, M. Ranaudo, R.E. Russo, Determination of vanadium/nickel proportionality in the asphaltene fraction of crude oil using thin-layer chromatography with femtosecond laser ablation–inductively coupled plasma–mass spectrometry, *Energ. Fuels* 27 (2013) 2431–2436. doi: 10.1021/ef3020052.
- [2] S. Acevedo, K. Guzmán, H. Labrador, H. Carrier, B. Bouyssiere, R. Lobinski, Trapping of metallic porphyrins by asphaltene aggregates: a size exclusion microchromatography with high-resolution inductively coupled plasma mass spectrometric detection study, *Energ. Fuels* 26 (2012) 4968–4977. doi: 10.1021/ef3002857.
- [3] N. Márquez, F. Ysambertt, C. De La Cruz, Three analytical methods to isolate and characterize vanadium and nickel porphyrins from heavy crude oil, *Anal. Chim. Acta* 395 (1999) 343–349. doi: 10.1016/S0003-2670(99)00304-9.
- [4] J.H. Chen, R.P. Philp, Porphyrin distributions in crude oils from the Jiangnan and Biyang basins, China, *Chem. Geol.* 91 (1991) 139–151. doi: 10.1016/0009-2541(91)90087-8.
- [5] S.M. El-Sabagh, Occurrence and distribution of vanadyl porphyrins in Saudi Arabian crude oils, *Fuel Process. Technol.* 57 (1998) 65–78. doi: 10.1016/S0378-3820(98)00068-X.
- [6] I. García-Cruz, J.M. Martínez-Magadán, F. Alvarez-Ramirez, R. Salcedo, F. Illas, Theoretical study of nickel porphyrinate derivatives related to catalyst dopant in

- the oil industry, *J. Mol. Catal. A Chem.* 228 (2005) 195–202. doi:
10.1016/j.molcata.2004.09.038.
- [7] E. Magi, C. Ianni, P. Rivaro, R. Frache, Determination of porphyrins and metalloporphyrins using liquid chromatography-diode array detection and mass spectrometry, *J. Chromatogr. A* 905 (2001) 141–149. doi: 10.1016/S0021-9673(00)01007-4.
- [8] R.H. Fish, J.J. Komlenic, B.K. Wines, Characterization and comparison of vanadyl and nickel compounds in heavy crude petroleums and asphaltenes by reverse-phase and size-exclusion liquid chromatography/graphite furnace atomic absorption spectrometry, *Anal. Chem.* 56 (1984) 2452–2460. doi: 10.1021/ac00277a043.
- [9] R.H.Fish, J.G.Reynolds, E.J.Gallegos, Molecular characterization of nickel and vanadium nonporphyrin compounds found in heavy crude petroleums and bitumens, *ACS Symp. Ser.* (1987) 332–349. doi: 10.1021/bk-1987-0344.ch021.
- [10] X. Zhao, Y. Liu, C. Xu, et al., Separation and characterization of vanadyl porphyrins in Venezuela Orinoco heavy crude oil, *Energ. Fuels* 27 (2013) 2874–2882. doi: 10.1021/ef400161p.
- [11] R. Ocampo, H.J. Callot, P. Albrecht, J.P. Kintzinger, A novel chlorophyll c related petroporphyrin in oil shale, *Tetrahedron Lett.* 25 (1984) 2589–2592. doi: 10.1016/S0040-4039(01)81238-7.
- [12] R. Ocampo, H.J. Callot, P. Albrecht, Identification of polar porphyrins in oil shale, *J. Chem. Soc., Chem. Commun.* 4 (1985) 198–200. doi: 10.1039/c39850000198.

- [13] R. Ocampo, H.J. Callot, P. Albrecht, Occurrence of bacterioporphyrins in oil shale, *J. Chem. Soc., Chem. Commun.* 4 (1985) 200–201. doi: 10.1039/c39850000200.
- [14] J. Verne-Mismer, R. Ocampo, C. Bauder, H.J. Callot, P. Albrecht, Structural comparison of nickel, vanadyl, copper, and free base porphyrins from OuladAbdoun oil shale (Maastrichtian, Morocco), *Energ. Fuels* 3 (1990) 639–643. doi: 10.1021/ef00024a003.
- [15] R. Ocampo, C. Bauder, H.J. Callot, P. Albrecht, Porphyrins from Messel oil shale (Eocene, Germany): Structure elucidation, geochemical and biological significance, and distribution as a function of depth, *Geochim. Cosmochim. Acta* 56 (1992) 745–761. doi: 10.1016/0016-7037(92)90095-Z.
- [16] S. Acevedo, A. Castro, E. Vásquez, F. Marcano, M.A. Ranaudo, Investigation of physical chemistry properties of asphaltenes using solubility parameters of asphaltenes and their fractions A1 and A2, *Energ. Fuels* 24 (2010) 5921–5933. doi: 10.1021/ef1005786.
- [17] S. Acevedo, L.A. García, P. Rodríguez, Changes of diameter distribution with temperature measured for asphaltenes and their fractions A1 and A2. Impact of these measurements in colloidal and solubility issues of asphaltenes, *Energ. Fuels* 26 (2012) 1814–1819. doi: 10.1021/ef201947h.
- [18] J. Burke, Solubility parameters: theory and application, *The Book and Paper Group Annual* 1984

- [19] A. Grubenmann, The solvent dependence of the solubility of organic solids and solubility parameter theory: investigation by means of an organic pigment, *Dyes. Pigments* 21 (1993) 273–292. doi: 10.1016/0143-7208(93)80005-L.
- [20] G. Caumette, C.-P. Lienemann, I. Merdrignac, B. Bouyssiére, R. Lobinski, Fractionation and speciation of nickel and vanadium in crude oils by size exclusion chromatography-ICP MS and normal phase HPLC-ICP MS, *J. Anal. At. Spectrom.* 25 (2010) 1123. doi: 10.1039/c003455j.
- [21] J. Barbier, J. Marques, G. Caumette, et al., Monitoring the behaviour and fate of nickel and vanadium complexes during vacuum residue hydrotreatment and fraction separation, *Fuel Process. Technol.* 119 (2014) 185-189. doi: 10.1016/j.fuproc.2013.11.004.
- [22] F.G. Wandekoken, C.B. Duyck, T.C.O. Fonseca, T.D. Saint'Pierre, Method for the quantification of vanadyl porphyrins in fractions of crude oils by high performance liquid chromatography–flow injection–inductively coupled plasma mass spectrometry, *Spectrochim. Acta B At. Spectrosc.* 119 (2016) 1–9. doi: 10.1016/j.sab.2016.03.001.
- [23] H.Liu, J. Mu, Z. Wang, et al., Characterization of Vanadyl and Nickel Porphyrins Enriched from Heavy Residues by Positive-Ion Electrospray Ionization FT-ICR Mass Spectrometry, *Energ. Fuels* 29 (2015) 4803–4813. doi: 10.1021/acs.energyfuels.5b00763.
- [24] A.M. McKenna, J.M. Purcell, R.P. Rodgers, A.G. Marshall, Identification of vanadyl porphyrins in a heavy crude oil and raw asphaltene by atmospheric pressure

- photoionization Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry, *Energ. Fuels* 23 (2009) 2122–2128. doi: 10.1021/ef800999e.
- [25] T. Liu, J. Lu, X. Zhao, et al., Distribution of vanadium compounds in petroleum vacuum residuum and their transformations in Hydrodemetallization, *Energ. Fuels* 29 (2015) 2089–2096. doi: 10.1021/ef502352q.
- [26] Hansen, Charles M. *Hansen solubility parameters: a user's handbook*. CRC press, 2007.
- [27] A. Desprez, B. Bouyssiere, C. Arnaudguilhem, G. Krier, L. Vernex-Loiset, P. Giusti, Study of the size distribution of sulfur, vanadium, and nickel compounds in four crude oils and their distillation cuts by gel permeation chromatography inductively coupled plasma high-resolution mass spectrometry, *Energ. Fuels* 28 (2014) 3730–3737. doi: 10.1021/ef500571f.
- [28] P.Giusti, Y.NuevoOrdóñez, C.PhilippeLienemann, D.Schaumlöffel, B.Bouyssiere, R.Łobiński, μ Flow-injection–ICP collision cell MS determination of molybdenum, nickel and vanadium in petroleum samples using a modified total consumption micronebulizer, *Anal. At. Spectrom.* 2288–92. doi: 10.1039/B611542J.
- [29] G. Caumette, C.P. Lienemann, I. Merdrignac, H. Paucot, B. Bouyssiere, R. Lobinski, Sensitivity improvement in ICP MS analysis of fuels and light petroleum matrices using a microflow nebulizer and heated spray chamber sample introduction, *Talanta* 80 (2009) 1039–1043. doi: 10.1016/j.talanta.2009.08.017.

Figure legends

Table 1. Distributions of vanadium in the separated fractions and its repartition to HMW, MMW and LMW species in Safaniya and Safaniya 2.

Fraction	Percentage	Percentage of V		
	distribution of total V	in HMW species	Percentage of V in MMW species	Percentage of V in LMW species
1	0.3	34.2%	41.1%	24.7%
2	0.5	61.5%	29.4%	9.1%
3	17.5	33.1%	57.1%	9.8%
4	46.3	53.9%	26.7%	19.4%
5	34.6	71.5%	11.2%	17.3%
6	0.8	89.3%	9.1%	1.6%
Safaniya	100	56.7%	25.4%	17.9%
1	0.1	21.7%	36.1%	42.2%
2	1.2	49.8%	49.1%	1.1%
3	27.8	13.6%	51.1%	35.3%
4	43.6	55.5%	30.3%	14.2%
5	23.9	67.2%	9.7%	23.0%
6	3.4	70.0%	10.0%	20.0%
Safaniya 2	100	56.3%	25.2%	18.5%

Table 2. Distribution of nickel in the separated fractions obtained from Safaniya and Safaniya 2.

Safaniya Fraction	Percentage distribution of total Ni	Percentage of Ni in HMW species	Percentage of Ni in MMW species	Percentage of Ni in LMW species
1	15.6	18.3%	57.3%	24.4%
2	9.6	39.5%	44.1%	16.4%
3	3.1	57.6%	25.8%	16.5%
4	27.1	67.3%	14.2%	18.6%
5	43.1	73.0%	8.7%	18.3%
6	1.4	91.4%	7.1%	1.5%
	100	62.9%	19.4%	17.8%
<hr/>				
Safaniya 2				
1	8.9	14.7%	15.4%	69.9%
2	14.3	18.2%	46.2%	35.6%
3	4.6	54.9%	37.1%	8.0%
4	37.7	71.2%	21.5%	7.3%
5	30.0	66.5%	8.7%	24.8%
6	4.4	71.2%	9.5%	19.3%
	100	63.8%	19.6%	16.6%

Table 3. Distribution of sulfur in the separated fractions of Safaniya and Safaniya 2.

Safaniya Fraction	Percentage distribution of total S	Percentage of S in HMW species	Percentage of S in MMW species	Percentage of S in LMW species
1	34.4	7.7%	63.5%	28.8%
2	13.2	27.4%	58.2%	14.5%
3	6.1	43.7%	47.7%	8.7%
4	33.2	47.7%	43.3%	8.9%
5	12.7	63.8%	19.3%	16.9%
6	0.4	81.0%	15.6%	3.4%
	100	33.6%	49.5%	16.9%
<hr/>				
Safaniya 2				
1	50.8	8.5%	60.2%	31.3%
2	7.9	24.2%	60.6%	15.3%
3	3.6	38.6%	50.4%	10.9%
4	29.6	48.7%	43.0%	8.3%
5	7.2	64.3%	15.9%	19.8%
6	1.0	66.0%	16.3%	17.6%
	100	30.9%	48.4%	20.6%

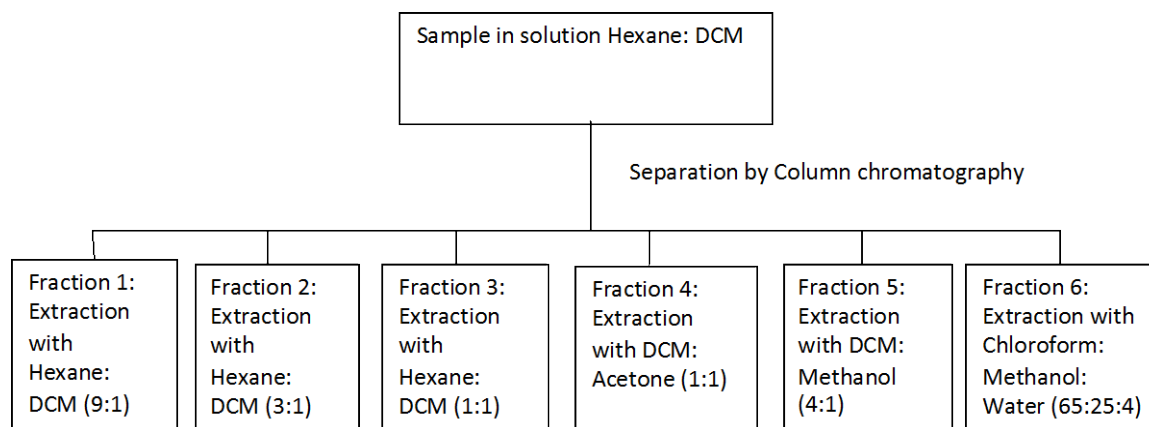


Figure 1: Separation by column chromatography

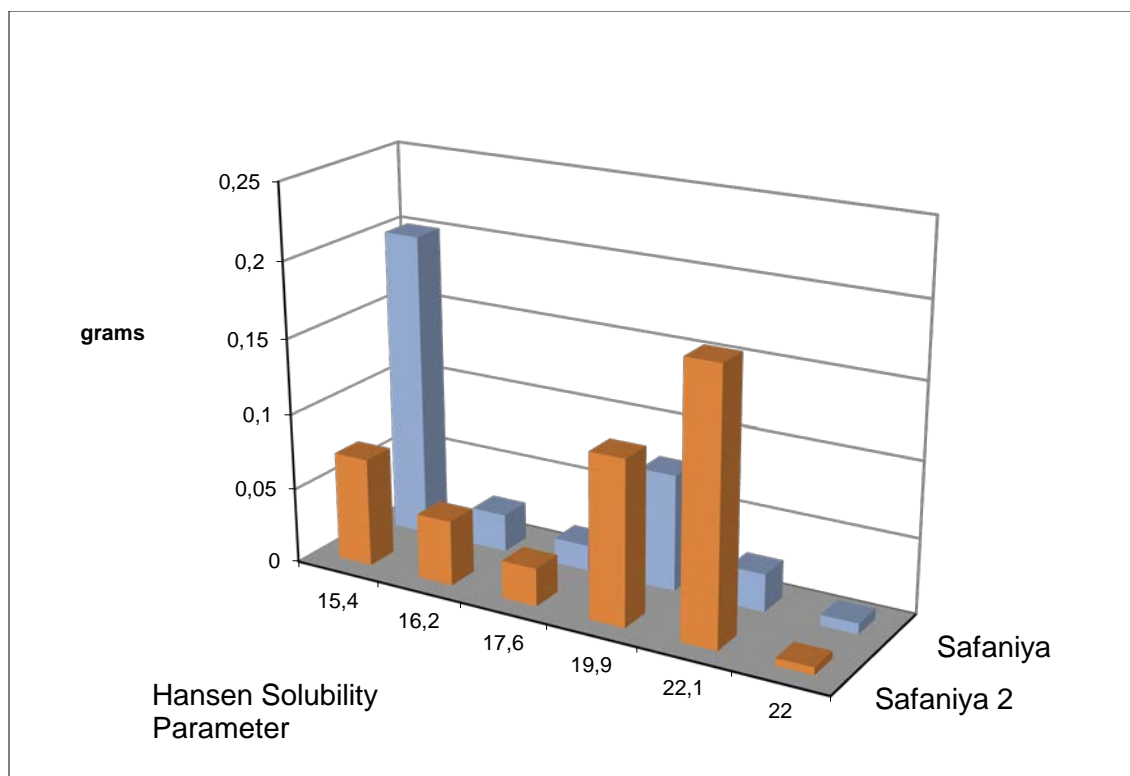


Figure 2. Hansen solubility parameters for the solvent mixtures used and fractions obtained from Safaniya VR.

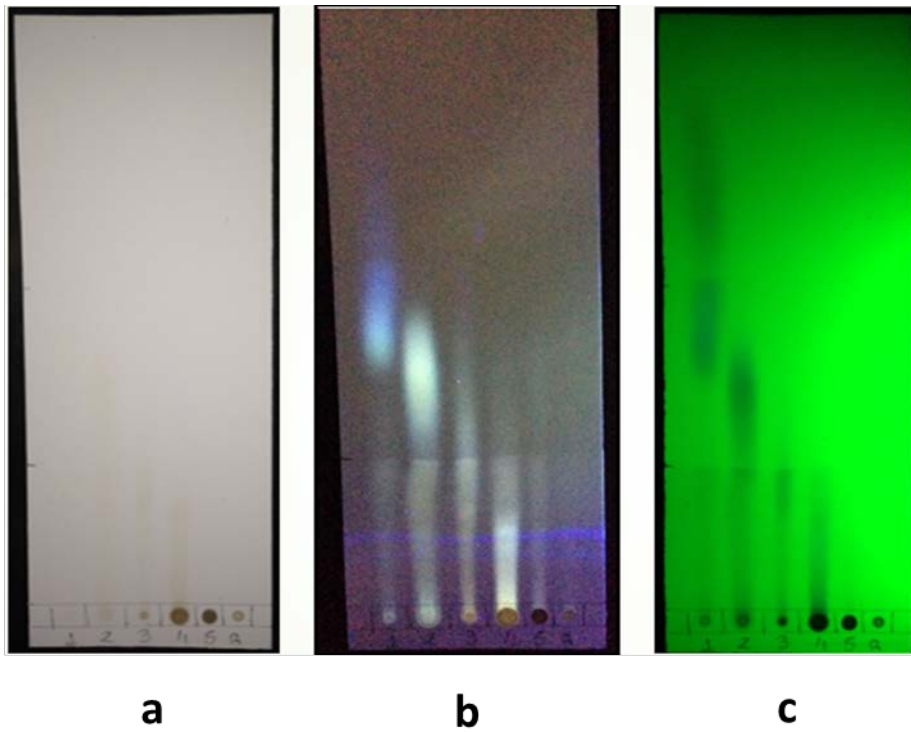


Figure 3: Separation of the fraction. Photo a: plate under white light. Photo b: plate under 254 nm UV light. Photo c: plate under 365 nm UV light

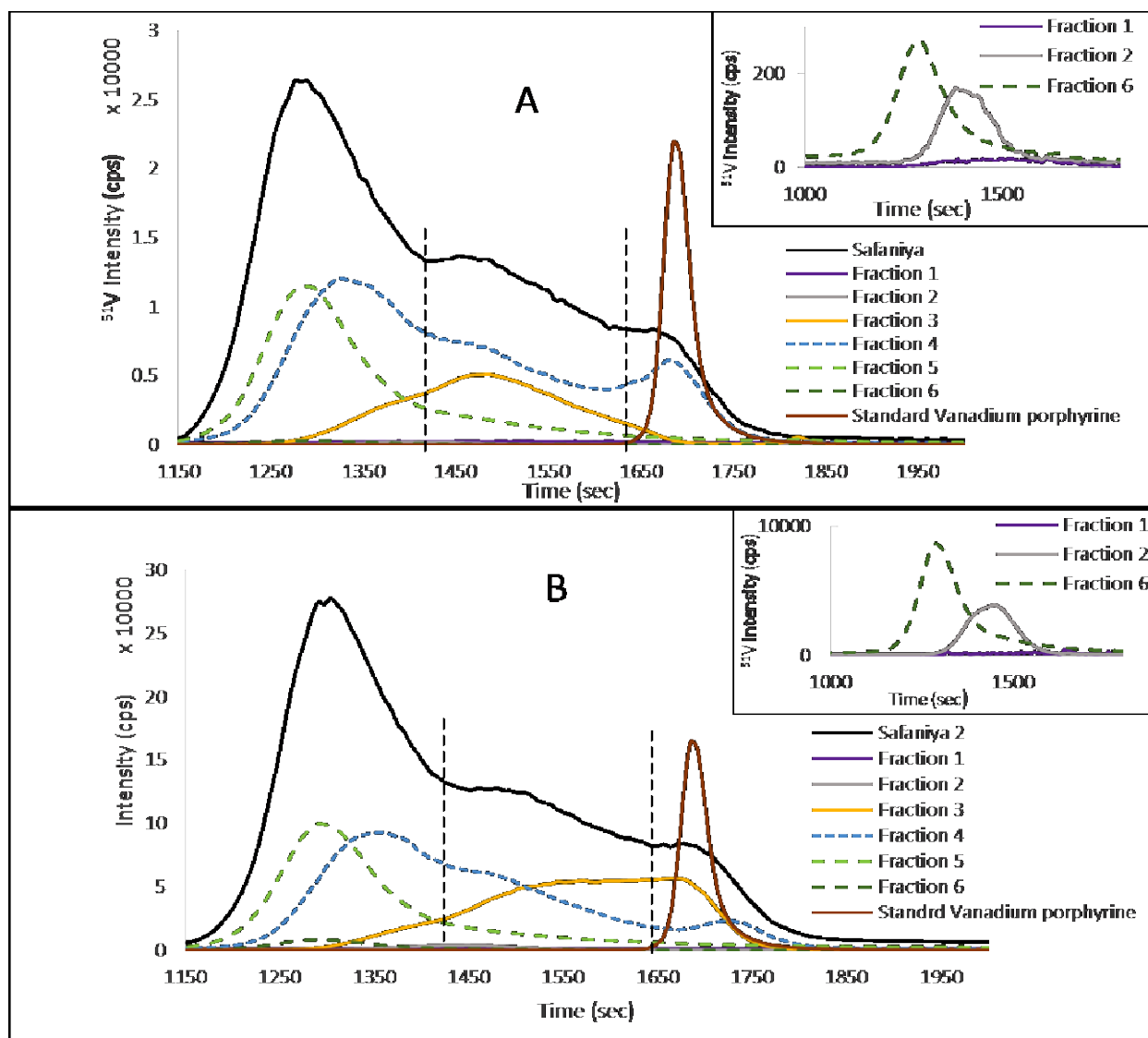


Figure 4. The profile of the fractions separated in GPC-ICP-HRMS, with vanadium detector for a) Safaniya and b) Safaniya 2.

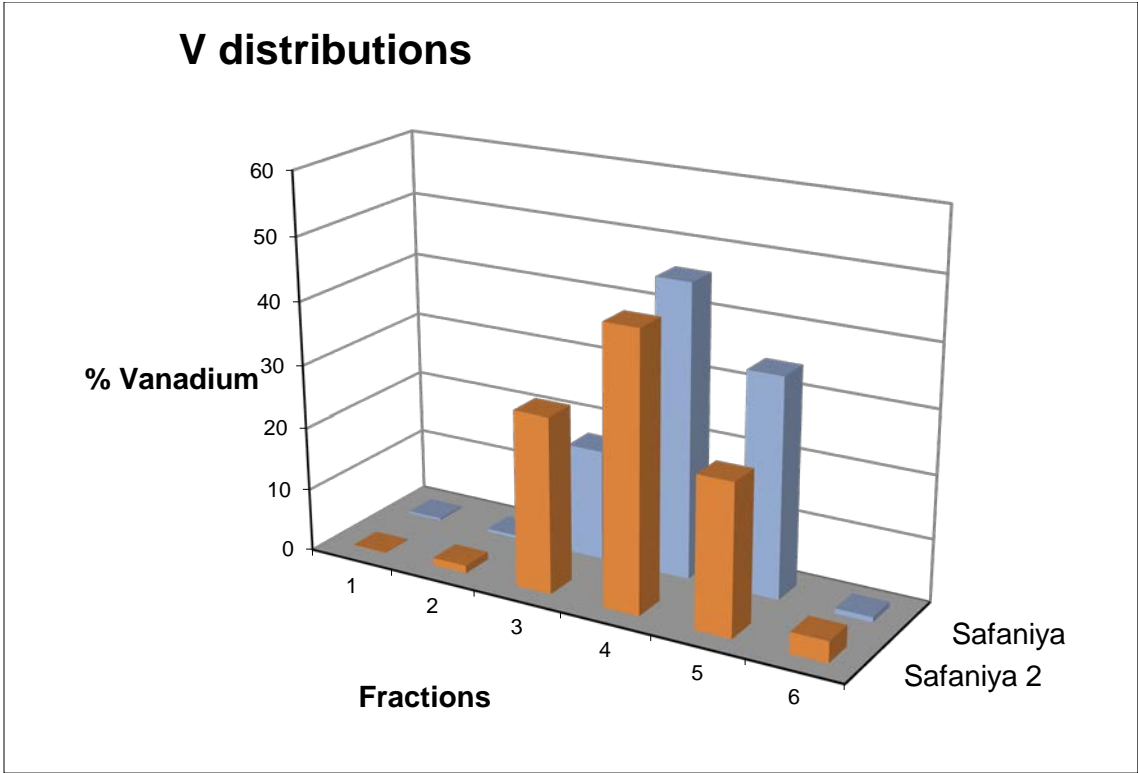


Figure 5. Percentage of Vanadium distribution in each fraction.

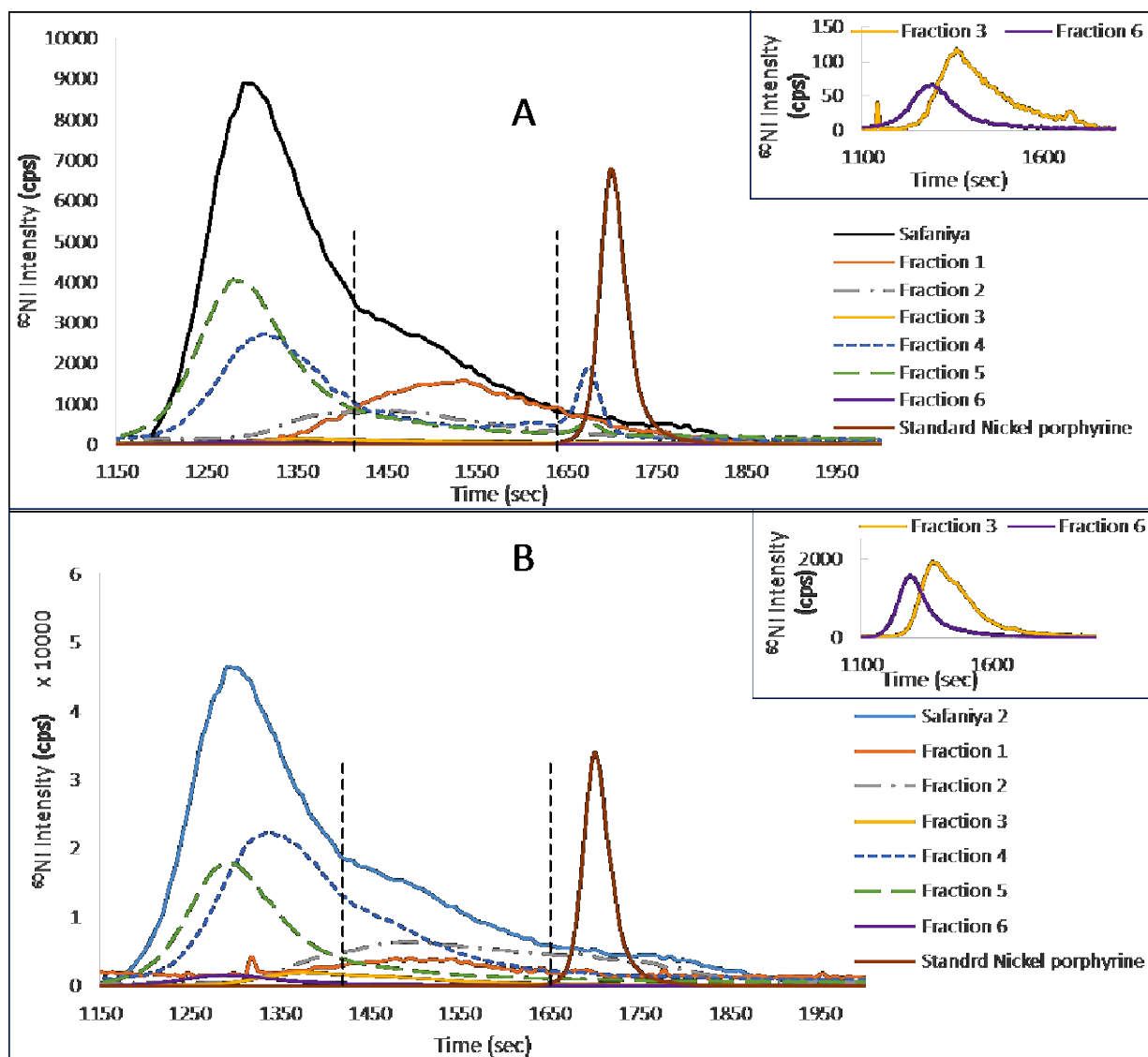


Figure 6. The profile of the fractions separated in GPC-ICP-HRMS, with nickel detector for a) Safaniya and b) Safaniya 2.

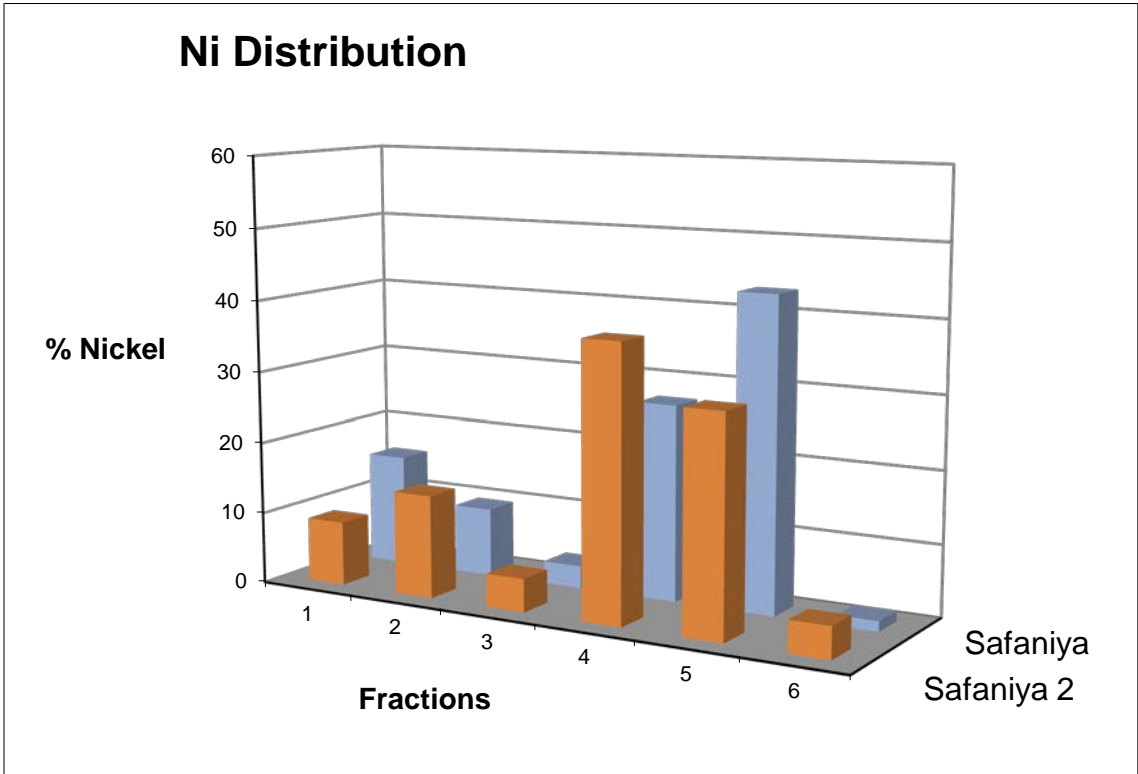


Figure 7. Percentage of Nickel distribution in each fraction.

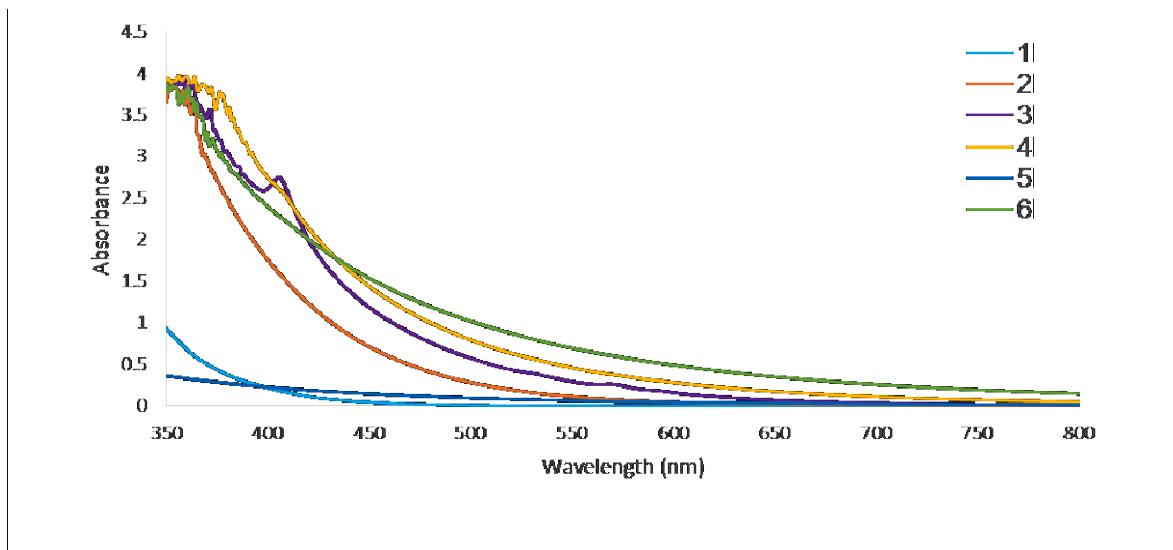


Figure 8. Absorbance spectra for separated fractions VR Safaniya

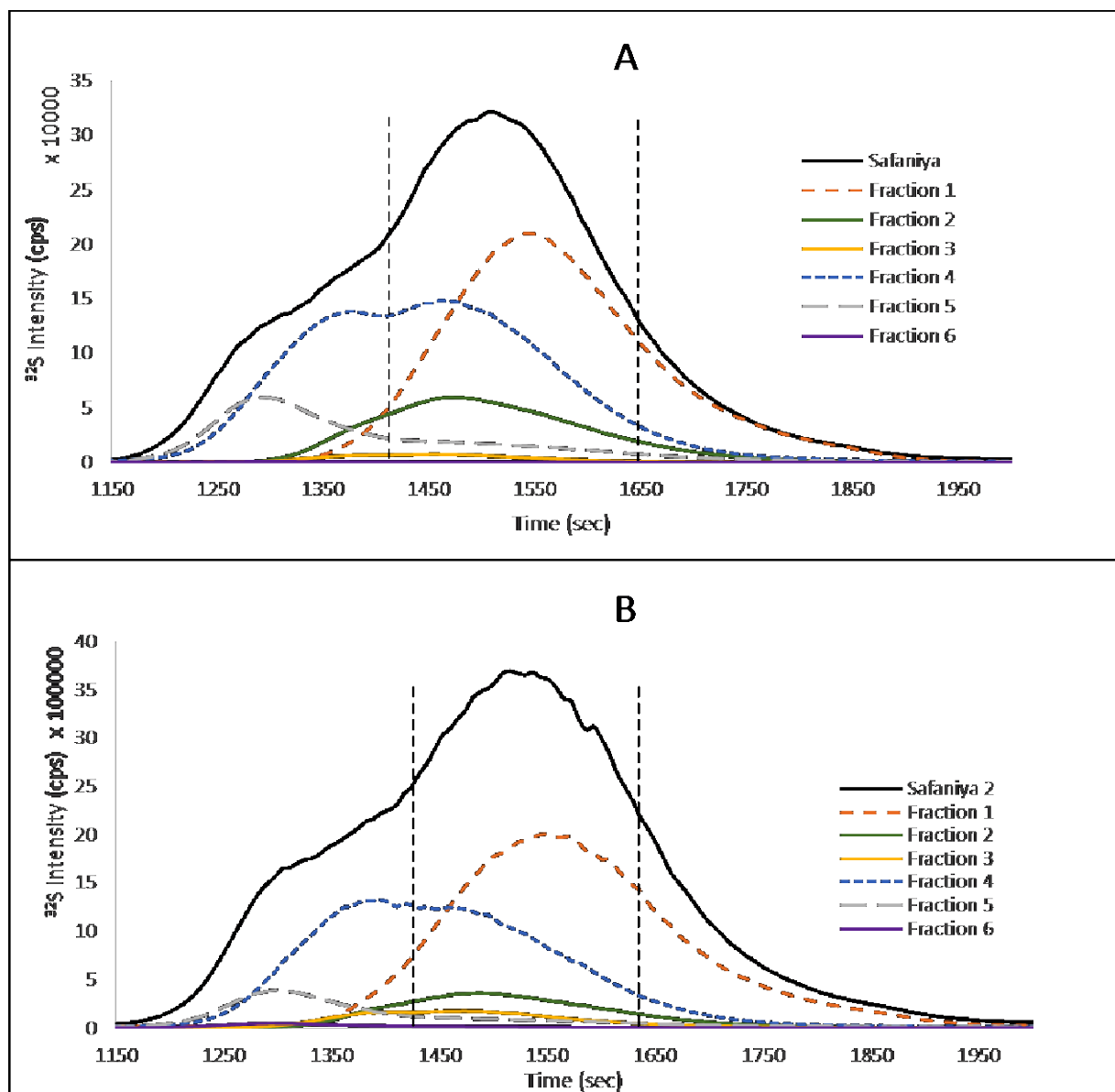


Figure 9. The profile of the fractions separated in GPC-ICP-HRMS, with sulfur detector for a) Safaniya and b) Safaniya 2.

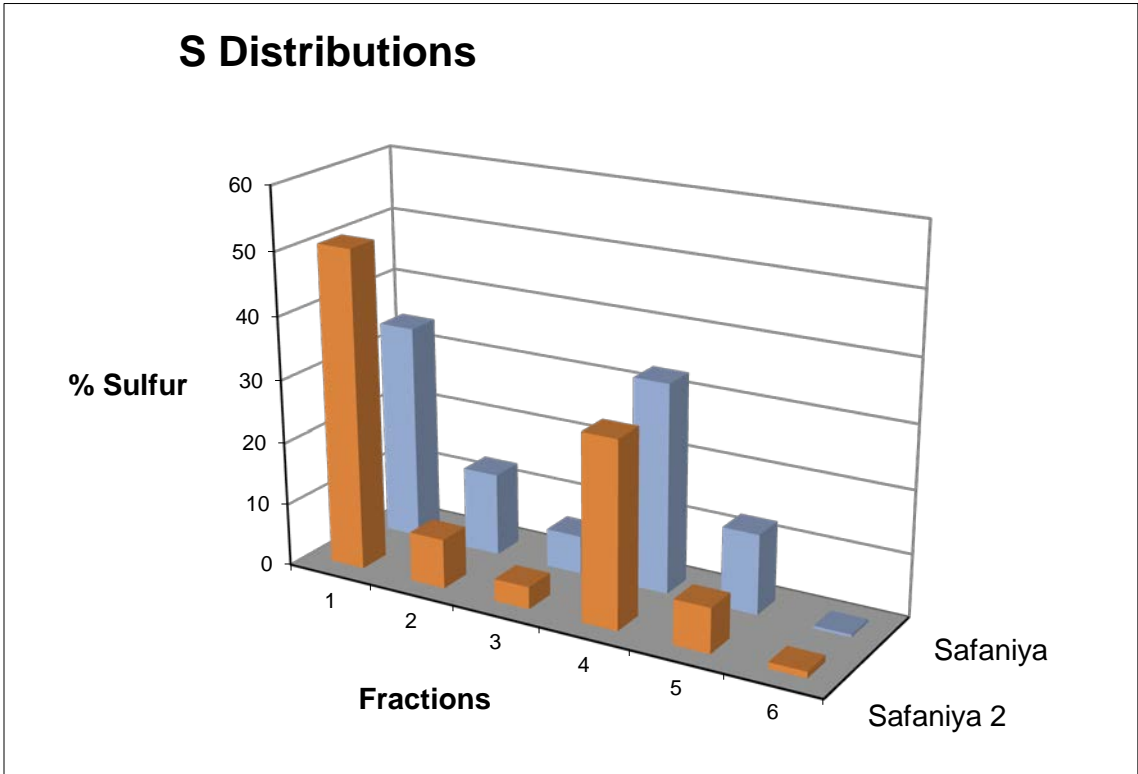


Figure 10. Percentage of Sulfur distribution in each fraction.