



**HAL**  
open science

## Simplification of heavy matrices by liquid-liquid extraction: Part I -How to separate LMW, MMW and HMW compounds in maltene fractions of V, Ni and S compounds

German Gascon, Juan Negrin, Victor Garcia-Montoto, Socrates Acevedo, Charles-Philippe Lienemann, Brice Bouyssière

### ► To cite this version:

German Gascon, Juan Negrin, Victor Garcia-Montoto, Socrates Acevedo, Charles-Philippe Lienemann, et al.. Simplification of heavy matrices by liquid-liquid extraction: Part I -How to separate LMW, MMW and HMW compounds in maltene fractions of V, Ni and S compounds. *Energy & Fuels*, 2019, 33 (3), pp.1922-1927. 10.1021/acs.energyfuels.8b03974 . hal-02122797

**HAL Id: hal-02122797**

**<https://ifp.hal.science/hal-02122797>**

Submitted on 7 May 2019

**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 destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Simplification of heavy matrices by liquid-liquid extraction: Part I -How to separate LMW, MMW and HMW compounds in maltene fractions of V, Ni and S compounds

*German Gascon<sup>a,b,c</sup>, Juan Negrin<sup>a</sup>, Victor G. Montoto<sup>b</sup>, Socrates Acevedo<sup>c</sup>, Charles-Philippe Lienemann<sup>d</sup>, Brice Bouyssiere<sup>b</sup>*

<sup>a</sup>PDVSA Intevep, Apartado 76343, Caracas 1070-A, Venezuela

<sup>b</sup>CNRS/ Univ pau & pays ADOUR/ E2S UPPA, Institut des Sciences Analytiques et de Physico-Chimie Pour L'environnement et les Matériaux, UMR5254, Helioparc- 2 Avenue du Président Angot 64000, Pau, France

<sup>c</sup>UCV, Facultad de Ciencias, Escuela de Química, Caracas, 1053, Venezuela

<sup>d</sup>IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

## ABSTRACT

A method using liquid-liquid extractions has been developed for matrix simplification and evaluated by gel permeation chromatography hyphenated with inductively coupled plasma and mass spectrometry (GPC ICP MS). In this method, maltenes were dissolved in n-heptane (HEP), and extractions with methanol (MeOH), acetonitrile (ACN) and dimethylformamide (DMF) were performed. The extraction with ACN is more efficient than that of MeOH for the removal of compounds with LMW containing V (our reference element) and more selective than that of DMF (with this solvent, compounds with LMW and MMW are extracted). Thus, a sequential extraction was performed by applying ACN to selectively remove LMW compounds, followed by extractions with DMF in the resulting maltene to separate the MMW compounds from the HMW compounds remaining in the final remnant maltene. The results show, for the first time in the literature, that it is possible to separate the three V and Ni species of compounds present in maltenes based on their molecular weight (HMW, MMW and LMW).

## INTRODUCTION

V and Ni are the most abundant metals that are naturally present in petroleum.<sup>1</sup> The high stabilities of these metals in crude oils, asphalts, and bitumens suggest that they mainly occur as tetrapyrrole complex-type metalloporphyrins. The predominance of Ni and V compounds compared to other organic metallocompounds is a consequence of the greater stability of nitrogen-vanadium or nickel bonds and their favorable electron configurations, among other factors.<sup>2,3</sup> A study performed using XAFS spectroscopy showed that the coordination shells of all compounds of V and Ni present in petroleum are very similar to those of vanadyl and nickel porphyrins.<sup>4,5</sup> In terms of their distribution in the products of petroleum, these compounds are almost all concentrated in atmospheric or vacuum residue based on their boiling points,<sup>6</sup> and they are present in asphaltenes and resins<sup>7-9</sup> when petroleum or residue is separated in their SARA fractions. Recently, three distinct families coexisting in the crude fraction of petroleum have been identified based on their molecular weight. These have been identified as compounds with high, medium and low molecular weights (HMW, MMW and LMW).<sup>6,9,10</sup> This approach is relatively recent<sup>6,9,10</sup> and is due to the improvements made in their possible detection with ICP MS. Regarding these compound families, we believe that compounds with LMW correspond to simple metalloporphyrins (MPs), whereas compounds with MMW and HMW correspond to MPs trapped or linked in nanoaggregates<sup>9,11</sup> due to the high capacities of some crude oil compounds to trap different compounds.<sup>12,13</sup> This idea is not new; since 1970, it has been accepted that some MPs behave as a single unit of the aromatic sheet in the generalized macrostructure of asphaltenes, as was proposed by Dickie and Yen.<sup>14,15</sup> Other authors have proposed that these V or Ni compounds may be assimilated as subunits in these aggregates,<sup>16-18</sup> so it has long been believed that in petroleum, there are two types of metallocompounds, one porphyrinic and a

second that is bound,<sup>14,19</sup> giving rise to Ni and V compounds with high molecular weights<sup>20</sup>

Over time, this classification was widely supported by the difference between the early direct determinations of metalloporphyrins by UV-Vis and the total contents of Ni and V obtained by atomic spectrometric techniques.<sup>19,21</sup> The part that do not absorb in the UV-Vis (based on total determination using UV-Vis detection) was then defined as non-porphyrinic compounds.<sup>19</sup>

However, no compound different than metalloporphyrins has yet been reported, even through the use of high-resolution techniques in the direct analysis of crude oil or asphaltenes.<sup>21-23</sup> On the other hand, it has been reported that the low contents of metalloporphyrins detected by UV-Vis are due to the limitations of the technique (UV-Vis), the association between the asphaltene molecules and MPs, and the poor efficiency of the extraction methods employed.<sup>24</sup> With respect to these observations, diverse methods have been developed using either Soxhlet extractions or chromatography<sup>25-29</sup> separations with a packed column. However, a regular to poor separation is obtained with these method to separation of compounds according to their molecular weight<sup>30</sup> possibly because asphaltenes are strongly adsorbed by the adsorbents used with these methods.

For all these reasons, we have decided to develop a new strategy of separation. Specifically, we have decided to develop a method by liquid-liquid extraction to maltenes and a method by liquid-solid extraction to asphaltenes. These methods are proposed to avoid the use of adsorbents, and therefore, the possible adsorption of compounds with V, Ni and S. In this context, the separation of maltenes is presented in this work (the separation in asphaltenes will be present in a second part) and it is divided. in two parts that are both developed here. In the first part, we present the results of the extraction performed with different solvents, and in the second part, we present the optimization of the method. The types of compounds obtained according to their MW with this procedure were evaluated by GPC ICP MS.

## EXPERIMENTAL SECTION

**Instrumentation.** A high-performance liquid chromatograph (HPLC) (UltiMate 3000, Dionex, Amsterdam, The Netherlands) was used for separation by gel permeation chromatography and was coupled with ICP MS. The detailed conditions for ICP MS detection have previously been reported<sup>9</sup> and are summarized here. A High-Resolution (Element XR, Thermo Scientific, ) ICP MS instrument operated at a resolution of 4000 was used. The ICP HRMS was equipped with an interface based on a microflow total consumption nebulizer without a drain maintained at 60°C to minimize the signal suppression and increase the sensitivity by a factor of 3–4.<sup>31</sup> An oxygen flow of 0.08 mL/min was continuously added to the nebulizer gas flow (Ar) to avoid the deposition of carbon on the cones.

**Samples, reagents, and materials.** In this work, a Venezuelan crude oil was used (8 °API). This was provided by PDVSA Intevep. N-heptane, methanol (MeOH), acetonitrile (ACN) and dimethylformamide (DMF) grade HPLC (Sigma Aldrich) were used for the liquid-liquid extractions, and tetrahydrofuran (THF) grade HPLC (Sigma Aldrich) was used for the dilution of the samples and GPC experiments. The GPC separations were carried out using a guard column (4.6x30 mm) and three styrene-divinylbenzene gel permeation columns (Styragel) connected in series (7.8x300 mm) in the following order: HR4, HR2, and HR0.5. The characteristics of these columns were already described elsewhere.<sup>6,9</sup>

**Obtaining maltenes.** Initially, 20 g of crude oil was placed in an oven at 80 °C for 24 hours to eliminate the presence of volatile compounds that could interfere in the mass balance calculations. Later, the crude oil was mixed with n-heptane at a ratio of 60:1 heptane:crude. To assure the complete precipitation of asphaltenes, this mixture was placed in ultrasound for 10 minutes, followed by 1 hour in agitation (with a magnetic stirrer) at 60 °C. To obtain the

maltenes, the mixture was filtered twice with No. 42 filter paper (with a pore size of 2.5  $\mu\text{m}$ , Whatman), and the solvent (of the filtered mixture plus the washes of the asphaltenes) was rotaevaporated.

**Part I. Solvent evaluations.** Five grams of maltenes were weighed and mixed with 25 mL of heptane in a beaker until they were completely dissolved. Later, this mixture was transferred to a decanting funnel with a capacity of 150 mL, and another 25 mL of heptane was added to maintain a ratio of 5:1 heptane:maltene. In the funnel, the volume occupied by the total mixture was marked to replace the volume of heptane lost by evaporation or partial dissolution during each extraction by MeOH, ACN and DMF. The extractions were made separately with each solvent, resulting in a total of 6 extractions of 50 mL each. Between each extraction, the complete separation of both phases was achieved. For each solvent, all extracts were combined. The mass extraction percentage was calculated by evaporating the solvent.

**Part II. Sequential liquid-liquid extraction.** To achieve sequential extraction, this experiment was performed in triplicate. As in the previous step, 5 g of maltenes were dissolved and transferred to the decanting funnel. A total of 8 extractions with 50 mL of ACN were performed initially; then, extractions were performed with the DMF in the remnant maltene. For the first two replicates, each extract was collected separately; in the third replicate, the extracts obtained with each solvent were combined.

**SEC - ICP MS detection.** All samples were diluted 100 times with THF. For the GPC – ICP MS detection, a 20  $\mu\text{L}$  sample was injected and isocratically eluted with a THF flow rate of 1 mL/min for 120 min. A post-column splitter was used to obtain a low-flow outlet (50  $\mu\text{L}/\text{min}$ ) to feed the ICP MS. A homemade Microsoft Excel program was used to deconvolute the chromatograms by summing the Gaussian curves.

## RESULTS AND DISCUSSION

**Part I. Direct extraction. Extraction efficiency of MeOH, ACN and DMF.** The total mass percentage extracted with each solvent is shown in Table 1. The solvent with the greatest extraction efficiency in terms of mass was MeOH (31%), followed by DMF (27%) and ACN (16%). However, by specificity, the DMF presented a better extraction efficiency for compounds containing V, Ni and S in comparison with the other solvents. As it can be observed, the particular distribution of the different compounds of V and Ni principally between the maltene dissolved in heptane and the solvents used as extractant (MeOH, ACN, and DMF) is very difficult to explain in terms of polarity, because this is very similar between the three solvents used (MeOH  $\epsilon=33$ , ACN  $\epsilon=37$  and DMF  $\epsilon=38$ ), suggesting that certain specific interactions between the solvents and the MPs play a fundamental role. We believe some of these specific interactions (not evaluated here) are based on different characteristic of the solvent used such as: size of the solvent molecule, type of interaction metal-solvent and periphery of MPs-solvent. However, the not correlation between the intensity of Soret band (Figure 1) and the percentage of V and Ni compounds extracted suggest that the interactions between part non-polar of the MPs (or aggregate that contain them) and the solvent are more important than a possible interaction metal-solvent due to the fact other compounds seem to be extracted and do not have this interaction (HC compounds). In this case, the results of the table 1 and Figure 1 show a higher interaction with the DMF.

***Size distribution of compounds containing V in extracts and remnant maltenes after extractions with MeOH, ACN and DMF.*** To simplify the discussion, we studied only the V



profile obtained after extraction with MeOH, ACN and DMF, and to obtain a clear comparison between the different chromatograms, the intensities of each sample were multiplied by its given mass balance. Figure 2a) shows the GPC ICP MS chromatogram obtained for all extracts, which are compared with the original maltene. As it can be seen, this reveals a particular extraction depending on the solvent used (this is not observed with the data of the table 1). So, only compounds in the LMW region are observed in the ACN and MeOH extracts, and a bimodal distribution is observed in the DMF extract. This is in good agreement with the high removal efficiency achieved with these solvents (Table 1). In terms of the remanent maltenes (Figure 2b), it can be observed that the size distributions of the V compounds complete the information obtained in Figure 2a). Also, it is important to observe how few V compounds with LMW are present in the remanent maltene after their extractions with MeOH. This demonstrates that this solvent does not remove all V LMW compounds. In contrast, only compounds with MMW and HMW are observed in the remanent maltene obtained after extractions with ACN, while most compounds with HMW are observed after extractions with DMF. Again, the difference observed are due to the specific interaction between the solvent and the MPs or with the aggregates that contain them, being these widely significant when the DMF is used, specifically with the MMW compounds

**Part II. Sequential extraction. Optimization of extraction.** Based on the fact that MeOH extracts show a lower efficiency than ACN (Figure 2b, Table 1), a sequential extraction with ACN and DMF was applied to the maltene solutions. So, ACN was applied to extract all of the LMW compounds followed by extractions with DMF to extract MMW compounds. Figure 3a shows the results obtained for each sequential extraction using ACN. The color of the extract

moves from red to yellow with a decrease in the intensity of the peak obtained in the LMW part of the chromatogram. As can be observed, by comparing the signal of the [vanadyl tetraphenylporphyrin](#) (TPPO VO) at 1646 s with the position of the maximum observed for each extract at 1695 s (to extractions with ACN), at 1519 s (to extractions with DMF) and, at 1367 s (to remanent maltenes), all of the compounds extracted with ACN have MW values that are very similar to or less than the TPPO VO (Figure 3a). On the contrary, all DMF extracts with colors moving from dark red to yellow present compounds in the MMW region (Figure 3b) and the remanent maltene solution (after all of these ACN and DMF extractions) with color dark, show compounds in the HMW region (Figure 3c). With regarding to the absorption in the UV-Vis of these extract, it can be observed how the [Soret is present in all the extract obtained with ACN](#) (Figure 4a) and, [initially in the extracts obtained with DMF until its absent complete](#) (Figure 4b) in the remanent maltenes after of the extraction with ACN and DMF (Figure 4c). These results confirm that a great part of V and Ni compounds do not absorb in the UV-Vis, even when these compounds can be separated by their MW as is showed here.

About the removal percentage obtained in each extraction, the Figure 5a and 5b shows the % of V in the extract versus the total V in the extractant (sum of the 8 extraction) for ACN and DMF. Concerning ACN extraction, the percentage of V, Ni and S decrease with each extraction but with different behavior between element. This might be due to the difference in molecular form of the extracted molecules containing V, Ni and S. Concerning ACN extraction, the behavior is more erratic, showing that after a first extraction with 10-20% of extraction, the second extraction is near 40%. This might be due to the fact that before extracting S, Ni and V compounds, other compounds have to be extracted (HC compounds).

*Size distribution of V, Ni and S compounds obtained by sequential maltene extractions.* A sequential extraction was applied to the maltene fraction, and all of the ACN and DMF extracts were pooled in two groups (ACN and DMF extracts) and evaporated. The size distributions of the compounds containing V, Ni and S are shown in Figures 6 a), b) and c), respectively. As it can be observed, the method of sequential liquid-liquid extraction in maltenes using ACN with 8 sequential extractions followed by 8 extractions with DMF allows for the separation of the three V, Ni and S compound families (HMW, MMW and LMW) originally present in the maltenes, which were previously identified.<sup>9</sup> The reconstructed chromatogram shows very good agreement with the original maltene chromatogram, indicating that there is minor loss during the extraction procedure. This agreement between the reconstructed and actual chromatograms of the maltene also demonstrates that no modification of the V, Ni and S species occurs during this extraction.

## CONCLUSIONS

It has been demonstrated that through liquid-liquid extractions with ACN, followed by extractions with DMF of the maltenes dissolved in heptane, it is possible to very effectively achieve the quantitative separation of V, Ni and S compounds in maltenes based on their hydrodynamic volume (LMW, MMW and HMW). Specifically, it has been made possible to directly extract the LMW compounds with ACN and to extract the MMW compounds with DMF, leaving the HMW in the matrices. These results show for the first time in the literature that it is possible, by extraction, to separate the trimodal distribution of V, Ni and S compounds. This extraction of LMW, MMW and HMW species is of great importance for future petrointeratomic studies.<sup>32</sup>

## AUTHOR INFORMATION

### **Corresponding Author**

\*Brice.bouyssi@univ-pau.fr

### **Funding Sources**

### **Notes**

The authors declare no competing financial interests.

## ACKNOWLEDGMENTS

The financial support of the Conseil Régional d'Aquitaine (20071303002PFM) and FEDER (31486/08011464) is acknowledged. This work is a collaboration between the University of Pau (UPPA), Total, IFP Energies Nouvelles, PDVSA INTEVEP, and the Central University of Venezuela (UCV) on behalf of the PCP project "Metalopetroleomic" financially supported by the MAE.

## REFERENCES

- (1) Speight, J. G. *The Chemistry and Technology of Petroleum*; Taylor & Francis: Boca Raton, FL, 1999.
- (2) Lewan, M. D. Factors Controlling the Proportionality of Vanadium to Nickel in Crude Oils. *Geochim. Cosmochim. Acta* 1984, 48 (11), 2231-2238.
- (3) Quirke, J. M. E. Rationalization for the Predominance of Nickel and Vanadium Porphyrins in the Geosphere. In *Metal Complexes in Fossil Fuels: Geochemistry, Characterization, and Processing*; Filby, R. H., Branthaver, J. F., Eds.; American Chemical Society: New York, NY, 1987; pp 74-83.
- (4) Goulon, J.; Retournard, A.; Friant, P.; Goulon-Ginet, C.; Berthe, C.; Muller, J. F.; Poncet, J. L.; Guillard, R.; Escalier, J. C.; Neff, B. Structural Characterization by X-Ray Absorption Spectroscopy (Exafs/Xanes) of the Vanadium Chemical Environment in Boscan Asphaltenes. *J. Chem. Soc., Dalton Trans.* 1984, pp 1095-1103.
- (5) Miller, J. T.; Fisher, R. B.; Van Der Eerden, A. M. J.; Koningsberger, D. C. Structural Determination by XAFS Spectroscopy of Non-Porphyrin Nickel and Vanadium in Maya Residuum, Hydrocracked Residuum, and Toluene-Insoluble Solid. *Energy Fuels* 1999, 13 (3), 719-727.
- (6) Desprez, A.; Bouyssiere, B.; Arnaudguilhem, C.; Krier, G.; Vernex-Loiset, L.; Giusti, P. 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. *Energy Fuels* 2014, 28 (6), 3730-3737.

- (7) Reynolds, J. G.; Biggs, W. R. Effects of Asphaltene Precipitation and a Modified D 2007 Separation on the Molecular Size of Vanadium-and Nickel-Containing Compounds in Heavy Residua. *Fuel Sci. Technol. Int.* 1986, 4 (6), 749-777.
- (8) Park, J. I.; Al-Mutairi, A.; Marafie, A. M. J.; Yoon, S. H.; Mochida, I.; Ma, X. The Characterization of Metal Complexes in Typical Kuwait Atmospheric Residues Using Both GPC Coupled with ICP–Ms and Ht Gc–AED. *J. Ind. Eng. Chem.* 2016, 34, 204-212.
- (9) Gascon, G.; Vargas, V.; Feo, L.; Castellano, O.; Castillo, J.; Giusti, P.; Acavedo, S.; Lienemann, C. P.; Bouyssiere, B. Size Distributions of Sulfur, Vanadium, and Nickel Compounds in Crude Oils, Residues, and Their Saturate, Aromatic, Resin, and Asphaltene Fractions Determined by Gel Permeation Chromatography Inductively Coupled Plasma High-Resolution Mass Spectrometry. *Energy Fuels* 2017, 31 (8), 7783-7788.
- (10) Caumette, G.; Lienemann, C. P.; Merdrignac, I.; Bouyssiere, B.; Lobinski, R. 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.* 2010, 25 (7), 1123-1129.
- (11) Acevedo, S.; Guzmán, K.; Labrador, H.; Carrier, H.; Bouyssiere, B.; Lobinski, R. Trapping of Metallic Porphyrins by Asphaltene Aggregates: A Size Exclusion Microchromatography with High-Resolution Inductively Coupled Plasma Mass Spectrometric Detection Study. *Energy Fuels* 2012, 26 (8), 4968-4977.
- (12) Derakhshesh, M.; Bergmann, A.; Gray, M. R. Occlusion of Polyaromatic Compounds in Asphaltene Precipitates Suggests Porous Nanoaggregates. *Energy Fuels* 2012, 27 (4), 1748-1751.

(13) Acevedo, S. C.; Cordero T, J. M.; Carrier, H.; Bouyssiere, B.; Lobinski, R. Trapping of Paraffin and Other Compounds by Asphaltenes Detected by Laser Desorption Ionization–Time of Flight Mass Spectrometry (LDI–TOF Ms): Role of A1 and A2 Asphaltene Fractions in This Trapping. *Energy Fuels* 2009, 23 (2), 842-848.

(14) Vaughan, G. B.; Tynan, E. C.; Yen, T. F. Vanadium Complexes and Porphyrins in Asphaltene, 2. The Nature of Highly Aromatic Substituted Porphins and Their Vanadyl Chelates. *Chem. Geol.* 1970, 6, 203-219.

(15) Dickie, J. P.; Yen, T. F. Macrostructures of the Asphaltic Fractions by Various Instrumental Methods. *Anal. Chem.* 1967, 39 (14), 1847-1852.

(16) Gray, M. R.; Tykwinski, R. R.; Stryker, J. M.; Tan, X. Supramolecular Assembly Model for Aggregation of Petroleum Asphaltenes. *Energy Fuels* 2011, 25 (7), 3125-3134.

(17) Strausz, O. P.; Mojelsky, T. W.; Lown, E. M. The Molecular Structure of Asphaltene: An Unfolding Story. *Fuel* 1992, 71 (12), 1355-1363.

(18) Murgich, J.; Abanero, J. A.; Strausz, O. P. Molecular Recognition in Aggregates Formed by Asphaltene and Resin Molecules from the Athabasca Oil Sand. *Energy Fuels* 1999, 13 (2), 278-286.

(19) Yen, T. F. *The Role of Trace Metals in Petroleum*; Ann Arbor Science Publishers: Michigan, US, 1975.

(20) Biggs, W. R.; Fetzer, J. C.; Brown, R. J.; Reynolds, J. G. Characterization of Vanadium Compounds in Selected Crudes I. Porphyrin and Non-Porphyrin Separation. *Liq. Fuels Technol.* 1985, 3 (4), 397-421.

(21) Qian, K.; Mennito, A. S.; Edwards, K. E.; Ferrughelli, D. T. Observation of Vanadyl Porphyrins and Sulfur-Containing Vanadyl Porphyrins in a Petroleum Asphaltene by Atmospheric Pressure Photonization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Rapid Commun. Mass Spectrom.* 2008, 22 (14), 2153-2160.

(22) Mckenna, A. M.; Purcell, J. M.; Rodgers, R. P.; Marshall, A. G. 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. *Energy Fuels* 2009, 23 (4), 2122-2128.

(23) Mckenna, A. M.; Williams, J. T.; Putman, J. C.; Aeppli, C.; Reddy, C. M.; Valentine, D. L.; Lemkau, K. L.; Kellermann, M. Y.; Savory, J. J.; Kaiser, N. K.; Marshall, A. G.; Rodgers, R. P. Unprecedented Ultrahigh Resolution Ft-Icr Mass Spectrometry and Parts-Per-Billion Mass Accuracy Enable Direct Characterization of Nickel and Vanadyl Porphyrins in Petroleum from Natural Seeps. *Energy Fuels* 2014, 28 (4), 2454-2464.

(24) Dechaine, G. P.; Gray, M. R. Chemistry and Association of Vanadium Compounds in Heavy Oil and Bitumen, and Implications for Their Selective Removal. *Energy Fuels* 2010, 24 (5), 2795-2808.

(25) Márquez, N.; Ysambertt, F.; De La Cruz, C. Three Analytical Methods to Isolate and Characterize Vanadium and Nickel Porphyrins from Heavy Crude Oil. *Anal. Chim. Acta* 1999, 395 (3), 343-349.

(26) Ali, M. F.; Perzanowski, H.; Bukhari, A.; Al-Haji, A. A. Nickel and Vanadyl Porphyrins in Saudi Arabian Crude Oils. *Energy Fuels* 1993, 7 (2), 179-184.



(27) Xu, H.; Yu, D.; Que, G. Characterization of Petroporphyrins in Gudao Residue by Ultraviolet-Visible Spectrophotometry and Laser Desorption Ionization-Time of Flight Mass Spectrometry. *Fuel* 2005, 84 (6), 647-652.

(28) Zhao, X.; Liu, Y.; Xu, C.; Yan, Y.; Zhang, Y.; Zhang, Q.; Zhao, S.; Chung, K.; Gray, M. R.; Shi, Q. Separation and Characterization of Vanadyl Porphyrins in Venezuela Orinoco Heavy Crude Oil. *Energy Fuels* 2013, 27 (6), 2874-2882.

(29) Liu, T.; Lu, J.; Zhao, X.; Zhou, Y.; Wei, Q.; Xu, C.; Zhang, Y.; Ding, S.; Zhang, T.; Tao, X.; Ju, L.; Shi, Q. Distribution of Vanadium Compounds in Petroleum Vacuum Residuum and Their Transformations in Hydrodemetallization. *Energy Fuels* 2015, 29 (4), 2089-2096.

(30) Vargas, V.; Castillo, J.; Torres, R. O.; Bouyssiere, B.; Lienemann, C. P. Development of a Chromatographic Methodology for the Separation and Quantification of V, Ni and S Compounds in Petroleum Products. *Fuel Process. Technol.* 2017, 162, 37-44.

(31) Caumette, G.; Lienemann, C. P.; Merdrignac, I.; Paucot, H.; Bouyssiere, B.; Lobinski, R. Sensitivity Improvement in ICP Ms Analysis of Fuels and Light Petroleum Matrices Using a Microflow Nebulizer and Heated Spray Chamber Sample Introduction. *Talanta* 2009, 80 (2), 1039-1043.

(32) Gutiérrez, S. S.; Farenc, M.; Barrère-Mangote, C.; Lobinski, R.; Afonso, C.; Bouyssière, B.; Giusti, P. Molecular Fingerprints and Speciation of Crude Oils and Heavy Fractions Revealed by Molecular and Elemental Mass Spectrometry: Keystone between Petroleomics, Metallopetroleomics, and Petrointeractomics. *Energy Fuels* 2018, 32 (4), 4593-4605.

## FIGURE CAPTIONS

**Figure 1:** Absorption in the UV-Vis obtained for the MeOH, ACN and DMF extracts

**Figure 2.** Vanadium GPC ICP MS chromatogram obtained for the MeOH, ACN and DMF extracts a) and for the maltene after extraction b).

**Figure 3.** Vanadium GPC ICP MS chromatograms obtained for the ACN extract a), DMF extract b) and maltene after extraction c).

**Figure 4:** Absorption at the UV-Vis obtained for the sequential extractions with ACN a), DMF b) and remanent maltene after extraction with ACN and DMF c).

**Figure 5.** Extraction percentage of V, Ni and S with ACN extract a) and DMF extract.

**Figure 6.** GPC ICP MS chromatograms of V a), Ni b) and S) obtained for the ACN extract, DMF extract and maltene after extraction.

**Table Caption**

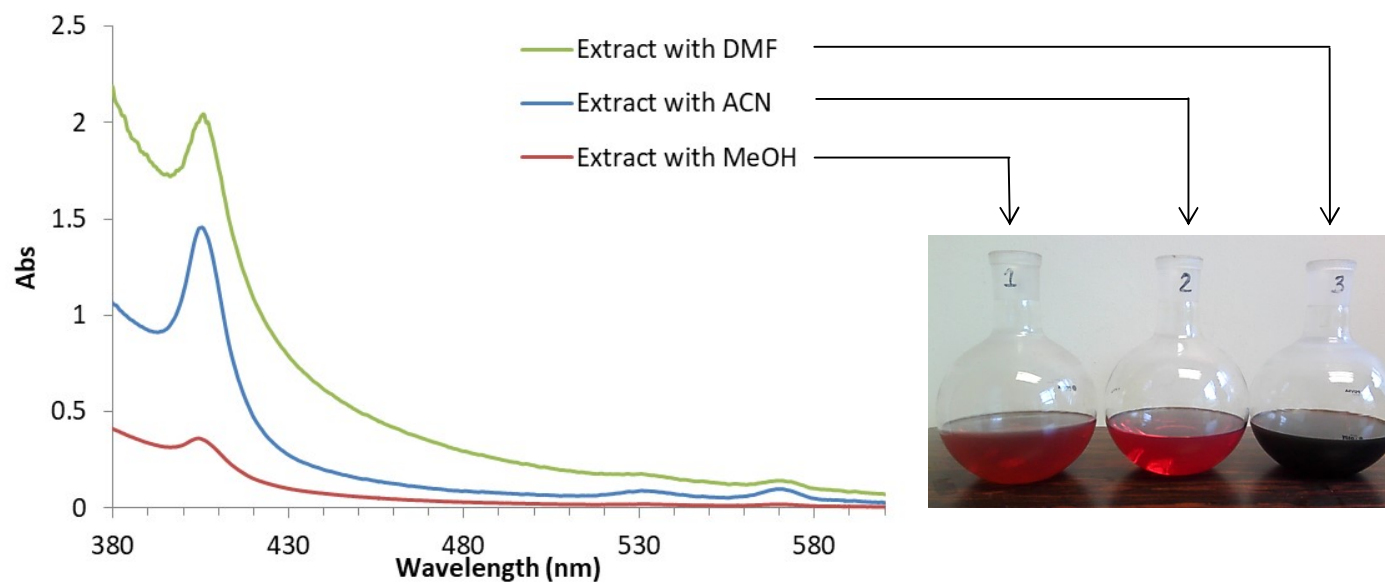
Table 1: Percentages (total and by element) of the masses extracted with methanol, acetonitrile, and dimethylformamide

## TABLES

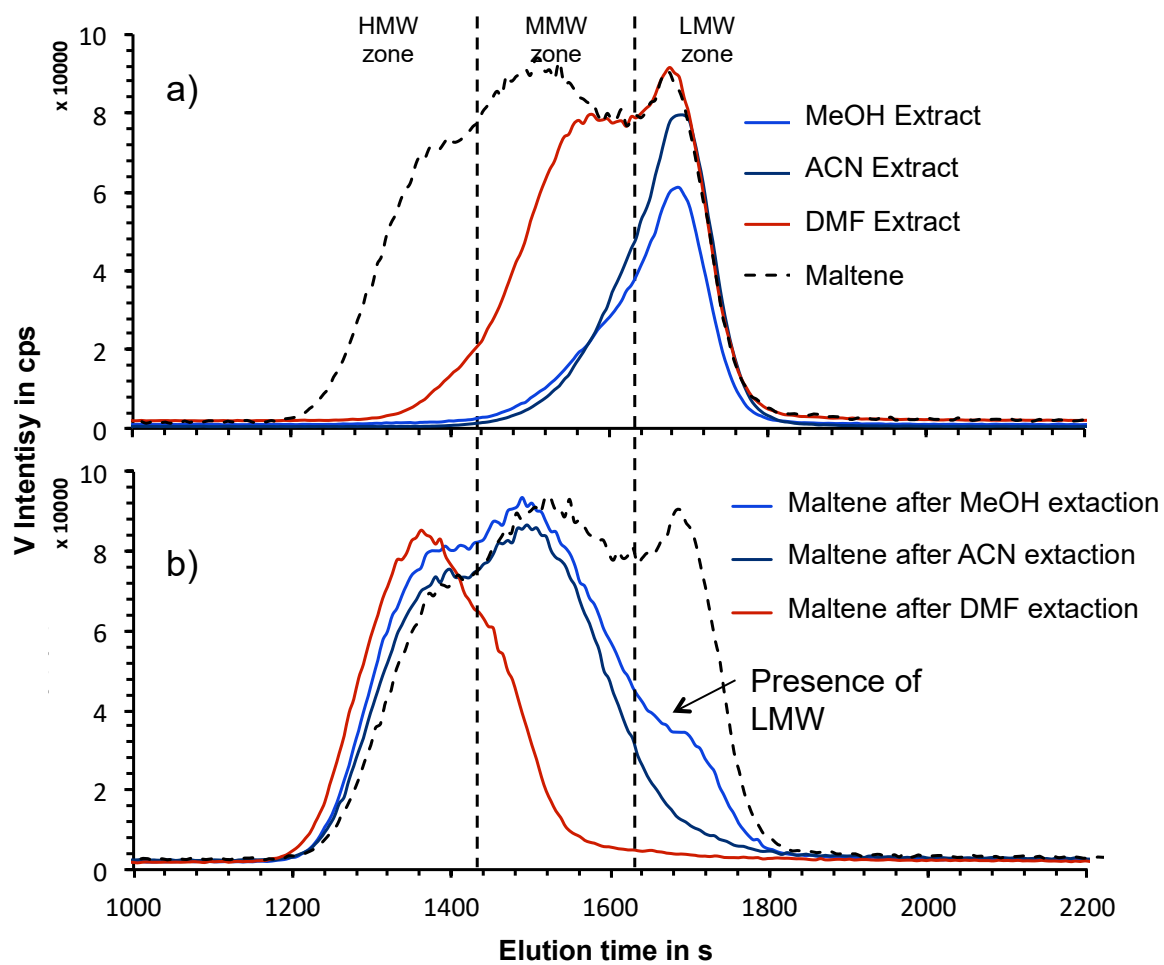
**Table 1.** Percentages (Total and by Element) of the Masses Extracted with Methanol, Acetonitrile, and Dimethylformamide

<b>Solvent</b>	<b>% removed</b>	<b>mass Element</b>	<b>% element extracted</b>
Methanol	31	S	<b>36</b>
		V	<b>22</b>
		Ni	<b>12</b>
Acetonitrile	16	S	<b>24</b>
		V	<b>30</b>
		Ni	<b>13</b>
Dimethylformamide	27	S	<b>46</b>
		V	<b>61</b>
		Ni	<b>48</b>

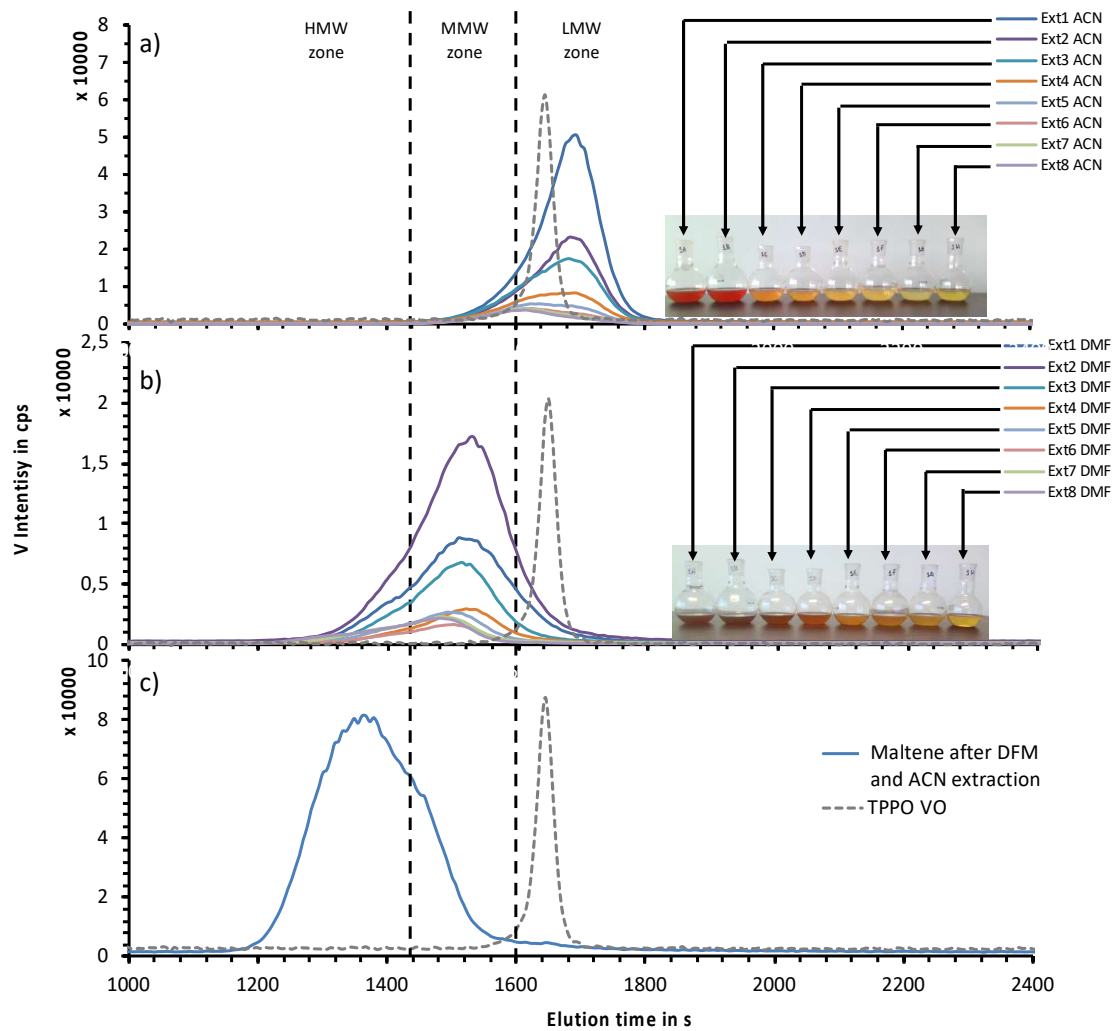
## FIGURES



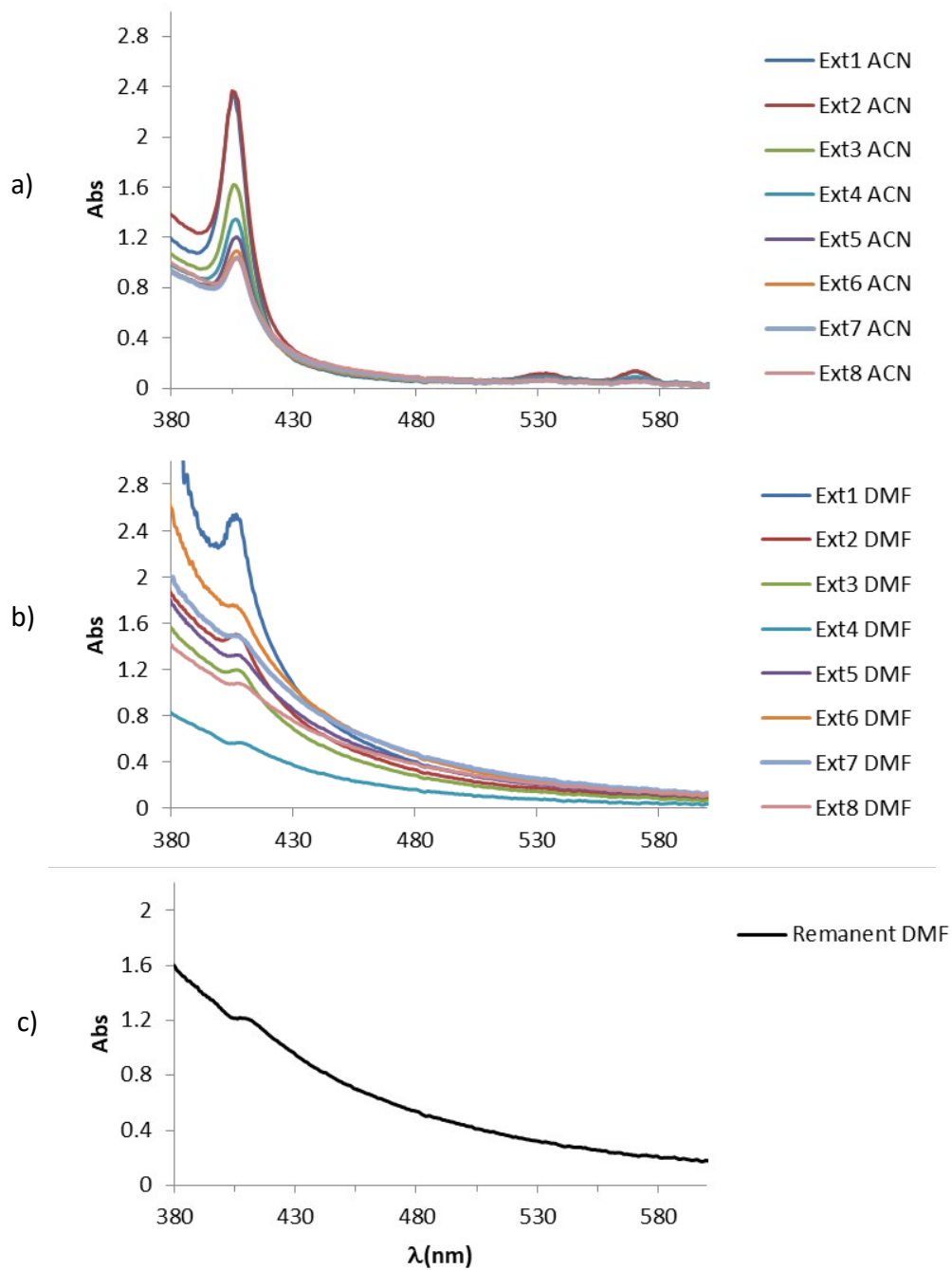
**Figure 1:** Absorption at the UV-Vis obtained for the MeOH, ACN and DMF extracts.



**Figure 2:** Vanadium GPC ICP MS chromatogram obtained for the MeOH, ACN and DMF extracts a) and for the maltene after extraction b).

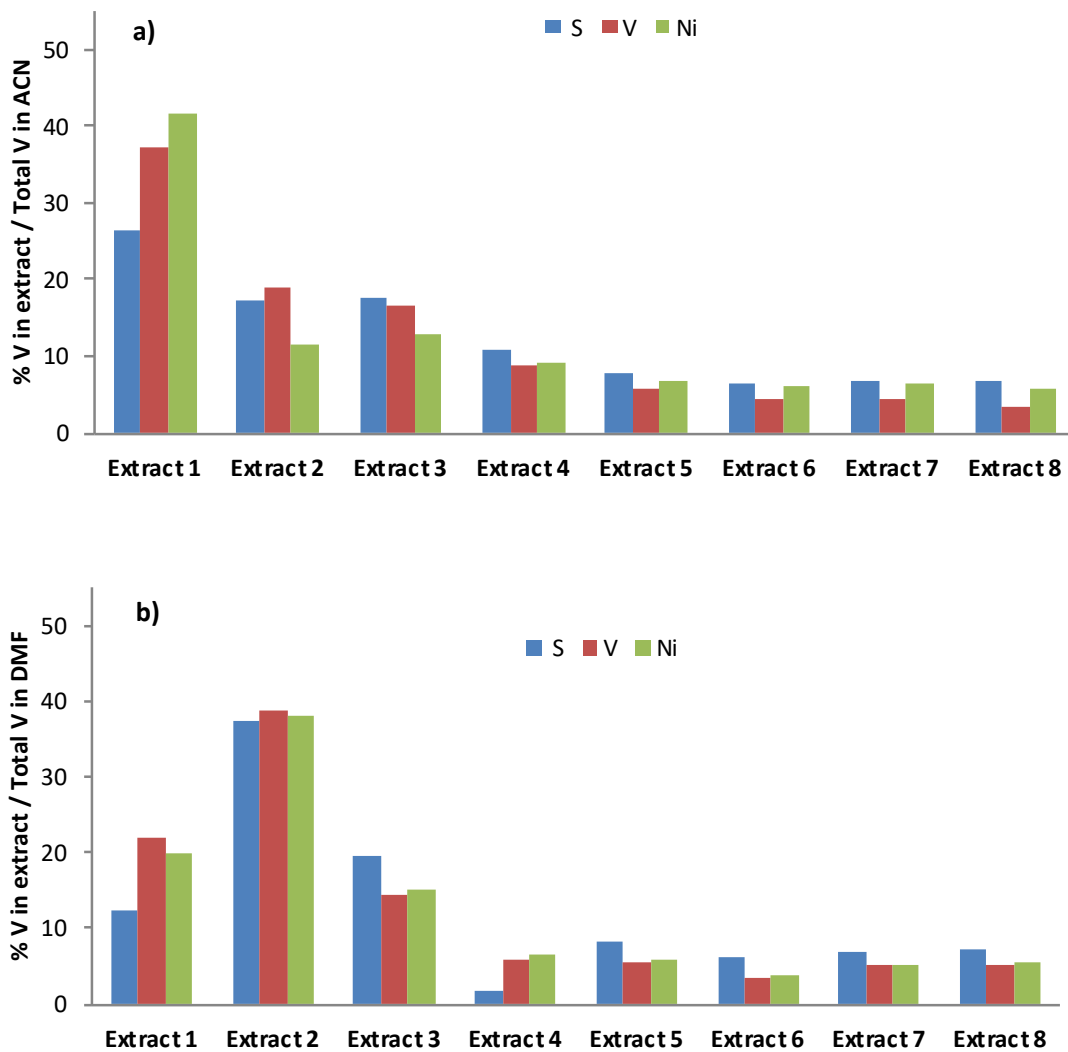


**Figure 3:** Vanadium GPC ICP MS chromatograms obtained for the ACN extract a), DMF extract b) and maltene after extraction c).

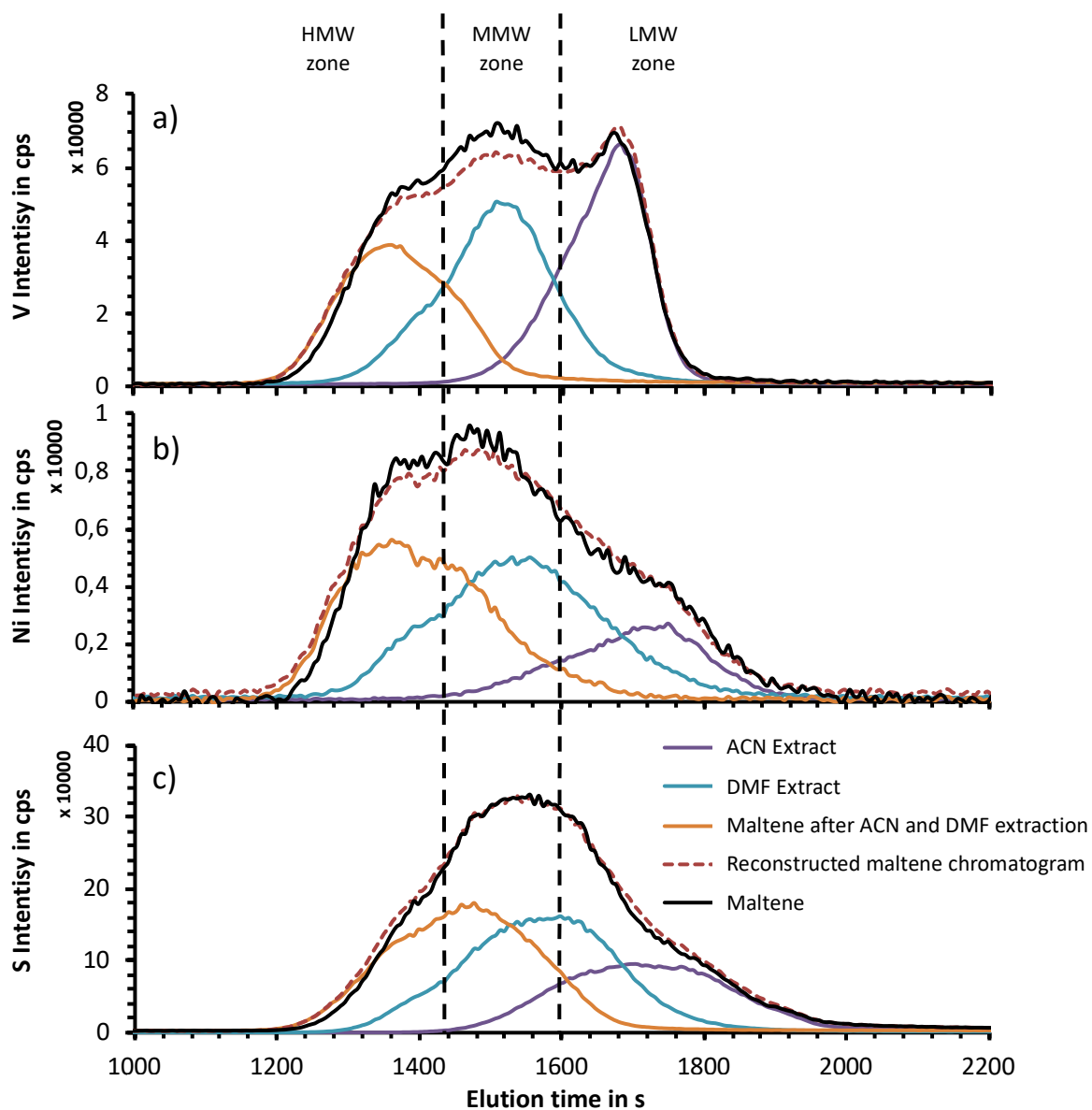


**Figure 4:** Absorption at the UV-Vis obtained for the sequential extractions with ACN a), DMF b) and remanent maltene after extraction with ACN and DMF c).





**Figure 5:** Extraction percentage of V, Ni and S with ACN extract a) and DMF extract.



**Figure 6:** GPC ICP MS chromatograms of V a), Ni b) and S) obtained for the ACN extract, DMF extract and maltene after extraction.