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Vacuum-assisted headspace solid-phase microextraction and gas chromatography coupled to mass spectrometry applied to source rock analysis

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ABSTRACT

Vacuum-assisted headspace solid phase microextraction (Vac-HSSPME) with high temperature of extraction was used for source-rock analysis. Optimization of extraction conditions was performed by Doehlert experimental design (DD) in gas chromatography coupled to mass spectrometer detector (GC–MS). Samples from the same oil well were mixed to obtain a mean stratigraphic characteristic for extraction optimization. Source-rock samples were analyzed in the DD optimal conditions and the proposed Vac-HSSPME+GC–MS method was compared to the classical procedure (SARA). The identification of important biomarkers like steranes and pentacyclic terpanes was possible. Fingerprint comparison between both methods shows similarity for steranes profile of overall chromatographic signal and compounds distribution. Also, it was possible to assess theoretical kinetic considerations for the system, as it differs from most conditions reported in literature. Furthermore, no organic solvent was used during the extraction or analysis with Vac-HSSPME. Classifying the procedure as a green methodology, while being faster and cheaper for oil bearing source-rock analyses.

1. Introduction

Petroleum is a complex chemical mixture formed by saturated hydrocarbons, and polar compounds including heteroatoms (N, O, S) of high molecular weight or not [1,2]. Physical-chemistry characterization of the oil is traditionally performed through determination of geochemical parameters. Those are dependent on quantity, absence, or presence of biomarkers, allowing one to extract information about the conditions during deposition of organic matter in the source rock. Such compounds may be direct related to organisms found in the organic matter during oil formation, and may also provide information about depositional environment and biodegradation process that occurs in the oil [1–3]. Classes like isoprenoids, steranes and terpanes are common in oil source rocks and may still provide information about its origin, and production potential of high-quality oil for the studied material.

Biomarkers are formed during sedimentation of organic matter and diagenesis processes conserving its structure [2]. Thus, its structure may be related to its biological precursor carrying information about the deposited organic matter. Specific characteristics differentiate biomarkers from other compounds found in oil and source rocks [4]:

- Precursors belong to a class of living organisms;
- They are partially or completely stable during sedimentation and subsequent physical, biological, and chemical process associated with it;
- The biomarker structure must be capable of indicating its biological origin.

The acquired data is interpreted by verifying the correlation between different biomarkers through ratios and relative abundance of those compounds in a qualitative manner [4–6]. Diagnostic parameters are a powerful tool to extract information about oil-oil and oil-source rock correlation. Comparison of different samples is usually promoted via direct ratio-to-ratio comparison or even 2D or 3D plots of ratio vs. ratio to distribute the samples in a graphical space [7,8]. Also, forensic analyses may be performed using such correlations to suggest a possible oil candidate or origin to a spilled oil studied [5,9–11]. Such correlations between components of a same sample have the function of minimizing concentration effects when different samples are compared. Thus, oils from different locations and similar analysis conditions may be compared and evaluated. Also, a multicriteria approach is required

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in geochemical evaluation, as source-rock characteristics are suggested by various biomarkers ratios, presence or absence of those [5].

The characterization and evaluation of a source rock as a possible oil producer is a challenge for the analyst due to the sample high complexity and number of constituents, usually found in low concentrations [1,12]. Traditionally, biomarkers analysis methodology in sediments requires the removal of the organic matter present in the source with Soxhlet extraction, concentration of the extracted material followed by open-column fractioning and GC-FID/MS analysis. The fractioning process aims to separate the extract into saturated, aromatics, resins, and light asphaltenes (SARA). The reference procedure is the ASTM D4124 09. However, it has been heavily modified by the petrochemical community throughout the years [13]. Such procedure is time consuming and costly, demanding sample pre-treatment and careful handling throughout the process. Also, those steps cannot be automated, which exposes the sample preparation method to innumerous errors and contaminants associated to the amount of unit operations required for biomarkers analysis [14]. Thus, alternative approaches in development of new methods compatible with sensibility, simplicity, and robustness demands are necessary.

In this scenario, the development of solid phase microextraction (SPME) more than two decades ago allowed the quantification of analytes with no need of exhaustive extraction [15,16]. This simple yet effective method has been used extensively in analytical chemistry, in fields like environmental, fragrancies, biological and many others. However, in petrochemical field its use is restricted due to sample nature and unsuitability for heavier compounds extraction. The capabilities of the technique to extract volatile and lighter compounds are well-known.

The theory for SPME is well stablished and discussed in the literature both in thermodynamic and kinetics terms [17,18]. The technique is based on partition coefficients of analytes in the different phases of the system. Thus, the amount of analyte a coating can extract depends on distribution constants of the analytes and the amount of free analyte in the sample. Also, direct immersion, headspace extraction, and experimental conditions affect how fast the thermodynamic maximum can be achieved. For highly volatile compounds in aqueous samples, extractions under equilibrium conditions are easily achievable due to enhanced kinetics. However, for semi volatile organic compounds (SVOCs) the equilibrium may not be practical for being too long. Thus, non-equilibrium extraction is performed for these analytes. In other to circumvent those limitations, Psillakis and coworkers demonstrated that the application of vacuum can improve the extraction kinetics of SVOCs via headspace extraction [19,20]. Considering the partial pressures of the analytes in vapor phase are independent of the total pressure, the amount of compounds extracted by Vac-HSSPME is essentially the same as in conventional HSSPME. However, lower pressure shortens the time needed for system equilibration, leading to fast extraction and enhancement of signal for higher mass compounds. For aqueous samples, the theory stated that mass transfer resistance from sample to vapor phase is related to two-films adjacent to the water-air interface which is related to Henry's constant. This is a parameter not affected by low pressure and compounds with lower K_H may have their transference to the headspace accelerated, as their mass transfer resistance relies on the gas-phase film term on the equation [19–21].

Considering that, in SPME factors like time of fiber exposition, temperature of extraction, fiber nature, stirring, and many others, may influence an extraction efficiency. Those parameters must be evaluated, and a surface plot generated to assess the best extraction conditions through experimental design [16]. Vacuum appliance during extraction requires only one additional variable in optimization process [19].

Design of experiment (DoE) techniques are applied as optimization tool to evaluate relevant variables within the studied system. A common approach is through factorial design model which allows a fast optimization in simple systems where the variables are just a few. However, when there are more variables to be tested at different levels, Doehlert design (DD) can be considered as a suitable option. Proposed by David Doehlert in 1970, DD allows more levels to be tested within the same variable while applying a point distribution model of the experimental values in a uniform way [22,23]. Comparing the number of experiments in other DoEs, DD requires significantly less experiments. When 7 variables were considered, Box-Behnken would require 85 experiments, and central composite design, 143. DD would require 57 while testing the variables in more levels [23]. Also, previously tested points can be reused in new models for a response surface approach [22,24]. Despite its advantages, DD is not commonly applied for gas chromatography analyses, but the determination of chlorides in human serum or water can be used as examples [25,26]. In our experience, this may be related to its low availability in DoE softwares, demanding a less automated approach and some programming knowledge in data treatment.

Considering the drawback of the conventional methods applied to oil source-rock analyses, Vac-HSSPME+GC–MS optimized via DD may be an interesting approach for biomarkers evaluation. The aim of this work is to provide a novel approach to oil source-rock screening, consuming less time, less human resources, while using no solvents in the extraction process.

2. Materials and method

2.1. Classical procedure (SARA)

The adopted procedure is based on ASTM D4124 standard method with some modifications. A detailed description can be found in the support information file.

2.2. Samples

All samples used were from the same oil well and their total organic carbon (TOC) was previously determined by the supplier using standard procedures; they were ground on a ball mill and sieved for d_p < 0,75 mm before use. The samples were identified as S0361, S0364, S0579, S0937 and S1830 were used as supplied and have TOC of 3,61%; 3,64%; 5,79%; 9,37% and 18,30% respectively. For optimization purposes, a blend of samples with total organic carbon (TOC) of 9,0% was prepared and identified through this paper as M0900.

2.3. Vacuum solid phase microextraction via headspace (Vac-HSSPME)

The Vac-HSSPME experimental setup and operation was adapted from Psillakis et al. [19] and is shown on Fig. 1. Aliquots of ground source rock were directly weighted inside 22 mL septum-sealable sample vials (Supelco, Bellefonte – PA, USA). The vial with sample was sealed with a Thermolite Shimadzu Plus plug-type high temperature pre-drilled silicone septa (Restek, Bellefonte – PA, USA), fit with a modified Mininert valve (Sigma-Aldrich, St. Louis- MI, USA). A detailed description and schematic of the vial and Mininert valve can be found elsewhere [27]. The vial headspace was evacuated down to 200 mbar (lowest possible with this model) using a GM-0.50 diaphragm vacuum pump (Jinteng Experiment Equipment Co., Tianjin, China), coupled to the mininert valve by a GC microsyringe barrel and needle. After an adequate time for evacuation of the headspace, the vial was inserted in a homemade heating block as soon as the vacuum pump is disconnected from the Mininert valve port. A 7 μm PDMS SPME fiber was introduced inside the vial through the pre-drilled septa and exposed after 5 min of equilibration time to its headspace for an appropriate extraction time. This particular fiber was chosen due to its high thermal stability and better performance for heavy compounds [17]. After extraction, fiber was immediately exposed to the heated injector of the GC–MS for desorption (5 min), separation, detection, identification, and quantitation of analytes.

2.4. Multivariate optimization through doehlert experimental design

The Vac-HSSPME method was optimized using a multivariate approach, through a set of experiments arranged according to a Doehlert

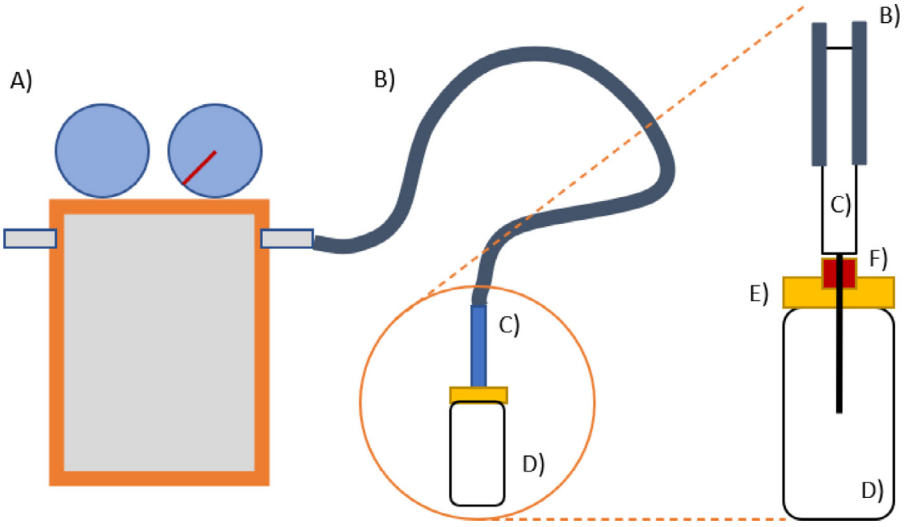

Fig. 1. Apparatus for pressure reduction inside the vial before HSSPME extraction. A) Vacuum pump, B) silicon hose, C) GC syringe, D) 22 mL vial, E) Modified Mininert® vial cap, F) GC septum fitted in the modified cap.

matrix experimental design [22,28]. Aliquots from the same single sample of source rock were used on all experiments. The operational variable studied and respective levels were: sample mass $\mathbf{m_s}$ (100, 300, 500, 700 and 900 mg); evacuation time $\mathbf{t_{PRE}}$ (5, 10 or 15 min); extraction temperature $\mathbf{T_{ext}}$ (100, 125, 150, 175, 200, 225 and 250 °C) and extraction time $\mathbf{t_{ext}}$ (15, 30, 45, 60, 75, 90 and 105 min) – for a total of 25 experiments, including triplicate runs on the central point (Table S1, Supplementary Material). The response optimized was the sum of all detected chromatographic peaks on chromatograms obtained monitoring the mass fragments with m/z = 217 Da (corresponding to steranes, a group of polycyclic alkanes which are some of the most relevant petroleum biomarkers) [1,4]. The processing of the data was carried out using scripts implemented on MATLAB v. 2011b (Natick, MA, USA) platform.

2.5. *Gas chromatography with mass spectrometry detection (GC–MS)*

Analyses were performed in a Shimadzu TQ8030 GC–MS. Injector temperature was set to 300 °C, splitless mode, SPME liner (0.75 × 5.0 × 95) mm. The column used was a 30 m × 0.25 mm-id × 0.25 µm SLB-5MS. H_2 was used as carrier gas with 0.8 mL/min @ constant flow rate. The GC oven was programmed from 70 °C (2 min hold) to 300 °C @ 4 °C/min with 30 min of holding time at the end. Acquisition was performed @ 10 Hz in selected ion monitoring (SIM) mode for 85, 191, 217 Da for DD optimization. The same acquisition rate was applied for the samples using SCAN mode from 50 to 600 Da. Interface between GC and the MS temperature was set to 200 °C, while the ion source was at 250 °C.

2.6. *Analytical performance of the optimized method*

Blends of M0900 sample and of ground rock sample exempt of organic matter from the same sample set were prepared, to simulate real samples with known and variable extractable content ranging from 0,56% to 9,0% TOC). For each blend, 160 mg were transferred to the 22 mL vial and extraction was performed according to the optimal conditions previously determined. Chromatographic conditions were the same described in Section 2.5 in SIM mode.

3. Results

3.1. *Doehlert experimental design*

Petrochemical samples are highly complex and geochemical studies are a multicriteria approach. The assessment of information despite its depositional environment and the organic matter deposited is often made by biomarkers ratio, ratio-to-ratio plots, and general chromatographic profile of the sample. Three classes of compounds are especially relevant: linear alkanes (monitored by GC–MS considering the mass fragment at 85 Da), pentacyclic terpanes (191 Da), and steranes (217 Da). For the optimization, the signal monitored at 217 Da was chosen, since steranes can be considered one of the biomarker classes more relevant concerning geochemical information.

The total area of detected peaks in extracted ion chromatograms for 217 Da was then defined as optimized response for the Doehlert multivariate optimization. A quadratic correlating this response and the optimized variables was found as adequate, considering the value for the F-test parameter of significance and the lack-of-fit test. Table S2 shows the p-value of significance for each variable and interactions calculated. Variables with p-value higher than 0.05 were not considered statistically relevant with 95% confidence. Eq. (1a) represents the model regression.

$$S = -59216 + 345\ X2 + 1000\ X3 - 3\ X2 \cdot X3 - 37\ X3 \cdot X4 + 122\ X4^2 \quad (1a)$$

Better assessment of the effects of the studied variables over the extraction efficiency can be made after inspection of Fig. 2, which represents surfaces correlating response with vacuum time, extraction time and/or extraction temperature.

Figs. 2 point out that the optimum extraction conditions are at 250 °C with 15 min of vacuum time and 15 min of extraction time. Since the sample mass did not significantly affect the extraction efficiency, it was fixed as 100 mg for the remaining experiments after evaluation of analytical performance in item 2.6 (results in supplementary material). When observing the regression curves (Figures S52 to S76), 100 mg provides maximum sensitivity without deviation from linearity. For n-alkanes, most of the determination coefficients are higher than 0.99 with few exceptions. Apart from the practical purpose – the determination of the best operational conditions – examination of the surfaces shown on Fig. 2 can provide some insight on basic and theoretical aspects of vac-HSSPME. The amount of analytes extracted increases for higher operational temperatures; this is consistent with a kinetically controlled extraction process where an increase on temperature leads to increment on the efficiency due to the acceleration of all mass transfer steps involved. The same stands for the extent of the vacuum time before extraction: longer evacuation periods of sample / headspace under vacuum should lead to continuous enrichment of the vapor phase with analytes (until equilibration or analyte depletion from sample, which seems not to be the case).

The behavior of the response surface in terms of vacuum and extraction times (Fig. 2A) deserves further examination. Two local maxima

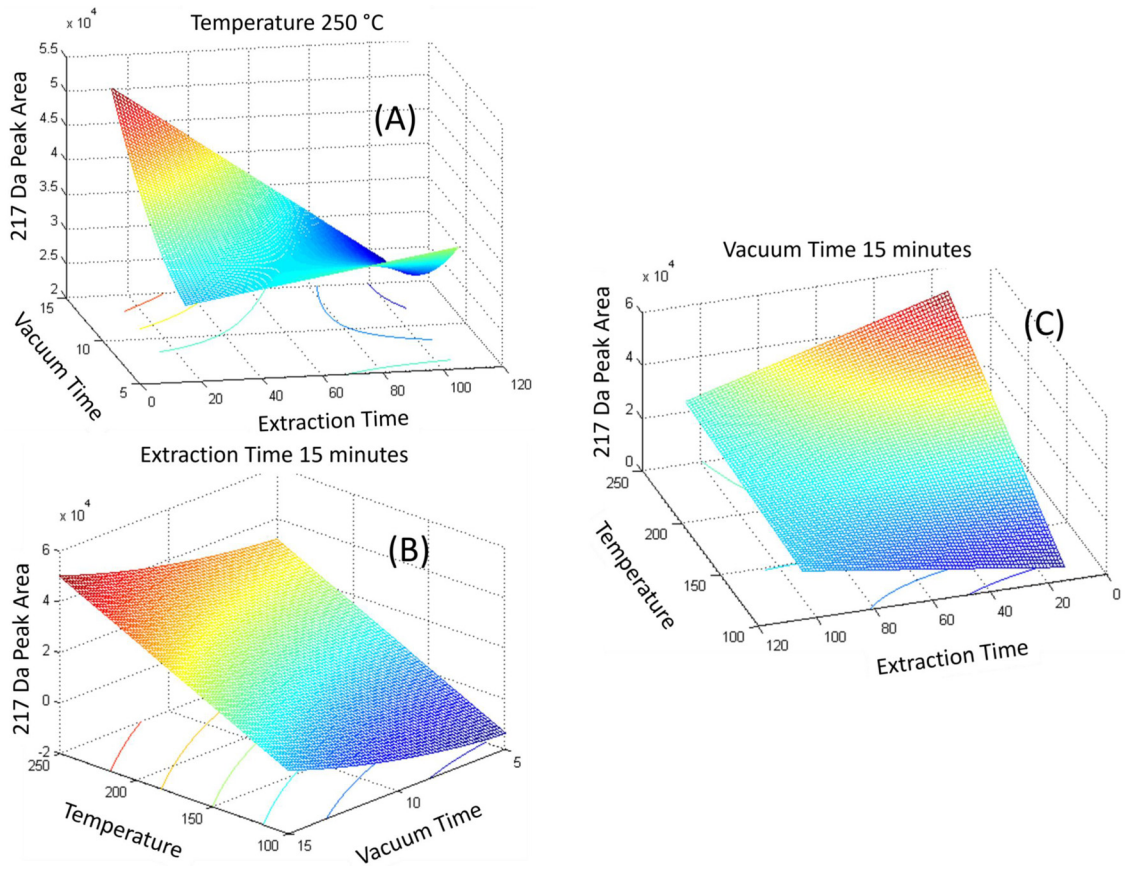

Fig. 2. Response surfaces for Doehlert experimental design. Predicted response is the peak area for 217 Da steranes in the model. (A) Temperature of extraction fixed at 250 °C. (B) Extraction time fixed at 15 min. (C) Vacuum time fixed at 15 min.

are observed, for shorter vacuum time with longer extraction time, and for longer vacuum time with shorter extraction time, the latter being the overall optimum condition. There is no straightforward correlation between fundamental kinetical and thermodynamical aspects of HS-SPME and this comportment – which therefore could be related to practical, operational aspects of the technique not predictable through its basic theory. A possible cause could be related to loss of analytes through septa, vial closure, tube connections or other interfaces after longer periods of operation but this is an aspect of the system which is still being assessed.

3.2. Qualitative and quantitative profiling of extractable volatile fraction of source rocks

The optimized vac-HSSPME was applied to samples of oil source rocks, and the results compared to the conventional Soxhlet + SARA fractioning extraction method. Figs. 3 and 4 compare total (scan) and 217 Da extracted ion chromatograms for a representative sample and allow a qualitative comparison between those approaches. Mass spectra comparison of each relevant peak is present in the supplementary material.

A visual inspection shows that the chromatographic profiles obtained using Vac-HSSPME and the conventional Soxhlet method are quite similar and comparable. However, a more meticulous examination shows, in fact, there are some remarkable differences. Less retained, and therefore more volatile analytes (t_R < ~ 20 - 25 min on Fig. 3) seem to be better detected using Vac-HSSPME – which is expectable, since it is a well-known fact that compounds with high vapor pressures are prone to be lost during Soxhlet extraction, as well as during posterior solvent evaporation, redissolution and transference between vials. Apart from this, either on the total ion or the SIM chromatograms, the distribution and relative intensities of the detected peaks on both techniques seem to be comparable save minor differences.

Although visual comparison of chromatograms can reveal some interesting information, better assessment of the potentiality and scope of applicability of this method needs quantitative information. Comparison between Vac-HSSPME and traditional Soxhlet + SARA results is not straightforward: both are, in principle, quantitative but the latter is a typically exhaustive where SPME, regardless of the particular format and approach being used, is an equilibrium / kinetically controlled extraction technique. Also, for Soxhlet + SARA, extracts are organic solutions (that usually are introduced on GC using split injections: although splitless mode is possible, it is not frequent on such dirt samples), where for SPME extracts are directly injected on chromatographic columns with injectors usually operating on splitless mode, without need of solvent evaporation or on-column band narrowing and reconcentration (when using liquid splitless injection). A simple and reliable way to compare both approaches for quantitative purposes could be carried out by appraisal of detection limits of relevant compounds for both techniques. Due to the nature of the samples here being studied (natural, non-synthetic oil source rocks) and since certified materials with known concentrations of relevant analytes are either unobtainable, extremely expensive or mostly not available, calculation of absolute detection limits would not be realistic. Traditionally, source-rocks evaluation is performed by biomarkers ratios, but the same approach would not be valid when applied to Vac-HSSPME. Considering the nature of the extraction, significant distortions in peak area values are expected. Table S3 presents a comparison of a normalized value of peak areas expressed as a percentage of the total peak area of each class. The ratio between vacuum and Soxhlet extraction reinforces the distortion in peak values for heavier compounds in most classes. Alternatively, signal-to-

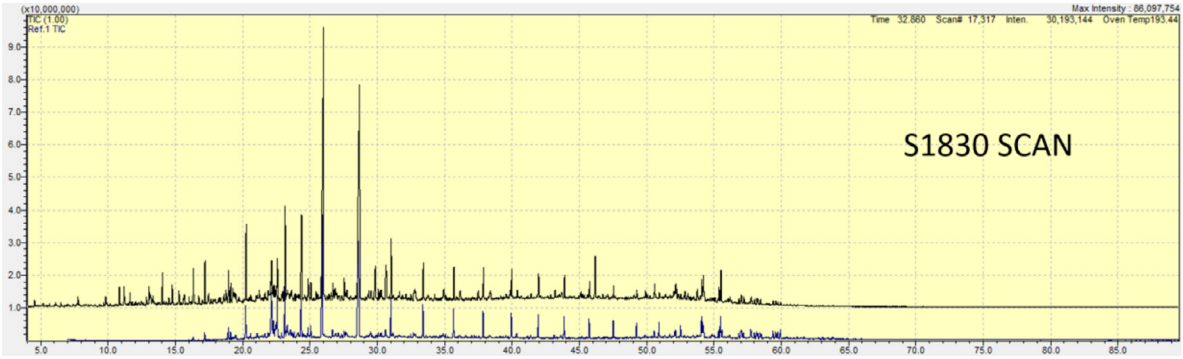

Fig. 3. Vac-HSSPME and Soxhlet fingerprints for the same source-rock compared. Above, Vac-HSSPME profile (black). Below, Soxhlet profile (blue).

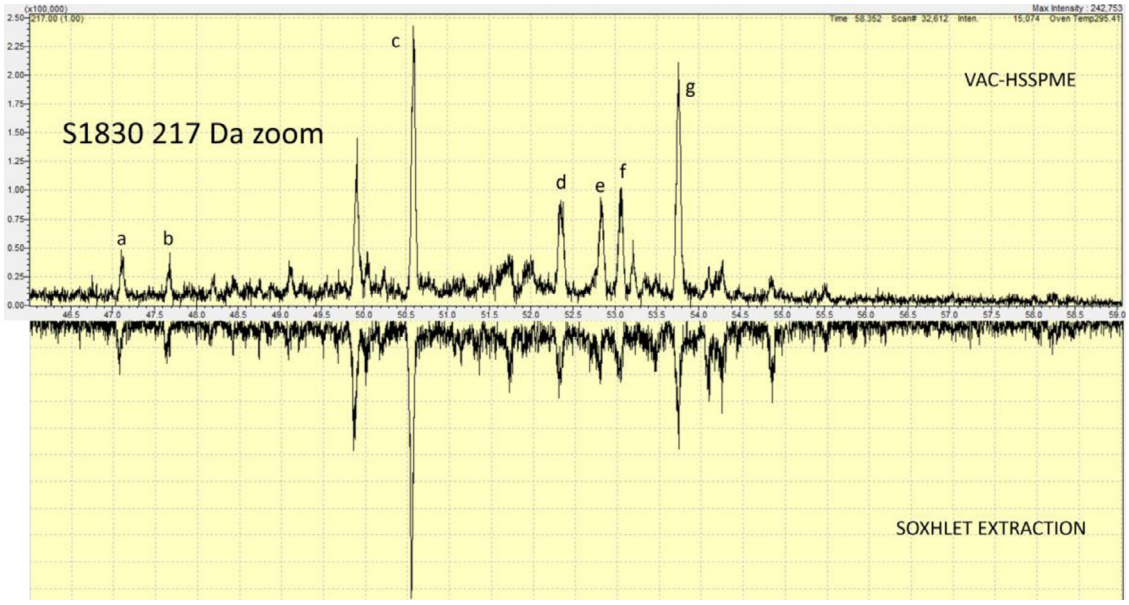

Fig. 4. Steranes 217 Da comparison between Vac-HSSPME method and Soxhlet extraction method. Retention time from 46 to 69 min.

noise ratios measured for peaks on the same samples corresponding to the same detected analytes could be a reliable parameter to compare chromatograms obtained in such different conditions. For each chromatogram, (S/N) ratios for relevant peaks (n-alkanes from C_{22} to C_{32} on total ion scan chromatograms, as well as steranes and terpanes on SIM chromatograms) were computed, and average values for each compound using Vac-HSSPME were calculated from them. Fig. 5 shows plots of the ratios of $(S/N)_{vac}$ values for n-alkanes as a function of the respective van den Dool – Kratz LTPRI (linear temperature programmed retention indexes) for each analyte.

Fig. 5 shows that, when compared to conventional Soxhlet extraction, there is an approximately linear correlation between S/N ratios for Vac-HSSPME and analyte LTPRI, except for the two heavier alkanes (were the detected amounts are marginally larger than the detection limits and, therefore, the uncertainty on the measured peak areas is quite large). Supposing that the conventional extraction method is exhaustive, this tendency should be attributed to features of Vac-HSSPME. Basic theoretical aspects of Vac-HSSPME have been discussed on the literature [19–21], and models correlating rate of analyte uptake, nature of analyte and operational parameters usually relies on Henry Law constants for aqueous solution / vapor equilibrium – which is not the case here, since there is no aqueous phase involved on the process. For n-alkanes, LTPRI are simply the size of the alkyl chain, and several relevant thermodynamic and kinetic molecular parameters pertinent to the extraction process can be directly correlated to it. For example, Pawliszyn and co-workers showed that, in equilibrium SPME operation, both fiber-headspace and sample-headspace distribution constants can be directly correlated with analyte LTPRI, if the nature of the SPME fiber coating and GC column stationary phase are the same [17,18]. Since Vac-HSSPME is usually conducted in non-equilibrium conditions, other parameters affecting the mass transfer rate should be considered. For the case here being assessed, a simplified discussion could be made considering that desorption of analytes from the sample surface is fast and that there is no significative diffusion from inside the solid matrix (and, therefore, after the evacuation period the analyte concentration on the headspace $\mathbf{C_{HS}}$ is directly proportional to the analyte concentration in the sample $\mathbf{C_S}$). It can be supposed also that the amount of analytes extracted are small compared to their concentration on the vial headspace in the beginning of the process. If these conjectures are true, the amount of analyte extracted **n(t)** can be correlated to the extraction time $\mathbf{t_{ext}}$ and to its concentration on the headspace $\mathbf{C_{HS}}$:

$$n(t) = \frac{2\pi D_G L}{\ln\left(\frac{b+\delta}{b}\right)} \cdot C_{HS} \cdot t_{ext} \tag{1b}$$

where $\mathbf{D_G}$ is the diffusion coefficient of the analyte in gas phase, L and b are the length and diameter of the SPME fiber, respectively, and δ is the thickness of the static diffusive boundary layer surrounding the fiber. As the sample headspace here is not stirred or mechanically perturbed, it is stagnant and therefore δ corresponds to the distance **r** between the fiber and the sample vial wall - which, if the fiber is centered in the system,

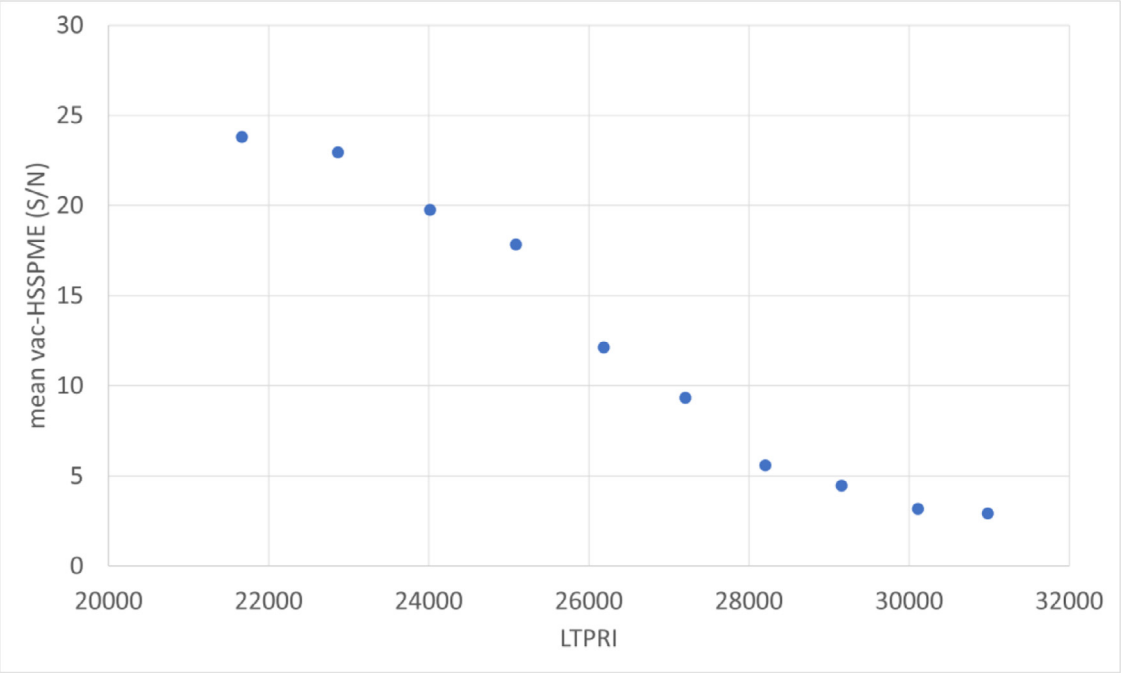

Fig. 5. van den Doon – Kratz LTPRI correlation with (S/N) in vac-HSSPME.

is approximately the vial radius. Since $\boldsymbol{r} >> \boldsymbol{b}$:

$$\ln\left(\frac{b+\delta}{b}\right) = \ln\left(\frac{b+r}{b}\right) \approx \ln\left(\frac{r}{b}\right) \tag{2}$$

Also, $\mathbf{C_{HS}}$ should be directly proportional to the concentration of the analyte in the sample surface, which on its turn is also proportional to the overall concentration in the sample $\mathbf{C_S}$, if the latter is homogeneous ($\mathbf{C_{HS}} = \boldsymbol{q}\bullet\mathbf{C_S}$, where $\mathbf{q}$ is a scalar proportionality constant). Therefore, Eq. (1b) reduces to:

$$n(t) = \frac{2\pi D_G L}{\ln\left(\frac{r}{b}\right)} \cdot q \cdot C_S \cdot t_{ext} = Q \cdot C_S \cdot t_{ext} \tag{3}$$

where Q is a scalar combining all constant terms on Eq. (3):

$$Q = \frac{2\pi D_G L q}{\ln\left(\frac{r}{b}\right)} \tag{4}$$

All terms in Eq. (4), except $\mathbf{D_G}$, are related to dimensions of fiber and sample vial. As for $\mathbf{D_G}$, according to the semi-empirical Fuller-Schettler-Giddings (FSG) model [20,29], it can be estimated from parameters related to the analyte, air and operational conditions:

$$D_G = \frac{10^{-3} T^{1.75} \sqrt{\left({}^1/_{M_A} + {}^1/_{M_{air}}\right)}}{P\left(V_A^{1/3} + V_{air}^{1/3}\right)^2}$$

where $\mathbf{T}$ is the temperature (K), $\mathbf{P}$ is the pressure (atm), $\mathbf{M_A}$ and $\mathbf{V_A}$ are the molar mass and molar diffusion volume of the analyte and $\mathbf{M_{air}}$ and $\mathbf{V_{air}}$ are apparent molar mass and apparent molar diffusion volume of atmospheric air. Molar diffusion volumes for the analyte can be calculated from the sum of the tabulated atomic diffusion volumes for each atom or structural feature (e.g., aromatic rings) on the molecular formula of the analyte. Therefore, for compounds in an analog series such as n-alkanes, $\mathbf{D_G}$ (as well as $\mathbf{M_A}$) is a direct function of the length of the alkyl chain.

In an n-alkane analog series $\mathbf{C_mH_{2m+2}}$, an expression for the "exact" dependence between $\mathbf{D_G}$ and $\mathbf{m}$ could be obtained expressing $\mathbf{M_A}$ and $\mathbf{V_A}$ in terms of $\mathbf{m}$ and re-writing the FSG model equation inserting there the corresponding formulae. The resulting complex polynomial expression obtained will be clearly non-linear in terms of $\mathbf{m}$ as it can be seen on Fig. 6– which shows a plot of $\mathbf{D_G}$ estimated from FSG model for n-alkanes from C_1 to C_{50} and on optimized operational $\mathbf{P}$ applied and $\mathbf{T}$ determined by Doehlert design (200 mbar and 250 °C). However, in practice the dependence between $\mathbf{D_G}$ and $\mathbf{m}$ for heavier hydrocarbons can be regarded as approximately linear: the insert to Fig. 6 shows $\mathbf{D_G}$ for alkyl chain range from C_{22} to C_{31} (the same as in Fig. 5) and the regression line shown on this insert has a determination coefficient equal to 0.995. Therefore and at least on a simplified basis, gas-phase diffusion coefficients can be a good parameter to assess and predict relative Vac-HSSPME extraction efficiencies, at least when considering non-aqueous solid samples.

4. Conclusion

Vac-HSSPME is presented as an alternative to classical sample preparation procedure based on Soxhlet extraction, which is time consuming and requires a lot of organic solvents. This simpler approach avoids many random errors during unity operations like weighting, transferring, solvent evaporation, open column chromatography and many others performed in ASTM D4124 or similar methods.

The studied correlation between the classical Soxhlet + SARA and vac-HSSPME provided insights on theoretical aspects. The extraction of analytes can be described mainly by their diffusion coefficients in the gas-phase based on FSG model for solid, non-agitated, and non-aqueous samples like oil source-rocks. For geochemical evaluation, the peak areas and biomarkers ratio obtained by Vac-HSSPME can not be direct correlated to ones obtained through Soxhlet. However, here we demonstrated that extraction of SVOCs from source rocks is possible and consistent. Further studies with a high number of samples may indicate correction factors for biomarkers ratio and support a simpler approach to source-rock characterization. Also, it is expected that Vac-HSSPME associated patterned recognition chemometrics methods may circumvent the laborious steps of manual parameters calculation and ratio-by-ratio plots in the final steps of geochemical analyses.

Besides being on its early stages, this novel technique presents great potential in geochemical analyses or even in analyses of other SVOCs rich matrices. The linearity and sensitivity showed that vacuum is a

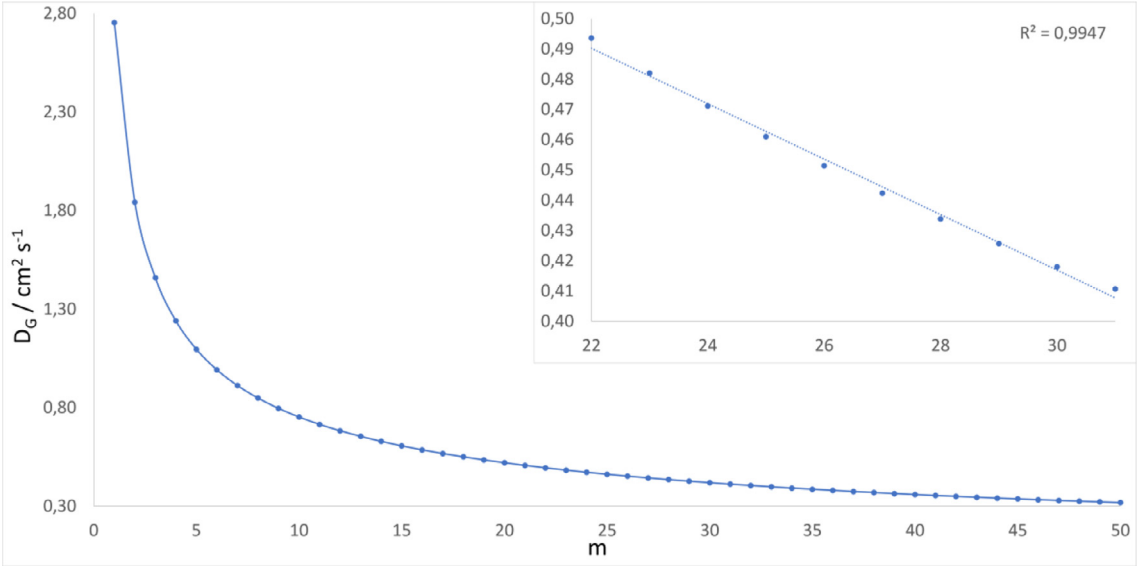

Fig. 6. Gas phase diffusion coefficients (D_G) calculated using FSG model at P = 200 mbar and T = 250 °C for n-alkanes from methane (C_1, m = 1) to pentacontane (C_{50}, m = 50). Insert shows D_G for the range between docosane (C_{22}) to hentriacontane (C_{31}).

quantitative capable technique for oil source-rock analyses providing a higher throughput when compared to the Soxhlet + SARA approach. Nonetheless, no hazardous solvents were used in vac-HSSPME method, which should reduce costs and environmental damage in petrochemical or related sediments analyses. Eq. (2)

Declaration of Competing Interest

The authors declare no conflict of interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.sampre.2021.100001.

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