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Direct elemental analysis of petroleum heavy fractions by means of ICP-OES equipped with a high temperature torch integrated sample introduction system

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The present work describes and discusses the use of the high temperature sample introduction system, hTISIS, for the analysis of crude oil and heavy petroleum fractions by means of inductively coupled plasma optical emission spectrometry, ICP-OES. A commercially available sample introduction system based on a conventional Cyclonic spray chamber operated at room temperature has been used for comparison purposes. The method has been based on the sample gentle heating while stirring, dilution and introduction into the spectrometer. A 5 μ L solution volume has been injected into an air carrier stream and driven to the sample introduction system. Therefore, a transient signal has been obtained. Meanwhile, the quantification strategy has consisted in an external calibration using a single set of multielemental standards prepared in xylene. The achieved results indicate that, for crude oil and its heavy cuts, the hTISIS operated at 400 °C provides signal enhancements in terms of peak height from about 4 to 15 times with respect to the Cyclonic spray chamber. Furthermore, the repeatability is improved and the limits of quantitation lowered when working with the high temperature device. The measured LODs for real samples have also been determined and it has been observed that the Cyclonic spray chamber affords figures from 2.5 to 50 times higher than the hTISIS at 400 °C. Moreover, for the latter design, matrix effects have been compensated for and it has been possible to apply the concept of universal calibration in which a single set of xylene multielemental standards has been applied to the simultaneous accurate quantification of silicon, vanadium, iron, aluminum and nickel in crude oil, atmospheric residue, fuel, vacuum residue and vacuum distillate.

Introduction

Petroleum fractional distillation yields light as well as heavy crude oil fractions.¹ Products such as naphtha, gasoline, diesel or kerosene are included within the former group and condense at lower temperatures than the remaining residue. Therefore, heavy products correspond to residues of distillation at either atmospheric pressure or vacuum conditions.² In the last years there has been an increased interest in using heavy fractions as a source of energy. In order to achieve this goal, high boiling point distillation residues undergo further refining aimed at producing light fractions.³

Among the different components of petroleum products, metals have a high interest for the crude oil industry for several reasons:⁴ (i) they help establishing relationships between the crude oil formation and the refining conditions; (ii) their content depends on the efficiency of the crude oil refining process; (iii) engine malfunction may be predicted; (iv) environmental risks are assessed as a function of the metal content; (v) they preclude the product stability; (vi) the

identification of the product geographical origin and maturity are based on the metal content and type;⁵ (vi) they may induce catalyst poisoning and fouling as well as equipment corrosion; and, (vii) some of them are incorporated to fuels as additives.

Metals have the tendency to concentrate in the residual oil fuel fraction. In fact, it has been claimed that 80% of the metal content is associated to the portion of crude oil that precipitates when it is mixed with an n-alkane (*i.e.*, asphaltene).^{6,7} In addition, these species may be transferred to light products. Therefore, it is compulsory to develop appropriate analytical methods able to provide metal and metalloid information in heavy petroleum cuts as well as in crude oil.

Inductively coupled plasma techniques, ICP-OES and ICP-MS, are highly appropriate for the determination of metals in heavy petroleum fractions and crude oil, basically because of their multielemental capability, low detection limits and high sample throughput.^{8,9} However, there are several challenges associated to the use of ICP methods for this kind of assays. Among them the fact that the samples have an intricate organic matrix that may vary significantly among products, the sample viscosity is high, elements can be present under very different chemical forms that are more or less strongly associated to the organic matter and the samples are usually difficult to bring into solution. Furthermore, ICP-MS is highly prone to the formation of soot deposits on the interface and to polyatomic spectral interferences when heavy petroleum residues are analyzed. Most of the proposed methods for elemental analysis of petroleum products are based on a previous preparation step

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including decomposition,¹⁰ open vessel wet digestion,¹¹ closed digestion,^{12,13} microwave digestion^{14,15} or combustion,¹⁶ emulsification,¹⁷ microemulsification,¹⁸ extraction induced by emulsion breaking^{19,20} and solid phase microextraction.^{21,22} In general terms, these procedures are time consuming, they may induce sample contamination or volatile losses and, hence, additional methods should be proposed. Sample dilution and direct introduction in the ICP spectrometer is a straightforward, fast, accurate and easy-to-automate method for carrying out the analysis of heavy petroleum products.^{23,24,25,26} Some of the problems of this methodology are related with the degradation of the limit of detection, the eventually sample incomplete solubilization and the generation of toxic residues. The chosen solvent should be able to completely dissolve the sample, it should have a low volatility, low toxicity, compatibility with the instrument materials and it should not induce additional ICP interferences.²⁷

The introduction of organic samples into the plasma has several disadvantages that have led to the selection of appropriate operating conditions.^{28,29} On this subject, the sample introduction system plays a role of capital importance and dedicated devices have been proposed as, for example, the use of a cooled spray chamber, desolvation system or the work with low sample consumption systems.³⁰ A good alternative consists in heating the aerosol generated by a micronebulizer before its introduction into the plasma. The so-called high temperature Torch Integrated Sample Introduction System (hTISIS) consists of a low inner volume single-pass spray chamber whose wall temperature is set at a 400 °C maximum value. In this case, the analyte transport efficiency becomes virtually 100% regardless of the sample matrix.³¹ As a consequence, the contribution of the spray chamber to the finally observed matrix effects is eliminated. This point is highly relevant for the petroleum analysis industry, because it is necessary to handle many fractions or cuts very different in terms of matrix composition and properties. Therefore, the concept of universal calibration can be applied in which external calibration using a single set of standards is used for the analysis of all kind of samples.³² So far, the hTISIS has been applied to the analysis of light petroleum products and biofuels through both ICP-OES³³ and ICP-MS.^{34,35} The obtained results reveal that, upon careful selection of the plasma operating conditions, the obtained sensitivities are more than one order of magnitude higher than those for a conventional spray chamber, limits of detection are lowered by an average factor typically close to 4-5, memory effects are mitigated and matrix effects are removed while the sample consumption goes from about 5 µL to 20-30 µL min⁻¹ in discrete and continuous sample aspiration modes, respectively. Within this context, it has been noticed that the hTISIS improves the ICP analytical figures of merit especially for the petroleum fuels with low volatilities (e.g., diesel).

The goal of the present work was thus to perform a systematic study about the performance of the hTISIS for the analysis of crude oil and its heavy cuts by means of ICP-OES. These products are much more difficult to vaporize than light fractions. Therefore, it is very interesting to evaluate whether such a concept for sample introduction can also be applied to heavy petroleum cuts. The elements evaluated (silicon, vanadium, nickel, aluminum and iron) were selected on the basis of their importance within the field.^{30,36,37,38,39} Thus, for instance, silicon has an abrasive nature and ability to form deposits and it can cause problems in transport and storage of petroleum and petroleum products; vanadium affects the efficiency of the catalytic cracking process and, together with nickel, gives indication of the geographical origin and age of the crude oil;

aluminum and iron, that increases the oxidation products, in turn, reveal corrosion problems in the machinery. DOI: 10.1039/C8JA00320C

Experimental

Reagents and real samples

Standards were prepared by appropriate dilution of a Conostan S-21 500 mg Kg⁻¹ multielemental solution in xylene. Five independent real samples were evaluated:

- a crude oil;
- an atmospheric residue, AR. This fraction corresponds to the residue issued of the atmospheric fractional distillation process and uses to have a boiling point about 340 °C.⁴⁰ AR can be transferred to a vacuum distillation unit or may be used as raw material for fuel production;⁴¹
- a fuel sample that is an intermediate product of the vacuum distillation process;
- a vacuum distillate, VD; and,
- a vacuum residue, VR, that describes the material at the bottom of the distillation tower having a boiling point close to 560 °C⁴⁰ and is usually employed to produce asphalt, for instance.⁴²

Physical properties of these samples are summarized in Table 1.

Table 1. Physical properties of the heavy petroleum fractions considered in the present work.[#]

Property	VD	AR	Fuel	Crude oil	VR
Density at 15 °C (kg m ⁻³)	909	969	1028	840	1006
Kinematic viscosity at 100 °C (mm ² s ⁻¹)	6.248	41.2	32.7	n.a.	457
Initial distillation temperature (°C)*	293.2	274	202	42	448
80% Final distillation temperature (°C)*	485	664	604	484	702
Flash point (°C) [#]	179.4	191.6	109	n.a.	n.a.

[#] VD: Vacuum distillate; AR: Atmospheric distillate; VR: vacuum residue.

*Determined according to Gas Chromatography simulated distillation.

[#]Determined according to ASTM D93-16a - Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester.

ICP-OES operating conditions and experimental procedure

An Optima 4300 DV Perkin-Elmer ICP-OES spectrometer (Überlingen, Germany) was used to axially take the intensities. The hTISIS was equipped with a 9 cm³ single-pass spray chamber. The operating conditions are gathered in Table 2. It has been recently claimed that heavy petroleum cuts may contain nanoparticles.⁴³ In order to prevent the nebulizer tip blocking, a glass pneumatic concentric nebulizer, TR-50-C0.5 (Meinhard Glass Products, Santa Ana, USA) was employed throughout the present study. This device has equipped with a 278 µm id sample capillary.

The solutions were delivered to the nebulizer by means of a peristaltic pump (Perimax 16 antiplus, Spetec) and a 0.19-mm id

flared end PVC-based tubing (Glass Expansion, Melbourne, Australia). The peristaltic pump continuously aspirated air. A given sample volume was measured with an automatic pipette (Eppendorf, Hamburg, Germany). Then, the nozzle was adapted to the flared end tubing and the solution was aspirated by means of the peristaltic pump. The sample plug was driven to the nebulizer thus avoiding sample dispersion, as the carrier stream was simply air.⁴⁴

Table 2. ICP-OES operating conditions.

	Plasma: 15
Ar flow rates/L min ⁻¹	Auxiliary: 0.2 Nebulizer: 0.4
Volume injected/μL	5.0
Air aspiration rate/rpm	350
Emission lines /nm	Al I 396.153 Ni II 231.604 Fe II 239.562 Si I 251.611 V I 290.880 Ar I 363.268
RF power/ kW	1.4
Number of replicates	6

Sample preparation

A very important issue related with heavy petroleum residues was the sample homogeneity. As mentioned before, heavy petroleum residues may contain solid particles.⁴³ Furthermore, viscosity for some products was fairly high (Table 1). In order to homogenize and fluidize the samples prior to their direct analysis, crude oil, AR, fuel, VD and VR were heated for 15 min at 100, 80, 60, 60 and 120 °C, respectively. These temperatures were low enough to prevent partial sample evaporation. Afterward, they were manually shaken for 2 minutes to take representative sub-samples. Finally, a given mass of sample was weighed and it was properly diluted with xylene.

Additionally, the samples were treated using a microwave digestion system Start D (Milestone, Sorisole, Italy). Approximately 250 mg of the sample, weighed with a precision of ±0.1 mg, were transferred to a digestion vessel and then 7 mL of 65% HNO₃ and 1 mL of 30% H₂O₂ were added. The sample was digested at 200 °C for 30 min. The digests were transferred to graduated glass flasks and diluted to 10 mL with Milli-Q water.

Statistical treatment

For further QC/QA assessment, the results generated by the dilution and direct analysis method were compared with those obtained after acid sample digestion. The F-test was applied to compare the variances of both procedures. In the cases where the variances could be considered as statistically comparable, the *t-Student* test was applied to verify statistical differences in terms of elemental concentration. However, when the variances could not be considered as statistically comparable, it was not appropriate to combine the sample standard deviations to give an overall estimate of this parameter. The unequal variance *t-Student* test involved calculation of a *t* statistic (Equation 1) that was compared with the appropriate value in standard *t* tables. The calculation of the degrees of freedom in this case was given by Equation 2.

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

Equation 1 View Article Online
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$$\text{Degrees of freedom} = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\left(\frac{s_1^4}{n_1^2(n_1-1)} + \frac{s_2^4}{n_2^2(n_2-1)}\right)}$$

Equation 2

where *x* was the mean value, *s* was the standard deviation, *n*₁ and *n*₂ were the number of replicates for both methods (*n*₁=*n*₂=6).

Results and Discussion

Effect of the hTISIS temperature on sensitivity

A relevant variable of the hTISIS is the temperature of the chamber. This parameter precludes the aerosol evaporation rate and, hence, the sample transport efficiency to the plasma. Figure 1 summarizes the peak height values obtained for silicon and the different products studied. As expected, the increase in the hTISIS temperature up to 200 °C led to a grow in peak height. The improvement factor was included within the 5.7 to 6.8 range with respect to the data at room temperature, depending on the product considered. A further increase in the temperature from 200 to 400 °C gave rise to a 15 – 30 % extra increase in sensitivity. It was therefore concluded that at 200 °C virtually all the solvent (xylene) was evaporated.

Up to now, the high temperature system has been applied to the analysis of samples having boiling points below the chamber heating temperature.^{26,32} Therefore, both the sample and the solvent used for dilution purposes evaporated inside the hTISIS before reaching the plasma. However, the products evaluated in the present work had boiling points above 400 °C that was the maximum studied chamber temperature. An experiment was performed in order to compare the trend depicted in Figure 1 with that found when a more volatile solution was introduced. On this subject a 1 mg kg⁻¹ silicon standard prepared in xylene (b.p. close to 140 °C) was introduced. It was verified that the peak height was 2.4 times higher at 200 °C than at room temperature. This enhancement factor was in contrast with those previously mentioned for heavy products (around 6 times, see Figure 1) and revealed that, as could be expected, the impact of the temperature on sensitivity was especially significant when working with non-volatile samples.

Figure 1. Silicon peak height for the four petroleum heavy fractions and crude oil found at three different hTISIS temperatures and the Cyclonic spray chamber. Error bars correspond to the standard deviation obtained from six consecutive injections. Dilution factor

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with xylene, 1:10. For the sake of clarity, signals for fuel and VR have been divided by 10.

Comparison with a Cyclonic spray chamber

One of the benefits of the hTISIS is that the signal enhances with respect to a conventional sample introduction setup.^{31,32} This is obviously due to the increase in the analyte transport efficiency. In order to avoid plasma degradation problems, the sample injected volume should be rather low. Note that the hTISIS was initially conceived to analyze microsamples. Later it was realized that, it was also possible to perform the analysis of complex organic samples (*i.e.*, fossil fuels) provided that a low amount of sample was consumed. Throughout the present study, it was verified that no drain was generated whereas the chamber walls remained virtually dry. This fact led us to assume a 100% solvent (xylene) transport efficiency. Obviously, samples were not evaporated because the operating temperature was too low (see Table 1). However, this variable was far above the xylene bp. Therefore, it could be indicated that, once the aerosol was generated, the solvent quickly evaporated and the sample transport as sub-micrometer droplets was favored. Figure 2 confirms this expectation, because it was clearly observed that the ICP-OES sensitivities were higher when working with the hTISIS than for the Cyclonic reference spray chamber.

In order to further verify the degree of evaporation of the sample inside the chamber at 400 °C, experiments corresponding to gas chromatography simulated distillation were performed for the petroleum residues.^{45,46} It was verified that, at this temperature, the percentages of evaporated sample were 30, 15 and virtually 0% for the VD, AR and VR, respectively. Therefore, the evaporation of the heavy residues inside the hTISIS could not be considered to be a dominating process.

It was interesting to notice that the signal improvement factor incorporated by the hTISIS over the conventional chamber depended on both the sample and the element considered (Figure 2). Thus, for instance, the silicon peak height was around 20 and 10 times higher for the hTISIS as compared with the Cyclonic design for the crude oil and the atmospheric residue, respectively. Interestingly, when nickel was under study, the normalized signal approached to 4 - 5 for four out of the five heavy cuts.

Additional data are shown for vanadium, iron and aluminum (see Figure S1). In the case of vanadium, it was found that, for the solutions resulting from AR, VR and fuel, at 400 °C the signal saturated because of its high content and, thus, it was not possible to evaluate the impact of the hTISIS in terms of signal improvement. More diluted samples or less sensitive vanadium emission lines would have been required to test the behavior of the hTISIS. The data for iron and aluminum in the case of crude oil are not included in Figure S1 because the Cyclonic spray chamber did not allow to detect the peaks corresponding to both elements. Collectively speaking, these results highlighted the benefits of the hTISIS especially when analyzing non-volatile samples. In order to illustrate the influence of the element on the signal improvement factor, the normalized peak heights were taken for VD. In this case, the relative values were 6.7, 1.3, 12.7, 1.8 and 3.9 for Si, V, Fe, Al and Ni, respectively. The characteristics of the emission line, together with the physical properties of the compounds in which these elements were present in petroleum could be argued to account for these discrepancies and will be the subject of further studies.

Figure 2. Peak height found with the hTISIS normalized with respect to that measured for the Cyclonic reference spray chamber. (a) Silicon; (b) nickel. White bars: hTISIS temperature: 200 °C; grey bars: hTISIS temperature: 400 °C. Samples dilution factor: 1:10

Precision

The repeatability of the achieved transient signals was evaluated by means of the peak height relative standard deviation. As Table 3 reveals, RSDs were lower than 3% when the hTISIS was utilized. This was in clear contrast with the Cyclonic spray chamber for which RSD values were as high as 19%. The fact that the hTISIS operated at 400 °C afforded lower RSDs than the conventional chamber highlighted the suitability of this design to carry out the analysis of microsamples having an organic matrix. In the case of the Cyclonic design, re-nebulization from the walls of the chamber and intense droplet impacts could be in the origin of the degradation of the signal repeatability. The data also suggested that, with the hTISIS, the aerosol heating was homogeneous, likely due to the high set temperature and the low sample injected volume.

In order to verify the aerosol and gas heating degree, a thermocouple was positioned inside the hTISIS at 3 cm from the nebulizer tip. When the nominal temperature was set at 300 °C and the nebulizer gas was on, it was verified that the temperature in the chamber centerline was close to 290 °C. This temperature dropped down to roughly 250 °C in presence of aerosol. Therefore, it was concluded that the work with low sample volumes did not originate strong temperature gradients (16% decrease in temperature according to the chamber main axis).

Plasma thermal characteristics

In order to evaluate the plasma state, the Ar 363.268 nm atomic emission intensity was registered for all the evaluated samples. As Figure 3 clearly demonstrates, it was observed that the Cyclonic spray chamber gave rise to higher Ar signals than the hTISIS whatever temperature was selected. This fact suggested that the plasma perturbation produced by the hTISIS when organic samples were introduced was more significant than that induced by the Cyclonic

design. This fact could be attributed to an increase in the amount of matrix delivered to the plasma when the aerosol generated by the nebulizer was heated. Furthermore, it was evidenced that the argon emission signal depended on the sample analyzed for the reference chamber. In contrast, the hTISIS afforded a similar plasma thermal state regardless of the sample being injected. This last result was typical for a robust plasma and revealed that the excitation cell was energetic enough to perform the analysis of heavy petroleum products with the hTISIS.

Table 3. Comparison between the signal repeatability (% RSD in terms of peak height, n=6) for the Cyclonic spray chamber and the hTISIS operated at 400 °C.#

	Ni		V		Fe		Si		Al	
	Cy	hTISIS	Cy	hTISIS	Cy	hTISIS	Cy	hTISIS	Cy	hTISIS
VD	@	0.8	14	2.5	7.0	0.7	8.9	1.7	7.0	2.0
AR	0.2	0.9	0.5	*	3.8	1.0	6.6	0.9	7.3	1.4
Crude Oil	7.9	2.6	19	2.0	@	1.1	7.2	1.4	4.5	1.1
Fuel	3.6	1.3	0.8	*	1.9	0.2	6.0	0.4	2.0	0.2
VR	3.1	0.3	0.8	*	3.2	1.7	3.0	0.5	5.8	1.1

Samples were 1:10 diluted with xylene. The samples elemental concentrations are given in Table 6.

@Concentrations below LOD

*Signal became saturated because of the increased sensitivity.

Figure 3. Ar signal at the maximum of peaks obtained for the studied elements. Black bars: Cyclonic; grey bars: hTISIS temperature: 200 °C; white bars: hTISIS temperature: 400 °C. Samples dilution factor: 1:10.

Limits of detection and quantitation

Detection limits were determined for the two evaluated sample introduction systems according to the $3 s_b/S$ criterion where s_b was the standard deviation of six consecutive injections of a blank. S , in turn, was the sensitivity found for a 1 mg kg^{-1} standard prepared in xylene. The results are gathered in Table 4. It was observed that, in agreement with the improvement found in terms of sensitivity, the LODs were from 1.6 to 3.2 times lower when the hTISIS was operated at 400 °C than for the Cyclonic spray chamber. Therefore, heating of the chamber walls did not degrade the blank stability, at least as it was determined in the present work, because the LOD enhancement factor corresponded to that in terms of peak height.

Table 4. Limits of detection ($\mu\text{g kg}^{-1}$) obtained for a xylene standard.

	Si	V	Fe	Al	Ni
Cyclonic	38	20	55	19	63
hTISIS 200 °C	26	17	14	15	28
hTISIS 400 °C	18	8	17	12	25

In order to experimentally evaluate the LODs for real samples, they were subsequently diluted and re-analyzed until the system was unable to provide reliable data. The standards were prepared in xylene and the quantification method was based on an external calibration. As discussed by Mermet et al.,⁴⁷ this procedure provided a minimum signal that was transformed into the concentration domain by means of a four standards based calibration line. The comparison of the obtained concentration with that measured through a sample digestion method provided a means for validation of the limit of quantitation. Clearly, quality control criteria were established in which the concentrations measured according to external calibration did not differ by more than 10% of those achieved by means of the conventional microwave digestion method. As an example, Figure 4 plots the analyte concentration versus the dilution factor. Data included corresponded to the Cyclonic spray chamber and the hTISIS at the two temperatures assayed. The results obtained when the samples were MW digested and analyzed using an aqueous set of standards were used as reference values in order to test for accuracy. The lowest analyte concentration for which there were not significant deviations (higher than 10%, see dashed red lines in Figure 4) between the results obtained according to the dilute-and-shot method and those corresponding to the digestion was the measured LOD. Thus, as it may be seen in Figure 4.a, for the 50-fold diluted AR (silicon concentration $40 \mu\text{g kg}^{-1}$), the Cyclonic spray chamber provided significantly higher concentrations than those obtained when applying a conventional dissolution procedure. This fact suggested that the Cyclonic device provided a quantitation limit for this sample above 40 parts per billion. Silicon may be present in petroleum products as volatile species, thus enhancing the analyte transport efficiency to the plasma and giving rise to an overestimation of the obtained concentration.⁴⁸ However, this effect was discarded in the present work, because more concentrated samples provided lower concentration than the reference value (see bars for Cyclonic chamber in Figure 4.a). Meanwhile, the hTISIS afforded accurate results at these concentrations (*i.e.*, no significant deviations between the concentrations determined according to the MW digestion and those found with the dilution-based analysis method). The same could be stated for the 10-fold diluted VD (Figure 4.b). The 10-fold diluted AR (Figure 4.a) and 5-fold diluted VD (Figure 4.b) presented a different situation, because it was found that the concentration measured with the Cyclonic design was lower than the actual one. It should be pointed out that matrices were different as a function of the dilution factor. Therefore, the results shown in Figure 4.a for AR suggested the appearance of a negative matrix effect. Indeed, the sensitivity for heavy petroleum products was expected to be lower than that for xylene.

Examples of the benefits of working at 400 °C are shown in Figure 4.c and 4.d. In this case, it may be observed that the obtained

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aluminum concentrations in AR were lower than the expected ones for the hTISIS at 200 °C whereas a subsequent increase in the chamber temperature provided concentrations not significantly different from those afforded by the digestion methodology. Therefore, the achieved results suggested that aluminum matrix effects were less severe for the highest temperature evaluated. Concentrations for aluminium in the case of the most diluted VD sample (Figure 4.d) were higher than the expected ones when working at 200 °C, whereas 400 °C provided, again, good results. As a conclusion, it could be indicated that quantitation limits were lower for the latter temperature than for the former one.

The results found for the remaining petroleum products and analytes tested agreed with those shown in Figure 4. Summarizing, the hTISIS operated at 400 °C provided the lowest deviation in concentration with respect to that measured following the digestion method for all the dilution factors evaluated. Table S1 recovers the concentrations obtained for the different elements, products, sample introduction systems and dilution factors. In general terms, it could be stated that the measured LOD was 2.5-25 times lower (Table S2) with the hTISIS as compared to the Cyclonic spray chamber depending on the sample and the element.

Figure 4. Correlation between the actual elemental concentration in the undiluted and diluted samples. (a) AR, silicon; (b) VD, silicon; (c) AR, aluminum; (d) VD, aluminum.

Analysis of real samples

Figure 5 plots representative peaks when samples were spiked at a 1 mg kg⁻¹ multielemental concentration. In order to obtain these peaks, the non-spiked samples were taken as blanks. It is interesting to point out that the signal obtained when injecting heavy petroleum products depended strongly on the sample considered when the Cyclonic spray chamber was utilized. A xylene standard yielded a peak signal from 4 to 9 times higher than those encountered for real samples. Meanwhile, the hTISIS operated at 400 °C afforded peaks whose height was approximately the same for all the evaluated compounds. Additional comments could be made regarding the peak width. In fact, it can be clearly observed that this parameter was 3-4 times lower in the case of the high temperature sample introduction system. Therefore, the sample throughput could be enhanced when using the hTISIS with respect to the conventional spray chamber.

Figure 5. Silicon peaks obtained for the different products analyzed when working with the Cyclonic spray chamber (a) and the hTISIS operated at 400 °C (b). Samples were 1:10 diluted in xylene.

The effect of the nature of the sample on the sensitivity (*i.e.*, matrix effects), suggested by some of the previously shown results, was thoroughly studied by determining the following ratio:

$$C_R = \frac{C_{\text{dilution and shot method}}}{C_{\text{microwave based method}}} \quad \text{Equation 3}$$

In absence of interferences, this ratio should be equal to the unity. On this subject, the sample dilution factor played a very important role. On the one hand, dilution mitigated matrix effects whereas, on the other, it degraded the limit of quantitation. Both points are evidenced in Figure 6 in which the obtained silicon C_R values are plotted for five different dilution factors. In the case of the Cyclonic spray chamber (Figure 6.a), this variable took values below 1 for VD, AR and crude oil samples when the dilution factor was low (*i.e.*, the concentration provided by the reference chamber was lower than the obtained when the digestion method was applied). Data for fuel and VR are only shown for dilutions higher than 1:10, because the signal was saturated when the dilution factor was below this level. However, when the dilution factor was too high, no signal was detected for silicon in the case of samples having a low content in this element (VD and crude oil). The use of the hTISIS at 200 °C led to C_R values close to the unity, instead. However, the determined concentrations were still lower (15 – 30%) than the actual ones. This deviation in C_R from the unity was especially relevant for low dilution factors. This was likely due to the fact that heating of the chamber at such a temperature was not enough to compensate for the great difference between the chemical composition of the samples and standards. In this way it could be anticipated that analyte transport efficiency still differed for samples and standards. A further increase in the hTISIS temperature improved the results and C_R were virtually equal to 1 irrespectively of the sample and dilution factor considered. This fact suggested that, for heavy petroleum fractions, matrix effects disappeared. Note that the quantification methodology consisted in an external calibration using a single set of standards prepared in xylene. Therefore, the possible reason for these results was based on the fact that, once the aerosol was generated, the solvent (xylene) evaporated and the remaining droplets corresponding to the sample were efficiently transported to the plasma. Therefore, analyte transport efficiency approached for the samples and the standards. This fact removed the contribution of the spray chamber to the non-spectral interferences. As revealed Figure 3, the plasma argon signal did not depend on the sample. In other words, the excitation cell was not sensitive to a modification in the nature of the aerosol reaching it. Therefore, the interferences were overcome when equipped the spectrometer with the hTISIS operated at 400 °C.

Figure 6. Silicon relative concentration, C_R , for five different dilution factors and the heavy products analyzed. (a) Cyclonic spray chamber; (b) hTISIS 200 °C; (c) hTISIS 400 °C.

These results were verified for all the analytes tested at low and high dilution factors. Table 5 contains the C_R for the 1:10 diluted samples. As it can be observed, the use of a Cyclonic spray chamber provided values of this relative parameter either lower (*i.e.*, matrix effects were present) or higher (*i.e.*, the concentration was lower than the limit of quantification) than 1 thus revealing that accurate results were not achieved. The hTISIS operated at 200 °C afforded C_R data closer to 1, although these results were not acceptable, because there was a residual deviation from the target value. It was necessary to heat the chamber walls up to 400 °C to achieve satisfactory C_R values. Therefore, under these circumstances, the concept of universal calibration would be applied. In other words, a single set of standards in which a Conostan® stock solution was diluted in xylene was useful to perform elemental quantification in petroleum heavy fractions, including crude oil, having very different physical and chemical characteristics.

The concentrations of the analytes when the hTISIS was used at 400 °C are included in Table 6. To evaluate whether the difference between the concentrations provided by the developed method and the microwave digestion method was significantly different, the statistical test previously described in section 2.4 was applied. No significant statistical differences were observed between the values obtained by both procedures.

As Table 6 shows, it was found that fuel sample and VR were the fractions generally enriched in elements such as Al, Fe, Al and Ni. Meanwhile, crude oil and VD appeared to be less concentrated in the five evaluated elements. The atmospheric residue contained an intermediate elemental concentration.

The data for Ni and V in AR and VR are on the same order as those provided elsewhere.⁴⁰ Druzian et al.,⁴⁹ used a method based on the sample treatment by microwave combustion and ICP-OES elemental analysis of petroleum distillation residues. These authors found that the iron concentration was higher in AR than in the VR. This observation differed as compared to the results found in the present work, although different samples were evaluated. However, the trends for vanadium and nickel were in concordance in both works.

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Table 5. Relative concentrations (see equation 3) obtained for the 1:10 diluted samples.

	Element	VD	AR	Crude oil	Fuel	VR
Cyclonic		3.90	0.71	3.60	0.72	0.74
hTISIS 200°C	V	2.80	*	3.00	*	*
hTISIS 400°C		1.05	*	1.06	*	*
Cyclonic		0.88	0.77	#	0.74	0.66
hTISIS 200°C	Fe	0.84	0.89	0.87	0.96	0.91
hTISIS 400°C		0.97	0.98	1.07	1.02	0.994
Cyclonic		4.81	0.76	1.82	0.58	0.7
hTISIS 200°C	Al	1.56	0.81	2.51	0.89	0.88
hTISIS 400°C		0.97	0.97	0.96	0.99	1.03
Cyclonic		#	0.76	0.74	0.78	0.62
hTISIS 200°C	Ni	0.76	0.83	0.89	0.88	0.94
hTISIS 400°C		1.05	1.01	0.98	1.00	1.01
Cyclonic		2.70	0.66	0.54	0.58	0.49
hTISIS 200°C	Si	0.97	0.91	0.94	0.89	0.94
hTISIS 400°C		1.04	0.95	1.00	1.01	1.03

*Detector was saturated.

#Concentration below the limit of quantitation.

Vanadium and nickel are the most abundant metals in petroleum.⁵⁰ Vanadium concentration in crude oil was close to 200 $\mu\text{g kg}^{-1}$ whereas that for nickel was on the order of 2 mg Kg^{-1} . These data likely indicated that a light crude oil sample was analyzed in the present study. Furthermore, these levels were in concordance with recent results found by dos Anjos et al. for some petroleum samples.⁵¹ Iron detected in the crude oil studied was found at a much lower concentration than other samples in which it was present at tens of mg Kg^{-1} .⁵²

Table 6. Elemental concentrations (mg Kg^{-1}) found for the five petroleum products using external calibration with a set of xylene multielemental standards.*

Sample	Si	V	Fe	Al	Ni
AR	1.968 $\pm$ 0.017	Sat	6.91 $\pm$ 0.07	0.808 $\pm$ 0.011	18.26 $\pm$ 0.17
VD	0.797 $\pm$ 0.013	0.401 $\pm$ 0.018	3.02 $\pm$ 0.02	0.303 $\pm$ 0.006	0.334 $\pm$ 0.003
VR	8.09 $\pm$ 0.04	Sat	52.2 $\pm$ 0.9	2.97 $\pm$ 0.03	32.22 $\pm$ 0.10
Crude oil	2.48 $\pm$ 0.03	0.200 $\pm$ 0.004	0.488 $\pm$ 0.006	0.158 $\pm$ 0.002	2.44 $\pm$ 0.06
Fuel	37.25 $\pm$ 0.14	Sat	44.13 $\pm$ 0.09	30.65 $\pm$ 0.06	25.2 $\pm$ 0.3

* hTISIS operated at 400 °C.

Conclusions

So far, the hTISIS had been applied to the analysis of light petroleum products including gasoline, diesel or kerosene. In that case, the improvement in signal varied strongly as a function of the volatility of the sample. The higher this property, the lower the sensitivity

improvement.³² The data shown in the present study confirmed that the hTISIS can be considered as a good alternative especially for the analysis of heavy petroleum products through ICP-OES.

Compared to a conventional sample digestion procedure, the method based on the use of the hTISIS for the analysis of diluted petroleum heavy cuts showed a dramatic shortening in analysis time together with a complete elimination of generated residues and reduction in requested sample amount. Analytically speaking, quantitation limits were reduced by a factor in between 2-20 depending on the sample and the element considered.

The data permit us to conclude quite positively that with the hTISIS operated at 400 °C it is possible to overcome matrix effects at sample dilution factors for which interferences are observed when using a conventional sample introduction system. This fact has several associated advantages. In a first place, universal calibration^{32,53,54} is possible in which a single set of standards prepared in xylene are used to perform external calibration with excellent accuracies. In a second one, it is possible to improve the sensitivity for three different reasons: (i) the high transport efficiency increases the analytical response by a factor close to one order of magnitude; (ii) it is possible to propose lower sample dilution factors than in the case of a conventional spray chamber; and, (iii) the peak is narrower than when using a conventional Cyclonic spray chamber what allows increasing the sample throughput by a factor close to two or three.

Additional features of the hTISIS combined with an air-segmented sample injection method include the fact that a very low sample amount is required to perform several replicates and, hence, it is possible to down-scale the total laboratory samples volume. In addition, no residues are generated thus matching the elemental analysis of petroleum products with the principles of green chemistry.

Conflicts of interest

There are no conflicts to declare.

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