Effect of solvent dilution on the ICP-AES based silicon sensitivity, the aerosol characteristics and the resulting organic solution properties in the analysis of petroleum products

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The effects of the solvent dilution factor on the physical properties of the resulting organic solutions, the aerosol characteristics and the silicon sensitivity were studied in ICP-AES for four different petroleum products by using near total sample consumption systems. The four samples were two gasoline products having very different volatilities along with a kerosene and a diesel sample. Petroleum product samples were diluted with xylene using four sample dilutions; 1 : 2, 1 : 5, 1 : 10 and 1 : 50. The sample introduction systems were a single pass spray chamber associated with a micronebulizer and a demountable Direct Injection High Efficiency Nebulizer (d-DIHEN). A cyclonic spray chamber also associated with a micronebulizer was taken as the reference system. Silicon was used as the test element, because it has been previously demonstrated that the ICP-AES Si sensitivity was significantly modified according to its chemical form. Silicon was spiked in each diluted solution with the same concentration to test sensitivity. When considering the dilution factor as the key variable, it was found that for the two gasoline samples and the kerosene one, the higher this variable, the lower the sensitivity. This result was explained in terms of changes in the solution volatility and/or in the aerosol characteristics. It was also observed that the total sample consumption systems were less sensitive to changes in the properties of the resulting organic solutions than the system based on the cyclonic spray chamber. However, for the latter chamber, the properties of the resulting organic solution had a marked influence on the extent of the effect of the silicon chemical form on the sensitivity. This fact demonstrated the appearance of an undefined interaction between the analyte and the organic solution during the aerosol transport step. However, both the single pass spray chamber and the d-DIHEN mitigated this effect for all the samples.

Introduction

The analysis of petroleum products through ICP techniques is one of the most challenging subjects in plasma spectrochemistry. Firstly, the matrix of this kind of samples is very complex. Secondly, the organic nature of the sample may produce severe degradation of the plasma performance because of its possible high volatility that may lead to a severe degradation of the plasma or even to its extinction. Furthermore, the analyte can be present in the sample under very different chemical compounds, which may significantly affect its sensitivity. Finally, most of the introduction systems are mainly designed for working with aqueous solutions. As a result, the accuracy of the analytical data may be degraded.

Because some petroleum products cannot be directly introduced into the plasma, significant dilutions with appropriate solvents are usually required which gives rise to constant physical properties such as viscosity, volatility or surface tension. The dilution factor influences the final properties of the organic solution, the extent of the interferences and obviously the sensitivity. Most of the new poisons known in the petroleum industry are effective at μg ml⁻¹ or sub μg ml⁻¹ levels (P and S in FAME, trace elements in diesel, As, Hg and Si in gasoline). Therefore, it is of crucial importance to better characterize the effect of dilution in order to choose the right factor representing the compromise between matrix effect and loss in sensitivity.

For organic solutions, it has been reported that the properties of a given solvent strongly modify the aerosol generation and transport processes. When pneumatic nebulizers are used, the most important physical properties in terms of aerosol characteristics are the surface tension and the viscosity. Once the aerosol is generated, the solvent volatility and density play a relevant role. Finally, some solvents modify the plasma thermal characteristics hence affecting the extent of the analyte excitation. For other nebulizers, such as the ultrasonic ones, aromatic compounds affect more severely the analytical signal than aliphatic solvents. All these issues are especially relevant in the context of the petroleum industry where heterogeneous samples (i.e., containing many and very different organic compounds) must be analyzed.

Due to the complex sample nature, the use of single matrix standards (i.e., universal calibration) has been considered to be virtually impossible to carry out quantitative analysis of this kind of samples through ICP techniques. Nonetheless there have been...
some attempts to achieve such an universal calibration. In some of them, the liquid sample introduction system has been modified. For example, Botto and Zhu used an ultrasonic nebulizer equipped with a conventional desolvation system and a microporous membrane, the basic idea being to remove most of the solvent before the plasma. According to these authors it was possible to carry out the analysis of gasoline or refinery naphtha with a single calibration line based on the dissolution of an organometallic standard in n-hexane. However, if the analyte was present in the solution as a volatile compound, it could be lost in the solvent elimination step of the desolvation system. Furthermore, for ultrasonic nebulizers, memory effects are severe. A more recent approach has used a modified dual-channel pneumatic nebulizer to carry out the analysis of organic samples with aqueous standards. In this case, one channel can be used to introduce the aqueous solutions whereas the other one is devoted to the nebulization of an immiscible solution (e.g., lubricating oils).

It is also worth mentioning that low sample consumption systems can be suitable for the introduction of organic samples such as fuels with minimum impact on the plasma thermal characteristics. Based on these devices, total sample consumption systems are very promising. In this case, the totality of the solution is delivered to the plasma. As a result, the differences in terms of aerosol transport phenomena are eliminated and, hence, the mass of analyte reaching the plasma is independent of the solution properties. Thus, for example, the Direct Injection Nebulizer and the Direct Injection High Efficiency Nebulizer (DIHEN) were used for the analysis of naphtha with the addition of an oxygen stream to avoid carbon deposits at its tip.

The aim of the present work was thus to characterize the effects of the petroleum product nature and dilution factor on the ICP-AES performance for three different liquid sample introduction systems. To achieve this goal, four petroleum products were spiked with silicon under three different chemical forms and diluted with xylene at different factors. The solutions were finally analyzed by ICP-AES. Two different approaches were evaluated: (i) a single pass spray chamber associated with a micronebulizer and; (ii) a demountable direct injection high efficiency nebulizer (d-DIHEN). The same micronebulizer adapted to a cyclonic spray chamber was used as the reference system.

### Experimental

Different fractions of petroleum products, such as two gasoline samples, kerosene and diesel were studied. Table 1 shows their boiling range distribution. In order to carry out the analysis through ICP-AES, the samples were 1 : 2, 1 : 5, 1 : 10 and 1 : 50 diluted with xylene. Additional physical properties were experimentally measured for the tested solutions (Table 2). Diluted samples were spiked with a 1 μg ml⁻¹ silicon to verify any change in the Si sensitivity. To determine surface tension at 25 °C, a stalagmometer (Brand, Germany) was employed. This method is based on the fact that the weight of a drop that flows through a capillary is proportional to the surface tension. Water surface tension value was taken as reference. Viscosities, in turn, were obtained at 25 °C by means of an Ostwald viscosimeter. To determine the so-called evaporated mass percentage, a beaker containing 20–25 g of sample was placed inside a ventilated oven at 40 °C. The beaker was weighted 1 h later and the following equation was applied:

$$\text{Evaporated} \% = \frac{m_{\text{initial}} - m_{\text{final}}}{m_{\text{initial}}} \times 100$$

where $m_{\text{initial}}$ and $m_{\text{final}}$ were the masses before and after the beaker was placed inside the oven. This parameter provided estimation about the solution evaporation rate.

Silicon was used as the test element because of its importance in the petroleum industry and its severe poisoning effect on hydrotreatment catalyst. This element was added to the solutions under three different chemical forms: octamethylcyclotrisiloxane (compound A); dimethyloctilchlorosilane (compound D); and, hexamethyldisiloxane (compound R). The codification was in agreement with previously published work. Their respective boiling points were 175, 218 and 100 °C. Compound D was selected as it was already used as a reference, while compound R exhibited the strongest ICP-AES signal enhancement effect. Compound A, in turn, also enhanced the ICP-AES sensitivity when compared to compound D but to a lesser extent than compound R. These compounds are also potential degradation products issued from polydimethylsiloxane (PDMS) that is used as an antifoaming agent in the petroleum industry.

A PFA concentric micronebulizer (CPI International) was fitted either to a 40 cm³ inner volume glass cyclonic spray chamber or to a 12 cm³ glass single pass spray chamber (Torch Integrated Sample Introduction System, TISIS). A demountable Direct Injection High Efficiency Nebulizer (d-DIHEN, Analab, Strasbourg, France) was also used in order to remove the aerosol transport step.

The solutions were delivered to the nebulizer by means of a peristaltic pump (Gilson Minipuls3 Model M312, Villiers-le-Bel, France) and a 0.19-mm id PVC-based material with plasticizer (Tygon, Ismatec, S.A.) tubing was employed.

Volume drop size distributions were measured for the aerosols generated by the nebulizer (i.e., primary aerosols) as well as those leaving the spray chamber (i.e., tertiary aerosols). These experiments were carried out by means of a laser Fraunhofer diffraction system (model 2600c, Malvern Instruments, Malvern Worcestershire, UK). The sizer was equipped with a 63-mm lens focal length, which enabled the system to measure droplets with diameters included within the 1.2–118 μm range. Either the nebulizer tip or the chamber exit was placed at 30 mm from the lens and at 5 mm from the laser beam centre.

The analyte mass transported to the plasma ($W_{\text{tot}}$) was measured by means of an indirect method. Prior to the experiments the TISIS chamber was washed with xylene. Then either 1 : 2 or 1 : 50 sample dilutions spiked with 100 μg g⁻¹ manganese (Alfa® Aesar®, Karlsruhe, Germany) were introduced into the

### Table 1: Initial and final boiling points for the studied samples

<table>
<thead>
<tr>
<th>Evaporated point (%)</th>
<th>Gasoline 1</th>
<th>Gasoline 2</th>
<th>Kerosene</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP (°C)</td>
<td>–42</td>
<td>0</td>
<td>174</td>
<td>222</td>
</tr>
<tr>
<td>50% (°C)</td>
<td>98</td>
<td>69</td>
<td>208</td>
<td>302</td>
</tr>
<tr>
<td>FBP (°C)</td>
<td>156</td>
<td>126</td>
<td>255</td>
<td>359</td>
</tr>
</tbody>
</table>

* Obtained as indicated in ref. 25.
system for twenty minutes at a 30 μl min⁻¹ liquid flow rate. Mn was selected because, unlike silicon, it was easily quantified through external calibration with xylene solutions. Drain from the chamber was recovered into a vessel. Once the experiments were completed, the chamber was washed again with xylene and the solution was added to the same reservoir as the drains. Then the total solution mass was made up to 10 g with xylene. Analyte concentration was determined through ICP-AES. Wtot was finally calculated by subtracting the mass recovered into the vessel to the total aspirated analyte mass. The analyte transport efficiency in turn was obtained by dividing Wtot by the total mass of analyte aspirated. The precision of the method was verified to be good the relative standard deviation being always lower than 3%.

An Optima 4300 DV Perkin-Elmer ICP-AES spectrometer (Uberlingen, Germany) was used and the emission signals were axially taken. Usually, in the petroleum analysis laboratories, the data are radially taken. In the present work the axial configuration was preferred because it offered an enhanced sensitivity. The system was equipped with a 40.68 MHz free-running generator and a polychromator with an echelle grating. Segmented-array Charge-coupled Device (SCD) detectors allowed for the simultaneous measurement of several lines in the UV and visible electromagnetic spectrum zones. Table 3 summarizes the instrumental conditions employed.

### Results and discussion

#### Effect of the dilution factor on primary and tertiary aerosol characteristics
In general terms, it can be stated that the dilution had little effect on the aerosol characteristics. By considering a given gasoline
sample, it was found that the median of the volume drop size distribution, i.e., $D_{50}$, for primary aerosols were slightly higher for the 1 : 50 (gasoline : xylene) dilution than for the 1 : 2 one. This fact may be attributed to the slightly higher surface tension and viscosity values when moving to higher dilutions (Table 2). Thus, for the gasoline 2 and a PFA pneumatic concentric micronebulizer, $D_{50}$ of primary aerosols were 10.5 μm and 11.9 for the 1 : 2 and 1 : 50 dilutions, respectively. In the case of the diesel and kerosene samples, similar trends were found (i.e., the higher the dilution factor, the higher the $D_{50}$ value). For the diesel sample, the increase in $D_{50}$ of primary aerosols as the dilution factor raised from 1 : 2 to 1 : 50 was remarkable (9.6 to 12.1 μm). For this sample, it was found that the higher the dilution factor, the lower the viscosity and the higher the evaporated mass fraction. As regards surface tension and density, no significant differences were encountered among diesel samples. The fact that finer aerosols were measured at low rather than at high dilution factors could be explained by considering that for the 1 : 50 solution aerosol finest droplets evaporated almost completely.

The trends found in the case of tertiary aerosols with dilution factor were similar to those described for primary aerosols irrespective of the chamber used. For example, for the diesel sample and TSIS, $D_{50}$ were 1.8 and 2.9 μm for the 1 : 2 and 1 : 50 dilutions, respectively. If the data for the cyclonic spray chamber were taken into consideration the corresponding $D_{50}$ values were 3.0 and 3.7 μm. These data were accounted for by considering that the higher the dilution factor the higher the solution volatility and, hence the finest droplets evaporated.

**Influence of the sample nature on the aerosol characteristics**

Fig. 1 summarizes the $D_{50}$ for the aerosols leaving the cyclonic spray chamber, the TSIS (i.e., tertiary aerosols) and those generated by the PFA micronebulizer and the d-DIHEN (i.e., primary aerosols). The four samples tested are considered. The 1 : 2 diesel samples led to the coarsest primary aerosols, with the highest $D_{50}$ values, both for the PFA and the d-DIHEN because this solution had the highest values of the surface tension and/or viscosity among the samples tested (Table 2). The kerosene solution, in turn, provided aerosols with $D_{50}$ values quite similar to those encountered for the two gasoline samples. This was observed in spite of the fact that surface tension and viscosities were higher for the former sample. The reason that could be argued in this case was related to the solution volatility. Table 2 shows that gasoline samples evaporated faster than kerosene ones. Therefore, once the aerosol was generated, the finest droplets could evaporate before the measurement area and, hence the aerosol mean diameter increased. The trends found for aerosols leaving the spray chambers were more complex. Thus, it was found that for the two chambers used, finer aerosols were found for the diesel and kerosene samples than for the remaining ones. An additional factor that helped to explain these results was that solution density was higher for the diesel and kerosene than for the gasoline samples (Table 2). Therefore, the loss of coarse droplets through inertial impacts and gravitational settling was favored for these two solutions. The analyte transport data confirmed this expectation. Thus for 1 : 2 dilutions of the four samples and the TSIS the analyte transport efficiencies were 50 and 68% for the diesel and kerosene solutions, respectively, whereas this parameter took values of 83 and 72% for gasoline 1 and 2, respectively. As these data also suggested, there was a direct relationship between analyte transport efficiency and solution volatility (Table 2).

**Effect of the sample dilution factor on silicon sensitivity**

The sample dilution factor is a very important variable that affects the sensitivity as well as the extent of the matrix effects. For each one of the four dilutions, spiked as well as non spiked solutions were prepared. The silicon concentration was identical for all the dilutions (i.e., 1 mg l$^{-1}$ Si). Non-spiked solutions were used as a blank. First of all it was verified that the optimum nebulizer gas flow rate in terms of silicon sensitivity remained unchanged irrespectively of the sample introduced. This was likely due to the so low liquid flow rate used what mitigated the impact of the solvent on the plasma fundamental conditions.

In order to evaluate the dilution effects a relative parameter was calculated: the *intensity ratio*. This factor was defined according to the following equation:

$$
\text{intensity ratio} = \frac{I_{\text{Si}}^{\text{dilution}^{-1}}}{I_{\text{Si}}^{\text{dilution}^{-1} \cdot 1:50}}
$$

(2)
where $I_{\text{silicon}}^{\text{dilution}}$ was the net emission intensity obtained for each one of the samples and $I_{\text{silicon}}^{\text{dilution:50}}$ was the corresponding signal found for the 1 : 50 dilution that was taken as reference. Note that in absence of dilution effects, the intensity ratio should take values close to the unity. The obtained data are included in Fig. 2 through Fig. 5.

Data for the most volatile gasoline (gasoline 1) are shown in Fig. 2. For this sample, the higher the dilution factor, the lower the measured silicon emission intensity. As it has been previously indicated, a decrease in the gasoline concentration due to dilution led to coarser primary aerosols. As a result, the mass of silicon reaching the plasma decreased thus degrading the sensitivity. Note that, for example, for the TISIS, the analyte transport efficiencies under the conditions used for Fig. 2 were 83 and 41% for 1 : 2 and 1 : 50 gasoline 1 solutions, respectively. Fig. 2 also shows that for gasoline 1 the design of the sample introduction system had little effect on the intensity ratio. In contrast, although the dilution factor effect was similar to that for gasoline 1, for the least volatile gasoline, gasoline 2 (Fig. 3) the TISIS was less sensitive to the dilution factor than the cyclonic spray chamber (the intensity ratio values were closer to 1 for the former, see compounds A and D). Likewise, the d-DIHEN mitigated dilution effects caused by a change in the xylene (or gasoline) concentration. The behaviour found for R was interesting, because both TISIS and the cyclonic spray chamber provided similar intensity ratio values. Therefore, for volatile solutions and volatile silicon compounds such as R, it appeared that the sample introduction system was not as critical as for less volatile solutions. Apparently this was due to an intensification of the solution transport caused by the sample evaporation inside the chamber.

Results were also evaluated for a kerosene sample (Fig. 4). Irrespective of the silicon compound, the cyclonic spray chamber was the most sensitive system to changes in the dilution because it showed the highest deviation from unity in the intensity ratios. The other two sample introduction systems showed lower differences in this relative parameter. As for the kerosene sample, the argon signal did not change with the dilution factor, the drop in silicon sensitivity with increasing this variable was attributed to a decrease in the total mass of silicon transported towards the plasma (69 and 35% for the 1 : 2 and 1 : 50 dilutions, respectively).

Finally, a diesel sample was similarly studied. It is interesting to note that the dilution effect was opposite to those previously observed for gasolines and kerosene, i.e. an increase in the intensity ration when diluting the sample (Fig. 5). However, for the diesel samples and the TISIS an increase in the dilution factor from 1 : 2 to 1 : 50 gave rise to a drop in analyte transport efficiency (i.e., from 50 to 34%). The measurement of the argon signal revealed a 6% drop by the argon emission intensity that could account for the drop in sensitivity as the dilution factor decreased. As regards the sample introduction system, it was...
observed that the smallest influence was obtained with the TISIS, which looks promising in the case of diesel analysis. Usually, dilutions higher than 1 : 10 are recommended in the different official methods for analyzing petroleum products. This fact is detrimental from the point of view of sensitivity. Summarizing the data obtained for the different products, it can be indicated that for TISIS, 1 : 10 is a very good choice because interferences are virtually eliminated in all the cases. For lower dilution factors (i.e., 1 : 5), the matrix induces changes in silicon intensity ratios ranging from 10 to 30% as compared to the 1 : 50 dilution.

**Effect of the sample nature on the emission signal**

Fig. 6 plots the silicon emission intensity found for the 1 : 50 dilutions of the four samples. The signals were normalized with respect to those encountered for gasoline 1 (i.e., that providing the highest sensitivity) so as to give an idea about the relative matrix effect. In the case of the cyclonic spray chamber (Fig. 6a) it was found that, even with a so high dilution, the two gasoline samples provided higher sensitivities than the diesel and kerosene samples. This was in concordance with the different initial boiling points (Table 1) as well as % of evaporated sample mass (Table 2 and Fig. 6). Similar results were found for the TISIS (Fig. 6b), although the influence of the matrix was less marked. Thus, for example, in the case of the diesel sample, the signal was 30 and 10% lower than that for the gasoline 1 for the Cyclonic and TISIS, respectively. The d-DIHEN was used because in this case the aerosol transport phenomena were minimized. The trends summarized in Fig. 6c were surprising, because it was found that for the kerosene and diesel samples, the d-DIHEN was the most sensitive device to changes in the sample matrix. The lower Ar emission intensity as compared to that measured for the remaining sample introduction systems could partially explain these results.

Data for silicon standards prepared in xylene are also included in Fig. 6. It can be observed that, for TISIS, the emission intensity encountered was similar to that found for the remaining solutions, thus confirming that this system was less sensitive to changes in the matrix composition than both the cyclonic spray chamber and the d-DIHEN.

When the sample concentration was increased (i.e., 1 : 2 dilutions), the signal variations versus the sample nature were intensified. In this case (Fig. 7) the drop in silicon sensitivity caused by the presence of kerosene and diesel was more pronounced than for the 1 : 50 dilutions. This is expected from the data of drop size distributions and volatilities. For these so concentrated solutions, the design of the liquid sample introduction system was also important, although none of the evaluated setups eliminated the matrix effect.

Fig. 6 and 7 also show the normalized argon net emission intensity as well as the percentage of evaporated sample mass. By considering the data obtained for the 1 : 50 dilutions (Fig. 6) it was observed that the argon signal did not change as a function of the matrix nature neither for the cyclonic spray chamber nor for the TISIS. In contrast, for the 1 : 2 dilutions (Fig. 7a and b) the argon signal was lower for the two gasoline samples (i.e., the most volatile ones) than for the kerosene and diesel ones (i.e., least volatile samples). Note that, silicon emission intensity for gasoline samples was higher than for diesel and kerosene solutions. Therefore, the behaviour found for silicon signal was not due to a change in the plasma thermal characteristics. In fact it was concluded that the changes in silicon signal as a function of the matrix were mainly due to a modification in the mass of solution transported towards the plasma. Globally speaking (Fig. 6 and Fig. 7), it can be indicated that there was a direct relationship between sensitivity and evaporated mass fraction because the most volatile samples (i.e., gasolines) yielded the highest silicon sensitivities.

**Effect of the silicon chemical form on the emission intensity**

In previous studies it was shown that for xylene solutions the sensitivity found in ICP-AES was dependent upon the silicon chemical form. In the case of xylene without petroleum products, these results were explained in terms of preferential silicon evaporation. In the present work, the three different silicon compounds (A, D and R) were added to the four different
petroleum products to test whether these products modified the extent of the effect. The so-called relative intensity was calculated as:

\[ I_{ri} = \frac{I_i}{I_D} \]  

(3)

Where \( I_i \) was the silicon emission intensity obtained for a given compound “i” and \( I_D \) was the signal for the compound D that was taken as a reference. The effect of the chemical form became more pronounced as the \( I_{ri} \) value deviated from 1. The \( I_{ri} \) precision (RSD) was close to 3% (10 replicates).

The dilution 1 : 2 was selected because as was shown before, it resulted in the strongest matrix effects. Fig. 8 summarizes the \( I_{ri} \) values for the three sample introduction systems and the four products under study. Fig. 8 also contains the data for a xylene standard. For the cyclonic spray chamber it was observed that, as for xylene matrices, \(^3\) sensitivity was enhanced for compound A when compared to compound D (i.e., \( I_{ri} \) values higher than unity). More interestingly, \( I_{ri} \) depended on the petroleum product, as it was much higher for the diesel-based sample than for the remaining ones. Relative intensities were also dependent on the sample nature. This dependence was more significant in the case of compound R. However, unlike for compound A, there was no significant difference between diesel and kerosene.

When considering the TISIS and d-DIHEN, it was found that, although sensitivity for compound R was still significantly enhanced with the TISIS system, results were less sensitive to the nature of the petroleum product than in the case of cyclonic spray chamber (Fig. 8).

**Conclusions**

Determination of silicon in petroleum products is particularly challenging as the analytical response depends not only upon its chemical form but also upon the nature of the petroleum products and the design of the sample introduction system. Based on the products used in this work, it has been demonstrated that the use of a conventional cyclonic spray chamber at room temperature led to a stronger influence on Si sensitivity with the gasoline having the lowest volatility (gasoline 2) and kerosene than the other two products. In contrast, the nature of the petroleum product had a lower effect when using the TISIS sample introduction system. The results for the d-DIHEN were slightly worse than those for TISIS. When conventional spray chambers are used, there is apparently an undefined interaction between silicon and matrix during the aerosol transport towards the plasma. A possible explanation can be related to the competition established between the matrix and the silicon evaporation. These problems are significantly minimized when near-total sample consumptions systems are used, particularly with a high dilution factor. However, dilution is to the detriment of sensitivity. The obtained results suggest that dilutions lower than 1 : 10 can be used thus mitigating the loss in sensitivity found for higher dilution factors (c.a., 1 : 50).
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