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## 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

Raquel Sánchez, José Luis Todolí, Charles-Philippe Lienemann and Jean-Michel Mermet

*J. Anal. At. Spectrom.*, 2010, 25, 178-185

DOI: 10.1039/B918692A, Paper

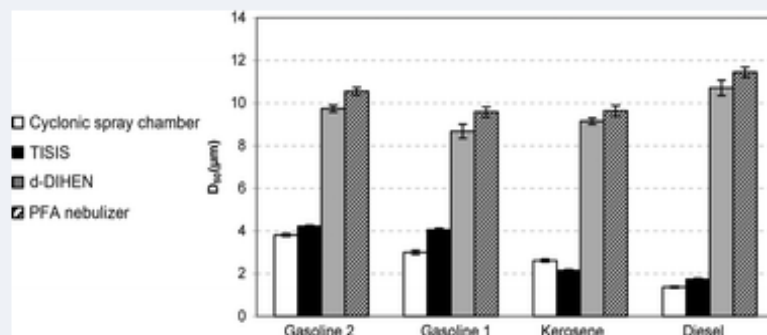


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The effects of the solvent dilution factor on the physical properties of the resulting organic solutions, the aerosol characteristics and the silicon sensitivity were studied in ICP-AES for four different petroleum products by using near total sample consumption systems.



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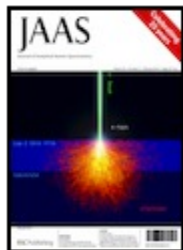
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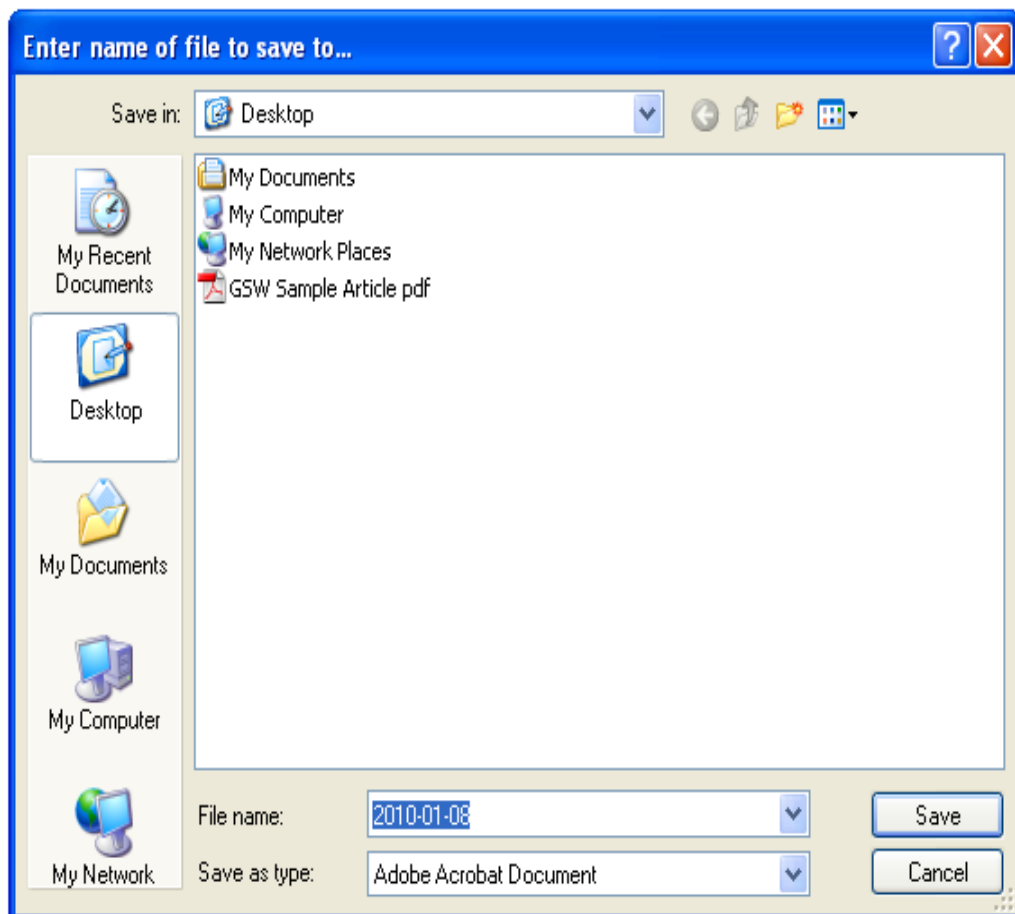
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## Abstract

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## 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

Raquel Sánchez,<sup>a</sup> José Luis Todolí,<sup>a\*</sup> Charles-Philippe Liénemans<sup>b</sup> and Jean-Michel Memet<sup>c</sup>

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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 micro-nebulizer and a demountable Direct Injection High Efficiency Nebulizer (d-DIHEN). A cyclonic spray chamber also associated with a micro-nebulizer 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 the 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 solution 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 unkind of interaction between the analyte and the organic solution during the aerosol transport step. However, both the single pass spray chamber and the d-DIHEN mitigate 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.<sup>1,2</sup> 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.<sup>3,4</sup> 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 give 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  $\mu\text{g ml}^{-1}$  or  $\text{sub-}\mu\text{g ml}^{-1}$  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 low Si sensitivity.

For organic solutions, it has been reported that the properties of a given solvent strongly modify the aerosol generation and transport processes.<sup>5</sup> 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.<sup>6</sup> For other nebulizers, such as the ultrasonic ones, aromatic compounds affect more severely the analytical signal than aliphatic solvents.<sup>6</sup> 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)<sup>7</sup> has been considered to be virtually impossible to carry out quantitative analysis of this kind of samples through ICP techniques. Nonetheless there have been

<sup>a</sup>Department of Analytical Chemistry, Nutrition and Food Sciences, P.O. Box 99, 0500 Alcala, Spain

<sup>b</sup>IFP-Lyon IFP Association Energy Resources, Molecular Characterization Department, Physics and Analysis Division, BP 1, F-69003 Solenn, France

<sup>c</sup>Spectroscopy Force, 0130 Trévoux, France

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