Original Paper

Comparison Between Two Sample Emulsification Procedures for the Determination of Mo, Cr, V and Ti in Diesel and Fuel Oil by ICP OES Along with Factorial Design

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Abstract. Inductively coupled plasma optical emission spectrometry (ICP OES) was used to determine Mo, Cr, V and Ti, in diesel and in used fuel oil. Samples were introduced into the ICP as emulsions to reduce interferences and allow the use of inorganic standards for quantification. A comparative study between one Triton X-100 emulsion and one detergentless emulsion was made. A 2^3 factorial design was applied to elucidate and establish the relationship between three experimental variables: presence of HNO_3, amount of diesel or fuel oil (between 5 and 25%) and the presence of O_2 into the Ar plasma gas flow rate. Results indicated that best performance were achieved using 10% sample (w/w) together with concentrated HNO_3 (0.5 mL) and using O_2 as auxiliary gas (0.047 L min^-1). The use of O_2 minimized both carbon deposits at the injector tip and plasma background. The addition of HNO_3 resulted in good correlation between inorganic standards used for calibration, and metallo-organic standards used for sample enrichment. Analyte enriched diesel and SRM 1634b were analyzed using the optimized conditions. Recoveries from 90.1 to 106.5% were achieved, with better results for detergent emulsions which enabled limits of detection at the ng g^{-1} range for Mo, Cr, V and Ti and at smaller background.

Key words: Diesel; emulsions; refractory elements; ICP OES; factorial design.

Metallic species may act as catalyst of oxidative reactions that affect the performance of petroleum based fuels (diesel, gasoline and kerosene) [1]. For instance, the refractory element vanadium, which is one of the most significant trace element in petroleum, may cause failure in internal combustion engines and produce deleterious effects in metal surfaces and coatings present in boilers employed in petroleum processing and in fuel oil propelled engines [2, 3]. In some cases, metallo-organic compounds are used in small quantities as additives in petroleum fractions. For example, naphtenates and alkilarilsulphonates of chromium and molybdenum are added in fuels to improve their combustion efficiency. These added quantities must be carefully controlled to guarantee best performance [2].

From the environmental point of view, the burning of fuels may cause significant pollution and human health problems. Therefore, the quantification of trace...
elements in fuels is useful to evaluate their potential as a pollutant [4, 5].

Electrothermal atomic absorption spectrometry (ETAAS) is an extensively used technique for trace metal determination in fuels since it combines high detection power and tolerance to samples with a high organic load [1, 2, 6]. However, in the case of the refractory elements, ETAAS is less suitable technique since these elements tend to form high melting point carbides and oxides which lead to small atomization efficiencies and consequently low sensitivities [7]. ICP OES can be used with a clear advantage over other spectrometric techniques for the determination of refractory metals because of the efficient analyte ionization and excitation achieved in the ICP. ICP OES has also multielement capability and wider linear dynamic ranges (4 to 6 orders of magnitude depending on the element). Other techniques such as flame atomic absorption spectrometry [8] and X-ray fluorescence spectrometry [9, 10], in many cases, does not enable adequate sensitivity. Inductively coupled plasma mass spectrometry (ICP-MS) [4, 11, 12] has also been used, however, this technique has a more complex instrumentation and are prone to problems related with the introduction of samples containing relatively high organic load. This latter limitation has been minimized with the use of alternative sample introduction systems such as electrothermal vaporization (ETV) [11, 13].

Spectroanalytical techniques usually require sample treatment in order to achieve compatibility between sample introduction systems and atomizers. For choosing the best sample preparation procedure, cost, preparation time, procedure complexity, potential for sample contamination and dilution factor must be considered. In the case of ICP OES, sample treatment must ensure reduction of sample organic load to be introduced into the plasma since it affects sensitivity and the correlation between signals from samples and standards.

The use of solutions is still the simpler and therefore the most commonly applied approach for ICP OES. The traditional way to introduce oil samples into the ICP is dissolving them directly in organic solvents (kerosene, MIBK, xylene, toluene etc) [5, 14, 15]. Such procedure reinforces problems associated with the high organic load (destabilization of the plasma, decreasing the energy available for analyte ionization/excitation and increasing background emission) and imposes the use of expensive and unstable analyte metallo-organic standards for calibration [1, 16]. Oil sample acid dissolution is also applied and enables the use of aqueous standards for calibration. However, this procedure is time consuming, and therefore has low throughput procedure [4].

Emulsions and microemulsions are being successfully applied for oil samples due to the homogeneously dispersion and stabilization of oil micro droplets in the aqueous phase which reduces oil viscosity and organic load of the system. For ETAAS, it has been demonstrated that the use of emulsions of fuels (gasoline and kerosene) acidified with HNO₃ enabled direct correlation between the signal of the analyte in the samples and the signal of analyte aqueous inorganic standards. This approach allowed the use of the analytical curve prepared with inorganic standards for the calibration procedure with the application range from 2 to a few hundreds of µg L⁻¹ of Sb, As and Se [6]. The introduction of oil samples as emulsions has been used for the analysis of fuel oil samples using ICP OES [3] and ICP-MS [17]. Surprisingly, for calibration purposes, metallo-organic standards have been systematically used in these methods. One exception is the work of Murillo and Chirinos who determined sulfur, vanadium and nickel in residual fuel oil using inorganic standards [18].

In this work, an ICP OES method for the determination of four refractory metals (Mo, Cr, V and Ti) in diesel and fuel oil has been developed. Two sample emulsification procedures (detergent emulsions using Triton X-100 and detergentless emulsion stabilized with propan-1-ol) were tested and compared to the direct sample introduction procedure. The optimization of the emulsification procedure and other experimental and instrumental parameters allowed the use of inorganic aqueous standards for calibration. The statistical method of 2³ factorial design was utilized in order to identify the influence of three parameters that may affect the introduction of emulsified samples into plasma and, therefore, the overall analysis results. The method was tested using diesel samples enriched with a metallo-organic analyte standard and a fuel certified reference material (SRM 1634b).

**Experimental**

*Instrumentation*

The inductively coupled plasma optical emission spectrometer employed for this study was a Perkin Elmer model Plasma P1000 (Perkin-Elmer, Norwalk, CT, USA) equipped with an Ebert type