



Multivariate optimization of dual-bed solid phase extraction for preconcentration of Ag, Al, As and Cr in gasoline prior to inductively coupled plasma optical emission spectrometric determination



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HIGHLIGHTS

- Preconcentration of trace metals in gasoline using dual bed SPE system.
- The experimental conditions of the method was optimized using factorial design.
- The method had relatively high enrichment factor with low LOD and LOQ.
- The column can be reused up to 200 cycles without loss of sorption performance.
- Method was applied for analysis of real gasoline samples.

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ABSTRACT

In this work, a dual-bed resin solid phase extraction (SPE) for preconcentration of Ag, Al, As and Cr prior to their inductively coupled plasma-optical emission spectroscopy (ICP-OES) determination has been developed. Dowex 50 W-x8 and Dowex 1-x8 packed in a column were used as metal ion sorbents. The optimization of the dual-bed SPE procedure was carried out using a two level full factorial design with three central points. Under optimized conditions, the limits of detection and quantification ($n = 21$) ranged from 0.16 to 0.22 and 0.52 to 0.76 $\mu\text{g L}^{-1}$, respectively. Enrichment factors of 100, 130, 130 and 150 and relative standard deviations ($n = 15$) of 1.2%, 2.0%, 1.8% and 1.3% were obtained in the determination of Ag, Al, As and Cr, respectively. The validity of the proposed method was checked by applying the standard addition method and the recoveries at the 20 $\mu\text{g L}^{-1}$ level using both inorganic and organic metal standards ranged from 95% to 99%. The proposed method presented an analytical throughput of about 18 samples per hour and was applied for the determination of metal ions in ten gasoline samples. In addition, the accuracy of the method was evaluated using microwave-assisted digestion method and the results were not significantly different (at 95% confidence level).

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1. Introduction

Controlling the levels of metals in petroleum products such as gasoline is a critical step in the petrochemical industry. This is because metal ions act as catalyst poisons thus cause deleterious effects on the refinery and processing operations unless they are added as additives [1,2]. Therefore, it is crucial to accurately determine metal content in liquid fuels which are also the main sources of energy for vehicles. Other effects of metal ions (even in trace concentrations) in liquid fuels are reported in the literature [1,3–5]. These include (i) poor fuel performance (ii) decrease in the

engine durability and efficiency and (iii) environmental pollution caused by the release of toxic metals into the atmosphere during fuel combustion [1,3–5]. Therefore, the development of sensitive and selective analytical techniques for the determination of metals in gasoline is one of the most important aspects of quality control in petroleum industries [1]. These techniques must be fast, simple, precise, accurate and economical to be easily employed in routine procedures. In addition, since metal ions in liquid fuel samples are usually present in trace levels, the analytical methods must be capable of resulting in high enrichment/pre-concentration factors enough to cope with the demands [1].

Analytical methods based on electrothermal atomic absorption spectrometry (ETAAS) are popular because they are associated with high sensitivity and tolerance to high organic matrix loads

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[2]. However, ETAAS is not common in routine analysis because of its low sample throughput as compared to inductively coupled plasma-based techniques [2]. Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely used in routine quantification of metal ions in different sample matrices [6–10]. This technique is attractive due to its multielement capability, relative sensitivity, wide linear range and high sample throughput. However, the direct introduction of fuels into the plasma requires special care, as the organic load may de-stabilize or extinguish the plasma [11–14].

Hitherto, different sample preparation approaches for determination of metal ions in fuels has been developed to overcome the problems associated with ICP-OES and are reported in the literature. These methods include conventional ashing and acid dissolution [14], microwave digestion [6,11,15], dilution with organic solvents [7], emulsion/microemulsion [9,10] and preconcentration using solid phase extraction [16,17]. However some of these sample preparation methods have some limitations, for instance conventional ashing and acid dissolution methods are time-consuming and also volatile elements may easily escape (be lost) [18]. Microwave digestion methods may be a good alternative to these methods and solve the problem of volatilization, but they increase the risks of explosion and cross-contamination. In addition, the use of concentrated acids could increase the blank values and cannot be supported by some analytical techniques such as ICP-OES [19]. Emulsion/microemulsion technique is one of the most promising approaches due to its short sample preparation time and the low risk of analyte losses by volatilization or sorption. However, its disadvantage is the low stability which then affects the sensitivity and reproducibility of the analytical instrumental signal [19]. Dilution with organic solvents is one of the simplest sample pretreatment procedures but does not reduce the problem of organic loading and plasma destabilization or extinction in case of the ICP techniques [13].

To overcome these difficulties associated with sample pretreatment methods, an accurate and reliable analytical procedure based on separation and preconcentration of analytes prior to analysis in fuel samples, is required. Preconcentration of the analytes from the organic matrices combines the advantages of separating the analyte from the complex fuel matrix, transferring it to an aqueous phase and enriching it at the same time [13]. Procedures based on solid phase extraction (SPE) for the separation and preconcentration of trace elements in gasoline and fuel kerosene are reported in the literature [16,17,20].

Recently, chemometric techniques have been used for optimization of different analytical methods. This is because, these techniques allow more than one variable to be optimized simultaneously [21]. The advantages of multivariate techniques include reduction in the number of required experiments, thus, lowering reagent consumption and significantly less laboratory work. They are faster to implement and more cost-effective than traditional univariate approaches [22,23]. In addition, chemometric methods are able to generate mathematical models that permit assessment of the relevance and statistical significance of factors being studied, and evaluation of interaction effects between them (factors) [21,22]. Full factorial design is one of the well-known statistical processes for multivariate optimization and is widely applied in analytical chemistry. This is due to its effectiveness in the identification of significant variables and the best conditions of an experimental procedure [21].

The aim of this work was to investigate the analytical performance and the potential applicability of a dual-bed resin column for preconcentration and determination of trace metals in gasoline via off-line SPE/ICP-MS system. The literature shows extensive focus on the methods for analysis of Cu, Zn, Ni, Pb, Cd, V, Mo and Fe, particularly in petroleum and its derivatives [9,12,15,16,20].

In the current study we focused on the selected elements due to their peculiar behavior. For instance, arsenic causes severe and irreversible catalyst poisoning, even at trace levels [24]. The rest of the elements mentioned above have been investigated in our previous studies [17,25,26]. Therefore, this study seek quantify the amount of Ag, Al, As and Cr in gasoline samples. A full two-level factorial design with a central point was used for optimization of experimental variables (pH, eluent concentration and sample flow rate) that affect the retention/desorption of metal ions. To the best of our knowledge, this is the first time that dual-bed resin column and the optimized preconcentration method are proposed for Ag, Al, As and Cr determination in gasoline. In addition, this study offers a simple system with no need of acid digestion prior to metal ion determination.

2. Experimental

2.1. Instrumentation

Metal ions (Ag, Al, As and Cr) were determined using a Spectro Arcos 165 ICP-OES (SPECTRO Analytical Instruments, GmbH, Germany) equipped with Cetac ASX-520 autosampler. The ICP-OES operating conditions are listed in Table 1. Sample introduction was achieved using a pneumatic cross-flow nebulizer mounted onto a Scott double-pass spray chamber. Sample solutions were pumped to the nebulizer using a built in four channel peristaltic pump. The most prominent atomic and ionic analytical spectral lines of the metal ions were selected for investigation, that is, Ag 329.068 nm, Al 167.078 nm, As 193.759 nm and Cr 283.563 nm. Solid phase extraction was carried out in a VacMaster-24 sample SPE station (Supelco, PA, USA). The latter was used to control the sample loading and elution flow rates. The microwave digestions were carried out in an Ethos D (Milestone, Sorisole, Italy) with maximum pressure 1450 psi and maximum temperature 300 °C.

2.2. Reagents, solutions and samples

All reagents were of analytical grade unless otherwise stated and Millipore water was used throughout the experiments. Absolute ethanol (99.9%) used to prepare model solutions and suprapur 30% hydrogen peroxide (H₂O₂) used for the acid digestion procedure were obtained from Merck, (Darmstadt, Germany). Spectrascan stock solutions (1000 mg L⁻¹) of Ag, Al, As and Cr (Teknolab, Norway) were used to prepare the working solutions for SPE at concentrations of 10 µg L⁻¹ for each analyte. Working solutions, as per the experimental requirements, were freshly prepared from the stock solution for each experimental run. A Spectrascan multi-element 100 mg L⁻¹ standard solution (Teknolab, Norway) was used to prepare working standard solutions at concentrations of 0–120 µg L⁻¹ for measurements of concentrations of analytes in all model and sample solutions. The cation exchangers used in this study as packing materials, that is, Dowex 1-x8 (Chloride form) and Dowex 50 W-x8 (sodium form) as well as solutions of nitric acid at concentration range of 1.0–4.0 mol L⁻¹ used for the elution of the analytes from the columns, were prepared from ultrapure concentrated acid (65%), were purchased from Sigma Aldrich (St. Louis,

Table 1
The operating parameters of determination of elements by ICP-OES.

RF power	1400 W
Plasma argon flow rate	13 L min ⁻¹
Auxiliary argon flow rate	2.00 L min ⁻¹
Nebulizer argon flow rate	0.95 L min ⁻¹
Sample aspiration rate	2.0 mL min ⁻¹
Replicate measurements (n)	3

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