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Alumina-titania (Al_2O_3-TiO_2) hollow fiber sorptive microextraction coupled to inductively coupled plasma mass spectrometry for determination of trace elements in diesel and gasoline samples

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Abstract

An alumina-titania (Al_2O_3-TiO_2) hollow fiber membrane was synthesized using the template method coupled with a sol–gel process. The crystal forms of the mixed oxides hollow fiber was evaluated using X-ray diffraction (XRD). The morphological structure and surface characteristics of the Al_2O_3-TiO_2 hollow fiber was characterized by scanning electron microscope (SEM) and nitrogen adsorption/desorption BET technique. The synthesized Al_2O_3-TiO_2 hollow fiber membrane was combined with inductively coupled plasma mass spectrometry for on-line preconcentration and determination of trace amounts of Co, Cr, Mo, Ni, Sb and V in diesel and gasoline samples. The optimization of the experimental parameters affecting the preconcentration and determination of target analytes was performed using a full 2^4 factorial and central composite designs. Under optimized conditions, limits of detection (LOD) (based on the original sample) and limits of quantification (LOQ) ranged 0.1-0.9 and 0.3-3.0 ng L^{-1}, respectively. The developed method was applied in the determination of trace elements in real diesel and gasoline samples.

Keywords: Alumina-titania hollow fiber; trace elements; sorptive microextraction, diesel; gasoline; inductively coupled plasma mass spectrometry

1. Introduction

The occurrence of metal ions in petroleum fractions such as diesel and gasoline is of substantial importance because of its effects on the use and performance characteristics of the

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desired products.[1] For instance, elements like copper, antimony, nickel and vanadium are known to catalyse oxidative reactions, degrading the thermal stability of the petroleum fractions and only low concentrations of such metals can be tolerated especially in diesel. [1,2] Therefore, accurate determination of trace metal ions in diesel and gasoline is a very important step in the industrial production processes to assure their subsequent use. In addition, their quantification helps in atmospheric pollution monitoring. For these reasons, different procedures have been developed for the elemental analysis of diesel and gasoline. These methods involve various sample pretreatments such as alcohol dilution[3], microemulsion[4] and microwave-assisted digestion[5], among others. Techniques employing preconcentration procedures to extract metal ions in fuel samples prior to their determination are also reported in the literature.[6-8] The benefit of using preconcentration techniques is that they combine the advantages of separating the analyte from the complex matrix, by transferring it to an aqueous phase and preconcentrating it at the same time.[9]

Recently, hollow fiber sorptive microextraction (HFSME) based on nanometer sized metal oxides has been reported as an attractive technique for preconcentration of metal ions in various sample matrices such as human serum and environmental water samples.[10,11] This technique integrates sampling, extraction and preconcentration into a single step.[10,11] Furthermore, it inherits the advantages of both the solid phase microextraction (SPME) and membrane separation.[10] Due to aforementioned advantages, HFSME can be used to separate trace elements from complex matrix samples without using special equipment.[10] The principle of HFSME is based on the retention of the analytes in the membrane. For this reason, the performance of the membrane is one of the key aspects that determine the sensitivity and the selectivity of the analytical method.[10,12] Most of the HFSME procedures employ a single metal oxide membrane such as titania,[13] alumina[11] and zirconia,[14] among others. Nanometer sized metal oxides gained special attention in preconcentration studies due to their excellent properties such as high specific surface area, high mechanical stability and low swelling capacity in different solvents.[15] Due to the high surface area of these nanomaterials, they can strongly adsorb many substances such as trace metals.[16]

In recent years, researches have reported that binary or ternary metal mixed oxides exhibit superior properties as compared to single metal oxides.[15] The properties of nanometer sized mixed oxides membranes or powders include increased adsorbent reusability, stability and adsorption capacity for metal ions in a wide pH range. In addition, these mixed oxides nanomaterials possess strong chemical activity as a result of the excess Lewis and Brønsted acid/base binding sites that permit high retention/adsorption of cationic and anionic metal species.[15]

Therefore, the objective of this study was to synthesize and characterize the binary hollow fiber membrane based on alumina/titania nanocomposite using the template method coupled with a sol–gel process. The performance of the resulting hollow fiber membrane was evaluated for preconcetration of Co, Cr, Mo, Ni, Sb and V ions liquid fuel samples. The membrane solid phase microextraction was coupled to inductively coupled plasma mass spectrometry (ICP-MS). The optimization of the experimental parameters associated with extraction and preconcentration of trace metal ions was performed by factorial and central composite designs.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Sciex ELAN 6000 (Perkin-Elmer SCIEX Instruments, Concord, Canada) inductively coupled plasma mass spectrometer was used for all measurements. Argon of 99.996% purity (Afrox, South Africa) was used. The operating conditions are presented in Table 1. The Accurel S6/2 polypropylene hollow fiber membrane used here was obtained from Membrana (Wuppertal, Germany). The wall thickness of the fiber was 450 µm, the inner diameter was 1800 µm, and the pore size was 0.2 µm. An on-line preconcentration system was performed using MinipulsTM 3 peristaltic pump (Gilson, Villiers le Bel, France). Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. A self-made PTFE micro-column (5.0 cm; 2.85 mm i.d), packed with Al_2O_3-TiO_2 hollow fiber membrane was used in the manifold for extraction and preconcentration of metals. Solvent Flex and PVC peristaltic pump tubing (Black/Black 0.76 mm i.d) were employed to propel the sample/ buffer and eluent, respectively. Minimum lengths of PTFE tubing was used for all connections.

Table 1 Operational ICP-MS parameters

RF power	1100
Gas flow rates	
Outer	15 L min^{-1}
Intermediate	1.2 L min^{-1}
Carrier	0.95 L min^{-1}
Resolution	0.7 a.m.u. (10% of the peak height)
Sweeps per reading	1
Dwell time	25 ms
Readings per replicate	100
Replicates	3
Auto lens	On
Isotopes	^{59}Co, ^{52}Cr, ^{95}Mo, ^{60}Ni, ^{121}Sb, ^{51}V ^{45}Sc (IS[a]), ^{103}Rh (IS), ^{209}Bi (IS)

[a] IS = Internal standard

Morphological structure of the Al_2O_3, TiO_2 and Al_2O_3/TiO_2 were observed using scanning electron microscope (SEM) (VEGAS-TESCAN, USA) after carbon coating and the diameter of the mixed metal oxide was measured by image processing software. The specific surface area value was determined from adsorption isotherms by the Brunauer, Emmett and Teller (BET) multipoint method using Surface Area and Porosity Analyzer (ASAP2020 V3. 00H, Micromeritics Instrument Corporation, Norcross, USA). All the gases used for analysis were of instrument grade. X-ray powder diffraction (XRD) measurements were carried out with a Philips X-ray generator model PW 3710/31 a diffractometer with automatic sample changer model PW 1775 (scintillation counter, Cu-target tube and Ni-filter at 40 kV and 30 mA).

2.2. Reagents and solutions

All reagents were of analytical grade unless otherwise stated and double distilled deionized water prepared by Millipore-Q-plus purification system (Bedford, USA) was used throughout the experiments. Aluminum isopropoxide, titanium butoxide, isooctane, n-heptane ammonia and ultrapure concentrated nitric acid (65%) were obtained from Sigma-Aldrich (St. Loius, MO, USA). Spectrascan multi element standard solution was purchased from Industrial Analytical (Pty) Ltd (South Africa) and glacial acetic acid was obtained from Merck (South Africa). Conostan custom made multi-element oil standard used in the experiment studies was obtained from SCP Science (Quebec, Canada). Aluminum isopropoxide and tetrabutyl titanate were used as a precursor for the preparation on alumina/titania. Synthetic gasoline was prepared by mixing appropriate amount of isooctane and n-heptane (Sigma-Aldrich, St. Loius, MO, USA), such that the final mixture contained 91% and 9% of isooctane and n-heptane, respectively. A multi-element standard solution (100 mg L^{-1}) was used to prepare working standard solutions for calibration of the ICP-MS instrument. Ultrapure concentrated nitric acid was used to prepare solutions of acid at different concentrations (used for the elution of the analytes from the hollow fiber membrane). The pH adjustments were performed with glacial acetic acid and ammonia solutions (Sigma-Aldrich)

2.3. Synthesis of alumina/titania sol

The synthesis of alumina/titania sol was prepared according to Jung *et al*.[17] To describe the procedure briefly, proper amounts (1:0.25 molar ratio) of aluminum isopropoxide and titanium butoxide were dissolved in ethanol, and the solution was then diluted with double distilled deionized water. The pH of the resulting solution was adjusted to 2 using 1.0 mol L^{-1} nitric and then it was stirred at 75°C for 24 h. It should be noted that alumina exhibits higher surface area as compared to titania. For this reason, higher aluminum isopropoxide content was chosen. Synthesis of pure nanometer-sized titania and alumina powders was according to Li *et al.*[14] and Rogojan *et al*.[18].

2.4. Preparation of alumina/titania *hollow fiber*

The preparation of Al_2O_3/TiO_2 hollow was carried out according to the methods reported by Cui *et al*.[11] and Huang and Hu.[10] Briefly, polypropylene hollow fibers were cut into equal segments (5 cm), ultrasonicated in acetone for 15 min and then removed and dried in air. For coating, the dried polypropylene hollow fibers were entirely immersed in the alumina-titania sol for 2 h, followed by a drying procedure with careful temperature control at 80°C for 1 h. The above immersion and drying processes were repeated several times until the dense alumina/titania submicron particles aggregates on the polypropylene hollow fiber templates. The coated hollow fibers were heated from room temperature to 1000°C at 2°C min^{-1} and maintained for 3 h to remove the polypropylene template and crystallize the alumina-titania hollow fiber membrane.

2.5. Preparation of the micro-column

About 5 cm of alumina/titania hollow fiber was fitted into PTFE tubing (2.85 mm i.d.) plugged with PTFE hard tubing (0.76 mm i.d.) at both ends. Before use, the column was washed by sequentially passing through it 1.0 mol L^{-1} HNO_3 and double distilled deionized water. This step was carried out to remove any possible impurities that might be adsorbed on the surface of the hollow fiber. The micro-column was then conditioned with 1.0 mol L^{-1} ammonium acetate buffer solution (pH 9).

2.6 Sample preparation and online preconcentration

The procedure for the preparation of gasoline–ethanol–water mixture was carried out according to Ozcan and Akman.[19] The model solutions were made up of synthetic gasoline (prepared as described in Section 2.2). The mixture was spiked with 1.0 mL of a 1.0 mg L^{-1} Conostan multi-element oil standard and made up to the mark with ethanol to obtain 10 µg L^{-1} concentration of each metal ion. The mixture was homogenized by shaking vortex. The samples were adjusted to appropriate pH with dilute acetic acid or ammonium hydroxide. On-line preconcentration step was carried out according to Cui et al.[11]

2.7. Multivariate optimization of an on-line HFSME preconcentration system

The optimization of the preconcentration system was carried out using a 2^4 full factorial and central composite design. Four variables i.e. sample pH, eluent concentration (EC), eluent flow rate (EFR) and loading flow rate (LFR) were regarded as important factors. Maximum, central point and minimum levels in Table 2 for each factor were chosen according to the data from previous experiments. All the experiments were carried out in random order. The experimental data was processed by using the STATISTICA 12.1 software program.

Table 2 Factors and levels used in 2^4 factorial design for separation and preconcentration of metal ions in fuel samples

Variable	Low level (-1)	Central point (0)	High level (+1)
pH	5	8	11
EC (mol L^{-1})	1.5	2.75	4
EFR(mL/min)	10	25	40
LFR (mL/min)	5	10	15

3. Results and discussion

3.1. Characterization of alumina/titania *hollow fiber*

The prepared alumina/titania hollow fiber was characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and low-temperature nitrogen adsorption/desorption measurements.

3.1.1 X-ray diffraction analysis

X-ray diffraction patterns (for 2θ diffraction angles from 10° to 80°) of the nanometer-sized alumina, titania and alumina/titania hollow fiber calcined at 1000°C for 3 hours are presented in Fig. 1. The XRD patterns showed well-crystallized structures when the calcinations metal oxides and mixed metal oxide hollow fiber were at 1000°C. The XRD patterns for pure alumina and titania powders were used as reference materials. It can be seen from Fig. 1C that the peaks for titania and alumina were not overlapping. This shows that the mixed oxides were not simply mixed phases of pure titania and alumina, but solid solutions with a single phase.[17]

3.1.2 Pore structure parameters

The pore structure of the alumina/titania hollow fiber and the polypropylene hollow fiber were investigated by nitrogen adsorption/desorption experiments. The surface area for alumina-titania nanocomposite hollow fiber membrane and the polypropylene hollow fiber were 135 and 26.6 m^2 g^{-1}, respectively.

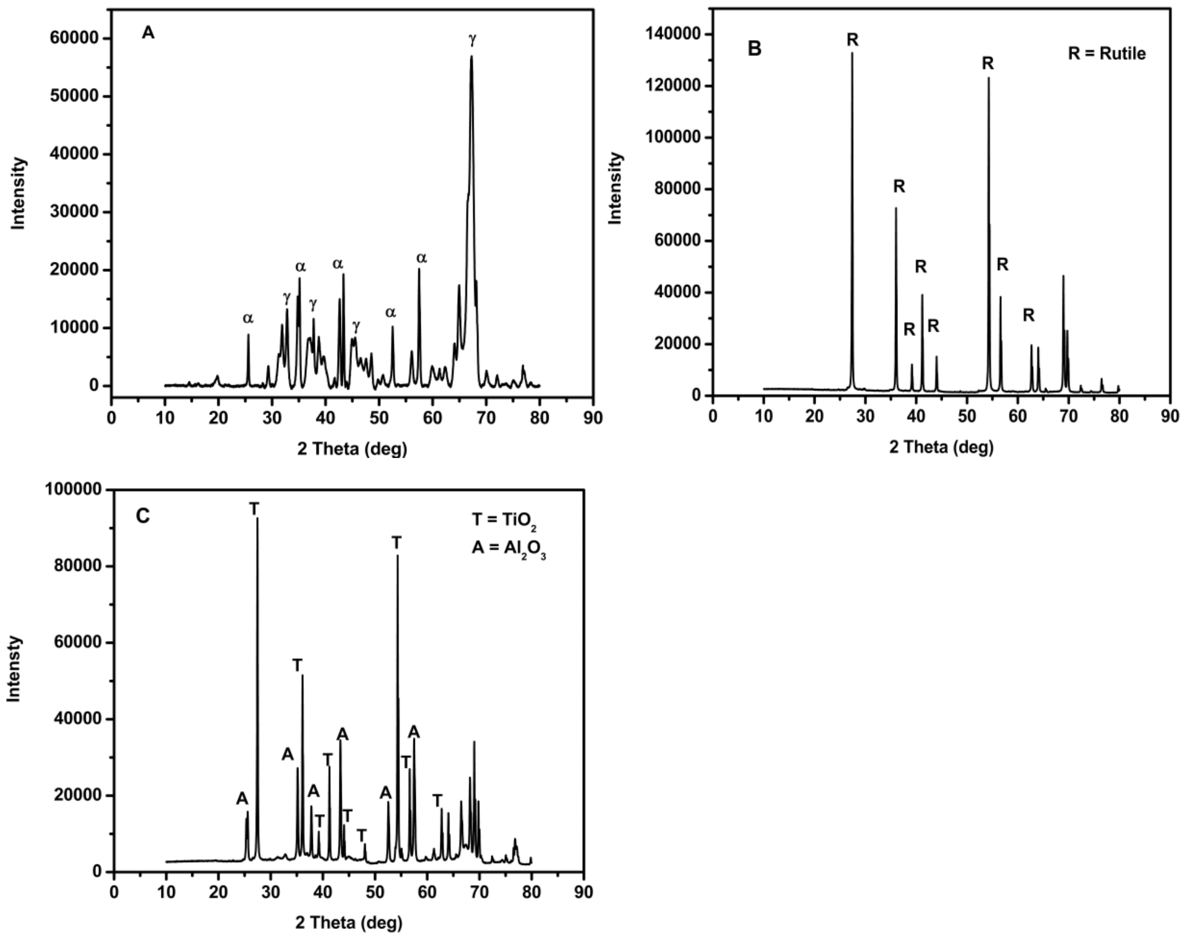

Fig.1. XRD spectra of nanometer-sized alumina powder (A), nanometer-sized titania powder (B) and titania-alumina hollow fiber (C) calcined at 1000°C for 3 hours. Theta phases: α = alpha-phase Al_2O_3, γ = gamma-phase Al_2O_3, R = rutile TiO_2, A= Alumina, T = Titania

3.1.3 Scanning electron microscopy (SEM) analysis

Fig. 2 shows the SEM textural images of the alumina/titania (A) and polypropylene hollow fiber (B). It can be seen from this figure that the textual image of alumina/titania hollow fiber had different nanopores sizes which was different from that observed for polypropylene hollow fiber. The diameter of the particles was estimated to range from about 5 nm up to a maximum of 45 nm. The polypropylene hollow fiber showed fibrous like structures. It is worth mentioning that the nanopores in the alumina/titania hollow fiber leads to an enhanced surface area and fast mass transfer for the analyte during the preconcentration process.[10,11]

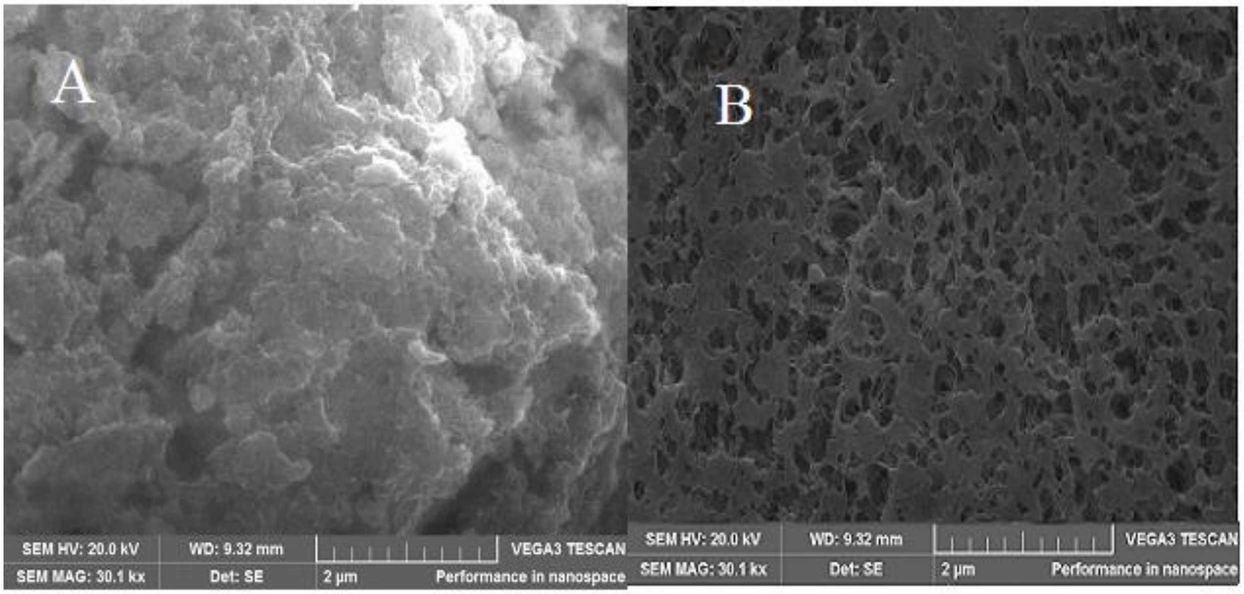

Fig. 2. SEM textural images of the titania-alumina (A) and polypropylene hollow fiber (B).

3.2 Screening of experimental variables using full factorial design

Two level (2^4) full factorial design was used as a screening method for optimization of on-line preconcentration system based on sorptive microextraction system using alumina-titania hollow fiber membrane. The effect of factors on the on-line sorptive microextraction system was investigated by using analysis of variance (ANOVA) taking into consideration the percentage recovery as the analytical response (Table S1). The ANOVA results for the main effects and their interactions are presented in the form of Pareto charts (Figs. S1-3).

In view of the overall ANOVA results, it was observed that that eluent concentration and sample pH were the most important variable for retention and recovery of the studied analytes. Based on the effect estimate for sample pH, the retention of all metal ions decreased significantly with increasing sample pH. This is because the properties of alumina and titania surface strongly depend on pH. It is reported that, below their points of zero charge 7.3 and 6.02 for alumina and titania, respectively, the surface is positively charged.[10,11,20] Therefore, the sample pH should be above the points of zero charge. Above these points the surface of the alumina-titania hollow fiber is covered with OH groups and negatively charged. Therefore, it attracts the analytes of interest and leads to an enhancement of the adsorption efficiency. The influence of eluent concentration for desorption of target analytes showed that higher levels must be employed to optimize the elution process. The flow rates were not or less significant at 95% confidence level as compared to the aforementioned variables. Therefore, loading and eluent flow rates were fixed at 5 and 0.5 mL min^{-1}, respectively.

3.3 Final optimization of on-line preconcentration system using central composite design

The overall results obtained for the screening analysis using 2^4 full factorial experimental design indicated that sample pH and eluent concentration require a final optimization. A central composite design containing a total of 14 experiments (Table S2) were carried out to optimize these two variables. The 3D surface responses (Fig S4) of the quadratic models were used to evaluate the interactive relationships between independent variables (pH and eluent concentration) and response. Based on quadratic equations resulted from the 3D surface response plots, the optimum pH and eluent concentration were 8.5 and 3.0 mol L^{-1}.

3.5 Adsorption capacities and regeneration of the hollow fiber

The investigation of adsorption capacities of an adsorbent is an important factor, because it determines how much of sorbent is required to quantitatively concentrate the analytes from a given solution.[10] The adsorption capacity of the alumina/titania hollow fiber membrane was studied and the experimental data were fitted into the general equation of the modified Langmuir model presented in Eq. 1.[21] The latter was used to calculate the maximum adsorption capacity.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L q_{\max}} \qquad 1$$

The results showed that adsorption capacity of the analytes probably differ due to their size, degree of hydration and the value of their binding constant with alumina/titania hollow fiber membrane. The maximum adsorption capacities were found to be 17.51, 18.74, 19.63, 15.39, 19.11 and 20.65 mg g^{-1} for Co, Cr, Mo, Ni, Sb and V, respectively. The adsorption capacities obtained in this study were better than those reported in the literature.[22,23]

The stability and regeneration possibility of the alumina/titania hollow fiber membrane were investigated. The adsorbent can be reused after regeneration with 5.0 mL of a 2.75 mol L^{-1} HNO_3 solution and 10 mL double distilled deionized water, respectively, and was relatively stable up to 60 runs without an obvious decrease in the recoveries for the studied ions (Table 3).

Table 3 Column stability and regeneration

Analytes	**No. of cycles**			
	1	**30**	**60**	**70**
Co	99.6±0.7	99.7±1.1	97.2±1.0	88.3±1.5
Cr	98.1±0.5	98.6±1.3	97.1±1.6	89.3±2.1
Mo	99.1±0.3	97.9±1.1	96.3±1.3	85.6±2.5
Ni	99.7±08	99.4±1.5	97.3±1.5	86.5±1.7
Sb	98.5±0.9	98.3±0.9	99.0±1.4	90.0±1.2
V	100.3±2.1	99.8.1±1.2	98.7.9±1.4	89.3±1.2

3.6 Analytical figure of merit

The online HFSME-ICP-MS system provided calibration graph that linear near the limits of quantification up to at least 250 µg L^{-1} (for all analytes except Mo which was 225 µg L^{-1}) with coefficients ranging from 0.9987-0.9995 (Table 4). The limits of detection (LOD) and quantification (LOQ) of the proposed preconcentration procedure were estimated under optimal experimental conditions and they were calculated according to IUPAC recommendation from $C_{LOD} = 3 \times SDm^{-1}$ and $C_{LOQ} = 10 \times SDm^{-1}$, where *SD* is the standard deviation of the blank (n=21) and *m* is the slope of the calibration curve. For 200 mL sample volume, the sensitivity, LOD, LOQ and precision (in terms of relative standard deviation) values are presented in Table 4.

Table 4 Analytical figure of merit of the HFSME system for preconcentration of metal ions obtained under optimum conditions

Analyte	Sensitivity (cps L µg^{-1})	LOD (ng L^{-1})	LOQ (ng L^{-1})	Precision (%RSD)	Calibration range (µg L^{-1})
Co	138.5	0.7	2.3	3.1	0.004-250
Cr	98.4	0.9	3.0	2.3	0.005-250
Mo	119.3	0.1	0.3	2.9	0.0009-225
Ni	128.1	0.9	3.0	3.0	0.005-250
Sb	113.7	0.8	2.7	1.5	0.003-250
V	141.8	0.6	2.0	1.2	0.003-250

A comparison of the proposed HFSME-ICP-MS method with other preconcentration procedures reported in the literature is summarized in Table 5. It can be seen from this table that the developed method has relatively lower detection limit for all investigated heavy metal ions. In addition, the relative standard deviation of the proposed method was comparable with Refs[7,23,24] and lower than those reported by Refs.[22,25,26] In view of the above, it can be concluded that HFSME-ICP-MS method is a simple, reproducible, sensitive technique.

Table 5 Comparison of the reported methods for the target analytes with the developed method

Analytes	Analytical method	LOD (ng L^{-1})	RSD (%)	Refs.
Co, Ni	DLLME-SFO-ICP-MS	2.2, 1.3	2.6, 4.5	22
Cr, V	SPE-ICP-OES	150, 90	1.7,2.9	23
Co, Cr, Ni, V	SPE-ICP-OES	90, 170, 280, 110	2.9, 3.5, 5.4, 2.5	24
Co, Cr, Ni	DLLME-SFO–GFAAS	1.3, 0.2, 1.3	7.2, 6.2, 7.2	25
Co, Cr, Mo, Ni, Sb, V	SPE-ICP-OES	4, 6, 36, 90, 27, 33	5.5, 2.0, 4.2, 4.5, 1.3, 1.4	26
Mo, Sb, V	SPE/ICP-OES	140, 50, 30	1.9, 1.2, 1.1	7
Co, Cr, Mo, Ni, Sb, V	HFSME-ICP-MS	0.7, 0.9, 0.1, 0.9, 0.8, 0.6	3.1, 2.3, 2.9, 3.0, 1.5, 1.2	Current work

3.7 Validation, application of HFSME-ICP-MS system to real samples and comparison with a standard method

In order to assess the accuracy of the optimized HFSME-ICP-MS methodology for preconcentration and determination of Co, Cr, Mo, Ni, Sb and V and their ICP-MS, diesel sample spiked with inorganic and organic standard solutions of the target analytes (5 µg L^{-1}) was analyzed. It is worth mentioning that certified reference materials (CRM) in suitable matrixes such as diesel or gasoline sample at the working concentration ranges (trace levels) were not available. The main objective of spiking the diesel sample with organic and inorganic standard solutions was to evaluate the alumina/titania hollow fiber membrane sorption efficiency to different metal species in liquid fuel samples. This is because trace element forms in petroleum products are not fully known and different species may display different adsorption behaviors.[6] All analyses were performed in triplicate and the analytical results obtained are given in Table 6. It can be seen from this table that the percentage recoveries range from 95-99% for both aqueous and organic standards. The obtained results attest to the accuracy of the proposed preconcentration procedure.

Table 6
Analytical results obtained in the analysis of spiked diesel sample. The concentration and recovery values are expressed as the mean ± standard deviation of the three replicates

Analytes	**Added (µg L^{-1})**	**Inorganic standard**		**Metallo-organic standard**	
		Found (µg L^{-1})	R (%)	Found (µg L^{-1})	R (%)
Co	0	ND	-	ND	-
	5	4.8±0.7	96.2±1.1	4.8±0.4	95.6±0.8
Cr	0	9.1±1.5	-	9.1±1.5	-
	5	14.0±1.5	97.3±2.1	14.0±1.2	98.1±0.9
Mo	0	104.8±3.0	-	104.8±3.0	-
	5	109.7±2.9	98.8±1.8	109.7±2.6	97.6±1.7
Ni	0	496.0±3.2	-	496.0±3.2	-
	5	500.9±4.3	97.5±1.5	500.8±3.8	96.1±1.0
Sb	0	ND	-	ND	-
	5	4.9±0.5	98.1±1.2	4.9±1.1	97.8±2.0
V	0	6.9±0.7	-	6.9±0.7	-
	5	11.9±0.9	99.2±1.3	11.8±1.3	97.5±2.2

The applicability of the proposed online HFSME-ICP-MS method was evaluated for preconcentration and determination of metal ions in gasoline and diesel samples. Table 7summarizes the results obtained for the preconcentration and determination of the target analytes in diesel samples. It can be seen from Table 7 that cobalt and antimony were not quantified in diesel samples as their concentrations were found to be below the LOD. The Ni concentrations were relatively higher in D1, G1 and D2 samples than in G2. It is worth mentioning that this element is quite abundant in the Earth's crust and also sample contamination during the diesel and gasoline production process should not be disregarded. The concentration of Mo was higher in diesel samples compared to gasoline sample. Molybdenum is normally used as a catalyst in the desulfurisation of petroleum, petrochemicals and coal-derived liquids to minimise sulfur dioxide emission from fuel combustion. Therefore, the relative high concentration in diesel samples might be due to residues of Mo leached out during the desulfurisation process. The concentration of other metal ions such as V, Cr (except in gasoline samples) and Co were quite low (ranging from 2.2 to 11.6 µg L^{-1}). The quantification of these metal ions required an analytical technique with high detection capability, such as the one reported in this study.

The samples were also analyzed by ICP-MS after microwave-assisted digestion. And the results were compared with those obtained by the HFSME-ICP-MS method. In the case of diesel samples, the two methods gave essentially similar results for quantification of Mo and Ni. While in the gasoline samples, the results were similar for determination of Cr, Mo, Ni and Sb in the case G1 samples and Cr, Mo and Ni for G2. Statistically, these results were not significantly different at 95% confidence level. This demonstrated the reliability of the proposed method. When using the comparative method (MAD/ICP-MS), the concentration of Co, Co, Sb and V were not quantifies in diesel samples as they present in trace levels (< 10 µg L^{-1}). Furthermore, Cr and V were not quantified in G1 sample as their concentrations were found to be below the LOD of the instrument. In the case of G2, Cr, Sb and V were also not quantified. It should be noted that the samples after acid digestions were diluted ten times. Therefore, the concentration of elements in diluted samples were less than or equal to 1.2 µg L^{-1}. In addition, the differences between the two methods might be attributed to incomplete mineralization (especially in diesel samples).

Table 7 Determination of Co, Cr, Mo, Ni, Sb and V (μg L^{-1}) in commercial diesel (D1 and D2) and gasoline (G1 and G2) samples by proposed HFSME-ICP-MS and comparative method MAD/ICP-MS (n = 3, at 95% confidence level).

Techniques	**Analytes**	**D1**	**D2**	**G1**	**G2**
		Concentrations (μg L^{-1})			
HFSME-ICP-MS	Co	ND	ND	11.6±1.4	7.7±0.3
	Cr	9.1±1.5	2.2±0.7	90.9±2.5	23.2±0.8
	Mo	104.8±3.0	73.2±2.7	47.5±1.4	20.9±1.3
	Ni	496.0±3.2	121.9±3.6	362.5±5.7	69.4±1.9
	Sb	ND	ND	70.9±0.9	4.8±0.3
	V	6.9±0.7	5.2±0.2	5.93±0.7	6.1±0.7
MAD/ICP-MS	Co	ND	ND	ND	ND
	Cr	ND	ND	90.4±3.1	22.8±0.7
	Mo	105.1±3.3	72.9±2.1	48.1±1.8	21.2±1.2
	Ni	494.6±4.1	122.3±4.2	363.4±6.4	69.1±2.3
	Sb	ND	ND	71.3±1.1	ND
	V	ND	ND	ND	ND

4. Conclusions

This study presents the preparation of alumina/titania hollow fiber membrane using polypropylene hollow fiber as the template. The hollow fiber membrane was characterized with XRD, SEM and BET. The prepared hollow fiber membrane was applied as a solid phase material for the sorptive microextraction technique. The latter was applied for online solid phase microextraction coupled to ICP-MS for preconcentration and determination of Co, Cr, Mo, Ni, Sb and V in diesel and gasoline samples. The experimental parameters of the proposed method were achieved using chemometric methods namely, 2^4 factorial and central composite designs. Under optimized conditions, the online HFSME-ICP-MS technique proved to be suitable for simultaneous preconcentration and determination of trace metal ions in diesel and gasoline samples. The preconcentration step permitted the elimination of the organic matrix, thus, reducing polyatomic interferences in ICP-MS. The developed method was applied for the determination of the target analytes in four liquid fuel (two diesel and two gasoline) samples purchased from different fuel filling stations. The developed HFSME-ICP-MS method can be considered as an alternative to other sample preparation techniques such as microwave acid digestion because it displays relatively low LOD and LOQ (0.1-0.9 and 0.3-3.0 ng L^{-1}, respectively).

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