Talanta 110 (2013) 153–159

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Preconcentration of molybdenum, antimony and vanadium in gasolsine samples using Dowex 1-x8 resin and their determination with inductively coupled plasma–optical emission spectrometry

Philiswa N. Nomngongo [a], J. Catherine Ngila [a,*], Joseph N. Kamau [a], Titus A.M. Msagati [a], Brenda Moodley [b]

[a] Department of Applied Chemistry, University of Johannesburg, PO Box 17011, Doornfontein, Johannesburg, Gauteng 2028, South Africa
[b] School of Chemistry and Physics, University of KwaZulu Natal, P/Bag X54001, Westville, Durban 4000, South Africa

ARTICLE INFO

Article history:
Received 28 November 2012
Received in revised form
12 February 2013
Accepted 13 February 2013
Available online 6 March 2013

Keywords:
Preconcentration
Gasoline
Dowex 1-x8
Metal ions
ICP–OES

ABSTRACT

Strong ion exchangers (Dowex 50W-x8 and Dowex 1-x8) were used for the separation and preconcentration of trace amounts of Mo, Sb and V in gasoline samples. Dowex 1-x8 resin was found to be suitable for the quantitative retention of these metal ions from organic matrices. The elution of the metal ions from Dowex 1-x8 resin was achieved by using 2.0 mol L^{-1} HNO_3 solution. The Dowex 1-x8 preconcentration and separation method gave an enrichment factor of 120 with limits of detection equal to 0.14, 0.05 and 0.03 μg L^{-1} for Mo, Sb and V, respectively. The limits of quantification were found to be 0.48, 0.18 and 0.10 μg L^{-1} for Mo, Sb and V, respectively. Under optimized conditions, the relative standard deviations of the proposed method ($n=20$) were $<4\%$. The accuracy of Dowex 1-x8 preconcentration procedure was verified by the recovery test in the spiked samples of gasoline sample. The Dowex 1-x8 preconcentration method was applied to Conostan custom made oil based certified reference material for the determination of Mo, Sb and V. The results of the paired *t*-test at a 95% confidence level showed no significant difference. The separation and preconcentration procedure was also applied to the gasoline samples collected from different filling stations.

1. Introduction

The knowledge of metal ion concentrations in fuel is of great interest with respect to economic and environmental issues [1,2]. For instance, the presence of metal ions such as antimony (Sb) and vanadium (V) in gasoline causes catalyst poisoning during the catalytic cracking of naphtha and gasoline [3]. Generally, metal ions in gasoline play a significant role in engine maintenance, since metallic species can catalyse the corrosion of engines or promote the formation of gums and sediments [4–6]. In addition, some metal ion compounds, especially vanadium, in gasoline are of environmental concern due to their potential impact in human health since they may cause mutagenic and carcinogenic effects [7–9]. Furthermore, their presence in gasoline causes fuel degradation, air pollution (especially in big cities) and reduces the efficiency of catalytic reactors in vehicle exhaust systems, thus increasing the emission of exhaust gases [4,6].

Many metals occur naturally in fossil materials and, as a result, they can be present in petroleum based products. The presence of metal ions in petrochemical compounds (e.g. fuel) can also be due to their incorporation during the production process, by contact with refinement or distillation equipment, storage and transport. Another source of these elements is that some can be added to the fuel improve its characteristics of the products [5,10]. Vanadium and molybdenum (Mo) are widely used as catalysts in the desulfurisation of petroleum, petrochemicals and coal-derived liquids to minimise sulfur dioxide emission from fuel combustion [11]. As such, residues of trace amounts of these metal ions can be found in the final product. The presence of metals in petrochemical organic products is undesirable, unless they are used as additives. Methods for the analysis of vanadium in fuel has been one of the most studied elements [1,8,12]. However, there is an increasing interest towards a number of other elements, such as Mo and Sb, among others, because they occur naturally in fossil fuels.

Direct determination of metals in fuel samples such as gasoline, by most analytical techniques is difficult. This is because of its volatility, low viscosity, corrosivity and immiscibility with water [13]. Inductively coupled plasma–optical emission spectrometry (ICP–OES) is a sensitive multi-element technique, but direct introduction of gasoline requires a special care [13,14]. This is because direct loading of organic samples to the ICP can destabilize or extinguish the plasma [14,15]. Therefore, a sample

* Corresponding author. Tel.: +27 115 596 196; fax: +27 115 596 425.
E-mail addresses: jcngila@uj.ac.za, jcngila2002@yahoo.com (J.C. Ngila).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.02.032

preparation step that will separate and preconcentrate trace metals in gasoline prior to ICP–OES detection, is required. Techniques involving separation and preconcentration procedures for the determination of trace elements in gasoline and fuel kerosene are reported in the literature [6,13,16,17]. In some of these preconcentration techniques, various sorbent materials have been functionalised with organo-functional groups in order to extract metal ions from complex matrices. Due to the leaching action of organic samples, the main limitation of these procedures in the analysis of metals in gasoline is to maintain the organofunctional group attached to the solid phase [6]. In addition, these techniques focus only on the preconcentration of Cu, Ni, Fe and Zn. Therefore, to the best of our knowledge, there are no reports on Mo, Sb and V.

The aim of the present study was to explore the applicability of commercially available ion exchange resins for the preconcentration and separation of Mo, Sb and V in gasoline prior to their determination using ICP–OES. The reason for choosing commercial resins is that they are the most commonly utilized cation exchangers for the removal of many metal ions from aqueous solutions and therefore well studied. The resins contain functional groups for metal ion binding and hence are effective in the extraction of heavy metals from organic phase matrices. In addition, procedures involving separation and preconcentration methods using commercially available ion exchange resins combined with ICP–OES for the determination of Mo, Sb and V in gasoline have not been reported in the literature. The retention performance of Mo, Sb and V ions on strongly acidic cation exchanger resin (Dowex 50W-x8) and strongly basic anion exchanger resin (Dowex 1-x8), was studied at different solution pH values for different resin columns. For the selected resin, that is, Dowex 1-x8, experimental conditions for retention/desorption of Mo Sb and V ions prior to their ICP–OES detection, were optimized. The validity of the separation and preconcentration procedure was verified by comparing the solid phase extraction (SPE)/ICP–OES results with those obtained by GFAAS after acid digestion. The spike-recovery experiments were conducted to evaluate the accuracy of the method. The procedure was applied for the determination of traces of Mo, Sb and V in Conostan custom made oil based certified reference material (CRM) and commercial gasoline samples.

2. Experimental

2.1. Instrumentation

Metal ions were determined using a Spetro Arcos ICP–OES (SPECTRO Analytical Instruments, GmbH, Germany) equipped with a Cetac ASX-520 autosampler. The operating conditions were as follows: forward power 1400 W, plasma argon flow rate 13 L min^{-1}, auxiliary argon flow rate 2.00 L min^{-1}, and nebulizer argon flow rare 0.95 L min^{-1}. The most prominent atomic and ionic analytical spectral lines of the metals studied, were selected for investigation, i.e. Mo 202.030 nm, Sb 206.833 nm and V 292.402 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 rate at 3.0 mL min^{-1}. Comparative experiments for the determination of metal ions were performed using A Perkin-Elmer (Norwalk, CT, USA) A Analyst 100 atomic absorption spectrometer equipped with a HGA-800 graphite furnace and an AS-72 autosampler. High purity nitrogen (99.996%, Afrox, South Africa) was used as purging gas. Appropriate hollow cathode lamps (HCL) from Perkin-Elmer were used in these experiments. The graphite furnace atomic absorption spectrometry (GFAAS) operation parameters and heating temperature program is presented in Table 1.

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 (Merck, South Africa), was used to prepare model solutions. Spectrascan stock solutions (1000 mg L^{-1}) of Mo Sb and V (Industrial Analytical Pty, Ltd, South Africa) were used to prepare the working solutions for SPE at concentrations of 10 μg L^{-1} for Mo and Sb and 12 μg L^{-1} for V. Working solutions, as per the experimental requirements, were freshly prepared from the stock solution for each experimental run. A Spectrascan multi-element standard solution at concentration of 100 mg L^{-1} (Industrial Analytical Pty, Ltd, South Africa) was used to prepare working standard solutions of 10–120 μg L^{-1} for measurements of concentrations of analytes in all model and sample solutions. Solutions of nitric acid at concentrations of 0.5, 1.0, 2.0 and 3.0 mol L^{-1} used for the elution of the analytes from the column, were prepared from ultrapure concentrated acid (65%, Sigma-Aldrich, South Africa). The pH adjustments were performed with glacial acetic acid and diluted ammonia solutions (Sigma-Aldrich, South Africa). Suprapur 30% hydrogen peroxide (H_2O_2, Merck, South Africa) was used for acid digestion procedure.

Ten gasoline samples from different local filling stations were used for method development and validation. Gasoline samples with and without additives are described as metal-containing unleaded gasoline (MCUG) and metal-free unleaded gasoline (MFUG), respectively.

The cation exchangers used in this study as packing materials namely Dowex 1-x8 (chloride form) and Dowex 50W-x8 (sodium form), were purchased from Sigma Aldrich. The properties of the resins are given in Table 2.

2.3. Preparation of column

Polyethylene columns of diameter 1.35 and 6.5 cm in height were used for preconcentration. Slurries of 1.5 g of Dowex 50W-x8

Table 1
Operation parameters and heating temperature program for GFAAS.

Spectrometer setup	Mo	Sb	V
Wavelength (nm)	313.3	217.6	318.40
Lamp type	HCL	HCL	HCL
Lamp current (mA)	10	15	15
Heating program for the atomizer			
Step	Step T (°C)	Ramp (°C s^{-1})	Hold time (s)
Drying 1	90	1	5
Drying 2	200	1	10
Pyrolysis	1800^{Mo}, 1000^{Sb}, 1000^{V}	5	20
Atomization	2450^{Mo}, 1500^{Sb}, 2400^{V}	0	6
Cleaning	2500	1	5

Table 2
Physical and chemical properties of the resins.

	Dowex 50W-x8	Dowex 1-x8
Type	Strong acidic cation exchanger	Strong basic anion exchanger
Functional group	Sulfonic acid	Quaternary amine
Matrix	Styrene-divinylbenzene	Styrene-divinylbenzene
Standard mesh size	100–200	200–400
Total exchange capacity (meq mL^{-1})	1.7	1.2
Water retention capacity%	50–58	39–45
pH range	0–14	0–14
Maximum operating temperature	120 °C	66 °C

or Dowex 1-x8 in Millipore water were prepared and packed into columns to heights of about 3–4 cm. A porous frit was placed at the bottom of the column and at the top of the packing material to hold and confine the adsorbent within the designated capacity/volume. The entrapment of the packing material serves to eliminate the dead volume. The columns were washed with Millipore water followed by conditioning with 10 mL ammonium acetate buffer (1.0 M, pH 9.0) and then 10 mL of ethanol.

2.4. Preconcentration and recovery of Mo, Sb and V in model organic solutions and real gasoline samples

Model metal ion solutions were prepared as follows: 1.0 mL of 1.0 mg L^{-1} of Mo and Sb solutions were separately transferred into 100 mL volumetric flasks and made up to the mark with ethanol to obtain 10 μg L^{-1} of each metal ion. The procedure was repeated for V to obtain 12 μg L^{-1}. Ethanol solutions of each metal ion (20 mL) were percolated through the ion exchange resin column with a flow rate of 3.0 mL min^{-1}. The column was washed with 10 mL of Millipore water to remove excess organic solution, followed by 5.0 mL of ammonium acetate buffer solution, to remove major cations (Na, Ca, K, etc). Lastly, the metal ions were eluted with 5 mL of 2.0 mol L^{-1} HNO_3 solution. All fractions obtained during the elution stage were collected separately and analysed with ICP–OES. It should be noted that the washings with Millipore water and ammonium acetate buffer solution were discarded. The same procedure was applied to the blank solutions. In between the experiments, the resin was washed as described in Section 2.3. The effect of pH sample solution, sample volume, eluent concentration and sample and eluent flow rates were investigated. In order to measure metal ions in real samples, 1.0 mL aliquot of gasoline was placed in a 100 mL volumetric flask and diluted with ethanol. The resulting solution was then subjected to the above mentioned preconcentration procedure. All analyses were performed in triplicate.

2.5. Procedure for the dilution of certified reference material

To validate the preconcentration method described in this study, a Conostan custom made oil based certified reference material (CRM) obtained from SCP Science (Quebec, Canada) containing 1.0 mg L^{-1} of each metal ions was used. The dilution of the CRM was performed as follows: a 1.0 mL aliquot of 1.0 mg L^{-1} CRM was dissolved in 10 mL of hexane. The solution was quantitatively transferred to a 100 mL volumetric flask and made to the mark with acetone to obtain 10 μg L^{-1} of each metal ion. Suitable aliquots (20 mL) of the solution were taken and preconcentrated by the proposed procedure and analysed with ICP–OES. The same procedure was applied to the preparation of blank solutions.

2.6. Procedure for acid digestion of gasoline samples

The acid digestion procedure was carried out according to Amorim et al. [1]. A brief Description of the procedure is as follows: 5.0 mL of gasoline sample was placed into a 100 mL Teflon beaker followed by the addition of 2.0 mL H_2O_2 (30%) and 6 mL concentrated HNO_3 and heated at 170 ± 10 °C in hot plate for 10 min. The digested content was left to cool down to room temperature, quantitatively transferred to a volumetric flask and then diluted with Millipore water to a final volume of 50 mL. Millipore water, applied to the same procedure, was used as the blank. The digested samples were then analyzed by GFAAS.

3. Results and discussion

In order to achieve quantitative adsorption of Mo, Sb and V onto the solid sorbent, the preconcentration method was optimized for various analytical parameters (such as the sorbent material selection, pH and eluent concentration). Flow rates, eluent volume and the amount of the sorbent fixed to 3.0 mL min, 5.0 mL and 1.5 g, respectively. The experimental conditions for the preconcentration of metal ions were investigated using absolute ethanol model solutions. The percentage recovery of analytes retained on the column was calculated from the concentration of the metal ions in the starting sample and the amounts of analytes eluted from Dowex 1-x8 and Dowex 50W-x8 columns.

3.1. Selection of stationary phase

In order to choose a suitable SPE stationary phase for the preconcentration of Mo, Sb and V, anionic (Dowex 1-x8) and cationic (Dowex 50W-x8) exchange resins were tested. Since the pH of the sample solution plays a vital role in the retention of metal ions, a comparison of recoveries of Mo, Sb and V at different pH values (4, 7 and 9) were carried out. The %recovery values for Mo, Sb and V were less than 50% at the three pH values when Dowex 50W-x8 resin was used. The lowest %recovery was 9.8% for Mo at pH 9 while the highest was 44.6% for Sb at pH 7. This shows that these elements were partially retained on the surface of the Dowex 50W-x8 resin. The reason for the partial adsorption might be the fact that these elements exist in various oxidation states and different ionic species in aqueous solutions. Pyrzyñska and Joñca [18] studied the behavior of Mo in aqueous samples. They found that Mo was partially retained on cation exchange resin because in solution, the dominant species is MoO_4^{2-}. When using the stronger anionic resin namely Dowex-1x8, improved results were obtained with the lowest recovery value being 54.9% for V at pH 4 while the highest value was 97.4 % for Sb at pH 7. Therefore, Dowex-1x8 was used for further investigations.

3.2. Effect of sample solution pH on retention of metal ions

Owing to competition for the exchange sites of the resin, between metal ions and hydrogen ions in solution, the effect of pH of the sample solution was studied as a significant factor for quantitative retention of the analyte [19]. The effect of the pH of the ethanol model solution on the retention of Mo, Sb and V onto Dowex 1-x8 was investigated in the pH range 4–10. The results are shown in Fig. 1. The recovery values for Mo, Sb and V were not quantitative at the pH values below 6. The recoveries increased with increasing pH and reached quantitative values at the pH range 6–8 for Mo and V ions and 6–7 for Sb. Therefore, pH 6 was selected for further investigations.

3.3. Effect of eluent concentration

The effect of eluent (HNO_3) concentration on elution of metal ions from Dowex 1-x8 resin was investigated by carrying out the elution with 0.5–3.0 mol L^{-1} HNO_3. In this work, the optimum eluent concentration was defined as the concentration of the eluent that can elute more than 95% of the retained metal ions. The results obtained indicated that elution of metal ions is dependent on the eluent concentration. Thus when [HNO_3] was increased from 0.5 to 2.0 mol L^{-1} the elution efficiency of the acid improved from 92.4 to 100.7% for Mo; 83.2 to 98.3% for Sb; and 91.0 to 96.5% for V. However, there was a slight decrease in elution efficiency when the acid concentration was increased from 2.0 to 3.0 mol L^{-1} in all the cases except for V which showed an increase from 96.5 to 100.1%. Therefore, for further investigations 5.0 mL of 2.0 mol L^{-1} HNO_3 was selected for elution of metal ions.

3.4. Effect of sample volume

The preconcentration of larger sample volumes at a defined sample flow rate improves the preconcentration factor of the SPE method [20]. In order to investigate the possibility of enriching low concentrations of analytes from large volumes, the maximum applicable sample volume must be determined. For this purpose, the concentrations of each metal ion were kept constant while increasing the sample volume. The recoveries of the Mo, Sb and V ions from different volumes of ethanol solutions containing 14 μg L^{-1} of each metal ion, are presented in Fig. 2. As it can be seen from the figure, the recoveries were found to be stable upto 500 mL for Sb and 600 mL for Mo and V. At higher volumes, the recoveries for analytes decreased. This decrease may be due to the saturation of the exchange sites of Dowex 1-x8. Therefore, the highest preconcentration factor of 120 was achieved when using 600 mL of the sample and 5.0 mL of final volume.

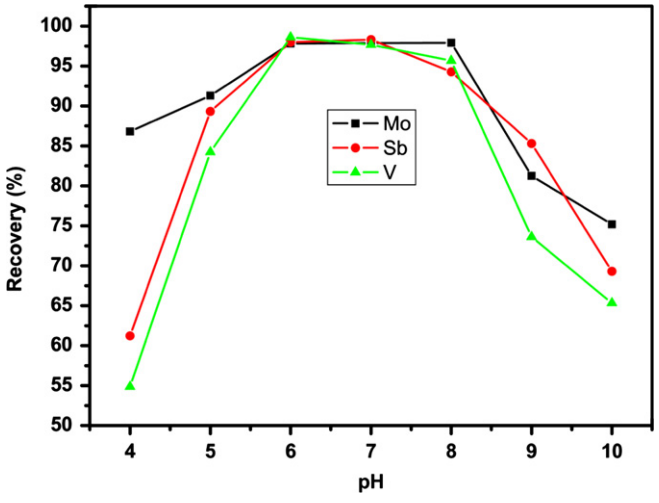

Fig. 1. Effect of sample pH on retention of the analytes in ethanol onto Dowex 1-x8 resin column. Sample volume: 20 mL; amount of resin 1.5 g; flow rates of sample and eluent 3.0 mL min^{-1}; replicates $n=3$).

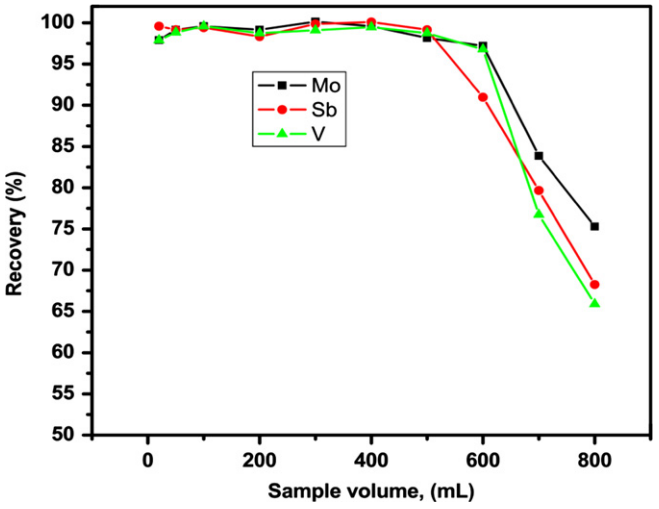

Fig. 2. Effect of sample volume on the recoveries of metal ions: pH 6; analyte concentration 14 μg L^{-1}; amount of resin 1.5 g; flow rates of sample and eluent 3.0 mL min^{-1}; eluent volume 5 mL; replicates $n=3$.

Table 3
Analytical performances for the proposed Dowex 1-x8 SPE method.

	Mo	Sb	V
Slope (cps L μg L^{-1})	26.39	53.43	113.1
Correlation efficient	0.9998	0.9987	0.9999
LOD (μg L^{-1})	0.14	0.05	0.03
LOQ (μg L^{-1})	0.48	0.18	0.10
%RSD	1.9	1.2	1.1

3.5. Analytical performances

The linearity of the method was checked by preconcentrating 20 mL aliquot sampled from 100 mL of 0.05 to 140 μg L^{-1} of Mo, Sb and V standards in ethanol solution, to obtain a final volume of 5 mL (preconcentration factor of 4). The analytes showed good linearity according to the results in Table 3. The sensitivity of the preconcentration method was defined as the slope of the calibration curve. The results in Table 3 indicated that the Dowex 1-x8 SPE method was more sensitive to V compared to the rest of metals studied. Thus the highest slope obtained was 113.1 cps L μg^{-1} for V while the lowest was 26.39 cps L μg^{-1} for Mo. Note that the ICP–OES signal intensity readings are given as counts per second (cps).

The reproducibility (precision) of the SPE method, calculated as the relative standard deviation ($n=12$), in model sample solutions containing 10 μg L^{-1} of Mo, Sb and V was in the range 1.1–1.9%. The IUPAC limit of detection (LOD) and limit of quantification (LOQ) under optimized conditions were obtained from the signals of 16 successive measurements of the blank and the slope (m) of the calibration curve. The LOD was defined as the lowest concentration of an analyte giving signals equal to three times the standard deviation ($3SD$) of blank signal divided by the slope of the calibration curve that the analytical technique can detect ($3SD/m$). The LOQ, on the other, was defined as the to the smallest concentration of an analyte giving signals equal to ten times the standard deviation of blank signal divided by the slope of the calibration curve which can be accurately and precisely measured with an analytical procedure ($10SD/m$). The calculated LOD and LOQ are presented in Table 3.

Table 4
Comparison of the proposed Dowex 1-x8 SPE method with some methods used for determination of Mo, Sb and V.

Analytes	Matrix	Sample preparation method	Detection	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)	Ref.
Sb	Gasoline and kerosene	Surfactant microemulsion	ETAAS	4.0	N.I[a].	[3]
V	Heavy oils	Direct determination	Tungsten coated-GFAAS	N.I.	N.I.	[21]
Sb	Naphta	Microemulsion	ETAAS	2.5	N.I.	[22]
V	Petroleum	Direct determination using solid sampling accessory	ETAAS	0.8	N.I.	[23]
V	Fuel oils	Microemulsion Acid digestion	GFAAS	100 250	300 800	[1]
V	Petroleum condensate, diesel and gasoline	Detergent emulsion	GFAAS	14	45	[8]
V	Diesel oil	Extraction induced by emulsion breaking	ETAAS	0.05	0.18	[24]
Mo and V	Petroleum products	Direct analysis	TXRF	65 and 75	N.I.	[25]
Mo and V	Gasoline	Multiphase emulsion	ETAAS	0.9 and 4.7	N.I.	[26]
Mo and V	Crude oil	Detergentless microemulsion	ICP–OES	4.1 and 2.4	13.7 and 7.9	[27]
Mo, Sb and V	Gasoline	SPE-Dowex 1-x8	ICP–OES	0.14, 0.05 and 0.03, respectively	0.48, 0.18 and 0.10, respectively	This work

[a] N.I.=not included, ETAAS=electrothermal atomic absorption spectrometry, GFAAS=graphite furnace atomic absorption spectrometry, TXRF=total reflection X-ray fluorescence, ICP–OES=inductively coupled plasma–optical emission spectroscopy.

Table 5
Effect of potential interfering ions on the recovery of metal ions.

Ions	Concentration of interfering ions ($mg\ L^{-1}$)	Recovery (%)		
		Mo	Sb	V
SO_4^{2-}	1000	99.3 ± 1.2	97.6 ± 0.8	100 ± 2.1
PO_4^{3-}	1000	98.7 ± 1.4	97.9 ± 2.1	99.2 ± 1.1
Cl^-	1000	100 ± 1.1	99.6 ± 0.5	98.9 ± 2.3
CO_3^{2-}	1000	97.0 ± 1.8	96.9 ± 0.7	99.3 ± 0.9
NO_3^-	1000	99.8 ± 0.3	99.1 ± 2.4	100 ± 0.2
Fe^{3+}	25	95.9 ± 3.1	99.1 ± 1.4	98.1 ± 1.1
Cu^{2+}	25	97.6 ± 2.1	97.8 ± 1.9	99.6 ± 2.1
Mn^{2+}	25	99.3 ± 0.5	98.9 ± 2.4	99.1 ± 3.8
Al^{3+}	25	96.8 ± 1.4	97.4 ± 2.8	98.9 ± 0.9

Experimental conditions: sample volume=50 mL, replicates $n=3$.

The Dowex 1-x8 SPE method was compared with the other previous works (Table 4). Comparison of analytical features of the present method with other sample preparation techniques indicated that the LOD and LOQ of the Dowex 1-x8 SPE were better than or comparable with other methods.

3.6. Effect of matrix ions interferences

Metal gasoline samples normally contain group I and II as well as some transition metals [5,15]. The effect of potential interfering ions was investigated in order to examine the possibility of selective recovery of Mo, Sb and V on Dowex 1-x8 resin in the presence of some anions and cations in the gasoline samples. Known amounts of anions and cations were added to the ethanol solution containing 20 $\mu g\ L^{-1}$ of Mo, Sb and V and the general preconcentration procedure was applied. The tolerance limit was set as the concentration of the ion required to cause $\leq 5\%$ error. The results are presented in Table 5. It should be noted that the effect of group I and II cations were not investigated because they were removed by washing the column with ammonium acetate buffer solution. It was found that ions normally present in gasoline samples did not interfere with the recoveries of the analytes. This suggests that the Dowex 1-x8 preconcentration method can be applied for selective removal of trace amounts of Mo, Sb and V in fuel samples that contains higher concentration of secondary cations and anions.

Table 6
Percentage (%) recovery results when 1 mL gasoline sample 1-MFUG was spiked with different metal concentrations (0–20 $\mu g\ L^{-1}$) and made up in ethanol (100 mL).

Element	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)
Mo	0	20.10 ± 0.76	–
	5	24.96 ± 0.35	97.2 ± 1.6
	10	30.03 ± 0.54	99.3 ± 1.2
	20	39.77 ± 0.10	98.4 ± 1.3
Sb	0	70.95 ± 0.82	–
	5	75.73 ± 0.25	95.6 ± 2.1
	10	80.64 ± 1.0	96.9 ± 3.1
	20	90.75 ± 0.12	99.0 ± 0.6
V	0	ND[a]	–
	5	4.89 ± 0.91	97.8 ± 1.2
	10	9.98 ± 0.34	99.8 ± 1.4
	20	19.7 ± 0.54	98.5 ± 2.1

Experimental conditions: sample pH=6, sample volume=20 mL, replicates $n=3$.
[a] ND=not detectable.

3.7. Regeneration studies

The regeneration of the column is one of the important parameters in evaluating the stability of the cation exchange resin material. In order to investigate the stability and recyclability of Dowex 1-x8 column, successive retention and elution cycles were performed by passing 20 mL of ethanol solutions (containing Mo, Sb and V) through the column. The stability and regeneration of Dowex 1-x8 column were evaluated by monitoring the changes in the recoveries of Mo, Sb and V through retention-elution cycles. The results showed that Dowex 50W-x8 column can be reused after regeneration with 20 mL Millipore water followed by 10 mL of 1.0 mol L^{-1} NaOH. The column was found to be stable up to 150 retention/elution cycles without any observable decrease in the recoveries of metal ions ($>95\%$). Therefore, recycling of the Dowex 1-x8 resin is possible.

3.8. Accuracy and validation of the separation and preconcentration procedure

An addition/recovery test was performed on the gasoline sample (1-MFUG) to estimate the accuracy of the Dowex 1-x8 SPE procedure. The results given in Table 6 showed good agreement between the added and found metal ion content.

The recovery values for Mo, Sb and V ions were quantitative ($\geq$95%). Therefore, the Dowex 1-x8 SPE method can be applied for the separation and preconcentration of analyte ions in gasoline samples.

The validity of the Dowex 1-x8 SPE method was investigated by analyzing a Conostan custom made oil based CRM. The results of the CRM certified values and those determined with Dowex 1-x8 SPE method for Mo and V are presented in Table 7. Satisfactory recoveries in the range 99.8–101% were obtained. The precision of the measurements (n=3) expressed as %RSD ranged between 1.3 and 1.5 %. According to the student t-test at the 95% confidence level, there was no significance difference between the certified and determined concentration values.

3.9. Application of the Dowex 1-x8 separation and preconcentration procedure in commercial gasoline samples

Dowex 1-x8 SPE method was used to separate and preconcentrate Mo, Sb and V ions in commercial gasoline samples collected from different petrol filling stations in Johannesburg (South Africa). The results obtained are presented in Table 8. In general, the concentrations of Sb were high (above 60 μg L^{-1}) in almost all gasoline samples irrespective of the source (manufacturer) except for 3-MCUG and 3-MFUG samples. Molybdenum and vanadium concentrations were the highest in 5-MCUG and 2-MFUG samples, respectively.

For comparison, the concentration of Mo, Sb and V in 10 gasoline samples were also determined by GFAAS after acid digestion (Table 9). The analyte concentrations obtained by Dowex 1-x8 preconcentration method (Table 8) were in agreement with the results obtained by GFAAS after acid digestion according to the paired t-test at 95% confidence level: t_{cal}=0.14, 0.72 and 0.87 for Mo, Sb and V, respectively. In all the cases t_{cal} was lower than t_{crit}=2.26 for Mo and Sb (n=10); t_{crit}= 2.44 for V (n=7). The determination of Mo, Sb and V by GFAAS after acid digestion was used as an additional procedure for quality check of the Dowex 1-x8 separation and preconcentration method. The main advantage of the Dowex 1-x8 column method described in this study is that it does not require rigorous acid digestion unlike the acid digestion method. In addition, the column method is advantageous because it minimizes the risks of cross-contamination and explosion during acid digestion. It should be noted that acid digestion followed by GFAAS determination was taken as the standard method in this study.

Table 7
Analysis of the oil-based certified reference material for the determination of metals after application of the preconcentration procedure.

Elements	Concentration (μg L^{-1})				
	Certified	RSD[a] (%)	Found	RSD (%)	Recovery (%)
Mo	1000	1.0	998.2	1.3	99.8
V	1000	1.0	1005	1.5	101

[a] RSD=relative standard deviation, replicates n=6.

Table 8
Concentrations (in μg L^{-1}) of metal ions in gasoline samples determined by ICP–OES in sample solutions resulting from Dowex 1-x8 preconcentration procedure.

Concentration (μg L^{-1})[a]			
Samples	Mo	Sb	V
1-MFUG[c]	20.10 ± 0.76	70.95 ± 0.82	ND[b]
2-MCUG[d]	17.10 ± 0.42	70.21 ± 1.80	16.11 ± 0.08
2-MFUG	36.85 ± 0.38	64.58 ± 0.81	43.89 ± 0.07
3-MCUG	21.98 ± 0.38	27.66 ± 1.00	ND
3-MFUG	22.01 ± 0.43	30.05 ± 0.62	ND
4-MFUG	32.58 ± 0.12	91.01 ± 0.87	2.78 ± 0.08
5-MCUG	70.73 ± 0.01	71.80 ± 0.01	14.65 ± 0.08
5-MFUG	50.06 ± 0.06	63.56 ± 0.02	3.96 ± 0.09
6-MCUG	47.86 ± 0.28	94.11 ± 0.48	9.89 ± 0.04
6-MFUG	19.63 ± 0.20	80.00 ± 0.97	4.30 ± 0.09

1–6 are the numbers allocated to the six gasoline filling stations.

[a] $X = st/\sqrt{n}$, X: Average value (n=3); t: Student's t ($p <$ 0.05); s: Estimation of the standard deviation, n: number of determinations.

[b] ND=not detectable.

[c] MFUG=metal-containing unleaded gasoline.

[d] MCUG=metal-free unleaded gasoline.

Table 9
Concentrations (in μg L^{-1}) of metal ions in gasoline samples determined by GFAAS in sample solutions resulting from acid digestion procedure.

Concentration (μg L^{-1})			
Samples	Mo	Sb	V
1-MFUG[c]	19.76 ± 0.67	71.24 ± 0.74	ND[b]
2-MCUG[d]	16.76 ± 0.42	66.61 ± 0.02	15.79 ± 0.08
2-MFUG	37.12 ± 0.73	85.44 ± 0.18	48.17 ± 0.07
3-MCUG	22.34 ± 0.95	28.41 ± 0.03	ND
3-MFUG	21.95 ± 0.53	29.31 ± 0.52	ND
4-MFUG	32.78 ± 0.13	90.79 ± 0.91	2.69 ± 0.79
5-MCUG	70.42 ± 0.14	71.70 ± 0.41	14.48 ± 0.52
5-MFUG	49.62 ± 0.13	63.38 ± 0.84	4.10 ± 0.41
6-MCUG	48.53 ± 0.16	93.72 ± 0.12	9.89 ± 0.51
6-MFUG	19.79 ± 0.93	79.37 ± 0.95	4.30 ± 0.43

1–6 are the numbers allocated to the six gasoline filling stations.

$X = st/\sqrt{n}$[a], X: Average value (n=3); t: Student's t ($p <$ 0.05); s: Estimation of the standard deviation, n: number of determinations.

[b] ND=not detectable.

[c] MFUG=metal-containing unleaded gasoline.

[d] MCUG=metal-free unleaded gasoline.

4. Conclusion

The separation and preconcentration of Mo, Sb and V presented in this study contributes to the growing field of fuel analysis and purification. The results obtained in the preliminary studies demonstrated that Dowex 1-x8 was suitable for preconcentration of Mo, Sb and V in organic matrices. Instead of using fresh resin for each analysis, the reusability of the Dowex 1-x8 was found to be about 150 cycles after desorption and regeneration treatment without any loss in its initial sorption performance. In addition, the Dowex 1-x8 SPE method was successful in pre-concentrating metal ions from large sample volume with a preconcentration factor of 120 achieved when using 600 mL of the sample and 5.0 mL of final volume. The elution of metal ions from the resin column was performed by 2.0 mol L^{-1} HNO_3. The positive features of the present separation and preconcentration method include relatively high selectivity, good precision and accuracy. The Dowex 1-x8 SPE procedure was successfully applied for simultaneous determination of trace amounts (μg L^{-1} range) of molybdenum, antimony and vanadium at in gasoline samples.

Acknowledgements

P.N. Nomngongo wishes to thank Sasol and NRF for financial assistance and the University of Johannesburg (Spectrau) for providing ICP–OES facilities.

References

[1] F.A.C. Amorim, B. Welz, A.C.S. Costa, F.G. Lepri, M.G.R. Vale, S.L.C. Ferreira, Talanta 72 (2007) 349–359.
[2] G.P. Brandão, R.C. de Campos, E.V.R. de Castro, H.C. de Jesus, Spectrochim. Acta, Part B 63 (2008) 880–884.
[3] R.Q. Aucelio, A.J. Curtius, J. Anal. At. Spectrom. 17 (2002) 242–247.
[4] R. Takeuchi, A. Santos, M. Medeiros, N. Stradiotto, Microchim. Acta 164 (2009) 101–106.
[5] E.S. Chaves, F.G. Lepri, J.S.A. Silva, D.P.C. de Quadros, T.D. Saint'Pierre, A.J. Curtius, J. Environ. Monit. 10 (2008) 1211–1216.
[6] D.S.S. Santos, M.G.A. Korn, M.A.B. Guida, G.L. dos Santos, V.A. Lemos, L.S.G. Teixeira, J. Braz. Chem. Soc. 22 (2011) 552–557.
[7] J.S.F. Pereira, D.P. Moraes, F.G. Antes, L.O. Diehl, M.F.P. Santos, R.C.L. Guimarães, T.C.O. Fonseca, V.L. Dressler, É.M.M. Flores, Microchem. J. 96 (2010) 4–11.
[8] R.E. Santelli, M.A. Bezerra, A.S. Freire, E.P. Oliveira, M.D.F.B. de Carvalho, Fuel 87 (2008) 1617–1622.
[9] M. Bettinelli, P. Tittarelli, J. Anal. At. Spectrom. 9 (1994) 805–812.
[10] M.N.M. Reyes, R.C. Campos, Spectrochim. Acta, Part B 60 (2005) 615–624.
[11] L. Zeng, C.Y. Cheng, Hydrometallurgy 98 (2009) 1–9.
[12] R.M. de Souza, A.L. Saraceno, C. Duyck, C.L.P. da Silveira, R.Q. Aucélio, Microchem. J. 87 (2007) 99–103.
[13] L.S.G. Teixeira, R.B.S. Rocha, E.V. Sobrinho, P.R.B. Guimarães, L.A.M. Pontes, J.S.R. Teixeira, Talanta 72 (2007) 1073–1076.
[14] M. Bettinelli, S. Spezia, U. Baroni, G. Bizzarri, J. Anal. Atom.Spectrom. 10 (1995) 555–560.
[15] T.D. Saint'Pierre, L.F. Dias, D. Pozebon, R.Q. Aucélio, A.J. Curtius, B. Welz, Spectrochim. Acta, Part B 57 (2002) 1991–2001.
[16] P.S. Roldan, I.L. Alcântara, J.C. Rocha, C.C.F. Padilha, P.M. Padilha, Ecl. Quím. São Paulo 29 (2004) 33–40.
[17] P.S. Roldan, I.L. Alcântara, C.C.F. Padilha, P.M. Padilha, Fuel 84 (2005) 305–309.
[18] K. Pyrzyñska, Z. Joñca, Anal. Lett. 33 (2000) 1441–1450.
[19] L. Zhang, X. Chang, Z. Hu, L. Zhang, J. Shi, R. Gao, Microchim. Acta 168 (2010) 79–85.
[20] P. Pohl, Z. Bogdal, B. Prusisz, Microchim. Acta 150 (2005) 253–259.
[21] Y. Nakamoto, T. Ishimaru, N. Endo, K. Matsusaki, Anal. Sci. 20 (2004) 739–741.
[22] G.P. Brandão, R.C. De Campos, E.V.R. De Castro, H.C.De Jesus, Spectrochim. Acta, Part B 62 (2007) 962–969.
[23] R.J Cassella, D.M. Brum, C.E.R. De Paula, C.F. Lima, J. Anal. At. Spectrom. 25 (2010) 1704–1711.
[24] A. Cinosi, N. Andriollo, G. Pepponi, D. Monticelli, Anal. Bioanal. Chem. 399 (2011) 927–933.
[25] D.S.S. Dos Santos, A.P. Teixeira, M.D.G.A. Korn, L.S.G. Teixeira, Spectrochim. Acta, Part B 61 (2006) 592–595.
[26] R. Cassella, B.S. Barbosa, R. Santelli, A. Rangel, Anal. Bioanal. Chem. 379 (2004) 66–71.
[27] R.M. De Souza, A.L.S Meliande, C.L.P. Da Silveira, R.Q. Aucélio, Microchem. J. 82 (2006) 137–141.