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Determination of Selenium(IV) by Electrothermal Atomic Absorption Spectrometry using Single Drop Extraction in Real Samples

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In this investigation, two new chemical modifiers for determination of Se(IV) are reported. The first, is coating of Pd in graphite tube and injection of Pd solution on top of sample solution in tube ($[Pd_{(c)} + Pd_{(i)}]$). Second modifier is concurrent coating with each of W, Rh and Pd in graphite tube ($[W.Rh.Pd]_{(c)}$). These modifiers showed very low detection limits, higher sensitivity and longer lived than other modifiers previously adapted for selenium. Second modifier is useful for determination of Se(IV) in inorganic compounds. For obtaining higher sensitivity method of single drop extraction for determination of trace amounts of selenium is reported. In this method Se (IV) is reacted with *o*-phenylenediamine, the piasoselenol complex formed was then extracted into micro drop of 1,2 dichloroethane. After extraction, the micro drop was retracted and directly transferred into a graphite tube modified by $[Pd_{(c)} + Pd_{(i)}]$. The detection limit was calculated to be 0.8 ng/mL (absolute value of 0.3 ng) based on $3S_b$. The relative standard deviation for five replicate analysis of 10 ng/mL Se was 4.8 %. The calibration curve was linear in the range of 0.8 to 40 ng/mL with a sensitivity of 0.25 ng/mL. Recovery of the method was 96 % for tap water spiked with selenium. In order to evaluate the applicability of the method, the amount of Se(IV) in plants, sea water and milk was determined.

Key Words: Seleium, Electrothermal atomic absorption spectrometry, Single drop extraction, Chemical modifier, *o*-phenylenediamine.

INTRODUCTION

Selenium(IV) is an essential trace element for several animal species, including humans. It is an integral part of glutathione peroxidase, catalyzing the reduction of reactive peroxides. This element is also applied to industrial products of semiconductor, glass, medical and product of colours. The high value of selenium is intensively toxic and at high level is lethal[1,2], hence it's determination is of great important. Electrothermal atomic absorption spectrometry (ETAAS) is a highly sensitive and relatively

selective technique for selenium determination. Chemical modifiers are an important factor in determination by ETAAS. Several chemical modifiers for determination of selenium by ETAAS have been reported. Among a wide variety of modifiers already suggested, Ni, Pd and Rh have been used with success. The modifier most commonly used for stabilizing Se species is Pd, alone or in combination with magnesium nitrate. When Pd is used alone, selenium can be stabilized up to 1000°C[3], whereas the (Pd + Mg) mixture stabilizes selenium up to 1200°C[4]. Another modifier commonly used is nickel[5]. Bulska and Pyrznska[6] studied the effect of Ni and Pd on the determination of selenium species in blood by ETAAS. For both modifiers, it was observed that selenium was stabilized up to 1200°C. Deaker and Maher[7] examined the effect of palladium and nickel on thermal stabilization of all forms of selenium in graphite furnace and observed that palladium was more effective than nickel as a modifier for Se(IV) in aqueous reference solutions, stabilizing the analyte to above 1400°C. Tada *et al.*[8] investigated 35 metals, including Rh, for the direct determination of Se in blood by ETAAS and they observed that Rh showed the largest enhancement effect and was also the most effective in preventing matrix interference. Mei *et al.*[3] reported that a solution containing $(NH_4)_3[RhCl_6]$ plus citric acid could be used for stabilizing selenium in biological tissue matrices at high pyrolysis temperatures (1200°C), allowing its determination in rich phosphorus containing samples. Volynsky and Krivan[9] compared the effect of Rh in pre-reduced form and as a solution of $RhCl_3$ on the behaviour of selenium in a transversely heated graphite atomizer for ETAAS, with other platinum group metals (Pd, Pt, Ru and Ir). Lima *et al.*[10] proposed a tungsten-rhodium coating as a permanent modifier for determination of cadmium, lead and selenium in waters by ETAAS. They observed this modifier can stabilize selenium to above 1400°C. Zanao *et al.*[11] reported W-Rh coated platform and co-injection of Rh modifier for determination of selenium. This modifier showed high sensitivity and longer lived than other modifiers used for selenium.

In order to determine trace levels of elements an extraction and preconcentration step is necessary. Conventionally, this can be accomplished by liquid-liquid extraction. However, liquid-liquid extraction is time consuming, tedious, requires too much of organic solvent and can be relatively expensive. Recently, solid phase extraction has gained favour as a replacement for liquid-liquid extraction, using low amounts of organic solvent and capability of automation. Solid phase microextraction was proposed by Belari and Pawliszyu[12]. For solid phase microextraction a small dimension fused silica fibre coated with a high temperature phase is applied, having the advantages of a higher enrichment factor, free of solvent and risk of contamination and ease of application to field sampling

and automation. Jeanton and Cantwell developed a newly method, liquid phase microextraction[13] which overcomes the problems of solvent evaporation in liquid-liquid extraction and solid phase extraction and fibre preparation in solid phase microextraction. It is based on the traditional liquid-liquid extraction technique but involves only a few microliters of organic solvent as an extractant. This method is quick, inexpensive and uses small volume of organic solvents. This technique uses simple equipment which is found in most analytical laboratories and is used for pre-concentration of organic components and has been coupled with chromatography methods. In this work the liquid phase microextraction method is reported for determination of selenium in a variety of samples. Despite the advantages of this method, no work has been reported so far on the coupling of liquid phase microextraction with spectrometry to determine inorganic compounds[13]. Bueno and Potin-Gautier[14] applied the solid phase extraction technique using Amberlite resin followed by high performance liquid chromatography.

EXPERIMENTAL

All reagents were of analytical reagent grade and triply distilled water was used throughout. A stock 1000 ppm of selenium solution was prepared from dissolving appropriate amounts of Na_2SeO_3 in 1 % HNO_3. Modifiers of 0.1 % Pd and Rh in HCl 2 %, 0.1 % W, 10 % Ni in water were used. 0.2 % *o*-phenylenediamine in 1:1 H_2O/C_2H_5OH was used as a complexing agent.

A 10 μL Hamilton syringe was used to suspend the drop of the acceptor phase and to inject it into the graphite furnace atomizer. A Shimadzu model AA-670 atomic absorption spectrometer with GFA-4B graphite furnace atomizer and D_2 lamp for background correction was used. A selenium hollow cathode lamp was used as radiation source adjusted at 12 mA. An atomic absorption signal at 196.0 nm line was recorded on a graphic printed PR-4 with peak height and gas stop mode for quantification. The temperature program for the furnace is as follows:

TABLE-1
GFA HEATING PROGRAM

Stage	Furnace temperature (°C)	Mode	Time (s)	Argon Flow rate (L min^{-1})
Drying	150	Ramp	15	1.5
Ashing	400	Step	15	15
Atomization	2100	Step	3	0 (gas stop)
Cleaning up	2500	Step	2	1.5

Determination of selenium *via* pre-concentration using single drop extraction technique

10 mL of Se(IV) solution was adjusted at pH = 2.5 and treated with 2 mL of 0.2 % *o*-phenylenediamine, heated at 60°C in water bath and then was transferred to a 15 mL vial. After cooling to 3-5°C in ice-bath it was extracted into a 4 μL 1,2-dichloroethane drop suspended on the tip of a Hamilton syringe for 25 min. The solution was stirred (2000 rpm) during the extraction (Fig. 1).

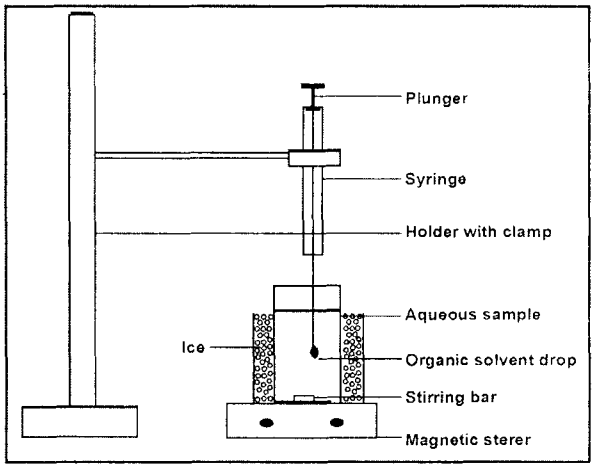

Fig. 1. Schematic setup for single drop extraction

After the extraction was completed, the solution was directly injected into the graphite tube modified with $[Pd_{(c)} + Pd_{(i)}]$.

Tube modification

Ni modifier was used by injecting 0.2 % Ni and sample solution with equal volumes. $[(W.Rh)_{(c)} + Rh_{(i)}]$ modifiers were used for coating containing 60 μg of each of W and Rh from 0.1 % of their solutions at temperatures of 2200°C and 2000°C, respectively and injecting 10 μL of 0.1 % Rh on top of 10 μL sample solution. $[Pd_{(c)} + Pd_{(i)}]$ modifier was used as coating of 60 μg Pd onto the graphite tube at 1800°C and injecting of 10 μL solution of 0.1 % Pd on top of 10 μL of sample solution. $[W.Rh.Pd]_{(c)}$ modifier was used as coating of 60 μg of each of W, Rh and Pd solution at the appropriate temperatures.

Direct determination of selenium in real samples

Sea water: 50 mL of sea water was reacted with 5 mL 37 % HCl and 5 mL 15 % H_2O_2 and boiling to half and diluting to 50 mL. The $[W.Rh.Pd]_{(c)}$ modifier was used for this determination.

Milk: 50 mL of milk was treated with 10 mL 65 % HNO_3 and after boiling for 10 min, 5 mL of 15 % H_2O_2 was added dropwise. After boiling and filtering, Se was determined using the $[Pd_{(c)} + Pd_{(i)}]$ modifier.

Plant: 4 Species of plant named Atriplex, Suaeda, Gamanthus and Koshia were analyzed. They were treated with 6 M HNO_3 and 6 M HCl (1:3) and after boiling for 15 min and filtering, they were analyzed using tubes modified by $[W.Rh.Pd]_{(c)}$.

RESULTS AND DISCUSSION

Optimizing the parameters

In order to investigate the effects of different parameters on Se determination by single drop extraction, 10 mL solution of 50 ng/mL selenium was used at all the following stages:

Modifiers: 46 Modifiers containing Pd, Ru, Rh, Ir, V, Mo, W, Ni, Mg, ascorbic acid separately or in their combinations were tested. The results of best performing modifiers are as follows:

TABLE-3
ANALYTICAL FIGURES OF MERIT FOR SELENIUM(IV) DETERMINATION USING DIFFERENT CHEMICAL MODIFIERS

Chemical modifier	Detection[a] limit (ppb)	Sensitivity[b] (ppb)	Linear range (ppb)	RSD[c] (%)
$Ni_{(i)}$	8.7	3.2	8.7-558.3	5.7
$[(W.Rh)_{(c)} + Rh_{(i)}]$	6.8	2.0	6.8-349.8	9.0
$[Pd_{(c)} + Pd_{(i)}]$	4.0	1.9	4.0-335.3	4.5
$[W.Rh.Pd]_{(c)}$	3.5	1.7	3.5-302.3	4.0

[a]Based on $3S_b$; [b]Calculated by dividing 0.0044 to the slope of calibration curve; [c]For 10 replicated analysis of 100 ng/mL Se.

$[W.Rh.Pd]_{(c)}$ modifier showed the best results in contrast to $[Pd_{(c)} + Pd_{(i)}]$ for direct determination of selenium. Also $[Pd_{(c)} + Pd_{(i)}]$ modifier showed the best results in determination of organic compounds of selenium than $[W.Rh.Pd]_{(c)}$ modifier.

Solvent: Different solvents were tested from the volatility and dissolving points of view. 1,2-Dichloroethane showed the best results for extraction of piasoselenol complex (Fig. 2).

Temperature: The extraction of complex into the drop was performed in the range of 3-20°C and the results showed no significant changes over this range. However temperature of 3-5°C was chosen for low volatility and higher mechanical stability (Fig. 4).

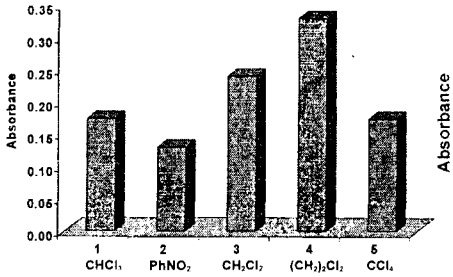

Fig. 2. Effect of solvent

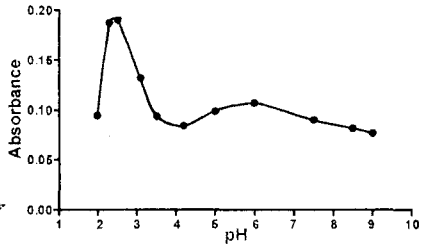

Fig. 3. Effect of pH

pH: Selenium complex solutions of different pH were tested. As can be seen from Fig. 3, the best pH was 2.5.

Extraction time: The time of extraction was varied from 5 to 30 min. As the results show (Fig. 5) the optimum time of extraction is 25 min.

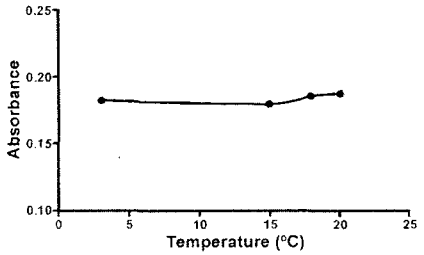

Fig. 4. Effect of temperature

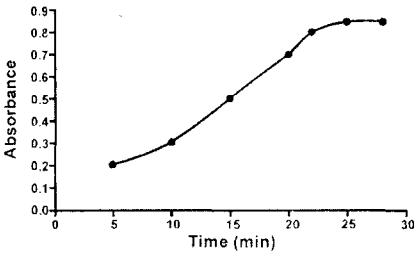

Fig. 5. Effect of time

Volume of aqueous and organic phase: Changing the organic volume from 1 to 4 µl increased the extraction efficiency. However higher volumes were avoided due to mechanical instability. 10 mL solution volume was chosen for the analysis as lower volumes caused falling of the drop due to agitation and higher volumes showed no benefit for the extraction process and were not used.

Effect of interferences: Interfering species at 100 fold excess were added to the Se(IV) solution and the extraction was followed. The following table shows the results:

The severe interferences were due to Ba^{2+}, AsO_3^{3-}, Sb^{3+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Sn^{4+}, Cu^{2+}, Mn^{2+}, Ag^{+}, Fe^{3+}, Co^{2+}, Mg^{2+} and Cr^{3+}.

Using the Chelex-100 resin and passing the solution of selenium containing interfering species at pH = 7 all of the interferences were removed except for Ag^{+} and Mg^{2+}.

TABLE-4
EFFECT OF INTERFERING IONS

Interfering ion	RE % in absorbance	
	Direct determination	Determination by Pre-concentration
Cl^-	-20.1	0.0
NO_3^-	-6.1	0.0
PO_4^{3-}	-3.3	-2.0
SO_4^{2-}	-2.8	-4.4
AsO_3^{3-}	-3.7	-35.6
SiO_3^{2-}	1.9	-11.2
Na^+	-5.1	0.0
K^+	-5.6	0.0
Mg^{2+}	-6.1	-29.3
Ca^{2+}	2.3	-0.5
Ba^{2+}	1.9	-17.1
Al^{3+}	-2.3	-1.5
Sn^{4+}	-4.7	-51.2
Sb^{3+}	-6.5	-25.8
Cr^{3+}	2.3	-28.3
Cu^{2+}	-4.2	-16.6
Hg^{2+}	-13.6	-19.0
Pb^{2+}	-43.9	-30.2
Cd^{2+}	-2.8	-22.9
Fe^{3+}	-0.9	-48.8
Zb^{2+}	-3.7	-8.3
Ag^{2+}	-2.8	-36.1
Mn^{2+}	1.4	-34.6
Co^{2+}	-13.6	-32.2

Analytical figures of merit

Calibration curve was calculated based on 2 mL of aqueous solution of selenium treated at the optimized conditions. The calibration curve was linear in the range of 0.8 to 40 ng/mL selenium with a correlation coefficient of 0.9936 and the sensitivity was 0.25 ng/mL. The detection limit was calculated to be 0.8 ng/mL based on $3S_b$. The relative standard deviation (RSD) for five replicate analysis of 10 ng/mL selenium was 4.9 %. Recovery test was performed using tap water spiked with 10 ng/mL selenium. The result shows a recovery of 96 % for the technique.

Application

Analysis of real sample: In order to evaluate the capability of the method different real samples were analyzed according to the method described earlier. The results are given in Table-2.

TABLE-2
RESULTS OF DIRECT DETERMINATION OF SELENIUM IN REAL SAMPLES

Sample	Value of Se	Sample	Value of Se
Sea water	0.54 ± 0.01 mg/L	Sueade	25 ± 3 μg/g
Milk	93.2 ± 0.7 μg/L	Gamanthus	45 ± 1 μg/g
Atriplex	6.4 ± 0.5 μg/g	Koshia	4.7 ± 0.6 μg/g

Conclusions

The results show a very promising technique for determination of selenium in a variety of samples at ng/mL levels without the needs for any sophisticated device. Apart from having extremely high sensitivity, the procedure is simple, nearly fast and benefits a very low detection limit. By the use a preliminary separation step using a resin, the method could be relatively free from interferences. The experimental parameter such as chemical modifier, organic solvent, pH of aqueous phase, sampling temperature, extraction time and volume of aqueous and organic phase have great effects on the sensitivity of method and should be optimized. The results show that selenium could be determined with high sensitivity and relatively good reproducibility in aqueous samples such as tap water and solid samples.

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