



Determination of Selenium in Biological Samples by Flame Atomic Absorption Spectrometry after Preconcentration on Modified Polyurethane Foam

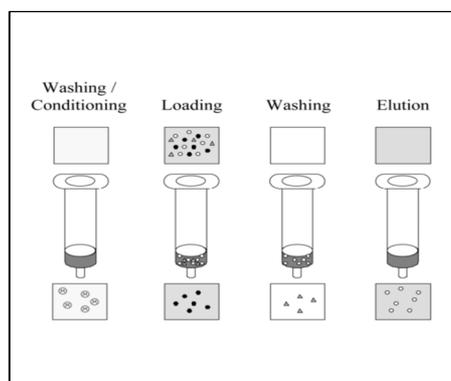
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Received: 27 December 2019 / Accepted: 07 January 2020 / Published Online: 15 March 2020

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ABSTRACT

An analytical method has been proposed based on the separation and determination of selenium(IV) ion using polyurethane foam as a solid sorbent coated with ammonium pyrrolidine dithiocarbamate (APDC). Different factors including the pH of sample solution, time of extraction, volume of sample, and amount of the loaded and unloaded polyurethane foam were examined and a preconcentration factor of 5 was obtained. The interference effects of some additional salts in the solution such as NaCl, FeCl₃, BaCl₂, CH₃COONa and Na₂SO₄ have been investigated. The improved limit of detection (LOD) for the method is 0.064 mg/L. The improved LOD is much lower than the LOD of FAAS and approaching the LOD of GFAAS. The new developed procedure SPE-FAAS has been Found to be successful in separating the complex matrices (human hair, bovine liver, pork liver, bovine muscle) and pre-concentrating selenium ion from real blood sample. The developed method for solid-liquid extraction is convenient, simple, sensitive and of low costs.



Keywords: Preconcentration; Solid phase extraction; Polyurethane foam.

Introduction

Selenium is a chemical element with symbol Se and atomic number of 34. It is a non-metal element with properties that are intermediate between those of its periodic table column elements Sulfur and Tellurium. It rarely occurs in its elemental state in nature or as pure ore compounds. Se (selene means moon in Greek)

was discovered in 1817 by Jones Jacopo, a Brazilian, who noted the similarity of the new element to the previously known tellurium (named for the earth). Selenium is found impurely in metal sulfide ores, where it partially replaces the Sulfur. The chief commercial uses for Se today are in glassmaking and in pigments. Se is a semiconductor and is used in photocells [1, 2].

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Solid Phase Extraction (SPE) Technique

The principle of SPE is similar to that of liquid–liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of two immiscible liquid phases, as in LLE, SPE involves partitioning between a liquid (sample matrix) and a solid (sorber) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorber. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retains the analytes. After passing all the sample through the sorber, retained analytes are subsequently recovered upon elution with an appropriate solvent. The first experimental application of SPE has been started fifty years ago. However, its growing development as an alternative approach to liquid–liquid extraction for sample preparation has been started from the mid-1970s [3-10]. SPE has been extensively used in the past fifteen years for the preconcentration of organic micro pollutants. A solid phase extraction method always consists of three to four successive steps, as illustrated in Fig. 1. First, the solid sorber should be conditioned using an appropriate solvent, followed by the same solvent as the sample solvent. This step is crucial, as it enables the wetting of the packing material and the solvation of the functional groups. In addition, it removes possible impurities initially contained in the sorber or the packaging. Also, this step removes the air present in the column and fills the void volume with solvent. The nature of the conditioning solvent depends on the nature of the solid sorber. The second step is the percolation of the sample through the solid sorber [11, 12].

Depending on the system used, volumes can be ranged from one ml to one L. The sample may be applied to the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample flow-rate through the sorber should

be low enough to enable efficient retention of the analytes, and high enough to avoid excessive duration. During this step, the analytes are concentrated on the sorber. Additionally matrix components may also be retained by the solid sorber; some of them pass through, thus enabling some purification and separation of sample matrix. The third step is washing the solid sorber with a suitable solvent, having a low elution strength, to eliminate matrix components that have been retained by the solid sorber, without exchanging the analytes. A drying step may also be advisable, especially for aqueous matrices, to remove traces of water from the solid sorber. This will eliminate the presence of water in the final extract, which may hinder the subsequent concentration of the extract and/or the analysis in some cases.

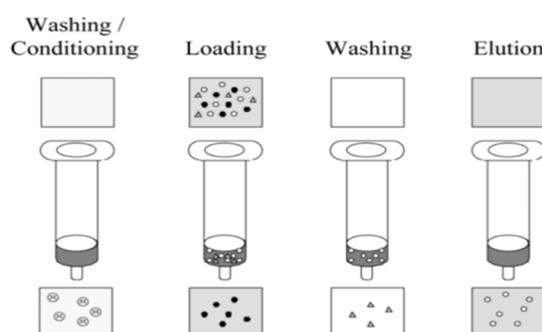


Fig. 1. Steps of solid phase extraction method.

The final step consists in the elution of the analytes of interest by an appropriate solvent, without removing retained matrix components. The solvent volume should be adjusted so that quantitative recovery of the analytes is achieved with subsequent low dilution. In addition, the flow-rate should be correctly adjusted to ensure efficient elution. It is often recommended that the solvent volume be fractionated into two aliquots, and before the elution to let the solvent soak the solid sorber.

Polyurethane Foam as a Sorber

Polyurethane foam (PUF) is a good sorber material in SPE, and it has been the subject of

several review articles. The first paper reporting sorption and recovery of some inorganic and organic compounds from aqueous solution using this sorbent was published in 1970 by Bowen. One year later, Gesser and co-workers suggested the use of untreated PUF for Sorption of organic contaminants from water using a batch technique. Braun and Farag published the first applications of PUF for chromatographic separation in 1972. These studies resulted in a number of papers, involving the use of unloaded and loaded PUF (polyether and polyester type) in separation and preconcentration procedures for the determination of both of inorganic and organic species using different types of analytical techniques [11-14].

Physical and Chemical Characteristics of Polyurethane Foams

Polyurethane foams (PUF) could be defined as plastic materials, in which a proportion of the solid phase is replaced by gas in the form of numerous small bubbles (cell). PUF has been prepared in soft, flexible and rigid form using a variety of polyesters and polyethers. Two important reactions in the preparation of urethane foams are those between isocyanate and hydroxyl compounds (polyester or polyether polyols) and those between isocyanate and water. Interferences during analysis of Se presence of highly interfering matrix are usually occurred, especially when Se is present at very low concentrations such as Se determination in body fluids and tissues [15].

Table 1: Effect of pH on the Se adsorption by unloaded and loaded PUF

pH Scale	Conc. of Se Obtained		Recovery E%	
	Unloaded PUF (20 ppm)	Loaded PUF (10ppm)	Unloaded PUF	Loaded PUF
2	11.7	0.832	41.5	100
4	8.0	5.670	60	43.3
6	17.0	7.620	15	23.8
8	19.0	8.920	5	10.8
10	19.5	10.00	2.5	0
12	20.0	10.00	0	0

The aim of this work is to separate and preconcentrate Se from different matrices in order to analyse Se at low concentration with higher accuracy and simple techniques.

Materials and Methods

Instrumentation and Equipment

An analytical jena model 2260 atomic absorption spectrometer was used for determination of metal concentration, pH meter and commercial polyurethane foam. Chemical Reagents, Solvents and Water Deionized water, purified by Elix3-MilliQ system (Millipore, USA) was used throughout. The metal standard solutions were prepared from a standard solution (1000mg/L). Appropriate dilutions were made, whenever

necessary with deionized water, nitric acid 65%, hydrochloric acid 36%, sodium chloride, ammonium pyrrolidinedithiocarbamate (APDC), tri-n-butylphosphate, Se standard solution 1000 ppm (SeO₂ in HNO₃), isobutyl methyl ketone (IBMK), buffer solution pH=7 phosphate, chloroform.

Preparation of Unloaded PUF

Approximately 5.0 g of flexible PUF was collected and cut into small cubes, washed with distilled water and then soaked in 1M HCl. The foam dried overnight at room temperature [16]. Preparation of PUF Loaded with Smmonium Pyrrolidine Dithiocarbamate Flexible polyurethane foam was cut into small cubes of about 1.00 cm edge, soaked

in 2M hydrochloric acid, and washed with distilled water and acetone and then dried in an oven at 80°C. To 10 g of this foam 10 ml of 2% APDC in try-

n butyl phosphate and 2 % chloroform were slowly added. Stirring the foam into the solution and the chloroform was finally evaporated off [17].

Table 2: Effect of amount of PUF on Se adsorption by unloaded and loaded PUF

PUF Amount (g)	Conc. of Se		Recovery E%	
	Unloaded PUF 25 ppm	Loaded PUF 10ppm	Unloaded PUF	Loaded PUF
1	15.45	7.199	38.2	28.0
2	13.03	3.320	48	66.8
3	8.075	2.017	65.2	79.8
4	5.556	1.068	77.7	89.3

Optimization of the parameters

Effect of pH on the Metal Adsorption

In this study pH values of the Se for 25 ml solutions were adjusted within the range between 2.7-4 by HNO₃ and NaOH for unloaded PUF, whereas the APDC-PUF the pH adjusted within the range of 1.9-2. Then, shaking the foam for 2 hours and eluted by IBMK and measured by FAAS. The percentage amount of the metal ions extracted by the foam

was calculated by difference. If metal ion concentration originally present in the aqueous feed solution before the extraction is (c_o , mass concentration) and its concentration in the aqueous solution after equilibration with the foam is (c). Thus, the extraction percentage (%E) can be calculated by eq. (1) [18].

$$\%E = (c_o - c) / (c_o) \times 100 \quad (1)$$

Table3: Effect of the immersing time on Se adsorption

Time per Hour	Conc. of Se (ppm)		Recovery E%	
	Unloaded PUF (25 ppm)	Loaded PUF 10 (ppm)	unloaded	loaded
2	9.8	6.292	60	37.08
4	11.7	4.033	52.2	59.67
6	17.97	2.744	28.12	72.56
8	19	4.560	24	54.40
24	21.10	6.876	16	31.24

Table4: Effect of sodium chloride on Se adsorption extracted by loaded PUF with APDC

Concentration of NaCl (ppm)	Concentration of Se (ppm)	Abs.	Recovery E%
0	9.87	0.1641	-
5	0.28	0.0047	97.15
10	1.58	0.0263	84.19
100	2.02	0.0458	79.98
1000	3.00	0.0495	70.00
10000	3.10	0.0512	68.90

Effect of the Immersing Time

Se solutions of 25 ppm were measured after periodic times of 2, 4, 6, 8, 10 hours and overnight,

for unloaded PUF. For loaded PUF, Se solutions 10 ppm were measured after 15, 30, and 45, 60, 120 min, 6 hours and overnight.

Effect of the Amount of PUF Sorbent

For unloaded PUF, 1, 2, 3, 4 g of samples were used for 20 ml of Se solutions 25 ppm, whereas the loaded PUF samples of 0.5, 1, 1.5, 2, 2.5 g were used and left for 2 hours and measured.

Effect of the Ligand Concentration

0, 1, 2, 3 % of APDC were studied for Se solutions after 2 hours, and then measured by FAAS after pH adjustment.

Effect of the Solution Volume

10, 20, 30, 40, 50 ml of 25 ppm Se solutions were added to 2.00 g of unloaded PUF and 10, 20, 30, 40, 50 ml of 10 ppm Se solution were added to 1 g

of loaded PUF –APDC and left for 2 hours then eluted by IBMK and measured.

Effect of Interfering Ions

The effect of foreign ions on the sorption of 10 mg of the metal ion in 25 ml of metal solution was examined. The experiments were carried out in beakers containing 25 ml of Se⁴⁺ ion with NaCl ion in portions of 1:0.5, 1:1, 1:10, 1:100, 1:1000. The sodium acetate, sodium sulphate, barium chloride and ferric chloride salts are also used in different concentrations to study their interference with Se ion extraction. The tolerance limit was defined as the amount that caused a deviation more than $\pm 5\%$ in the extraction percentage.

Table 5: Effect of sodium acetate on Se adsorption extracted by loaded PUF with APDC

Conc. of CH ₃ COONa (ppm)	Conc. Of Se	Abs.	Recovery E%
0.00	10.00	0.2055	-
1	1.016	0.0208	89.84
5	3.611	0.0611	63.89
15	3.813	0.0644	61.87
20	3.911	0.0645	60.89
25	4.429	0.0730	55.71

Table 6: Effect of sodium sulphate on Se adsorption extracted by loaded PUF with APDC

Conc. of Na ₂ SO ₄ (ppm)	Conc. of Se (ppm)	Abs.	Recovery E%
0.0	9.881	0.1592	-
0.5	3.702	0.0596	62.98
1	2.246	0.0396	77.54
5	2.136	0.0376	78.64
15	1.702	0.0297	82.98
20	1.004	0.0258	89.96
25	0.391	0.0100	96.09

Table 7: Separation and determination of Se in certified reference biological tissues

Sample	Certified ($\mu\text{g/g}$)	Found ($\mu\text{g/g}$)	Recovery E%	RSD%
Pork liver	0.602	0.480	97.7	2.3
Human hair	0.580	0.530	91.3	6.8
Bovine muscle	0.181	0.207	114.3	1.9
Bovine liver	0.323	0.315	97.5	5.0

Results and Discussion

Unloaded polyurethane foam in different shapes have been successfully used in the determination and separation of the metal ions using different sorption techniques. A lot of studies focused on polyurethane foam published their results in a number of papers, involving the use of unloaded and loaded PUF (polyether and polyester type) in separation and preconcentration procedures for their determination of inorganic and organic species using different analytical techniques [19]. Loaded PUF offers a wider field of applications than unloaded PUF. The loaded ligand could be determined if an extraction process is selective or nonselective, i.e. multi element loaded PUF can also be used in batch or online operation.

In this work, the foam was loaded with chelating agent of dithiocarbamate compounds, among dithiocarbamate $[RR-N-CS(=S)-]$ ammonium pyrrolidine dithiocarbamate (APDC) is most widely employed for sorption of metal ions with IBMK as eluent on PUF. APDC is a pale yellow crystalline solid (m.p. 153°C) with molecular mass of 164.29 g/mol.

On the other hand, isobutyl methyl ketone (IBMK) is used as eluent because it is convenient with APDC complexes, also IBMK is considered to be a better eluent for FAAS than alcohols (ethanol or methanol) or halogenated hydrocarbons (chloroform). Attiyat and Christian have shown that using IBMK instead of other organic solvents as carrier, highest enhancement factors were obtained. In addition, IBMK is almost completely immiscible with water, less polar solvent and the use as eluent in an on line SPE preconcentration system may enhance the sensitivity of FAAS due to the fact that increases the flame temperature, producing lower dispersion and better elution of the complexes than a aqueous eluents. Preliminary experiments between ethanol, methanol, chloroform and IBMK as eluents showed that the last one produced higher and

sharpest signals. In addition with ethanol and methanol as eluents, the baseline was unstable and the absorbance was lower because of the greater dispersion. With chloroform the recorded signals were lower although the baseline was stable thus, IBMK was chosen as eluent [20].

Application of the Proposed Method

Separation and Determination of Se in Certified Reference Biological Tissues (Pork Liver, Human Hair, Bovine Muscle, and Bovine Liver)

The certified reference materials of biological specimens that used are: R.M NO. 184 bovine liver 0553, certified reference GBW human hair 09101, certified reference GBW pork liver 08551, community bureau of reference BCR bovine muscle No.0553.

Digestion of the Samples

Approximately 0.5 to 1.00 g of powdered tissues is weighed into a beaker and 10 ml of concentrated HNO₃ are added and left for 20-24 hours until the digestion is completed. Samples are then diluted to a final volume of 25 ml with distilled water and then the pH was adjusted to 2 then 1 g of APDC-PUF to each samples for 2 hours. After that the foam was removed and squeezed gently then kept to dry then recovered in 25 ml of IBMK after 1 hour and metal ion concentration in each one was determined by using FAAS.

Preconcentration and Determination of Se⁴ in Real Blood Sample

When the analyzed sample contains a highly interfering matrix, or the element to be analyzed present in very low concentration to be correctly analyzed and evaluated, then the technique of the standard additions can be applied to the analytical method used in order to overcome matrix effect. When using the method of standard additions, the unknown sample is split into several samples which are then spiked with different (and known)

quantities of the element under investigation. Then, the relation between the measured instrument response and the analyte concentration is plotted and the intercept of the obtained straight line of the x-axis at which $y=0$ indicates the concentration of the unknown analyte in the original samples. It means that this value given by a/b , the ratio of the intercept and the slope of the regression line [21].

Table 8: Analysis results of real blood sample spiked with Se using loaded PUF with APDC

Se (mg) Added	Found	Abs.
0	0.8611	0.0143
10	10.29	0.1582
12.5	12.86	0.2002
15	15.07	0.2110
25	25.51	0.3460

In this work, the standard addition method was applied, after the digestion step the sample solution was passed through the proposed method; the Se level in human male blood is 0.069 mg/L and after elution with 5 ml of IBMK. The standard addition curve obtained is represented in Fig. 2.

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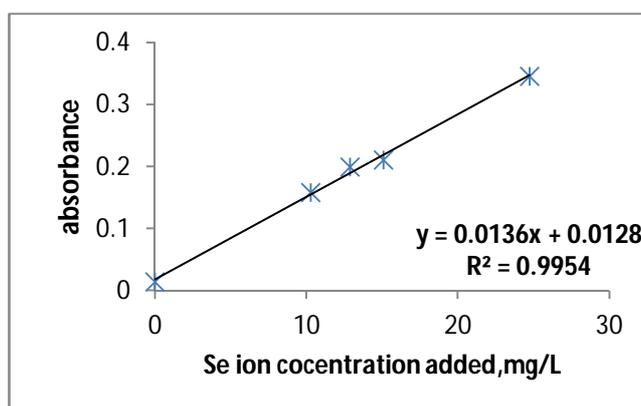


Fig. 2. The standard addition curve obtained for Se in real blood sample eluted by 5ml of IBMK

Conclusion

The proposed analytical method is based on the separation/pre-concentration of Se ions using solid sorbent of polyurethane foam uncoated and coated with ammonium dithiocarbamate. The development of solid-liquid extraction is convenient, simple and low cost; the coating of polyurethane foam by APDC is very simple.

Acknowledgments

The authors would like to thank the University of Benghazi that provided the equipment and materials to accomplishing this work.

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How to cite this article: Ambarak MF, Asweisi AA. Determination of Selenium in Biological Samples by Flame Atomic Absorption Spectrometry after Preconcentration on Modified Polyurethane Foam. *Adv. J. Chem. B.* 2020;2(1):10–17. doi: [10.33945/SAMI/AJCB.2020.1.3](https://doi.org/10.33945/SAMI/AJCB.2020.1.3)