



Determination of Trace Selenium in Urine and Water Samples by Hydride Generation Atomic Absorption Spectrometry After Preconcentration/ Separation with Modified Organobentonite with Dithizone

DONG ZHANG^{1,*} and GUANG SHENG ZHAO²

¹School of Environmental and Chemical Engineering, Shenyang Ligong University, Shenyang 110159, P.R. China

²Liaoning QingYang Chemical Industry Corporation, Liao Yang, P.R. China

*Corresponding author: Tel/Fax: +86 24 24680345; E-mail: sylgdxdong@sina.com

(Received: 4 February 2013;

Accepted: 18 October 2013)

AJC-14264

This paper describes a novel application of modified organobentonite with dithizone (D-O-bentonite) to the preconcentration and separation of selenium using a hydride generation-atomic absorption spectrometry (HG-AAS). A new method for the determination of trace selenium in urine and water has been introduced using a solid-phase extraction agent of D-O-bentonite. Optimal experimental conditions for the adsorption and elution of the selenium, including amount of acid, contact time, eluent volume and co-existing ions have been investigated. The result showed that the selenium could be adsorbed on the D-O-bentonite because of the complexation of dithizone with Se(IV). The adsorbed quantity was affected by the type and amount of acid and contact time. In 50 mL solution, when the dosage of HCl was 20-30 mL and the shaking time was 10 min, the adsorption capacity was 12.09 mg/g. The selenium adsorbed on the D-O-bentonite could be completely eluted by using 5 mL of 1 g/L sodium hydroxide solution. With a preconcentration factor of 100, the detection limit of this method for selenium was 0.0076 µg/L. The proposed solid-phase extraction methodology has been successfully applied to the preconcentration/separation of selenium in the human urine and water samples with satisfied results.

Key Words: Selenium, Preconcentration, Separation, Urine, Water, Dithizone, Organobentonite.

INTRODUCTION

It is well known that the selenium is an essential trace element fundamental to human health. It is an important part of antioxidant enzymes that protects cells against the effects of free radicals that are produced during normal oxygen metabolism. Selenium is also essential for normal functioning of the immune system and thyroid gland and it also has additional important health effects in relation to the immune response and cancer prevention¹. Selenium intake is usually provided by a normal diet and water and it is mainly excreted in urine². Thus, the selenium content in urine is a useful indicator of selenium status in the organism³. So, the determination of selenium in urine and drink water is indispensable. At present, several analytical techniques have been applied to the determination of selenium in biological and water. The most important are fluorometry, voltammetry, hydride generation atomic absorption spectrometry (HG-AAS), hydride generation atomic fluorescence spectrometry, graphite furnace atomic absorption spectrometry and mass spectrometry⁴⁻⁸. Hydride generation atomic absorption spectrometry is usually the method of choice where simplicity, sensitivity and short analysis

time is required⁹⁻¹¹. Although HG-AAS methods is powerful analytical tools for determining trace selenium, pre-concentration and separation techniques are still necessary, due to high salt content in addition to the presence of a number of organic constituents¹².

The widely used techniques for the preconcentration and separation of trace selenium include thiol cotton extraction¹³, coprecipitation¹⁴, adsorption¹⁵, flotation¹⁶, iron (Fe³⁺) oxide/hydroxide-based nanoparticles sol (NanoFe)¹⁷ and on-line ionic liquid dispersive microextraction¹⁸, *etc.* However these conventional techniques have their own inherent limitations such as less efficiency, using health hazardous reagents, sensitive operating conditions, production of secondary sludge and further the disposal is a costly affair. Hence, there is great demand for a sensitive, low-cost and non-polluting pre-separation and enrichment method for determination of trace selenium.

Recently, as a new solid-phase extraction (SPE) agent, the modified organobentonite by dithizone (D-O-bentonite) has been applied to enrichment and separation of lead, cadmium and thallium with satisfied results¹⁹⁻²¹. But the D-O-bentonite use in pre-concentration/separation of selenium has

not been studied. In this work, D-O-bentonite was used as a solid-phase extraction agent to preconcentration and separation of selenium in the human urine and water.

EXPERIMENTAL

Modified organobentonite with dithizone (D-O-bentonite) was prepared according to our previous work^{19,20}. Selenium(IV) stock solution (0.1 mg/mL), (Tian Jin Hua Te Hua Yan Science and Technology Co., Ltd.). The working standard solutions were prepared daily by successive dilution from the stock solution. Standard solution of each interfering ion was prepared from its analytical soluble salt. All the reagents used in this study were of analytical reagent grade. Distilled water was used throughout.

Atomic absorption spectrometer (WYX-9003A, Shenyang Yi Tong Analytical Instrument Co., Ltd.). A selenium hollow cathode lamp was used as a light source, a WHG-102A hydride generator. The operating parameters are as follows: the wavelength for selenium was 196.0 nm; spectral band-pass of 0.4 nm; lamp current is 5.0 mA, Argon gas consumption, 200 mL/min; reductant agent, 1 % NaBH₄ solution; carrier liquid, 1 % HCl.

A constant temperature bath shaker (Jintan Experiment Instrument Factory, Jiangsu China).

Adsorption experiments: A 50 mL calibrated colorimetric cylinder with plug was prepared; Se(IV) solution was added into it. Added to 25 mL HCl and dilution to the mark with water, then 0.5 g of D-O-bentonite was added. Being shaken for 10 min, the solution was separated from the adsorbent using a percolator. Then the concentrations of Se(IV) were determined by the hydride generation-atomic absorption spectrometer and adsorption capacity was calculated.

After adsorption, the Se(IV) loaded adsorption agent was washed with 6 mol/L HCl to remove any unadsorbed Se(IV). The adsorbed Se(IV) was eluted with 5 mL of 1 g/L sodium hydroxide solution. The concentration of the Se(IV) in the eluent was determined by HG-AAS and the recoveries were calculated from concentrations of eluent.

RESULTS AND DISCUSSION

Acid and its dosage: It is known that the acid and its dosage of the medium governing the complexation of dithizone with Se(IV). The acid and its dosage of medium has been the most important variable governing Se(IV) adsorption onto D-O-bentonite. The effect of H₂SO₄, HCl and HNO₃ and their dosage on the adsorption were investigated (Fig. 1). The results showed that adsorption percentage had maximum in HCl when the dosage was 20-30 mL/50 mL. So, in this study, the dosage of HCl was 25 mL/50 mL.

Effect of contact time: The influence of shaking contact time on the adsorption was studied. From the Fig. 2, it could be seen that the amount of adsorption increased with increasing the shaking time. The maximum adsorption capacity was observed after 10 min, beyond which there was almost no further increase in the adsorption. So, the shaking time chose 10 min in this work.

Static adsorption capacity: At room temperature, in 50 mL solution, when the dosage of HCl was 25 mL and the shaking time was 10 min, the adsorption capacity of D-O-bentonite to Se(IV) was 12.09 mg/g.

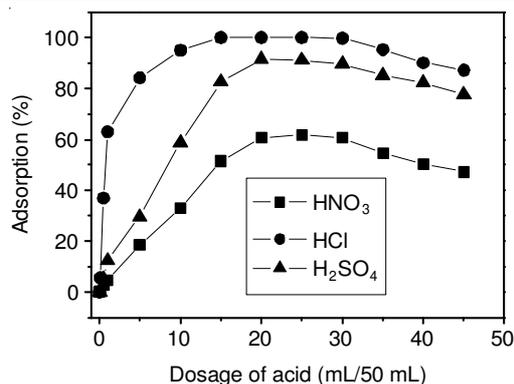


Fig. 1. Effect of acid and its dosage on adsorption

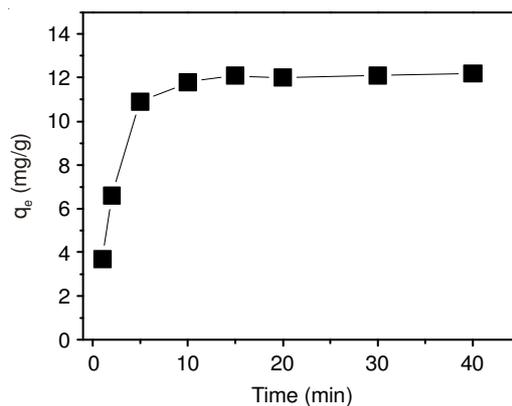


Fig. 2. Effect of contact time on adsorption

Elution: According to the Fig. 1, the adsorption of Se(IV) could be negligible when used acid content were less than 0.1 mL. Therefore, after adsorption under the optimized adsorption conditions, 5 mL of sodium hydroxide solution at different concentration were chosen to be eluents in desorption of Se(IV) adsorbed on D-O-bentonite by shaking 5 min. The results showed that recovery of using 5 mL of 1 g/L sodium hydroxide solution was up to 99 %. So, in this paper, 5 mL of 1 g/L sodium hydroxide solution was chosen.

After elution, the D-O-bentonite was dried under 50 °C and reused 10 times. Its adsorption performance did not decrease, indicating that D-O-bentonite was very stable.

Enrichment factor and detection limit: For studied the possibility of enriching low concentrations of Se(IV) from large volumes, 0.050 µg of Se(IV) was dissolved in various volume (including 20, 50, 100, 250 and 500 mL) of water together. After adsorption, the samples were eluted. The amounts recovered are listed in Table-1. It could be seen that when the solution volume was 500 mL, the recovery was above 90 %. The enrichment factor was 100. The detection limit of Se(IV) was 0.0076 µg/L.

TABLE-1
PRECONCENTRATION AND RECOVERY OF Se(IV)

Volume of the solution (mL)	Quantity in eluent (µg)	Recovery (%)	Enrichment factor
20	0.0481	96.2	4
50	0.0493	98.6	10
100	0.0479	95.8	20
250	0.0483	96.6	50
500	0.0457	91.4	100

Interferences: The effects of common coexisting ions on the extraction of Se(IV) were investigated, various interference ions were added into a 50 mL volumetric flask containing 0.1 µg of Se(IV). The experimental results showed that recoveries of the Se(IV) remained above 90 % even in the presence of ions in the following concentrations: 1000 mg/L for Na⁺, K⁺, NH₄⁺ and NO₃⁻; 500 mg/L for Ca²⁺, Mg²⁺, Al³⁺, Cr(III), Ag⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Pb²⁺ and Zn²⁺; 10.0 mg/L for Cr(VI), Fe³⁺. It will be seen that the recovery of Se(IV) was essentially quantitative in the presence of foreign ions. Therefore these ions produce no interference in the extraction of Se(IV).

Analysis of real samples: The solid-phase extraction method was applied to the preconcentration/ separation and determination of selenium in the human urine samples and tap water. According to normal method¹¹, the samples were pretreatment and the selenium level found in the samples. The results obtained are reported in Table-2. The recoveries were 92.5-106.9 %.

TABLE-2
DETERMINATION OF SELENIUM IN
URINE AND WATER SAMPLES (n = 6)

Samples	Added (µg/L)	Found (µg/L)	RSD (%)	Recovery (%)
Urine sample 1	0	38.34	2.24	–
	10	49.03	4.61	106.90
	50	87.22	1.22	97.76
Urine sample 2	0	27.51	2.37	–
	10	36.76	3.28	92.50
	50	76.39	2.01	97.76
Tap water	0	0.2080	4.69	–
	0.1	0.3019	5.88	93.90
	0.5	0.7022	3.65	98.84
Well water	0	21.92	2.96	–
	10	31.58	1.07	96.60
	50	70.44	3.64	97.04

Conclusion

We have proposed a novel application of modified organo-bentonite with dithizone (D-O-bentonite) to the preconcentration

and separation of selenium. In HCl medium, the adsorption time was 10 min, the selenium could be adsorbed on the D-O-bentonite. The adsorbed capacity was 12.09 mg g⁻¹. The selenium adsorbed on the sorbent could be completely eluted by using 5 mL of 1 g/L sodium hydroxide solution. The proposed method has been applied to the pre-concentration/ separation of selenium in human urine, tap water and well water samples with satisfactory results.

REFERENCES

- M.P. Rayman, *Lancet*, **356**, 233 (2000).
- O.M.S. Guñas Para la Calidad del Agua Potable, Vol. 2, Organización Panamericana de la Salud, Washington, Ch. 14, p. 142 (1987).
- W. Wasowicz and B.A. Zachara, *J. Clin. Chem. Clin. Biochem.*, **25**, 409 (1987).
- Y.K. Lu and H.W. Sun, *J. Insturm, Anal. Chim. Acta*, **19**, 190 (2000).
- I. Marawi, J. Wang and J.A. Caruso, *Anal. Chim. Acta*, **291**, 127 (1994).
- H. Elfering, J.T. Anderson and K.G. Poll, *Analyst*, **123**, 669 (1998).
- D. Beauchemin, *J. Anal. At. Spectrom.*, **13**, 1 (1998).
- P.N. Vijan and G.R. Wood, *Analyst*, **101**, 966 (1976).
- P. Smichowski and S. Faryas, *Mikrochem. J.*, **67**, 147 (2000).
- A.G. Howard and C. Salou, *J. Anal. At. Spectrom.*, **13**, 683 (1998).
- D.L. Tsalev, L. Lampugnani, A. D'Ulivo, I.I. Petrov Jr., R. Georgievac, K. Marcuccid and R. Zambonid, *Microchem. J.*, **70**, 103 (2001).
- A.K. Das, R. Chakraborty, M.L. Cervera and M. Guardia, *Mikrochim. Acta*, **122**, 209 (1996).
- L. Marin, J. Lhomme and J. Carignan, *Talanta*, **61**, 119 (2003).
- M. Tuzen, K.O. Saygi and M. Soylak, *Talanta*, **71**, 424 (2007).
- K. Pyrzyńska, P. Drzewicz and M. Trojanowicz, *Anal. Chim. Acta*, **363**, 141 (1998).
- M.A. Akl, D.S. Ismael and A.A. El-Asmy, *Microchem. J.*, **83**, 61 (2006).
- G. Zelmanov and R. Semiat, *Sep. Purif. Technol.*, **103**, 167 (2013).
- E.M. Martinis, L.B. Escudero, P. Berton, R.P. Monasterio, M.F. Filippini and R.G. Wuilloud, *Talanta*, **85**, 2182 (2011).
- D. Zhang, J. Zhang, L.Z. Xu and G.J. Ren, *Met. Anal.*, **28**, 57(2008).
- D. Zhang, G.J. Ren and L. Z. Xu, *J. Chem. Ind. Eng.*, **59**, 1535 (2008).
- D. Zhang and Y. Cheng, *Asian J. Chem.*, **24**, 5279 (2012).