Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(8):73-77
(http://derpharmachemica.com/archive.html)

Ultra-trace analysis of selenium by HGAAS: A plausible reduction approach using silver nanoparticles

Ruttiya Poonyaka and Saksit Chanthai*

Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

---

ABSTRACT

In general, selenium that is determined by most spectroscopic techniques usually results in total selenium (Se). Relatively few analytical methods have been applied for the selective determination of the different selenium species present in various sample matrices. This review aims to propose the method development of Se under catalytic activation of silver nanoparticles in association with flow injection-hydride generation atomic absorption spectrometry (FI-HGAAS). In this aspect, colloidal silver is an alternative choice as the reducing agent, and of particular interest due to a lot of distinctive properties such as good conductivity, chemical stability, and catalytic and antibacterial activity. Silver nanoparticles were freshly prepared and calibrated by visible absorption spectrum. This will demonstrate the catalytic activation of Se speciation by using Ag nanoparticles in comparison with borohydride solution indicating certainly increase in its sensitivity for selenium analysis.

Key words: selenium, silver nanoparticles, hydride generation, ultra-trace analysis

---

INTRODUCTION

Water, which is odorless, tasteless, transparent liquid, is almost colorless in nature, in fact, with ultra-trace amounts of chemicals but exhibits a bluish tinge in large quantities such as deep sea water or water vapor in the sky. Most of the living tissue of a human being is made up of water; it constitutes about 92% of blood plasma, about 80% of muscle tissue, about 60% of red blood cells, and over half of most other tissues. It is also an important component of the tissues of most other living things [1]. The presence of nutritive and toxic elements in water samples depends on type of water, the accumulation of metals varies greatly both between species and cultivars [2]. Elemental water composition data are important to both consumers and health professionals, and recent water labeling legislation has highlighted this importance.

For human body selenium is essential element playing important role in body antioxidation system; it is considered individual antioxidant that can cooperate with other antioxidants, such as C and E vitamins and in processes protecting the cells from free radicals. In such manner selenium protects a body from development of cancer, cardiovascular diseases and masculine sterility [3]. Selenium participates in thyroid hormone metabolism and immune system, inhibits virulence, and slows down the development of AIDS through reducing the speed of HIV development. Furthermore, it can reduce the risk of spontaneous abortions as well [4]. Balanced content of selenium in human food helps in the case of complications connected with diabetes and also affects the prevention of asthma. Through free radicals inhibition selenium moderates harmful effects of radiation [5]. Selenium is important for proper function of cerebral neurotransmitters and reduces epileptic waves at children. Selenium deficiency is connected with acceleration of senility and development of Alzheimer´s disease. It also affects in a positive manner human mind and mental wellness [6].

However, the levels of selenium in water are highly variable, depending on the location. In toxicology it has long been known that great differences in toxic properties occur among the various species of an element, because they follow different metabolic pathways. In particular, selenium absorption, retention and distribution within the body, and the amounts, forms and routes of excretion vary with the chemical forms and amounts of the element ingested [7]. It can be found naturally in four valence states including selenide, Se (-II), elemental Se(0), selenite, Se(IV) and selenate, Se(VI). Although precise feeding comparisons of the relative toxicity or nutritional activities of the different selenium compounds have not yet been made, it is known that selenite is more toxic than selenate [8]. Thus, the study of the selenium species in water would provide a better understanding of the requirements of this element in the living system.

Most methods for selenium determination were reported in total selenium [9]. However, relatively few analytical methods have been applied for the selective determination of the different selenium species present in various matrixes. Chromatographic techniques coupled with different detector systems have been extensively used for the separation and determination of all selenium species. This approach minimizes interferences from the matrix. However, errors may arise from a lack of efficiency in the separation, e.g. due to incomplete retention on the column, decomposition of the species, incomplete recovery of the eluate or peak overlap [10]. There are few electrochemical methods that can be applied for selenium speciation in biological fluids, or electrochemical methods that can be applied for selenium speciation in biological fluids and environmental samples [9,11,12]. However, the complete mineralization or conversion of Se(VI) to Se(IV) (the electro active form) makes sample preparation more complex and increases the risk of sample contamination and of losses of selenium. Spectrofluorimetric methods have been also used for the determination of the different inorganic species of selenium [9,11]. Although very sensitive, an initial acid digestion step is required for this technique and the analytical figures of merit may be markedly influenced by an extractant, temperature and the hydrogen ion concentration. The detection of methyl selenide species is carried out after gas chromatographic (GC) separation on the basis of their different retention times with a wide variety of the detection methods such as electrothermal atomic absorption spectrometry (ETAAS) [13] and microwave-induced helium plasma detection [14]. The most commonly applied technique for inorganic selenium species determination is based on hydride generation (HG) with atomic absorption spectrometry (AAS) [11]. In all of these techniques, Se(IV) is determined directly after derivatization process, whereas Se(VI) is determined by difference after reduction, and the organic selenium content is also determined by difference after destroying organic compounds by oxidation. These techniques are highly sensitive and yield detection limits in the ngL^{-1} and are not subject to major interferences or high background noise levels [15]. The severe and systematic imprecision reported for this technique are almost due to the use of improper sample decomposition [9]. The tolerance limits for other hydride-forming elements in the determination of selenium could be improved by one or two orders of magnitude by using a flow injection (FI) instead of a batch system and optimizing the analytical conditions systematically [16]. According to the literature on total selenium determination in biological and environmental materials, the combination of FI techniques with HGAAS is an accepted method [17-22]. To our knowledge, only one paper has described the FI closed system with thermal heating at 140°C for the determination of Se(IV) and Se(VI) by HGAAS with on-line pre-reduction of Se(VI) to Se(IV) [23]. No losses of selenium occur and the method has been successfully applied to the speciation of both inorganic species.

Even, FI-HGAAS can be used to determine Se(IV) only from the mixture of Se(IV) and Se(VI) solution, and the concentration of Se(VI) can be calculated by the difference between total inorganic Se and Se(IV). In the present study, for its reducing reason the prevention of the back-oxidation of Se(IV) to Se(VI) is introduced. Only Se(IV) forms its hydride compound, and so Se(VI) must be completely pre-reduced to Se(IV), if total selenium is needed to be determined. When $NaBH_4$ is used as a common reducing agent for the determination of selenium by HGAAS, only SeH_2 is formed. The Se(IV) redox state is determined directly. Total inorganic Se is determined after quantitative reduction of selenate to selenite. Considering that HGAFS cannot detect Se(VI) directly, Se(VI) has to be certainly reduced to Se(IV) first. Thus, the pre-reducing step to convert Se(VI) to Se(IV) is still necessary.

Pre-reducing agent is normally achieved using HCl with various concentrations and heating temperatures. For instance, the reduction with HCl solution in a closed system at room temperature takes almost a week [24]. If its reduction step works at elevated temperature (90-100°C), it is faster [25,26]. The reaction time usually varies from 20 to 45 min [25,27]. However, too long heating can lead to the appearance of elemental Se [24,28]. The pre-reduction can also be using a warm co-reducing agents i.e. KBr and HBr [29] or a mixture of KBr and HCl [29,30], thiourea with the addition of HCl [31] and a 20%(w/v) KI solution with HCl and thiourea. The later system restricts the interference of some transition metals [27].

Table (1): Literature reviews for speciation analysis

Sample	Analyst	Technique	LOD	Pre-reducing agent	Recovery (%)	Ref.
water and garlic	Se species	on-line ionic liquid dispersive microextraction coupled to electrothermal atomic absorption spectrometry (ETAAS)	15 ng L^{-1}	HCl 5 mL, 100°C, 20 min	Se(IV) 96.0 Se(VI) 104	41
garlic	total Sb, Se, Te and Bi	HGAFS	1.0 ng g^{-1}	HCl and KBr, 70-75°C, 30 min	Se(IV) 94.3 Se(VI) 94.0	42
natural water	Se species	graphite furnace atomic absorption spectrometry (GFAAS)	0.03 µg L^{-1}	-	Se(IV) 99.0 Se(VI) 96.0	43
agricultural drainage water	Se species	ion chromatography-HGAAS	Se(IV) 0.68 mg L^{-1} Se(VI) 0.55 mg L^{-1}	HCl 130 °C	Se(IV) 93.1 Se(VI) 108	44
vegetable, pulse and cereal	As, Sb, Se, Te and Bi	HGAFS	0.7 ng g^{-1}	HCl and KBr, 70-75°C, 30 min	95.4 - 97.0	45

Table (2): Literature reviews for speciation analysis of inorganic selenium by HGAAS

Sample	Condition for HG	Pre-reducing agent	Digestion method	LOD	Ref.
water and orange juice	0.75% (w/v) $NaBH_4$/0.5 mol L^{-1}NaOH carrier, 10.0% (v/v) HCl	10%(v/v) HCl/HBr	microwave (MW), prereduction	Se(IV) 0.25 mg L^{1} Se(VI) 0.30 mg L^{-1}	46
beef, milk, fish, chicken, rice, wheat flour and egg	0.1%(w/v) $NaBH_4$/0.025%(w/v) NaOH carrier,1.2 mol L^{-1} HCl	6 mol L^{-1}HCl 15 mL at 90°C, 30 min (heat block)	heat block, soak overnight in HNO_3 at 90 °C, 2 h add 5 mL HNO_3/H_2O_2	2.0-7.0 µg kg^{-1}	47
tomato	0.6%(w/v) $NaBH_4$/0.5%(w/v) NaOH carrier, 10 mol L^{-1} HCl	7 mol l^{-1}HCl 4 ml at 80 °C, 30 min (heat block)	autoclaves: 140 °C, 120 min add HNO_3/H_2O_2	0.00049 mg L^{-1}	48
lemon juice and geothermal water	0.5%(w/v) $NaBH_4$/0.5%(w/v) NaOH carrier, 1%(v/v) HCl	Se(VI),12 molL^{-1} HCl Se(IV), 4 molL^{-1} HCl	microwave (MW)	Se(IV) 1.0 µg L^{-1} Se(VI)1.5 µg L^{-1}	49
urine	0.3%(w/v) $NaBH_4$/0.05%(w/v) NaOH carrier, 1 mol L^{-1} HCl	32%(v/v) HCl 3 mL	microwave (MW)	3 µg L^{-1}	50

Speciation analysis of inorganic Se

Speciation is the identification and quantitative determination of different forms or phases in which a given element occurs in a given substance, established in so-called speciation analysis [32]. In the context of the study of water, the form or phase of occurrence of a given element can be defined according to different criteria [33,34]: (i) a certain compound or degree of oxidation of a given element, their identification and determination is the subject of individual or detailed speciation, (ii) certain functional groups or forms of particular biochemical or hydrogeochemical functions: bioavailable, mobile, exchangeable forms and others, (iii) according to analytical procedures used for their identification and determination: reagents, instrumental procedures, etc. (iv) according to the physical distribution of substances: suspended and dissolved forms (similarly, according to cytological presence of elements - the forms of the elements as they occur in different cellular organs), and (v) combining compounds of similar properties, or a similar form, e.g. combining compounds with a given element at the same oxidation degree, e.g. the speciation analysis of Se(IV)/Se(VI); this is a pragmatic approach when it is impossible or too difficult to perform individual speciation analysis.

The significance of the determination is not only the total content of a given element but its speciation follows from different toxicological effects of different speciation forms of a given element on the ecosystem. For example the inorganic compounds of selenium are a few hundred times more toxic than the methylated forms. The speciation analysis of selenium using atomic absorption spectrometry with generation of hydrides is based on the established different kinetics of the reaction of hydride generation by elements at different degrees of oxidation, depending on the pH of the reaction environment.

Nevertheless, few analytical methods for the selective determination of the Se species include inductively coupled plasma-mass spectrometry (ICP-MS), chromatographic techniques coupled with different detectors, or flow injection-hydride generation atomic absorption spectrometry (FI-HGAAS). However, ICP-MS approaches interferences between the dominant isotope of Se and the argon dimer (both mass 80) [35]. Chromatographic techniques rather give any decomposition of species and peak overlapping problems [36].

Hydride generation is a chemical derivatization technique in which some elements of the periodic table mentioned above form their volatile hydrides as indicated in the following reactions[37]when they react with sodium borohydride, $NaBH_4$, as a strong reducing agent and hydrochloric acid, HCl, as a carrier solution.

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8H^+$$
$$8H^+ + M^{m+} \rightarrow MH_n + H_2(\text{excess}) \rightarrow M^{m+}: \text{Se, As, Sb}\ldots.$$

Here, M is the desired metal, *m* is the oxidation state of the metal and does not necessarily equal to nMH_n which is the volatile metal hydride. In this technique, elements are separated from other accompanying materials in the form of gaseous hydrides and are introduced to the sample cell for atomization leaving the sample matrix in the liquid waste. Thus, spectral and chemical interferences can be eliminated. Therefore, the significant increase in sensitivity, by 10-100 folds, over commonly used liquid sample introduction techniques has been reported [38-40].

However, relatively few analytical methods have been applied for the selective determination of selenium species present in water and food samples. In further study, higher sensitivity of Se analysis is a main subject to develop under other catalytic activation of any reactive nanoparticles in association with modern atomic spectrometry.

Acknowledgements

This review article is financially supported by the Higher Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission, through the Food and Functional Food research Cluster of Khon Kaen University, and Materials Chemistry Research Center, and Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education are gratefully acknowledged.

REFERENCES

[1] Niedzielski P., Siepak M., Siepak J., Przybyłek J., *Polish Journal of Environmental Studies*, **2002**, 11, 219-224.
[2] Miteva E., Maneva S., Hristova D., Bojinova P., *Journal of Phytopathology*, **2001**, 149, 179-184.
[3] Mach I., *Selenium-nutritive deficiency and efficacy in supplements.* Vitamins, Nutrition and Diagnostics. The Abstract Book. Univerzita Tomáše Bative Zlíně. **2008**.
[4] Rayman M.P., *The Lancet*, **2000**, 356, 233-241.
[5] Surai P.F., *Selenium in nutrition and health.* Nottingham University Press, **2006**.
[6] Kvíčala J. *Internímedicína pro praxi*, **2003**, 7,354-359.

[7] Underwood E.I., *Selenium In: Trace Elements in Human and Animal Nutrition.* Academic Press, New York, **1977**.
[8] Frost D.V., *Critical Reviews in Toxicology*, **1972**, 1, 467-513.
[9] Sanz Alaejos M., Diaz Romero C., *Chemical Reviews*, **1995**, 95, 227-257.
[10] Raptis S.E., Kaiser G., Tolg G., *Fresenius' Zeitschriftfür Analytische Chemie*, **1983**, 316, 105-123.
[11] Mufioz R.O.,DonardO.F.X.,C~maraC.,OuevauvillerP.,*AnalyticaChimicaActa*,**1994**, 286, 357-359.
[12] Bryce D.W., Izquierdo A., Luque de Castro M.D., *Analytica ChimicaActa*, **1995**, 308, 96-101.
[13] Jiang S., Robberecht H., Adams F., van der Berghe D., *Toxicological & Environmental Chemistry*, **1983**, 6, 191-201.
[14] Olsen K.B., Sklarew D.S., Evans J.C., *SpectrochimicaActa Part B: Atomic Spectroscopy*, **1985**, 40, 357-365.
[15] Verlinden M., Deelstra H.A., Adrianensses E., *Talanta*, **1981**, 28, 637-646.
[16] Welz B., Stauss P., *Spectrochimica Acta Part B: Atomic Spectroscopy*, **1993**, 48, 951-954.
[17] Chan C.C., *Analytical Chemistry*, **1985**, 57, 1482-1485.
[18] Fang Z., XuS., Wang X.,Zhang S., *Analytica Chimica Acta*, **1986**, 179, 325-340.
[19] Ikeda M., *Analytica Chimica Acta*, **1985**, 170, 217-224.
[20] Pyen G.S., Browner R.F., *Applied Spectroscopy*, **1988**, 42, 508-512.
[21] Negretti de Bratter V.E., Bratter P.,Tomiak A., *Journal of trace elements and electrolytes in health and disease*, **1990**, 4, 41-48.
[22] Xiu W.,Fang Z.,*Kexue Tongbao*, **1986**, 31, 11.
[23] Cobo F.M.G., Palacios M.A., Chmara C., *AnalyticaChimicaActa*, **1993**, 283, 386-392.
[24] Pyrznska K., Siepak J., Kowalczuk Z., *Journal of Environmental Studies*, **1999**, 8, 183-187.
[25] Olivas R.O., Donard O.F.X., Camara C, *Analytica ChimicaActa*, **1994**, 286, 357-370.
[26] Cobo M.G., Palacios M.A., Camara C., Reis F., *Analytica Chimica Acta*, **1994**, 286, 371-379.
[27] Dulivio A., *Analyst*, **1997**, 122, 117-144.
[28] Pyrzynska K., *Analytica Chimica Acta*, **1998**, 363, 141-146.
[29] Brindle I.D., Lugowska E., *Spectrochimica Acta Part B: Atomic Spectroscopy*, **1997**, 52, 163-176.
[30] D'Ulivo A., *Journal of Analytical Atomic Spectrometry*, **1989**, 4, 67-70.
[31] Niedzielski P., Siepak M., Siepak J., Przybyalek J., *Journal of Environmental Studies*, **2002**, 11, 219-224.
[32] Lobinski R., *Applied Spectroscopy*, **1997**, 51, 260A-278A.
[33] Hulanicki A., *Speciation in waters and sediments*.ed. J. Siepak, Speciation analysis of metals, in Polish 7-18, Wyd.UAM, Poznan **1998**.
[34] Bernhrad M., Brincman F.E., Sadler P.J, *The Importance of Chemical "Speciation" in Environmental Processes*, Springer-Verlag, **1986**.
[35] Jackson B.P., Miller W.P., *Environmental Science & Technology*, **1999**, 33, 270-275.
[36] Raptis S.E., Kaiser G., Tolg G., *Fresenius Journal of Analytical Chemistry*, **1983**, 316, 105-123.
[37] Dedina J., Tsalev D., *Hydride Generation and Atomic Absorption Spectrometry*. Wiley and Sons, New York, **1995**.
[38] Thakur M., Pandey S., Meweda A., Shah R., OzaG., Sharon M., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2003**, 109, 344-347.
[39] Maria B.S., Devadiga A., Kodialail V.K.S., Saidutta M.B., *Cross Mark*, **2015**, 5, 755-762.
[40] Sohn E.K., Johari S.A., Kim T.G., Kim E., Lee J.H., Chung Y.S., Yu I.J., Hindawi, *BioMed Research International*, **2015**, 2015:893049. doi: 10.1155/2015/893049.
[41] Martinis E.M., Escudero L.B., Berton P., Monasterioa R.P., Filippini M.F., Wuilloud R.G., *Talanta*, **2011**, 85, 2182-2188
[42] Matos Reyes M.N., Cervera M.L.,de la Guardia M., *Analytical and Bioanalytical Chemistry*, **2009,** 394, 1557-1562
[43] Tuzen M., Saygi K.O., Soylak M., *Talanta*, **2007**, 71, 424-429
[44] Goldberg S., Martens D.A., Forster H.S., Herbel M.J., *Soil Science Society of America Journal*, **2006**, 70, 41-47.
[45] Matos-Reyes M.N., Cervera M.L., Campos R.C., de la Guardia M., *Food Chemistry*, **2010**, 122, 188-194.
[46] Gallignani M., Valero M., Brunetto M.R., Burguera J.L., Burguera M., Petit de Penã Y.,*Talanta*, **2000**, 52, 1015-1024
[47] Sigrist M., Brusa L., Campagnoli D., Beldoménico H., *Food Chemistry*, **2012**, 134, 1932-1937.
[48] Hegedűs O., Hegedűsová A., Šimková S., Pavlík V., Hegedűs K.J.O., Hegedűsová A., ŠimkováS., Pavlík V., Jomová K., *Journal of Biochemical and Biophysical Methods*, **2008**, 70, 1287-1291
[49] Burguera J.L., Carrero P., Burguera M., Rondon C., Brunetto M.R., Gallignani M., *SpectrochimicaActa Part B: Atomic Spectroscopy*, **1996**, 51, 1837-1847
[50] Li F., Goessler W., Irgolic K.J., *Analytical Communications*, **1998**, 35, 361-364.