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Recent Developments in Speciation Analysis of Selenium

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The review concerns the specific problems of selenium speciation analysis. The distribution of the element, sample storage, its decomposition prior to analysis as well as the preconcentration and separation techniques is discussed. Recent developments in the determination of inorganic and organic selenium compounds are presented.

Przegląd dotyczy problemów związanych z badaniem specjacji selenu. Przedyskutowano formy występowania pierwiastka, pobieranie, i techniki mineralizacji próbek do analizy oraz metody zatężania i wydzielania selenu. Przedstawiono ostatnie dane literaturowe dotyczące zastosowania różnych metod analitycznych do oznaczania nieorganicznych i organicznych połączeń selenu w próbkach naturalnych.

The physiological effect of selenium have been realized; there is a narrow concentration range between selenium as an essential nutrient and as a toxic substance for animals and humans [1]. This element is contained in the enzyme glutathione peroxidase, which affords cells protection against oxidative damage [2,3]. The antagonistic selenium action towards toxic metals, such as cadmium, arsenic, mercury and tin, has been summarized by Magos and Webb [4]. On the other hand, there is also some evidence that in higher concentration toxicity effect of selenium can occur [2,5]. In 1980 the National Academy of Science of the USA proposed daily intake of 50–200 μg Se for adult humans as safe and adequate. Now, the recommended dietary allowances is 55 μg for women and 70 μg for men [6]. The maximum allowed selenium concentration in drinking water recommended by WHO is 10 μg l^{-1} [7]. The toxicity and essential nature of Se in the environment depends on its chemical forms, with different toxicity for organic and inorganic compounds.

Selenium naturally exists in several oxidation states: -II, 0, IV, VI. The most important inorganic selenium species in environmental matrices are selenites

(SeO_3^{2-}) and selenates (SeO_4^{2-}). Selenites have high affinity for metal hydroxide and are adsorbed onto insoluble compounds [8]. Under acidic conditions, selenites are rapidly reduced to elemental red selenium by mild reductants such as ascorbic acid or sulphur dioxide. Alkaline and oxidizing conditions favor the formation and stabilization of selenate.

During the last years several organic selenium compounds were identified in biological samples (animals, plants, microorganisms) [2,8]. Among these compounds are dimethylselenide (DMSe), dimethyldiselenide (DMDSe), trimethylselenonium ($TMSe^+$), selenoamino acids, selenoenzymes and their derivatives. A number of bacteria are able to transform inorganic selenium species into volatile DMSe and DMDSe, which are exhaled and excreted through the skin. TMSe+, the major product of selenium metabolism, leaves the body of humans in urine. These methylation reactions are considered to be detoxification steps, because DMSe and $TMSe^+$ are less toxic than other selenium compounds.

Apart from natural sources (mainly metal–sulphur minerals) selenium compounds can widely spread throughout the environment as a result of combustion of coals, industrial and agricultural processes. Many problems in selenium speciation analysis are associated with the low concentration of each species to be determined. Total selenium levels in environmental samples range from 0.1–400 $\mu g\ l^{-1}$ in natural waters to about 1 $ng\ l^{-1}$ in the atmospheric aerosols and 1–80 $\mu g\ g^{-1}$ in soils, but depending on geological factors, ground water may reach much higher concentrations up to 6 $mg\ l^{-1}$ [9,10]. Thus the development of reliable techniques to study the speciation of selenium in waters, soils and biological materials has been a necessary step to understand the biochemical cycle mobility and uptake of selenium as well as its toxicity.

Sampling and storage

Various factors affect the loss of selenium or interconversion of one species into another during sampling, sample storage and analysis.

Sampling of the alkylselenium compounds is based on cryogening trapping system. Effects of cryogenic trap temperature and several adsorbents on the collection efficiency have been investigated by Jiang *et al.* [11]. The volatile selenium species are then thermally desorbed [12,13] or extracted from the adsorbent with organic solvents [14] prior to gas chromatography (GC) analysis. However, when high volume of air sample is used some losses of selenium may occur [15].

During a storage of selenium solutions, adsorption, desorption, volatilization processes *etc.* may occur, altering the original concentration. These processes depend on pH, ionic strength, presence of dissolved gases (*e.g.* oxygen), temperature, container material and the ratio of surface area per unit volume [9,10,16,17]. Se(VI) is more stable than Se(IV) in aqueous solutions and less dependent on the acidic conditions of the sample. Use of polyethylene or Pyrex containers and adjustment to pH 1.5 (with H_2SO_4) provided preservation conditions for Se(IV) and Se(VI) in natural water samples [16]. The optimum temperature at which there is no significant risk of selenium losses at 10 and 50 $\mu g\ l^{-1}$ concentration over the twelve months

tested was -20°C [10]. Samples stored at this temperature need not to be acidified, which is an advantage if acids interfere with a detection method, such as HNO_3 with hydride generation (HG). The maximum time of sample storage at room temperature (at pH 6) was two months and 9 months in polyethylene and PTFE containers, respectively [10].

Also the containers walls can give off blank, if the vessel is not carefully cleaned. Thus, *e.g.*, 0.2 and 0.8 ng cm^{-2} of Se were given off from PTFE containers in one week upon leaching with HNO_3 (1:1) and HCl (1:1), respectively [18]. Cleaning of the vessel by soaking in 0.5%(V/V) HNO_3 and careful rinsing with deionized water is a suitable preatreatment technique [9,18].

Decomposition

For the destruction of organic and biological materials combustion in a pure oxygen atmosphere in the closed systems and dynamic mode have been applied [19,20]. During that process selenium is volatilized as SeO_2, condensed in a cold finger and then dissolved with HNO_3 or HCl, which ensures complete dissolution. From metals selenium can rapidly be volatilized in a stream of oxygen at 1100°C using a tube furnace and collected in a U-shaped trap, which is cooled with liquid nitrogen [21]. Compounds containing selenium can be also decomposed in an oxygen plasma of a high frequency discharge [18] and in a plasma asher run with low power [22].

Wet digestion with nitric acid or mixtures of this acid with other oxidizing agents [23–26] and ultraviolet irradiation [27,28] have been used for decomposition of selenium compounds. The comparison between the efficiencies of six destruction methods for various organoselenium compounds from water followed by their determination with HG method was presented by Ornemark *et al.* [29]. They found that the use of peroxodisulphate at pH≥2 is the most efficient. This method decomposed also very acid-resistant trimethylselenonium salts, which were not decomposed by permanganate or by oxidative UV-irradation. Selenomethionine and $TMSe^+$ from biological samples can only be converted into inorganic selenium after a nitric–sulphuric–perchloric acid digestion at 310°C [30]. A critical review of some digestion methods for selenium compounds is given [31–33]. The mechanized decomposition techniques for organic and inorganic samples were proposed by Knapp [34].

Conversion of Se(VI) to Se(IV)

Most methods for selenium speciation analysis require the conversion of selenium species into Se(IV), because Se(VI) does not react with most of the complex forming agents used for spectrophotometric determinations. Moreover, the hydride generation process is the most efficient when selenium occurs as Se(IV). For this reason after decomposition of organoselenium species, prior reduction of any selenate present in the sample is necessary. Although several reducing agents have been proposed, such as KI and HBr [35], the reduction with hydrochloric acid is mostly applied. This approach suffers, however, from the loss of information on the original

selenium species present in the sample and depends on many factors, *e.g.*, concentration of HCl, reduction time, temperature and accompanying metal ions. Statements on the concentration of HCl range from 4 mol l^{-1} to 7 mol l^{-1} [17,36]. The reduction time varies from 20 to 45 min at boiling temperature of the solution [37,38]. However, if the sample is boiled for too long, reduction to elemental selenium may result [17] or selenium may be lost owing the formation of volatile selenium chloride or other volatile compounds [10]. On-line reduction in a closed system at 140°C proposed by Cobo *et al.* [39] prevents losses of selenium during this step.

A microwave energy source in conjunction with a flow injection system was applied also for reduction of Se(VI) [40]. Automation of the system has resulted in much shorter analysis time, with greater reduction efficiencies than conventional heated digestion methods.

Preconcentration and separation

Despite the very sensitive analytical methods available for selenium, it is often impossible to make its direct determination at the concentration levels present in natural samples. The preconcentration step improves the detection limit and increases the precision of the results. Moreover, this can also serve as a convenient method for removal of the matrix. Flow injection analysis (FIA), with on-line sample pretreatment procedures, offers improvements, particularly in separation and preconcentration processes [41–45].

The formation of SeH_2 in the HG technique has come into general use for separation of selenium from non-volatile matrix components. However, the presence of several elements, also forming volatile hydrides, may be the source of errors during the transport and atomization steps [46–49]. To avoid the use of sodium tetrahydroborate as a reducing agent, which is unstable, an electrochemical HG technique has been developed [50]. The enrichment of hydrogen selenide can be achieved using cold trap system at liquid nitrogen temperature [28,29] or appropriate adsorbing solution [49]. Also the commercial graphite furnaces (in AAS method) can be used as both the trapping medium and atomization cell [49,51,52].

Coprecipitation by hydroxides of metals, such as Fe(III) and La(III) have proved to be an effective approach for improving the sensitivity of the determination of selenium trace amounts [53,54]. Batch mode in this technique is rather tedious and time consuming. Recently, Hansen *et al.* [55] have described an automated procedure for the determination of Se(IV), which combines hydride generation atomic absorption spectrometry (HG-AAS) with on-line preconcentration of the analyte by coprecipitation with the generated $La(OH)_3$. The precipitate was quantitatively collected on the inner walls of a knotted reactor made of Microline tubing and then dissolved by a stream of 1 mol l^{-1} HCl, which was introduced into the HG-AAS system.

Se(IV) can be preconcentrated by complexation with diethyldithiocarbamate [56,57], pyrrolidinedithiocarbamate [58] or dithizone [57,59] and extraction into organic solvents. These preconcentration procedures have been often combined with graphite furnace atomic absorption spectrometry (GF-AAS) detection. In addition Se(IV) forms piazselenols with a range of aromatic *o*-amines (the most popular are

3,3′-diaminobenzidine and 2,3-diaminonaphthalene) that can be extracted by organic solvents and used for spectrophotometric or fluorimetric determinations [18,60].

Supercritical fluid extraction with on-line detection by AAS was reported by Wang and Marshall [61]. Selenium in aqueous medium was derivatized by *in situ* complexation with tetrabutylammonium dibutyldithiocarbamate and the product complex was mobilized into supercritical carbon dioxide.

Solid sorbents are often used for preconcentration of selenium species. Moreover, their separation by fractional elution can be also obtained. This approach will increase the accuracy in the determination of Se(VI) and organic selenium species, the content of which is usually obtained by difference after reduction to Se(IV). The combination of on-line preconcentration on solid sorbents with FIA–HG method have proved to be very efficient [62]. The acid medium used for most common elutions is quite similar to that required for the HG reaction, so that in principle no further adjustment of acidity should be necessary between the two processes. Cellulose filters with immobilized 2,2′-diaminodiethylamine functional groups [63] and zirconium-loaded activated charcoal [64,65], after a simple filtration step, were used for direct determination of Se by X-ray fluorescence spectrometry. Application of solid sorbents for preconcentration and separation of selenium species has been recently reviewed [65]. A variety of sorbents have been also used for the separation of selenium from a wide range of interfering matrix components [66–68].

Gas chromatography is the technique most frequently used for separation of volatile selenium species, such as DMSe and DMDSe [70]. Both packed and capillary columns have been applied. The former can be conventiently cleaned and have large sample capacity. On the other hand, capillary columns or megabore open-tubular columns with thin methylsilicone coating provide much better resolution [70–73]. Atomic spectroscopic techniques are the most common detectors used.

The separation of selenium species by liquid chromatography (LC) offers a number of potential benefits. This include minimal preparation of liquid samples and separation at ambient temperature avoiding thermal decomposition risks for unstable compounds. Another advantage is that both the stationary and mobile phases can be varied simultaneously to achieve better separation [8]. The technique is mainly applied as HPLC, in which the size of particles used for the stationary phase is very small to ensure good separation. Conductivity cells [74–77], UV absorption spectrometers [78,79] and fluorescence spectrometers [80] have been used as detectors. Interferences in suppressed LC from several anions were reported [74,77,80,81]. Application of selenium-specific detectors, such as GF-AAS [81], HGAAS [82] or inductively coupled plasma atomic emission spectrometry (ICP-AES) [83,84] is very useful for elimination of these interferences. One of the main problems in coupling a chromatographic separation with plasma detectors is the perturbation introduced by the solvent from the analyte. An alternative approach is the introduction of a sample in the gaseous state, such as in HG technique [85].

Analytical methods

Several analytical techniques are now available for the determination of selenium at the trace levels. In many of them, Se(IV) is determined directly after derivatization process (*e.g.* hydride generation, complexation), whereas Se(VI) is determined by difference after reduction with HCl. The content of organoselenium species is also determined by difference after oxidation of organic compounds.

For a better quantification of a studied sample, it is usually necessary to combine the preconcentration/separation technique with determination method having higher detection limit than it is required for evaluation of the total selenium content. The selective method for determination of selenium species, not requiring any or minimal chemical treatment of a sample, is still needed to provide more information about its environmental and biomedical distribution.

The methods for selenium determination have been reviewed; they include atomic absorption spectrometry [86], UV–VIS spectrophotometric [87] and X-ray fluorescence methods [88]. The articles also reviewed the determination of selenium species in various types of matrix: water [9,89,90], urine [91,92], blood [88,93], biological [17,18,94,95] and environmental [2,18,95] samples.

The slow rates of many color-forming reactions involving selenium have precluded their wider use. Catalytic spectrophotometric methods are more simple and selective. While their detection limits are such that they cannot compete with HG-AAS technique, they are still appropriate to meet many analytical needs [96–100]. Recently, few automatic flow injection systems have been used for selenium determination [101–103].

Electrochemical techniques, such as cathodic or anodic stripping voltammetry, offer a highly sensitive approach to the determination of Se in most samples. However, they are associated with matrix effects and a time-consuming standard additions method must be employed [104–106].

Graphite furnace atomic absorption spectrometry has become an important method for the trace selenium determination. One of the difficulties occurring in this method is connected with the volatility of selenium compounds. The stabilizing effect of several chemical modifiers on inorganic as well organic selenium species has been reported [107–109]. Mechanisms of selenium vaporization with palladium modifiers and palladium-induced stabilization processes were reported by Styres *et al.* [110]. Palladium and Rh-plating of the graphite furnace has been evaluated as a method for introducing the metallic form of Pd and Rh for chemical modification [111]. The resulting metallic layer is very efficient in inhibiting the loss of volatile selenium compounds, as well as extending analytical lifetime of tubes up to 160 firings. The graphite tubes coated with boron nitride were tested for their behavior with selenite and selenate [112]. After the conversion to a volatile piazselenol, a quantitative preatomization separation of Se(IV) from Se(VI) was possible. However, this type of tubes showed two serious disadvantages: the need for long preconditioning and their rapid deterioration.

The emission methods have been popular as detection techniques used in selenium speciation analysis with combination of chromatographic separation. This

approach offers the possibility of multielement detection and access to a variety of heteroatoms not directly available with AAS techniques. Detection of optical emission generated by microwave-induced plasma (MIP) has been especially popular with GC and the effluent can be introduced directly into the flame without extinguishing it. Selenium species have been determined by GC-MIP-AES with the detection limits in the range 20–50 pg [113,114].

Plasma techniques are sensitive to organic solvents present in the HPLC effluents. Another problem with HPLC–ICP system is the low efficiency of sample nebulization, which has a major effect on sensitivity. Several different sample introduction techniques have been investigated but direct injection nebulization gives the best reported detection limits. The plasma excited ICP-AES has been coupled to HPLC for determination of Se(IV), Se(VI) and $TMSe^+$ [83,84].

Radiochemical neutron activation analysis (RNAA) has very low detection limit, allowing the determination of Se in solid samples at levels down to 0.5 $\mu g\ g^{-1}$ [43]. Most interfering species could be removed by the radiochemical separation. But the time for analysis is very long as a delay of a few days is often required post-irradiation to allow short-lived interfering isotopes to decay.

Mass spectrometric (MS) detection was applied for the determination of different selenium species after their separation on solid sorbents [115]. The internal calibration by an enriched spike isotope was used. The most recent development in coupling scheme that considerably improved the sensitivity is HG-ICP–MS [116]. The absolute detection limit of 6.4 pg for total Se in pure solution was obtained, whereas the detection limit of 1.3 ng was found for routine analysis of 1 g samples by isotope dilution. This technique is suitable for plant as well as animal materials. Interference from copper was eliminated by addition of sodium iodide or by maintaining a high concentration of HCl in the sample solution. Despite the fact that selenium has six isotopes, its determination in biological samples by ICP–MS is seriously hampered by spectral interferences. The resolution of quadrupole mass analyzers is insufficient to resolve Se^+ from molecular species having the same nominal mass [117]. Recently, the addition of CH_4 to the nebulizer gas [118] or EtOH to the sample solutions [119] was successfully applied to selenium determination in clinical samples. Goossens *et al.* [120] proposed a mathematical correction method based on signal ratio measurements of $^{78}Se^+/^{76}Se^+$ and $^{78}Ar_2^+/^{76}Ar_2^+$. Although ICP–MS is not yet currently fully established for trace-level analysis of selenium, it shows exceptional potential as the future method for determining its species in all environmental matrices.

In a recent review [95], different analytical methods used for determination of selenium compounds were presented. Recent developments (since 1992) in the quantification of inorganic and organic selenium species are presented in Table 1. Compared with the extensive investigations on total selenium or selenite and selenate determination, very little work has been done with organic selenium compounds, although the majority of selenium compounds in the natural selenium cycle have at least one C–Se bond. Systematic investigations and applications to natural samples are rare.

Table 1. Recent developments in the analysis of selenium compounds

Species	Matrix	Analytical method	Detection limit	Ref.
Total Se	groundwater	HG-AAS	2 ng l^{-1}	29
Total Se	sediment	HG–ICP-AES	0.40 μg l^{-1}	48
		fluorimetry	0.28 μg l^{-1}	
Total Se(urine)		HG-AAS	20 ng l^{-1}	52
Se(IV), Se(VI)	coal ashes	IC-CD	50 μg l^{-1}	77
Total Se	urine	GF-AAS	20 μg l^{-1}	84
Se(IV)	shampoo	spectrophotometry	1 μg l^{-1}	99
Total Se	human hair	polarography	–	105
Total Se	soil	CSV	0.75 μg l^{-1}	106
Total Se	plants	HG-ICP–MS	1.3 ng l^{-1}	116
Se(IV), Se(VI)	soil	IC-CD	30 μg l^{-1}	121
DMSE	soil	GC–AAS	5 pg	122
DMDSe				
Total Se	biological samples	HG-AAS	0.02 μg l^{-1}	123
Diphenyl selenide	drain water	MEKC	30 pg l^{-1}	124

Abbreviations: CD – conductometric detection, CSV – cathodic stripping voltametry, MEKC – micellar electrokinetic chromatography.

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