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REVIEW ARTICLE

Methods of Spectroscopy for Selenium Determination: A Review

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ABSTRACT:

Selenium (Se) is cumulative nonmetallic element that occurs naturally in a range of oxidation states as volatile species or analogues of organic sulphur compounds. At low concentrations, selenium is an essential element; however at higher concentrations it possesses toxicological properties. Its determination requires a sampling procedure to be followed, an initial digestion stage of the sample matrix and the reduction of Se (VI) to Se (IV). Spectroscopic methods for the determination of Se including hydride generation atomic fluorescence spectrometry, hydride generation, graphite furnace, flame atomic absorption spectrometry and spectrophotometric methods are described detailing detection limits and sensitivity.

KEYWORDS: Selenium; spectroscopic methods; review; detection limits; sensitivity.

INTRODUCTION:

Selenium is a cumulative nonmetallic element found in high concentrations in food and water. It has received high attention of researchers because of its dual role as an essential trace nutrient and a toxic element [1,2]. This dual effect has been recognized for many naturally occurring chemicals[1]. Selenium speciation has been attracting much attention in recent years because selenium compounds have been reported to have anticarcinogenic activity and prevent heavy metal toxic effects[3-5]. Selenium is extensively used not only in medicine but also in other fields such as material sciences and in the agronomical area[6]. Since that time many papers appeared devoted to determination of selenium in the environment and biological material. The most common spectroscopic methods used for determination of various species of selenium were hydride generation atomic fluorescence spectrometry[7,8], hydride generation [9,10], graphite furnace[11-13] and flame atomic absorption spectrometry[14,15]. In spite of some of the above methods, spectrophotometric methods are popular because of their simplicity and are based on complex formation between the reagents and selenium. In view of the profound recent interest in selenium and its vital biological importance in human health, reviewing modern spectroscopy methods of determination of this element seemed worthwhile.

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Methods of spectroscopy for selenium determination

Visible absorption spectroscopy:

A wide number of rapid, highly sensitive and selective spectrophotometric methods for the determination selenium (IV) were reported. These methods are based on piazselenol complex formation between the reagents and selenium. Selenium was detected in blood samples based on the oxidation of phenylhydrazine –p sulphonic acid coupled with acetyl acetone in an alkaline medium with a detection limit of 0.07µg/ml[16]. 5,6-diaminouracil hydrochloride reagent was developed and used for the determination of Se (IV). The reagent formed a yellow complex with the aqueous solutions of selenium in acidic medium with a detection limit of 0.05µg/ml[17]. Krishnaiah *et al.* developed a rapid and sensitive method for the determination of selenium in environmental samples based on either the oxidation of 2,4-dinitrophenyl hydrazine hydrochloride by selenium in HCl medium and coupling with N-(1-naphthyl) ethylenediamine dihydrochloride with a maximum absorption peak at 520nm or the oxidation of 4-aminoresorcinol hydrochloride by selenium in H_2SO_4 medium and coupling with 4-aminoresorcinol hydrochloride to yield a orange red colored product with a maximum absorption peak at 495nm. The detection limits reported were 0.0165 and 0.0335µg/ml, respectively[18]. A similar detection limit of 0.0124µg/ml resulted from the reaction of selenite ions with hydroxylamine hydrochloride, which in turn diazotizes p-Nitroaniline and then coupled with N-1-naphthyl-ethylenediamine dihydrochloride to form a red colored azo compound with a maximum absorption peak at 545 nm[19]. Soruraddin *et al.* recently developed a new spectrophotometric method for the determination of trace amounts of selenium (IV) after pre-concentration with cloud point extraction. The colored complex was formed using dithizone at pH < 1 in micellar medium (Triton X-100) and extracted to a surfactant rich phase by centrifugation. The proposed method was highly sensitive with a detection limit of 0.0044µg/ml[20].

Hydride generation atomic absorption spectrometer (HG-AAS):

Over the last decade, significant instrumental and methodological progress has led to HG-AAS being widely applied to an extensive range of metal sample types such as As, Sb and Se which are vaporized by converting them into volatile hydrides[21,22]. This method of analysis is one of the most preferred methods because of its simplicity, sensitivity and rapidity[23]. Nevertheless, the first step of this procedure is the mineralization of any organic selenium compound and the reduction of Se (VI) to Se (IV) prior to hydride generation[10]. Different methods have been suggested to accomplish this step including digestion of the sample using a mixture of a wide number of mineral acids such as HNO_3, HCL, H_2SO_4, HClO and H_2O_2[24]. Several parameters such as the type of acid, its concentration and the reaction temperature and time should be optimized to assume a complete destruction of the organic compounds for better recovery. Heating the acidified sample greatly enhanced the reduction of Se (VI) to Se (IV) but unfortunately a wide number of interfering species could be formed[25]. Thus, the reduction of Se (VI) is currently carried out using L-cysteine 0.5% at 100ºC for 25 min [26]. The use of solid reagents was also investigated by Maleki *et al.* as a simple and fast procedure that could reduce the interference effects[9]. The effects of several solid acids such as oxalic, tartaric, adipic, salicylic and some amino acids were evaluated and results proved that tartaric acid gave the highest sensitivity. It was also proved that the increase of solid reagent and the use of higher volumes of selenium solution improved the sensitivity[27]. However, acid-resistant organoselenium compounds and high fat samples demand the use of agents with high oxidation potential for complete destruction. Furthermore, selenium readily forms volatile species that could be lost during an uncontrolled decomposition[28]. The use of a closed microwave digestion system was developed as fast procedure that has the advantage to minimize the potential loss of analyte due to an open system mineralization[29]. Shalt out *et al.* proved that the use of microwave-assisted digestion with nitric acid and hydrogen peroxide was appropriate for the complete mineralization of organo-selenium compounds, avoiding the use of more hazardous reagents, such as sulfuric or perchloric acid [10]. Finally, in order to achieve higher sensitivity in hydride generation of selenium, sodium tetrahydroborate (III) ($NaBH_4$) is used as the most suitable reductant for hydride generation because of its short reaction time coupled with a rapid transfer of the products to the gas phase. At first, $NaBH_4$ pellets were favorites, but currently more concentrated $NaBH_4$ dissolved in concentrated NaOH or KOH is the most popular and most convenient agent[30]. The metal hydride was then introduced to the atomizer of AAS by inert carrier gas (N_2, He) and absorbance is recorded and plotted against concentration[25]. Several operational parameters should be optimized as they could influence the sensitivity of the HG-AAS method such as the system design and operating conditions, the type and amount of the acid, the amount of sodium borohydride, and the generation temperature. The sensitivity of this method for selenium determination ranged from 10.6µg/l to 0.0035µg/l with the best detection limit of 0.0055ng/l found by Busheina *et al.* who used a HGAAS method for the determination of Selenium content in soil samples, alfalfa, animal feed, and water samples[25,30,31].

Hydride generation atomic fluorescence spectrometry (HG-AFS):

Atomic fluorescence spectrometry has been widely used in single- and multi-elemental determinations since 1964 due to its flexibility with a wide variety of light sources, optical designs, atomizers, and electronics[32]. Tsujii and Kuga appear to be the first to report the use of non-dispersive AFS for the hydride forming elements such as As, Sb, Se and Te[33,34]. This approach offers several advantages due to the heating process necessary to convert the metal hydride into an atomic vapor[35].

Lopes dos Santos *et al.* evaluated several conditions for the measurement of the total selenium content in oysters using HG AFS after digesting by HNO_3 and HCl. Under the optimized conditions, the detection and the quantification limits were 6.06 and 21.21µg/1, respectively[36]. Stibilj *et al.* developed a method for very lowlevel selenium determination in water soluble protein and peptide fractions. The sample was treated using HNO_3 and H_2O_2 and detected by HG-AFS after various separation procedures. The LOD was 0.2 µg/l[37]. A new method was proposed for simultaneous determination of traces of arsenic (As) and selenium (Se) in biological samples by HG-AFS from tartaric acid media. The detection limits for arsenic and selenium were 0.13 and 0.12µg/l, respectively[38].

Flame atomic absorption spectrometry (FAAS):

Flame atomic absorption spectrometry (FAAS) is one of the techniques most extensively used for determining various elements with a significant precision and accuracy. This analytical technique is remarkable for its selectivity, speed and low operation cost[39]. It is based on the light absorption process that passes through the atomized analyte. The most important stage in the FAAS is the method of atomization of the element that is analyzed into neutral atoms in the form of gases[40]. Mariam *et al.* proposed a method based on the separation and determination of selenium (IV) ion using polyurethane foam as a solid sorbent coated with ammonium pyrrolidine dithiocarbamate (APDC). The sample was digested by HNO_3 and the detection limit for this method was 0.064mg/l[41]. Another method was improved in atomic flame absorption spectroscopy to determine the concentrations of AS and Se. Results of the method showed that FAAS is more sensitive to Se with an LOD of 1.0mg/l[15]. FAAS is found to be suitable for the measurement of a limited range of elements present at concentrations greater than approximately 1 µg/ml. FAAS is a sufficiently sensitive and precise technique; however, when the concentrations of elements are lower than 100ng/ml the greater sensitivity of Graphite furnace atomic absorption spectrometry (GF-AAS) is required[42].

Graphite furnace atomic absorption spectrometry (GF-AAS):

Graphite furnace atomic absorption spectroscopy (GF-AAS) (also known as Electro-thermal Atomic Absorption Spectroscopy (ETAAS)) is a type of spectrometry that uses a graphite-coated furnace to vaporize the sample[43]. Briefly, the technique is based on the fact that free atoms will absorb light at frequencies or wavelengths characteristic of the element of interest and correlated with their concentrations[44,45].

Abdel-Lateef *et al.* developed a method for the determination of total selenium in human hair and nails using GF-AAS with palladium/ascorbic acid as a chemical modifier. The detection limit is estimated to be 0.8µg/l[46]. Another method is reported for measuring Se and Sn in human brain tissue. Microwave energy was applied to digest the brain samples which were analyzed without dilution by transversely heated graphite atomizer for atomic absorption spectrometry with longitudinal Zeeman background correction at 2100°C[47]. Cassia *et al.* studied the influence of sample preparation strategy of vegetables on the electrothermal behaviour of Se without and with chemical modifiers. Best conditions, such as thermal stability, signal profile, repeatability and sensitivity were attained using Pd $(NO_3)_2$ as chemical modifier. The limits of selenium detection were 2.0mg/l and 0.6mg/l for digestates and slurries, respectively[48]. Selenium has been determined in sixty five geological reference materials of different origins by graphite furnace atomic absorption spectrometry after decomposition with a mixture of nitric and hydrofluoric acids and a reduction with hydrochloric acid. The limit of determination was 0.02µg/g[49]. Selenium was measured in chicken meat either by HG-AAS or by GF-AAS. Acid digestions were carried out with mixtures of HNO_3 and $HClO_4$. The limits of detection for HG-AAS and GF-AAS were 1µg/l and 0.6µg/l, respectively [50].

CONCLUSION:

A wide number of rapid, highly sensitive and selective spectrophotometric methods for the determination selenium (IV) were reported. However, comparative studies have shown that in the past decade atomic absorption spectroscopy has been established as an adequate method for the determination of selenium in the sub-ng/ml range. The choice of a particular method will depend on the type of sample studied, accessible equipment and analytical experience of the analyst.

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