



Determination of selenium compounds in food supplements using reversed-phase liquid chromatography–inductively coupled plasma mass spectrometry

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ABSTRACT

A reversed phase HPLC–ICP–MS method for the speciation of selenium compounds is described. Chromatographic separation was performed in a gradient elution mode using 2 mmol L⁻¹ sodium 1-pentanesulfonate and 5 mmol L⁻¹ citric acid in 3% methanol (pH 2.70) and 5 mmol L⁻¹ NaH₂PO₄ and 5 mmol L⁻¹ citric acid in 3% methanol (pH 2.77). The potentially interfering ³⁸Ar⁴⁰Ar⁺ and ⁴⁰Ar⁴⁰Ar⁺ at selenium masses of *m/z* 78 and 80 were reduced in intensity significantly by using 1.0 mL min⁻¹ CH₄ as a reactive cell gas in the dynamic reaction cell. Calibration curves were linear in the range 0.1–10 μg L⁻¹. The detection limits of the procedure were in the range of 0.04–0.07 μg Se L⁻¹. This method has been applied to determine various selenium compounds in NIST SRM 1567a Wheat Flour and food supplements purchased locally. The accuracy of the method has been verified by comparing the sum of the concentration of individual species obtained by the present procedure with the total concentration of the element. The selenium compounds were quantitatively extracted with a mixture of Protease XIV and mobile phase solution in a microwave field at 37 °C during a period of 30 min. The extraction efficiency was better than 91%. The spike recoveries were in the range of 92–104% for all determinations. The electrospray ionization-mass spectrometer has been tested to identify the unknown selenium compounds detected in the food supplements. γ -glutamyl-methyl-Se-cysteine was identified in one brand of the Selenium Tablet.

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1. Introduction

Elemental speciation in environmental samples is essential as different species of an element show varying toxicities [1]. Selenium is used vastly in the semiconductor and optoelectronic industries. The determination of selenium in environmental and biological systems is important, mainly because of the ubiquitous nature of this element and the toxic characteristics of some of its species. Selenium is well known not only as an essential element for biological systems, but also as a potential toxicant at higher levels. Although, Selenium is available in our food, its content in food varies widely among different world regions depending on the selenium content in the soil. To compensate for selenium deficient food dietary supplements are being administered. However, in view of their toxicity, it is necessary to determine various species of selenium in food supplements, such as Selenium Tablets and vitamins [2]. Inductively coupled plasma mass spectrometer (ICP–MS) is a trace-element detection method with superior analytical capabilities. Several procedures based on high performance liquid chromatography (HPLC) [3–13], gas chromatography (GC) [14] and capillary electrophoresis (CE) [15–18] coupled

with ICP–MS have been reported for selenium speciation analysis. Coupling of HPLC to ICP–MS gained much attention due to its easiness of sample preparation, simplicity of the interface to the detector and specificity of the signal intensity of the determined element [19]. Moreover, the use of HPLC will enable the separation of more species of selenium in a single run. The determination of selenium by quadrupole ICP–MS is typically compromised by isobaric interferences from ⁴⁰Ar⁴⁰Ar⁺ on ⁸⁰Se⁺ and ⁴⁰Ar³⁸Ar⁺ on ⁷⁸Se⁺. These interferences are reported to be alleviated by employing the dynamic reaction cell (DRC) technique with CH₄ as the reaction gas [20,21].

To perform selenium speciation analysis, extraction methods adopted must be capable of quantitatively extracting selenium from the sample without altering the individual selenium compounds under the extraction conditions. Microwave-assisted extraction method was used for the extraction of selenium compounds in cereal and food supplement samples which is reported to be simple and suitable for the rapid sample preparation of solid samples for elemental speciation analysis [3,17,22].

The aims of the present work are to develop an effective microwave-assisted extraction procedure and an accurate method of speciation analysis of selenite (Se(IV)), selenate (Se(VI)), Se-methylselenocysteine (Se-MeSeCys), selenocystine ((SeCys)₂) and selenomethione (SeMet) in food supplements using HPLC–DRC–ICP–MS. The optimization of the extraction method, HPLC–DRC–ICP–MS operating conditions, and

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its analytical figures of merit, as well as its application to selenium speciation analysis in extracts of food supplements is described. Electrospray ionization-mass spectrometry (ESI-MS) provides molecular and structural verification of the compounds. Consequently, the use of ESI-MS is gaining importance in the field of speciation. In recent years some studies have used ESI-MS for achieving molecular and structural information on selenium compounds [23–25]. In this study ESI-MS method was employed to identify selenium compounds in food supplements without standards.

2. Materials and methods

2.1. Equipment and operating conditions

An ELAN 6100 DRC II ICP-MS (Perkin-Elmer SCIEX, Concord, ON, Canada) was used for these experiments. Samples were introduced by a cross-flow pneumatic nebulizer with a Scott-type spray chamber. The operating conditions of ICP-MS were optimized by continuous introduction of a solution containing $5 \mu\text{g L}^{-1}$ Se in a mobile-phase solution. The solution flow rate was maintained at about 1.0 mL min^{-1} . The ICP-MS operating conditions used in this work are summarized in Table 1. The optimum conditions could vary slightly with time. An amaZon SL Ion Trap Mass Spectrometer (Bruker Daltonics, Bremen, Germany) was employed for the identification of unknown selenium compounds [26].

Two HPLC pumps (Hitachi, Model L-6000 & L-6100), an injector (Rheodyne 7125) and an Alltech Econosphere C18 column ($5 \mu\text{m}$ diameter particles, $250 \text{ mm length} \times 4.1 \text{ mm i.d.}$) comprised the HPLC system. Samples were loaded with a syringe onto a $100 \mu\text{L}$ sample loop. All separations were performed at room temperature. The separation conditions used in this work are summarized in Table 1. The column outlet

was connected to a pneumatic nebulizer of the ICP-MS device through polytetrafluoroethylene (PTFE) tubing ($0.18 \text{ mm i.d.} \times 470 \text{ mm length}$).

2.2. Chemicals

Analytical-reagent grade chemicals were used without further purification. Purified water ($18.2 \text{ M}\Omega\text{-cm}$), from a Milli-Q water purification system (Millipore, Bedford, MA), was used to prepare all of the solutions. Se-methylselenocysteine (Se-MeSeCys), selenocystine ((SeCys)₂), selenomethione (SeMet) and Protease XIV were obtained from Sigma (St. Louis, MO). Methanol and Suprapur nitric acid (65%) were purchased from Merck (Darmstadt, Germany). Sodium selenite(IV) and sodium selenate(VI) were procured from Alfa Chemical (Danvers, MA). Citric acid and sodium dihydrogen phosphate monohydrate were obtained from Fluka (Buchs, Switzerland). Sodium 1-pentanesulfonate was from TCI (Tokyo, Japan). Stock solutions of all the selenium compounds were prepared in pure water and diluted appropriately before use. The Ar gas used was provided by Hsin E Li Gases Co., Ltd. (Kaohsiung, Taiwan). CH₄ gas used was of 99.999% purity (Air Liquide, Taiwan).

2.3. Sample preparation and extraction

The applicability of the developed procedure on real samples has been carried on NIST SRM 1567a Wheat Flour standard reference material (Gaithersburg, MD, USA) and also two brands of Selenium Tablet and multiple vitamin tablet samples purchased locally.

A simple and rapid microwave-assisted extraction procedure was used for the extraction of selenium compounds from wheat flour and food supplement samples [22,27]. A CEM MARS (Matthews, NC) microwave digester equipped with temperature and pressure sensors was used for wheat flour and food supplement sample extraction and digestion. Approximately 0.5 g each of wheat flour and food supplement samples was accurately weighed into 15 mL polyethylene centrifuge tubes; 50 mg Protease XIV and 5 mL of mobile phase A solution were added. The centrifuge tube was then put into a beaker. The microwave system was programmed to maintain the water temperature at $37 \text{ }^\circ\text{C}$ for 30 min with a ramp time of 10 min. After microwave heating, the samples were allowed to cool and directly centrifuged for 10 min at 3743 g (MIKRO 22R, Hettich, Germany). The supernatant of SRM 1567a, Multiple Vitamins, Selenium Tablet 1 and Selenium Tablet 2 was diluted by another 4, 500, 400 and 1000-fold, respectively, with mobile phase A and then filtered through a PVDF filter (Pall Corporation, Ann Arbor, MI, USA) of $0.2 \mu\text{m}$ porosity before HPLC separation. The concentration of selenium species was determined by an external calibration method based on the peak area. The spike recoveries of the individual species were determined by spiking various samples with suitable amounts of selenium standards, dried and then extracted by the extraction solution. The selenium standards spiked were $10 \mu\text{g g}^{-1}$ each in Multiple Vitamins, $200 \mu\text{g g}^{-1}$ each in Selenium Tablet 2, 400 ng g^{-1} each of Se(VI), Se(IV), (SeCys)₂, Se-MeSeCys and $1.2 \mu\text{g g}^{-1}$ of SeMet in NIST wheat flour, and $8 \mu\text{g g}^{-1}$ each of Se(VI), Se(IV), (SeCys)₂, Se-MeSeCys and $160 \mu\text{g g}^{-1}$ of SeMet in Selenium Tablet 1, respectively. The amounts of Se presence in the extracts were quantified by HPLC–DRC–ICP-MS. Recovery was then calculated against the theoretical concentration.

The accuracy of the method was verified by comparing the sum of the concentrations of individual species obtained by the HPLC–ICP-MS method with the certified values and/or those obtained from the dissolution method. The wheat flour sample was digested in a closed microwave oven (MARS 5, CEM) using 3.5 mL HNO₃ and 1.5 mL H₂O₂ for 0.5 g of powder sample and analyzed for total concentration of Se by DRC ICP-MS using solution nebulization after suitable dilution. In case of food supplement samples, 0.1 g of grinded samples was dissolved in 5 mL HNO₃ and heated in the microwave oven.

Table 1
Equipment and operating conditions.

ICP-MS instrument	Perkin-Elmer SCIEX ELAN 6100 DRCII
Plasma conditions	
RF power/w	1100
Plasma gas flow/L min ⁻¹	15
Auxiliary gas flow/L min ⁻¹	1.325
Nebulizer gas flow/L min ⁻¹	0.98
Mass spectrometer settings	
Resolution	0.7 amu at 10% peak maximum
Dwell time/ms	50
Sweeps per reading	5
Readings per replicate	1100
Ions monitored	⁷⁸ Se ⁺ , ⁸⁰ Se ⁺ , ⁸² Se ⁺
Reaction gas	CH ₄
Reaction gas flow rate/mL min ⁻¹	1.0
Rejection parameter q	0.45
Rejection parameter a	0.0
Axial field voltage/V	175
HPLC conditions	
Pump	Hitachi, Model L-6000 and L-6100
Injector	Rheodyne 7125
Column	Alltech Econosphere C18 column, 5 μm diam. particles, 4.6 mm i.d. × 250 mm length
Mobile phase	
	A: 2 mmol L ⁻¹ sodium 1-pentanesulfonate, 5 mmol L ⁻¹ citric acid in 3% v/v methanol (pH = 2.70)
	B: 5 mmol L ⁻¹ NaH ₂ PO ₄ , 5 mmol L ⁻¹ citric acid in 3% v/v methanol (pH = 2.77)
	0–0.1 min: 100% mobile phase A up to 100% mobile phase B
	0.1–8 min: 100% mobile phase B
Mobile phase flow rate	1.0 mL min ⁻¹
Sample loop	100 μL

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