Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Chromatography A, 1114 (2006) 1–20
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Review

Selenium speciation analysis using inductively coupled plasma-mass spectrometry

C. B'Hymer, J.A. Caruso *

Department of Chemistry, University of Cincinnati, Mail location 0172, Cincinnati, OH 45221-0172, USA

Received 28 November 2005; received in revised form 14 February 2006; accepted 21 February 2006
Available online 23 March 2006

Abstract

Selenium exists in several oxidation states and a variety of inorganic and organic compounds, and the chemistry of selenium is complex in both the environment and living systems. Selenium is an essential element at trace levels and toxic at greater levels. Interest in speciation analysis for selenium has grown rapidly in this last decade, especially in the use of chromatographic separation coupled with inductively coupled plasma-mass spectrometry (ICP-MS). Complete characterization of selenium compounds is necessary to understand selenium's significance in metabolic processes, clinical chemistry, biology, toxicology, nutrition and the environment. This review describes some of the essential background of selenium, and more importantly, some of the currently used separation methodologies, both chromatographic and electrophoretic, with emphasis on applications of selenium speciation analysis using ICP-MS detection.

Keywords: Reviews; Inductively coupled plasma-mass spectrometry; Selenium; Organoselenium compounds

Contents

1. Introduction: selenium and speciation analysis 2
   1.1. A summary of the biochemistry of selenium 2
   1.2. Selenium in the environment 4
2. Inductively coupled plasma-mass spectrometry and basic interfacing 4
   2.1. ICP-MS and selenium 4
   2.2. Interfacing with ICP-MS 6
      2.2.1. HPLC interfacing 6
      2.2.2. CE interfacing 6
      2.2.3. GC interfacing 7
3. Separation of selenium compounds 8
   3.1. HPLC separations of selenium compounds 8
      3.1.1. Reversed-phase and ion-pair HPLC 8
      3.1.2. Ion-exchange HPLC 9
      3.1.3. Size-exclusion HPLC 9
      3.1.4. Chiral HPLC 10
      3.1.5. Miscellaneous HPLC 10
   3.2. Capillary electrophoretic separation 10
   3.3. Gas chromatographic separation 11
4. Sample preparation and preservation of selenium species 12
   4.1. Sample collection, storage and treatment 12

* Corresponding author.
E-mail address: joseph.caruso@uc.edu (J.A. Caruso).

0021-9673/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2006.02.063

4.2. Non-volatile species extraction 12
4.2.1. Traditional techniques 12
4.2.2. Enhanced techniques 12
4.3. Volatile species extraction 13
5. Further applications of selenium speciation analysis 13
6. Conclusions and future trends 16
Acknowledgement 17
References 17

1. Introduction: selenium and speciation analysis

Selenium has a major nutritional and biological role in living systems, and speciation analysis of inorganic and organoselenium compounds to define exact biological roles is a major analytical challenge. Selenium is an essential nutrient and has been known to be a necessary component of the human diet for many years [1]. Selenium is also toxic at levels above the rather narrow range of that considered a health level in the human diet; daily consumption of less than 0.1 mg kg^{-1} of body weight will result in selenium deficiency while levels above 1 mg kg^{-1} are considered toxic [2,3]. This leads to a demand of high accuracy and precision in the measurement of selenium in its various chemical forms and oxidation states. Analysis of this type falls under the field of elemental speciation analysis; specifically, selenium speciation analysis has been reviewed in the literature [4–8]. Elemental speciation analysis is defined as the analytical activity of identifying and quantifying the actual chemical form, the chemical species of an element and has been described in general detail by various review articles [9–19]. Elemental speciation usually requires coupling of two techniques: a technique to separate the element's chemical forms of interest and a sensitive detection method to provide detection of the analyte at low levels [11].

For practical purposes, method specificity is necessary for selenium speciation analysis. The most practical approach for selenium speciation analysis, therefore, is the use a separation technique combined with a specific and sensitive detection system. The coupling of chromatography or capillary electrophoresis to accomplish analyte separation with highly sensitive detector such as inductively coupled plasma-mass spectrometry (ICP-MS) has proven to be an effective hyphenated system in recent years [4]. Selenium speciation analysis has been conducted with various means of detection including conductametric, ultraviolet, inductively couple plasma-atomic emission (ICP-AES), electrospray ionization mass spectrometry (ESI-MS) and neutron activation analysis which has been covered in other reviews [4,6]; the use of inductively coupled-mass spectrometry (ICP-MS) detection is widespread and will be covered extensively within this review. ICP-MS detection offers high sensitivity and relative ease of interfacing with common chromatographic and separation techniques. Although ESI-MS is the best approach for identification of selenium compounds [20], ICP-MS offers the highest sensitivity and offers the best quantitiative methodology when reference compounds are avaliabile. Some selenium compounds or species of interest which are commonly studied in the literature are listed in Table 1. Various selenium containing enzymes and proteins are also of interest from a biochemical standard point; thioredoxin reductase (TR), glutathione peroxidase (GSH-Px), phospholipid hydroperoxide gluthathione peroxidase (phGSH-Px) [2,21,22], and Selenoprotein P [23] are a few common selenium containing biochemicals of interest. The endocrine system is known to have at least 30 selenoproteins, many which have well defined funtions [24].

1.1. A summary of the biochemistry of selenium

Selenium is an essential nutrient and is found in various forms within human body fluids [25]. It is present as a necessary component to form the active center, a selenol group (–SeH), in numerous selenoenzymes, a few which have been mentioned in the previous section. Some studies in recent years have implied that selenium may reduce the incidence of some types of cancers, including an implied role in the prevention of prostrate cancer [26–29]. Cancer chemoprevention has been associated with inorganic selenium salts, selenoamino acids and other organoselenium compounds. Methylselenol (CH_3SeH) and other monomethylated forms of selenium have been considered important chemopreventive selenium metabolites [30]. Other selenium compounds have been evaluated and shown to reduce certain tumor cell proliferation in the rat [31] and tumorigenesis in the mouse [32]. The dietary considerations of selenium, along with the cancer preventative considerations, have lead to widespread commercial interest in selenium diet supplements sold in various chemical forms. Augmenting the food supply and diet by inclusion of selenium-enhanced plants has also been suggested [33]. Selenium speciation often parallels sulfur chemistry, except that selenium analogs can be present at three orders of magnitude lower than sulfur. These trace levels of selenium compounds make detector/method sensitivity an important consideration for speciation analysis. Selenocysteine (see Table 1) is functionally the most used selenium species in biochemical processes and in active selenium proteins, and it has been classified as the 21st amino acid in terms of ribosome-mediated protein synthesis [34,35]. Selenomethionine, a major species of selenium found in selenium rich foods, is usually incorporated non-selectively into proteins as a substitute for sulfur containing methionine [22].

The primary metabolic pathway of selenium by animals is the reduction of the elemental form followed by methylation leading to dimethylselenide and trimethylselenonium cation [36–38]. Hydrogen selenide has been described as an intermediate in this process [39], although some animal studies have suggested the