Applied Radiation and Isotopes 111 (2016) 45–49

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Determination of selenium in biological samples with an energy-dispersive X-ray fluorescence spectrometer

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HIGHLIGHTS

- The high-energy (100 kV, 600 W) linearly polarized beam energy-dispersive X-Ray fluorescence spectroscopy (EDXRF) was used to determine 0.1 – 5.1 μg g^{-1} levels of selenium in biological samples.
- High-pressure pressed powder pellet technique (1500 kN) is used for sample preparation.
- The detection limit of selenium in biological samples found to be 0.1 μg/g.

ARTICLE INFO

Article history:
Received 4 November 2015
Received in revised form
29 January 2016
Accepted 2 February 2016
Available online 20 February 2016

Keywords:
Selenium
Biological samples
High-energy polarized X-ray fluorescence spectrometer
Limit of detection

ABSTRACT

Selenium is both a nutrient and a toxin. Selenium—especially organic selenium—is a core component of human nutrition. Thus, it is very important to measure selenium in biological samples. The limited sensitivity of conventional XRF hampers its widespread use in biological samples. Here, we describe the use of high-energy (100 kV, 600 W) linearly polarized beam energy-dispersive X-Ray fluorescence spectroscopy (EDXRF) in tandem with a three-dimensional optics design to determine 0.1–5.1 μg g^{-1} levels of selenium in biological samples. The effects of various experimental parameters such as applied voltage, acquisition time, secondary target and various filters were thoroughly investigated. The detection limit of selenium in biological samples via high-energy (100 kV, 600 W) linearly polarized beam energy-dispersive X-ray fluorescence spectroscopy was decreased by one order of magnitude versus conventional XRF (Paltridge et al., 2012) and found to be 0.1 μg/g. To the best of our knowledge, this is the first report to describe EDXRF measurements of Se in biological samples with important implications for the nutrition and analytical chemistry communities.

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1. Introduction

The selenium concentration in biological samples is an important issue because it has a very narrow therapeutic window. That is, the concentration that is both safe and effective is narrow. At the proper concentration, Se is a nutrient, but at too high of a concentration it is toxic while low concentrations can lead to malnutrition (Bidari et al., 2007) Indeed, recommended allowances of Se in foodstuffs fall in a very narrow range: consumption of food containing below 0.1 mg kg^{-1} will result in deficiency, whereas dietary levels above 1 mg kg^{-1} will lead to toxic events such as gastric distress or problems with hair and nails loss and poor productivity (Fordyce, 2005). Since Schwarz and Foltz (1957) demonstrated the nutrition of selenium, more and more attention has been given to its unique physiological role. Many studies have indicated that selenium is a trace element essential to organisms with anti-cancer activity. It can scavenge free radicals and has anti-oxidation and anti-aging effects (Panigati et al., 2007; Rotruck et al., 1969). It can protect cell membrane structures and function, and enhances immunity. Studies have shown that the physiological activity of selenium is closely related to the selenium form. Selenium—especially organic selenium—is a core component of human nutrition. While animal-based foods can supply Se in the food chain, plant sources are much more common. Therefore, biological selenium resources directly affect human selenium nutritional status. Thus, measuring selenium in biological samples including foodstuffs is very important to prevent both overdose and underdose effects.

The abundance of Se in biological samples is only 10^{-8} to 10^{-6} and it is often difficult to measure such low concentrations especially in complex matrices such as food—this hampers most

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http://dx.doi.org/10.1016/j.apradiso.2016.02.010
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Table 1
Spectrometer operation conditions.

Target	Type	Filter	Counting time (s)	Analyte
Zr	Fluorescent target	Al100, Al500, Cu100, Zr125, Mo250	1000	Se
Mo	Fluorescent target	None	500	Se
B_4C	Barkla target	None	500	Se
Al_2O_3	Barkla target	None	500	Se
KBr	Fluorescent target	None	500	Se
W	Fluorescent target	None	500	Se
CaF_2	Fluorescent target	None	500	P,K
Ti	Fluorescent target	None	500	Ca
Ge	Fluorescent target	None	500	Fe
KBr	Fluorescent target	None	500	As
Zr	Fluorescent target	None	500	Br

spectroscopic techniques. High sensitivity is required for the determination method of selenium, and various methods have been used to measure selenium in biological samples. On-line chemical vapor generation-ICP OES (dos Santos and Beatriz Herrmann et al., 2009), hydride generation–inductively coupled plasma mass spectrometry (Moor et al., 2000), dynamic reaction cell inductively coupled plasma mass spectrometry (DRC-ICP-MS) after microwave digestion (Wei et al., 2014), electrothermal atomic absorption spectrometry (Viitak and Volynsky, 2006), and hydride generation-atomic fluorescence spectrometry (Zhao et al., 2010) potentially have high sensitivity and low interference. However, these methods also suffer from complicated sample preparation steps including dry ashing and wet ashing acid digestion process—this can lead to a loss of volatile elements. While neutron activation analysis has simple sample preparation (Czauderna, 1988), but the analysis is time-consuming and expensive.

X-ray fluorescence (XRF) is a non-destructive measurement approach that offers simple sample analysis. However, conventional XRF has been hampered by poor elemental sensitivity due to high background from instrumental geometries and matrix effects. In XRF, the relatively low sensitivity often makes a decomposition and preconcentration step mandatory. One tool to increase sensitivity is energy-dispersive XRF. This has been used for zinc, iron and selenium analyses in whole grain wheat with a Se limit of detection of 2 mg kg^{-1} (Paltridge et al., 2012). Previously EDXRF has been used for trace selenium measurements in organic and biological matrices after rapid acid digestion and thin-film deposition (Raptis et al., 1980). Shenberg et al. (1988) determined selenium in human serum (0.75 μl samples) via EDXRF, and the minimum limit of detection is 0.06 μg g^{-1}. Margui et al. (2010) explored the possibilities of several analytical approaches combined with total reflection X-ray (TXRF) spectrometry for soil Se determinations. A dispersive liquid–liquid microextraction procedure (DLLME) was used before the TXRF analysis of the soil digest. The limit of detection (LOD) using this analytical methodology (0.05 mg/kg of Se) was comparable to or lower than those obtained in previous studies. Selenium has also been measured in biological sample by hydride evolution and wavelength dispersive X-ray fluorescence spectrometry; the limits of detection was 0.13 μ g g^{-1} (Bohmer and Psotta, 1990). Suitable limits of detection have also been achieved for the determination of Se in biological and fluid samples with and without preconcentration strategies (Bellisola et al., 1999; Griessel et al., 2006; Mukhtar et al., 1991). Here, we used EDXRF with a high-energy polarized spectrometer to determine 0.1–5.1 μg g^{-1} levels of selenium in biological samples. This process uses minimal sample preparation steps and is compatible with a general EDXRF spectrometer. To the best of our knowledge, this is the first report to use EDXRF with a high-energy polarized spectrometer to measure Se in biological samples. The results have important implications for the dietary and analytical chemistry community.

2. Materials and methods

We used an Epsilon 5 EDXRF (Holiland, Panalytical com.) with a maximum voltage of 100 kV, maximum power of 600 W, and 24 mA, ScW synthetic anode. This was configured with 15 secondary targets, PAN32 Ge-detector, a side window, and a beryllium window thickness of 150 μm. The activity area of the crystal is 30 mm^2, and the resolution for MnKα is less than 140 eV. The efficient energy detection range is 0.7–100 keV; the detector is cooled with liquid nitrogen. The WinAxil (based on AXIL) software package provided with the instrument was used for evaluation of the EDXRF spectra. The data of peak fitting, integral peak area, net peak area and background signal were obtained directly from the deconvolution software. And the background signal is subtracted from the integral peak area automatically. The instrument operation condition is given in Table 1.

2.1. Sample preparation

We used 30 certified biological materials including liver, huangqi, ginseng, spinach, milk powder, wheat flour, rice flour, corn flour, soybean powder, cabbage, tea, chicken, and apple. These were prepared by Institute of Geophysical and Geochemical Exploration (IGGE), China and were used as calibrators. To make a calibration curve, 5 synthetic standards were made with certified reference materials.

First, the biological sample was pulverized to 180 μm (80 mesh), and dried at 60 °C for 24 h in the oven. Next, 6.0 g of sample is weighed and subjected to 1500 kN to form pellet using a liquid press developed in house.

3. Results and discussion

Generally hundreds of mgs or several grams of biological samples were used to press pellet under 150–400 kN pressure. The powder on the surface of this pellet (pressed under 150–400 kN pressure) is easily detached. This will lead to contamination of the EDXRF measurement chamber and decrease the longevity and stability of the instrument. The pellet is not stable and is easily deformed. Thus, the time between sample preparation and determination should be as short as possible to prevent deformation of the specimen surface (Queralt et al., 2005; Margui et al., 2005). The addition of a binder can make the pellet more stable, however it is critical that the source material be homogeneous but without excessive sample preparation. The approach we used here accomplished this. We used a high-pressure pressed powder pellet technique, without a binder, to solve the sample preparation issues related to biological samples XRF analysis. This is a major technological breakthrough for XRF sample preparation. This technique eliminates the need for a binder, thus increasing the analytical sensitivity, decreasing the relative standard deviations, and improving detection limits for most of components.

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