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Determination of selenium in domestic or imported buckwheat and barley using inductively coupled plasma-mass spectrometry

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Abstract

Inductively coupled plasma-mass spectrometry (ICP-MS) was applied to determination of selenium (Se) in food samples. When the concentration of nitric acid in the sample solution was adjusted to 1.0 to 1.5 M, a suitable analytical value of Se was obtained without using any internal substances. The concentration detection limit was 25 ng/g in the dried food samples. In quadruplicate assays of 7 biological reference materials using the proposed ICP-MS method, measured Se concentrations were not significantly different from their certified values. Using the proposed method, Se concentrations in domestic or imported buckwheat and barley were determined. Imported cereals grown in Manitoba (Canada) or North Dakota (USA), known to be high Se areas, showed high Se values at a level of more than 300 ng/g, while most domestic cereals showed low Se values at a level of less than 100 ng/g. These results indicate that the proposed method is reliable and suitable for the determination of trace levels of Se in foods.

Introduction

Selenium (Se) is an essential trace element in human nutrition and is involved in integral parts of several selenoenzymes[1]. In the assessment of the Se nutrition of a human population, quantification of Se in food based on a precious determination method is essential. In many studies on Se determination in foods, fluorometrical analysis (FA) or atomic absorption spectrometry with hydride generation (AAS-HG) has been used[2]. In these analyses, Se present as differential chemical forms in foods has to be converted to selenite during a wet incineration using nitric acid, perchloric acid and hydrochloric acid[3, 4]. However, because of an incompletion of the chemical conversion of Se in this process, an inadequate analytical value is often obtained[4].

Recently, inductively coupled plasma-mass spectrometry (ICP-MS) has been developed for the determination of several trace elements in foods. In this analytical method, differences in chemical species of Se may not influence the quantification of selenium. In the present study, we attempted the determination of Se in several cereal samples using ICP-MS.

Materials and methods

Reagents and samples

Nitric acid (metal-free grade), distilled water (HPLC grade) and standard Se solution (1000 μg/ml Se as SeO_2 in 0.1 M HNO_3) were purchased from Wako. Standard tellurium (Te) solution (1000 μg/ml Te as TeO_4^{2-} in 1M HCl) was purchased from Kanto Chemical (Tokyo). Standard reference materials [bovine liver (SRM 1577a), whole egg powder (RM 8415), wheat flour (SRM 1567a), rice powder (SRM 1568a), spinach leaves (SRM 1570a), apple leaves (SRM

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1515), and peach leaves (SRM 1547)] were purchased from the National Institute of Standards & Technology (Gaithersburg, MD). Samples of barley and buckwheat were kindly supplied by Kyoto Grain System (Kyoto, Japan) and Japan Buckwheat Millers Association (Tokyo, Japan), respectively.

Analysis of Se

Approximately 1 g of sample was mixed with 10 ml of nitric acid in a 30 ml-Kijeldahl flask and kept at room temperature overnight. The mixture was heated at 90℃ in a water bath until the disappearance of insoluble components. The digestion mixture was diluted to 100 ml with 0.5 M HNO_3 and filtrated with a membrane filter (0.45 μm). Titration showed that the HNO_3 concentration of the diluted solution was 1.0 to 1.5 M. Standard Se solution was diluted with 1.2 M HNO_3. To determine the Se contents in the diluted sample solution, the ion intensities of ^{78}Se and ^{82}Se were monitored by ICP-MS with direct nebulization of the sample and standard solution. The operating conditions of ICP-MS are described in Table 1.

Table 1 Operating conditions of ICP-MS in the detection of Se

Instrument	ICPM-8500 (Shimadzu, Kyoto)
Forward power	1200 W
Coolant gas flow rate	7.0 l/min
Auxiliary gas flow rate	1.50 l/min
Nebulizer gas flow rate	0.58 l/min
Sampling depth	5.0 mm
Integration time	2.0 s
Number of running	20
Mode of analysis	Pulse
Isotopes monitored	^{78}Se and ^{82}Se

Results and discussion

Figure 1 shows the relative ion intensities derived from ^{77}Se, ^{78}Se, ^{82}Se, ^{128}Te and ^{130}Te in 50 ng/ml of standard Se or Te solution containing a graded level of HNO_3. The ion intensities of both Se and Te isotopes were decreased with elevation of the HNO_3 concentration. However, the extent of the decrease was different between the Se and Te isotopes; the relative intensities of both ^{78}Se and ^{82}Se were 64%, while those of the two Te isotopes were 75% at a concentration of 1.0 M. These results indicate that Te cannot be used as an internal substance in the quantification of Se using ICP-MS. When the concentration of HNO_3 was more than 1.0 M, the relative intensities of ^{78}Se and ^{82}Se were 40% lower but were found to be at an almost constant level. As described in the previous section, the concentration of HNO_3 in the sample solution could be adjusted at 1.0 to 1.5 M. Thus, we measured ion intensities derived from Se isotopes in the sample and standard solution containing 1.0 to 1.5 M of HNO_3 and did not use an internal substance in the determination of Se by ICP-MS.

Table 2 shows the analytical results of Se in several standard reference materials. In the present analysis, two Se isotopes, ^{78}Se and ^{82}Se, were monitored. Since the ion intensity at m/z 82 provides better sensitivity and signal-to-noise ratio than m/z 78, it was used for the quantification. The analytical values of Se for the reference materials were coincident with the certified values. The detection limit was 0.25 ng/ml when nebulizing to ICP-MS; the concentration detection limit was 25 ng/g of sample. This detection limit is close to that of FA or AAS-HG. Thus, the ICP-MS method established is by no means inferior to the FA or AAS-HG method for Se determination in foods.

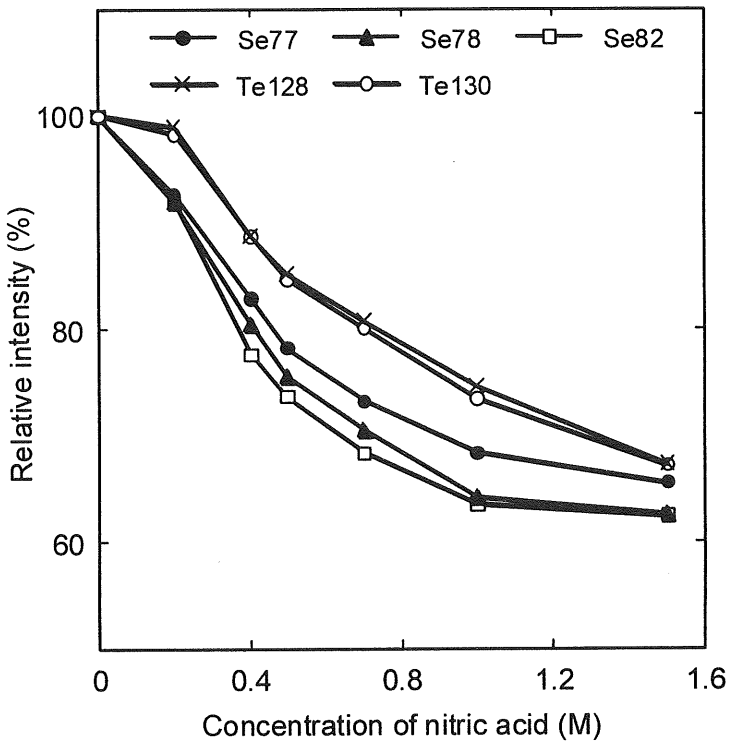

Fig. 1 Effect of nitric acid concentration on ion intensity from selenium (50 ng/ml) and tellurium (50 ng/ml) isotopes

Table 2 Validation with biological reference materials

Reference materials	Certified vaiue (μg/g)	Observed value* (μg/g)
Bovine liver (SRM 1577a)	0.71 ± 0.07	0.741 ± 0.055
Whole egg powder (RM 8415)	1.39 ± 0.17	1.261 ± 0.182
Wheat flour (SRM 1567a)	1.1 ± 0.2	1.017 ± 0.150
Rice powder (SRM 1568a)	0.38 ± 0.04	0.434 ± 0.079
Spinach leaves (SRM 1570a)	0.117 ± 0.009	0.135 ± 0.038
Apple leaves (SRM 1515)	0.050 ± 0.009	0.062 ± 0.023
Peach leaves (SRM 1547)	0.120 ± 0.009	0.142 ± 0.034

*Values are means ± SD for 4 assays.

Table 3 shows the Se contents in domestic or imported buckwheat and barley, determined using the ICP-MS method. Among the same cereals, the variation of Se content was remarkable. Buckwheat and barley grown in Manitoba (Canada) or North Dakota (USA) showed high Se values at a level of more than 300 ng/g, while most domestic samples showed low Se values at a level of less than 100 ng/g. Other imported cereals showed median Se values. This variation pattern of Se content observed in buckwheat and barley is similar to that in wheat[5] or soybeans[6]. Since Manitoba and North Dakota have been recognized as high Se areas[7], most crops grown in these areas are expected to show high Se content. Accordingly, the present analytical results are reasonable and the measurement of Se using ICP-MS is applicable to several food samples.

Table 3 Selenium content in buckwheat and barley cultivated in various places

Samples	Places	Se content (ng/g)
Buckwheat, whole	Canada, Manitoba	372[2]
	USA, North Dakota	533[2]
	USA, Washington	118[3]
	Australia, New South Wales	156
	China, Nèi-ménggu	158
	China, Liàoning	176
	China[1]	54
	Japan, Hokkaido	69[3]
	Japan, Aomori	92
	Japan, Yamagata	113
	Japan, Fukushima	126[3]
	Japan, Ibaraki	94
	Japan, Nagano	30
	Japan, Fukui	36
Barley, whole	Canada, Manitoba	762
	China[1]	101
	Japan, Hokkaido	46

Each value was obtained from quadruplicate analyses of one sample unless otherwise noted.
[1] Detail of the place was not identified.
[2] Mean of three samples.
[3] Mean of two samples.

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