

Determination of arsenic, antimony, and selenium by FI-HG-AAS in foods consumed in Slovakia

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Summary

A flow injection hydride generation atomic absorption spectrometric (FI-HG-AAS) method was developed for the determination of arsenic in fish, rice and yeast; of selenium in vegetable, fruit, and dairy products; and of antimony in vegetable, fruit, dairy and bakery products after microwave digestion of samples. Individual steps of the method were optimized and analytical as well as statistical parameters of the method were determined (detection limits: arsenic - $0.068 \mu\text{g.kg}^{-1}$, selenium - $0.060 \mu\text{g.kg}^{-1}$, antimony - $0.15 \mu\text{g.kg}^{-1}$; quantification limits: arsenic - $0.22 \mu\text{g.kg}^{-1}$, selenium - $0.20 \mu\text{g.kg}^{-1}$, antimony - $0.51 \mu\text{g.kg}^{-1}$; type C combined standard uncertainties: arsenic - 10.8%, selenium - 8.4%, and antimony - 14.3%). Accuracy of the method was evaluated using BCR-150 skim milk, BGW 08502 Rice Flour and P-ACHK reference materials. The method was used for the determination of arsenic, selenium and antimony in foods consumed in Slovakia.

Keywords

arsenic; antimony; selenium; foods; FI-HG-AAS

Arsenic is widely distributed in the general environment, and all humans, plants and animals are exposed to low levels of this element and its compounds. Arsenic is mainly used for production of pesticides, plant desiccants, and wood preservatives. Inorganic arsenic is an established human carcinogen: lung cancer may develop following occupational exposure via inhalation, and skin cancer may result from ingestions and consumption of water and food containing high concentrations of arsenic [1]. Antimony and its compounds are used in several industries: fireproof materials, ceramic products, pharmaceutical industry, metallurgy and mailings [2]. Also, several natural processes including weathering of rock and soil run-off may be sources of higher antimony concentrations in the air and waters. The background of Sb (III) toxicity is its irreversible binding to thiol-containing enzymes [3]. The trace mineral selenium is an essential nutrient of fundamental importance to human biology as Se is a component of glutathione peroxidase. Some epidemiological studies have revealed an inverse correlation between Se status and cardiovascular disease [4]. Selenium deficiency has been suggested to play a role in the etiology of other pathologies, such as oxidative stress or inflammatory conditions, diabetes mellitus, hepatopathies, HIV infection [5, 6].

The flow injection hydride generation technique combined with atomic absorption spectrometry (FI-HG-AAS) offers the advantage of high sensitivity, together with reduction of matrix interference. Determination of arsenic, antimony and selenium concentrations in foods by this technique also requires destruction of the organic matter and complete reduction of As (V), Sb (V) and Se (VI) to As (III), Sb (III) and Se (IV).

MATERIALS AND METHODS

Fruit, vegetables, fish, oils, rice, baking products, and dairy products were obtained from the retail network in Bratislava. Samples were digested in consumption form by microwave digestion system (Milestone MLS 1200 MEGA, Sorisole, Italy). Standard reference materials - arsenic, antimony and selenium stock solutions 1 g.l^{-1} in 2% HNO_3 were obtained from Slovak Institute of Metrology, Bratislava, SR. All reagents were of the highest purity grade available: nitric acid, 65%, Suprapur (Merck, Darmstadt, Germany); hydrochloric acid, 37%, Suprapur (Merck); sodium tetrahydroborate, 99% (Merck); sodium hydroxide p. a. (Lachema, Brno, Czech Republic); potassium iodide solution p. a., (Lachema); ascorbic acid p. a., (Merck).

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Tab. 1. Parameters of the method.

Element	As	Sb	Se
wavelength [nm]	193.7	217.6	196.0
slit [nm]	0.7 high	0.2 high	2.0 high
type of lamp	EDL	EDL	EDL
lamp Current [mA]	310	290	210
signal type	AA-BG	AA-BG	AA-BG
time of measurement [s]	15	25	20
sample value [μ l]	500	500	500
cell temperature [°C]	900	900	900
carrier gas	argon	argon	argon
gas flow rate [ml.min ⁻¹]	40	50–80	40–100
carrier solution	3 % HCl	3 % HCl	3 % HCl
reagent	0.5% NaBH ₄ in 0.05% NaOH	0.05% NaBH ₄ in 0.05% NaOH	0.05% NaBH ₄ in 0.05% NaOH

EDL - electrodeless discharge lamp.

Tab. 2. Analytical characteristics of the method.

Element	As	Sb	Se
LD [mg.kg ⁻¹]	0.00015	0.00015	0.00006
LOQ [mg.kg ⁻¹]	0.00035	0.00051	0.0002
type A uncertainty [%]	5.24	9.75	3.26
type B uncertainty [%]	6.33	10.47	7.76
type C uncertainty [%]	8.20	14.41	8.40
recovery [%]	94–112	76–109	88–111
linearity range [mg.dm ⁻³]	0.0003–0.025	0.0005–0.025	0.0002–0.025

LD – detection limit, LOQ – quantification limit.

Volatile arsenic, antimony, and selenium were generated in a FIAS 400 flow injection analysis system (Norwalk, Connecticut, USA), transported by means of an argon carrier gas to a quartz cell of the Perkin–Elmer 4100 atomic absorption spectrometer (Norwalk, Connecticut, USA) with deuterium correction. In the quartz cell heated to 900 °C, the hydrides were converted to gaseous metal atoms and the amount of light absorbed was measured.

Optimised parameters of the method are summarised in Tab. 1 [7, 8].

Digestion of samples

Weighed samples of 1.0–2.0 g of vegetable, fruit and sea fish or 0.5 g of oil, rice, dairy, bakery products were placed in a teflon microwave digestion vessel, and 2 ml HNO₃ and 2 ml HCl (3 ml HNO₃ and 1 ml HCl) were added. The vessel was closed and fastened in the rotor. The rotor with 6 loaded vessels was placed into the microwave oven. The microwave digestion program was applied: 250 W (1 min), 0 W (1 min), 250 W (5 min), 400 W (5 min), and 650 W (5 min). Then, 0.5 % KJ and 0.5 % ascorbic acid were added to the digested samples to ensure reduction of As(V) to As(III)

(for 60 min). Selenium(VI) was reduced to Se(IV) with HCl (1:1) and heating to 90 °C for 30 min, and antimony(V) was reduced to Sb(III) with KI and ascorbic acid (for 5 min) and adjusted to 10 ml with 3% HCl. The different elements were determined by FIA-HG-AAS with optimized parameters. The concentrations of the elements studied were calculated from peak areas or absorbance peaks. The results shown represent averages of triplicate measurements.

Tab. 2 summarizes the analytical characteristics of the method. The trueness of method was tested by determining arsenic concentration in the reference material GBW 08502 Rice Flour (Beijing Municipal Environmental Monitoring Center, Beijing, China); the value obtained was 0.0525 mg.kg⁻¹, $s_x = 0.010$ mg.kg⁻¹, whereas the certified value was 0.051 mg.kg⁻¹, $s_x = 0.005$ mg.kg⁻¹. For selenium, the reference material was BCR-150 skim milk (Community Bureau of Reference, Brussels, Luxembourg), with the measured and certified concentration being 0.128 mg.kg⁻¹, $s_x = 0.004$ mg.kg⁻¹ and 0.132 mg.kg⁻¹, $s_x = 0.010$ mg.kg⁻¹, respectively. For antimony, P-ACHK seaweed (SMU, Bratislava, Slovak Republic) was used as the reference mate-

rial, with the measured and certified concentration being 0.0933 mg.kg⁻¹, $s_x = 0.0091$ mg.kg⁻¹ and 0.0916 mg.kg⁻¹, $s_x = 0.0048$ mg.kg⁻¹, respectively.

Detection limit was defined as the element concentration of reagent blanks corresponding to three times the standard deviation of the blanks ($n = 10$). Similarly, the quantification limit corresponded to ten times the standard deviation of the reagent blanks. The combined standard uncertainty (u_C) was defined as $\sqrt{(u_A^2 + u_B^2)}$. Type A uncertainty (u_A) is the standard deviation of the matrix measurement. Type B uncertainty (u_B) included a sample mass, volume, slope of calibration curve, and signal measured. Recovery of the method was assessed in the matrix by analyzing fortified samples. The samples were fortified before microwave digestion using solutions of As(V), Se(VI) and Sb(V) (0.005 and 0.020 mg.dm⁻³).

RESULTS AND DISCUSSION

The results obtained with the optimised FI-HG-AAS method are presented in Tables 3, 4, 5.

In frozen sea fish and yeast, very low levels of arsenic (0.006–0.102 mg.kg⁻¹ and 0.034–0.113 mg.kg⁻¹, respectively) were measured as compared with the limits set by the Slovak legislation. The concentrations of arsenic measured in oils reached the maximum limit (0.018–0.096 mg.kg⁻¹). Concentrations of arsenic found in rice (0.003–0.096 mg.kg⁻¹) were comparable to those measured in rice from the US market basket [9]. Relatively higher arsenic concentrations have been reported for marine fish from Canada, the values reported for edible oil were comparable with our results [10].

Tab. 3. Contents of arsenic in sea fish, rice and yeast consumed in Slovakia.

Sample	n	Minimum [mg.kg ⁻¹]	Maximum [mg.kg ⁻¹]	Mean [mg.kg ⁻¹]	s_x [mg.kg ⁻¹]	LH [mg.kg ⁻¹]
sea fish	8	0.006	0.103	0.039	0.054	5.0
rice	10	0.003	0.096	0.036	0.046	1.0
yeast	6	0.045	0.111	0.075	0.031	2.0
oils	10	0.018	0.096	0.049	0.033	0.1

LH - hygienic limit set by Slovak legislation, n - number of samples analyzed, s_x - standard deviation.

Tab. 4. Contents of antimony in fruit, vegetable, dairy, and bakery products consumed in Slovakia.

Sample	n	Minimum [mg.kg ⁻¹]	Maximum [mg.kg ⁻¹]	Mean [mg.kg ⁻¹]	s_x [mg.kg ⁻¹]
tangerines	8	0.002	0.020	0.013	0.006
apples	10	0.006	0.011	0.008	0.003
garlic	8	0.002	0.004	0.003	0.002
onions	9	0.006	0.011	0.008	0.003
peppers	5	0.009	0.016	0.012	0.003
cucumbers	2	0.008	0.010	–	–
cabbage	10	0.004	0.021	0.013	0.008
tomatoes	2	0.011	0.014	–	–
carrots	6	0.002	0.008	0.005	0.003
flour	10	0.003	0.023	0.011	0.010
rolls	5	0.005	0.009	0.007	0.003
bread	2	0.006	0.007	–	–
biscuits	2	0.009	0.012	–	–
pastry	5	0.003	0.010	0.008	0.003
oat flakes	5	0.003	0.012	0.007	0.005
milk	5	0.005	0.007	0.006	0.002
fermented milk	5	0.004	0.008	0.006	0.003
cheese	5	0.005	0.021	0.012	0.011
spread cheese	6	0.009	0.030	0.022	0.010
milk powder	5	0.011	0.020	0.016	0.006

n - number of samples analyzed, s_x - standard deviation.

Tab. 5. Contents of selenium in fruit, vegetable, and dairy products consumed in Slovakia.

Sample	n	Minimum [mg.kg ⁻¹]	Maximum [mg.kg ⁻¹]	Mean [mg.kg ⁻¹]	s _x [mg.kg ⁻¹]
apricots	5	0.005	0.024	0.014	0.009
apples	10	0.003	0.111	0.040	0.053
plums	10	0.016	0.111	0.064	0.048
pears	5	0.037	0.158	0.077	0.073
grapes	5	0.008	0.064	0.036	0.027
grape-fruits	5	0.004	0.008	0.005	0.003
bananas	5	0.002	0.018	0.009	0.007
peppers	10	0.006	0.102	0.050	0.047
tomatoes	5	0.015	0.076	0.051	0.026
carrots	5	0.001	0.015	0.007	0.006
cucumbers	5	0.007	0.030	0.015	0.014
kohlrabi	5	0.030	0.045	0.039	0.006
cabbage	4	0.041	0.064	0.051	0.011
cauliflower	5	0.017	0.070	0.043	0.025
milk	5	0.007	0.011	0.008	0.003
cream	5	0.025	0.069	0.049	0.021
yogurt	10	0.006	0.119	0.044	0.051
acid milk	5	0.024	0.075	0.041	0.025
cheese	8	0.010	0.176	0.072	0.063

The levels of antimony found in fruits (0.002–0.020 mg.kg⁻¹), vegetables (0.003–0.021 mg.kg⁻¹), bakery products (0.003–0.023 mg.kg⁻¹) and cheese (0.009–0.030 mg.kg⁻¹) were low.

Also, low concentrations of selenium were measured for vegetables (0.001–0.102 mg.kg⁻¹) and fruits (0.002–0.158 mg.kg⁻¹). Pears and plums showed relatively higher selenium concentrations (0.037–0.158 mg.kg⁻¹). The values of selenium measured in dairy products (0.006–0.176 mg.kg⁻¹) were comparable with those reported for dairy products, e. g. from Spain [11], Ireland [12], and Australia [13]. Selenium concentrations measured in foodstuffs in Slovakia are suboptimal, with the daily intake of this element representing as little as 60% of the recommended value [14].

CONCLUSION

The optimised method presented herein is more economical than the routine procedure recommended by the FIAS system manufacturer because the former uses lower concentrations of reduced agents and carrier solution, as well as smaller carrier gas flow rates. The method was implemented to be used for the determination of arsenic, antimony, and selenium in vegetables, fruits, marine fish, rice, oils, yeast, dairy and bakery products consumed in Slovakia. The values of total

arsenic concentrations measured for the tested samples did not exceed the hygienic limits.

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