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ELECTROTHERMAL AAS FOR THE DETERMINATION OF ARSENIC AND SELENIUM IN HAIR

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Abstract. The level of arsenic and selenium in the hair of Estonian children living in different industrial and traffic-polluted areas was determined. The similarity in the chemical behaviour of arsenic and selenium can be used in the chemical preparation of hair and AAS.

Key words: hair, As, Se, AAS, determination.

In this study the levels of arsenic and selenium were determined in the hair of Estonian children who lived in different industrial and traffic-polluted areas. The compounds of arsenic and selenium have some similar chemical properties, but they differ in their physiological influence. Arsenic is a toxic element while selenium is a bioelement.

Arsenic

All the biochemical actions of As are attributed to its trivalent forms. These compounds can covalently react with sulphhydryl groups (—SH) and enzymes (E), inactivating these. Since —SH groups are often required for certain enzyme activity, arsenic compounds inactivate these enzymes, leading to eventual cell death.

Arsenic trioxide and the derivative arsenites and arsenates are the principal causes of occupational and environmental poisoning. The symptoms of chronic arsenic exposure are exfoliation and pigmentation of the skin, neurological symptoms, polyneuritis, altered hematopoiesis, and degeneration of the liver and kidneys.

Hair is an easily accessible biological matter for determining arsenic. It seems that arsenic in the hair is a good indicator of the amount of inorganic arsenic absorbed during the growth period of the hair. The normal level in the hair is under 0.3 μg/g [1].

Selenium

Selenium is known as an essential trace element for man. It is a component of enzyme glutathione peroxidase, which has been demonstrated by the isolation of glutathione peroxidase from human erythrocytes.

Selenium is also found in type I and type III iodothyronine deiodinases. Proteins with unknown enzymatic function that contain selenium include Selenoprotein P and Selenoprotein W. The former is a highly unusual molecule in that it contains several selenocysteine residues per polypeptide chain. Progress in our understanding of selenium metabolism is also evolving rapidly with the identification of selenophosphate synthetase and its possible regulatory role in controlling selenium transformation at the cellular level.

Attempts to link selenium deficiency with human diseases, especially the chronic degenerative disease, are continuing. In particular, much effort has been devoted toward elucidating any possible relationship between low dietary selenium intake and an increased risk of cancer.

The US Environmental Protection Agency has promulgated an official toxicological standard known as the Reference Dose (RfD), which is defined as "an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects during a lifetime". The RfD for selenium is 5 µg/kg/d or 350 µg/d for the typical 70 kg male [2].

The normal values of selenium are in the range from 100 to 190 µg/l in whole blood and in the range from 0.4 to 0.8 µg/g in the hair [1, 3]. In principle, three methods are used for arsenic and selenium determination in biological materials: determination by the hydride atomic absorption technique, electrothermal furnace atomic absorption spectrometry, and the neutron activation analysis after wet digestion as a nondestructive technique.

MATERIALS AND METHODS

Sample preparation

From the collected hair only the first 3 cm proximal to the scalp was used for analysis. The hair samples were washed with 1 M nitric acid and bidistilled water and dried at 40 °C. Thereafter, 0.2–0.6 g of washed and dried hair samples was mineralized by concentrated nitric acid and hydrogen peroxide (5 : 1) in a Teflon bomb at 140 °C for 6 h. The solution was cooled and diluted up to 25 ml with bidistilled water.

Experimental apparatus

A Philips Model PU 9100X atomic absorption spectrophotometer equipment with a Philips HGA/P3105 graphite furnace and a deuterium

background corrector was used for all measurements. A pyrolytically coated graphite tube was used.

Instrumental conditions for As and Se:

Principal line (nm) – As 193.7; Se 196
Lamp current (mA) – As 12; Se 6
Bandpass (nm) – As 0.5; Se 0.5

Stock solutions:

1.000 mg Se/l and 1.000 mg As/l (Merck)

Standard solutions:

As – 5 and 10 or 10 and 20 ng/ml
Se – 5 and 10 or 10 and 20 ng/ml

The graphite furnace settings consisting of drying, charring, and atomizing cycles are listed in Table 1. The purge gas used was argon. During the atomization cycle the purging gas stream was interrupted by programming the stopped flow control to increase the residence time of the arsenic and selenium atoms in the light beam and to enhance sensitivity.

Table 1

Temperature programme of the graphite furnace for the determination of As and Se in hair

Step	Temperature, °C		Hold time, s
	for As determination	for Se determination	
Drying	100	100	10
	500	500	20
Ashing	1000	1200	10
Atomization	2200	2400	3
Cleaning	2400	2600	2

To 0.5 ml of the sample was added 0.2 ml of the solution of nickel nitrate (1 mg Ni/ml, Merck) and mixed. Then, 20 ml of the solution was injected into the graphite tube.

The method developed in this study was checked with a GSV-1 reference sample (Standard reference material GBW 07602), where the certified concentration for As is 0.095 ± 0.08 μg/g and for Se 0.184 ± 0.011 μg/g.

RESULTS AND DISCUSSION

1. The addition of nickel nitrate solution stabilizes the vaporization and allows of the use of high ashing temperatures. Without nickel solution the maximum ash temperature for As is 400 and for Se 300 °C and with nickel solution respectively 1000 and 1200 °C (Figs. 1 and 2).

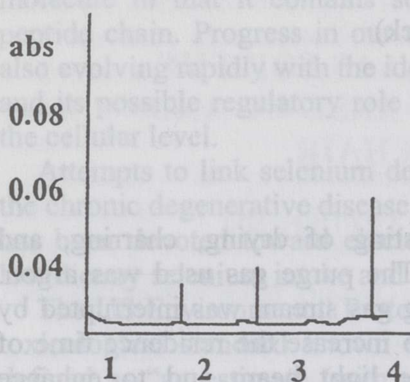

Fig. 1. Absorptiogram for Se without a Ni-matrix. Steps: *1*, drying; *2*, ashing; *3*, atomization; *4*, cleaning.

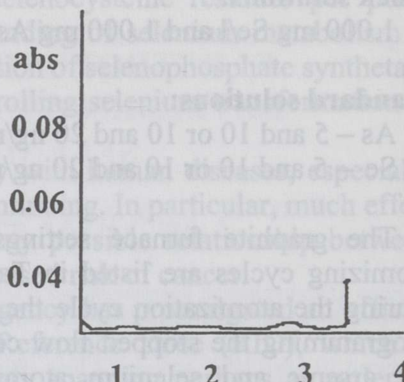

Fig. 2. Absorptiogram for Se with a Ni-matrix. See Fig. 1 for legend.

2. The application of pyrolytically coated graphite tubes improves the sensitivity.

3. The application of the deuterium lamp background correction helps avoid the light scattering effect.

4. One of the most serious problems was the interference of the high concentration of nitric acid in samples with the determination of arsenic and selenium. A high concentration of nitric acid in the mineralized sample changed the absorption of the blank sample and impaired the accuracy and the sensitivity of the determination (Figs. 3 and 4).

The program used for the graphite furnace allowed us to completely separate the fumes of the matrix and to receive a better ratio of the arsenic and selenium to the background signal.

The sensitivity defined in atomic absorption spectrometry was 1 ng/ml As and 1 ng/ml Se. The sensitivities for hair are 5 ng As/ml and 4 ng Se/ml. The relative error is 6% at 20 ng and 4% at 40 ng.

Optimal absorption for AAS graphite furnace determination for arsenic and selenium is at the concentration 5 ng/ml in the range 0.12–0.13 abs. For the blank solution the absorption must not be more than 0.04–0.05 abs.

Arsenic and selenium concentrations in the hair of Estonian children are presented in Table 2.

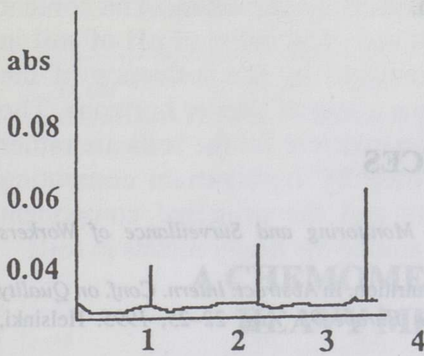

Fig. 3. Absorptiogram for Se with a high nitric acid concentration. See Fig. 1 for legend.

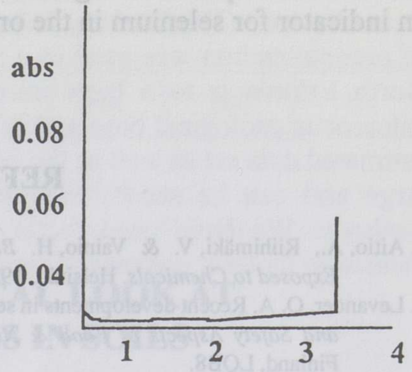

Fig. 4. Absorptiogram for Se with a low nitric acid concentration. See Fig. 1 for legend.

Table 2

The mean concentration of As and Se in hair ($n = 190$)

Metal	Concentration, µg/g	Mode
As	0.34 ± 0.08	0.26
Se	0.64 ± 0.24	0.46

The levels of arsenic in the hair of Estonian children are therefore normal, not surpassing the toxicity limit of 3 µg/g [1]. The levels of selenium in the hair of Estonian children can be compared with the values usually mentioned in literature [1–4], but we can say nothing about the normal level.

In our earlier investigations [3, 4] the mean concentration of selenium in the blood serum and whole blood of a group of adults of 146 persons was shown to be 0.15 and 0.18 mg/l, respectively. The serum selenium level was lower for the inhabitants of the island of Saaremaa and higher among the population of the town of Pärnu. Very low concentrations of selenium in blood serum (0.06 mg/l) and milk (0.01 mg/l) were found for mothers in North Estonia [3]. As nothing is known about the concentration of selenium in the food, we cannot make any conclusions about selenium deficiency.

We have no information on the possible correlation between hair and blood. It is not possible to give an assessment on the application of hair as an indicator for selenium in the organism.

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JUUSTE ARSEENI- JA SELEENISISALDUSE MÄÄRAMINE AAS-ELEKTROTERMILISEL MEETODIL

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On määratud arseeni- ja seleenisisaldus Eesti eri piirkondades elavate laste juustes. Tulemused näitasid, et arseenisisaldus ei ületa toksilisuse piiri ning on sellest keskmiselt kümme korda madalam. Seleenisisaldus juustes on normväärtuse piirides, kuid olemasolevate andmete põhjal ei saa otsustada, kas tegu on seleeni defitsiidiga organismis. Eestis ei ole veel tehtud uuringuid seleenisisalduse kohta toiduainetes.

On välja töötatud metoodika arseeni- ja seleenisisalduse määramiseks juustes AAS-elektrotermilisel meetodil.