Determination of zinc in plants and grains by atomic absorption spectrometry

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Determination of zinc in different objects by atomic absorption spectrometry (AAS) has been performed. The selectivity of the method has been investigated. The interfering Zn/Me ratios were considered as limiting when the determination error was ±10%. All metals according to their obstruction characteristics make the following sequence: Cr > Cd > Sr ≈ K > Co ≈ Ca ≈ Mg ≈ ≈ Li > Fe > Cu ≈ Mn > Ni ≈ Pb > Na.

The method has been applied for the determination of zinc in plants and grains. This method is more simple and selective than the previously reported photometric method.

Key words: atomic absorption spectrometry, zinc, plants, grains

INTRODUCTION

High concentrations of heavy metals are generally found in the industrial regions. Excessive amounts of heavy metals (*e.g.*, Zn, Cu, Mn, Cr) are accumulated in different environmental objects, being available to humans and animals along the food chains. To understand the role of metals in biochemical and geochemical processes, determination of their concentrations in different environmental objects is very important.

Zinc is essential for the normal growth of plants, although elevated concentrations of zinc can result in growth inhibition and toxicity symptoms. Zinc is also an essential micronutrient for humans, because it activates a large number of enzymes. In particular, zinc has been recognized as a co-factor of the superoxide dismutase enzyme, which is involved in protection against oxidative processes [1]. Certain groups of people appear to be at risk with regard to zinc nutrition. By contrast, excess of Zn causes inhibition of apoptosis thus suggesting increased survival of genetically mutated cells and higher cancer risks in exposed populations [2].

One of many methods of determination of the total contents and speciation analysis of heavy metals of their environmental concentrations is atomic absorption spectrometry [3–5]. This method is simple and very selective. In this paper we present determination of zinc by the method of flame atomic absorption spectrometry in plants and grains.

EXPERIMENTAL

Materials and Procedures

All solutions were prepared from chemical and analytical grade reagents with double-distilled water.

The standard solution of zinc. ZnO (1.2447 g) was dissolved in 10 ml of diluted HCl (1:1), and then the solution was diluted to 1000 ml with double-distilled water (1 μg/ml Zn).

The standard working solution of zinc. 1 ml of Zn standard solution was diluted to 100 ml with double-distilled water (10 μg/ml Zn).

HCl (1:1), 2 mol/l and conc.

HNO_3 (1:1) and conc.

H_2SO_4 (1:4) and conc.

Hydroxylamine hydrochloride solution (20%).

Acetate buffer (pH 5).

Thiourea solution (10%).

Potassium thiocyanate solution (20%).

Rhodamine C solution (0.02%).

Methyl orange solution (0.1%).

NH_3 *solution (1:1).*

Li, Na, K, Ca, Mg, Sr, Cu, Mn, Cr, Pb, Fe, Ni, Co and Cd solutions. These solutions were prepared from reagent levels, witch contain 1 g of pure metal ions.

Metal Cu, Pb, Co, Mn, Fe, Cd and Ni_2O_3 were dissolved in 10 ml of diluted HNO_3 (1:1).

CaO and metal Mg were dissolved in 10 ml of diluted HCl (1:1).

Metal Cr was dissolved in 10 ml of diluted H_2SO_4 (1:4).

All these solutions were diluted to 50 ml with double-distilled water.

KCl, NaCl, Li_2SO_4 and $Sr(NO_3)_2$ were dissolved in double-distilled water and diluted to 50 ml.

1 ml of resulting solutions contains $2.0 \cdot 10^4$ μg metal ions.

2.5 ml of the standard working zinc solution (10 μg/ml), 1 ml of the corresponding metal ions solution ($2.0 \cdot 10^4$ μg/ml) and 5 ml of HCl (2 mol/l) were placed in a volumetric flask and diluted to 50 ml with double-distilled water. Zinc solution of 0.5 μg/ml with addition of a corresponding metal was prepared for studies of interference effect. For comparison, solution of 0.5 μg/ml zinc without addition of metals was also prepared.

Calibration was performed with aqueous standards. Aqueous standards were prepared by taking different aliquots (0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 7.5, 8.0 and 8.5 ml) and diluting to 100 ml with double-distilled water. 10 ml of HCl (2 mol/l) was added to all solutions. Thus, the aqueous standards of 0.00, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.75, 0.8 and 0.85 μg/ml were prepared.

Determination of zinc in solid environmental samples must be preceded by their mineralization. Mineralization can be carried out with a mixture of mineral acids [6] or heating in a muffling furnace [7, 8]. In this work, for determination of zinc in plants and grains the method of heating mineralization was used. Homogenized samples of plants (0.25 g) and grains (1.00 g) were placed in a sand beaker and heated at 825 ± 25°C for 2 h in a furnace. The cooled remnants were digested by addition of 10 ml diluted HNO_3 (1:1). The resulting solutions were filtered and diluted to 25 ml with double-distilled water. Zinc determination was carried out by direct aspiration into an air-acetylene flame atomic absorption spectrometer fit with a zinc hollow cathode lamp. Then the sample was aspirated into the air-acetylene flame lower zinc detection limit, and interference of some metals in comparison with propane-butane-air flame was obtained [9].

Instruments

A Hitachi 170–50 atomic absorption spectrometer (Japan) was used for the determination of zinc.

Samples were atomized at 213.8 nm.

Air-acetylene gas was used for all of the experiments.

The strength of the current was 15 mA.

For the photometric determination of zinc, a KFK-3 photometer was used.

RESULTS AND DISCUSSION

A correlation between absorption and zinc concentration (calibration curve) is shown in Figure 1.

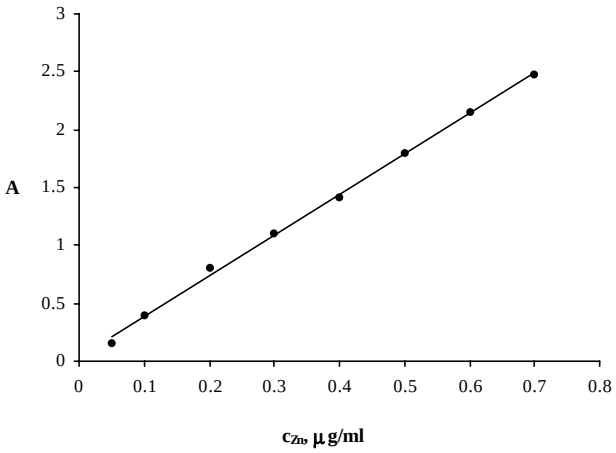

Fig. 1. Correlation between absorption and zinc concentration

The parameters of calibration curve are listed in Table 1. One can see that the linear correlation between absorption and zinc concentration exists when zinc concentration lies in the range 0.05–0.7 μg/ml. The observed detection limit of zinc is about 0.05 μg/ml.

Table 1. **Parameters of calibration curve**

$C_{Zn,}$ μg/ml	y = ax + b		Zn detection limit, μg/ml
	a	b	
0.05–0.7	3.4	0.06	0.05

To studyd the effect of interference, the following metals were selected: Li, Na, K, Ca, Mg, Sr, Cu, Mn, Cr, Pb, Fe, Ni, Co and Cd. The Zn/Me interfering ratios are considered as limiting when the determination error is ± 10%. The results obtained are summarized in Fig. 2–5. The interferen-

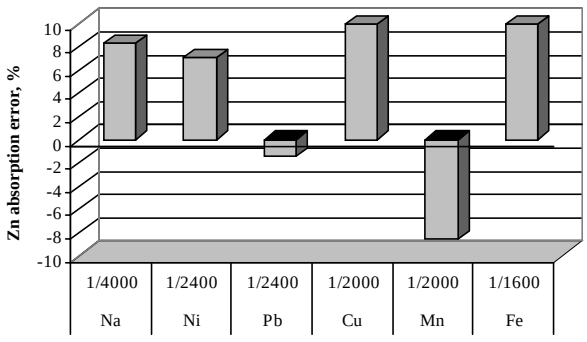

Fig. 2. Influence of Na, Ni, Pb, Cu, Mn and Fe on zinc absorption

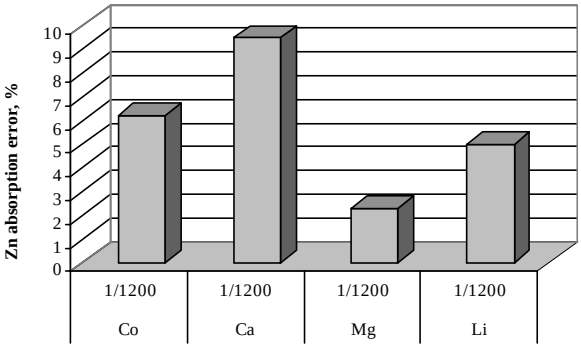

Fig. 3. Influence of Co, Ca, Mg and Li on zinc absorption

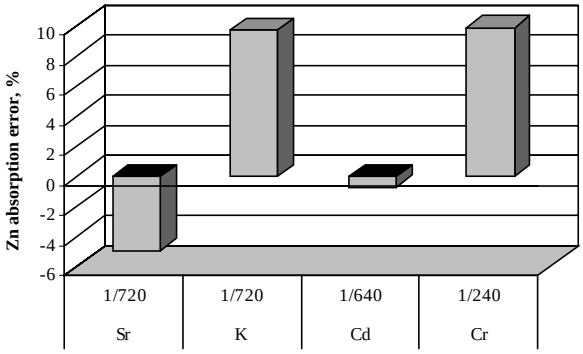

Fig. 4. Influence of Sr, K, Cd and Cr on zinc absorption

ce of Na (see Fig. 2) is not significant at its concentration 4000-fold higher than that of zinc. The interference of Ni and Pb is not significant when their concentrations are 2400-, Cu and Mn at 2000-, and Fe (Fig. 2) 1600-fold higher than that of zinc. Then the interference of Co, Ca, Mg and Li (Fig. 3) is not significant at their concentrations 1200- and of Sr and K (Fig. 4) 720-fold higher than that of zinc. Finally, the interference of Cd and Cr (Figure 4) is not significant at their concentrations 640- and 240-fold higher than that of zinc, respectively.

According to the obtained results, all metals can be put in the following order by their obstruction characteristics: Cr > Cd > Sr ≈ K > Co ≈ Ca ≈ ≈ Mg ≈ Li > Fe > Cu ≈ Mn > Ni ≈ Pb > Na. For the determination of zinc by AAS, interferences from the metals can appear when these metals occur at concentrations much higher than in ordinary environmental samples. Thus, we can conclude that the AAS method is very selective and might be successfully used for the determination of zinc in plants and grains.

Zinc was determined in different kinds of plants from different regions of Lithuania. The determined levels of zinc in plants are shown in Table 2. The highest concentration of zinc was found in samples of *Calamagrostis arundinacea*. Zinc levels were higher in *Calamagrostis arundinacea* and *Hylocomium splendens* from the Dzūkija region than in plants from the Aukštaitija region.

Zinc was determined also in different grains. The levels of zinc in grains are shown in Table 3. The

Table 2. **Zinc concentrations in plants**

Region	Plants	Zn concentration, mg/kg (AAS method)		Zn concentration, mg/kg (photometric method)	
		(n= 5, P = 0.95)	Sr, %	(n = 5, P = 0.95)	Sr, %
Dzūkija	*Calamagrostis arundinacea*	100.3 ± 0.6	0.6	108.2 ± 2.5	0.9
Aukštaitija	*Calamagrostis arundinacea*	59.2 ± 0.9	1.2	57.5 ± 5.0	3.5
Dzūkija	*Hylocomium splendens*	53.1 ± 0.7	1.1	51.5 ± 6.1	4.8
Aukštaitija	*Hylocomium splendens*	25.4 ± 0.4	1.3	26.4 ± 3.8	5.8
Saldutiškis	*Festuca pratensis* L.	73.2 ± 1.3	1.5	70.5 ± 8.0	4.6
Josvainiai	*Festuca pratensis* L.	40.4 ± 0.8	1.6	39.5 ± 3.9	4.0

Table 3. **Zinc concentrations in grains**

Grains	Zn concentration, mg/kg (AAS method)		Zn concentration, mg/kg (photometric method)	
	(n = 5, P = 0.95)	Sr, %	(n = 5, P = 0.95)	Sr, %
Wheat (Lithuania)	20.6 ± 0.3	1.5	18.3 ± 0.7	1.6
Wheat (France)	18.2 ± 0.4	1.5	19.3 ± 1.7	4.5
Barley (Lithuania)	22.6 ± 0.4	1.8	20.2 ± 1.5	3.0
Green peas (Lithuania)	24.6 ± 0.5	1.6	24.3 ± 1.1	1.8
Rice (India)	16.3 ± 0.3	1.2	14.3 ± 0.5	1.6
Buckwheat (Lithuania)	22.6 ± 0.5	1.8	23.2 ± 1.3	2.5

concentrations of zinc in different grain samples were almost equal. The highest level of zinc was found in green peas (24.6 mg/kg) and the lowest in rice (16.3 mg/kg). Zinc level in wheat from Lithuania was higher than in wheat from France.

For comparison, the content of zinc in plants and grains was also determined by the photometric method using Rhodamine C as a complexing agent [10]. The concentrations of zinc determined by AAS were statistically equal to the concentrations determined by the photometric method (see Tables 2 and 3). However, the proposed AAS method is more simple and selective than the photometric method.

CONCLUSIONS

1. The parameters of the calibration curve were determined. A linear correlation between absorption and zinc concentration exists when zinc concentration lies in the range 0.05–0.7 μg/ml. The observed detection limit of zinc was about 0.05 μg/ml.

2. For the investigation studied of interference effect the following metals were selected: Li, Na, K, Ca, Mg, Sr, Cu, Mn, Cr, Pb, Fe, Ni, Co and Cd. The Zn/Me interfering ratios are considered as limiting when the determination error is ±10%. All metals according to their obstruction characteristics made the following sequence: Cr > Cd > Sr ≈ K > > Co ≈ Ca ≈ Mg ≈ Li > Fe > Cu ≈ Mn > Ni ≈ ≈ Pb > Na. For the determination of zinc by AAS, interferences from other metals can appear when these metals occur at concentrations much higher than in ordinary environmental samples.

3. The proposed method has been applied for the determination of zinc in plants and grains by flame atomic absorption spectrometry. This method is more simple and selective than the photometric method.

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CINKO NUSTATYMAS AUGALUOSE IR GRŪDINĖSE KULTŪROSE ATOMINĖS ABSORBCINĖS SPEKTROMETRIJOS METODU

S a n t r a u k a

Atominės absorbcinės spektrometrijos metodu ištirtos pagrindinės cinko nustatymo charakteristikos. Nustatyta, kad, naudojant dujas acetilenas–oras, absorbcijos ir cinko kiekio tiesinė priklausomybė yra koncentracijų intervale nuo 0,05 iki 0,7 μg/ml. Mažiausia cinko nustatymo riba 0,05 μg/ml. Taip pat buvo ištirtas cinko nustatymo metodikos atrankumas. Nustatyti leidžiamieji ribiniai santykiai Zn/Me, kuriems esant nustatymo paklaida būna ne didesnė kaip ±10%. Visus metalų jonus pagal trukdantį poveikį galima surašyti į eilę: Cr > Cd > Sr ≈ K > Co ≈ Ca ≈ Mg ≈ ≈ Li > Fe > Cu ≈ Mn > Ni ≈ Pb > Na.

Parengta ir praktikoje pritaikyta metodika cinkui nustatyti augaluose ir grūdinėse kultūrose AAS metodu. Palyginti su fotometriniu metodu, AAS metodas yra paprastesnis, spartesnis, atrankesnis, rezultatai geriau sutampa.