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Determination of selenium in garlic (*Allium sativum*) and onion (*Allium cepa*) by electro thermal atomic absorption spectrometry

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Abstract

A separation/enrichment procedure has been developed for the determination of selenium in garlic and onion samples by electrothermal atomic absorption spectrometry (ET-AAS) as a slurry sampling after preconcentration with 3,3-diaminobenzidine (DAB) reagent on the activated carbon. The influences of pH, time, amount of carbon and complexing reagent were outlined. The effect of acids used in the digestion of samples was also studied and compared. Selenium level was found to be 0.024 μg g^{-1} for onion ($n = 5$; LOD – 0.5 μg L^{-1}; LOQ – 1.7 μg L^{-1}) and 0.015 μg g^{-1} for garlic ($n = 5$; LOD – 1.3 μg L^{-1}; LOQ – 3.3 μg L^{-1}). Three different samples of garlic were analyzed by k_0-instrumental neutron activation analysis (k_0-INAA) at the Jozef Stefan Institute (JSI). The data obtained by k_0-INAA show that the content of selenium overlapped the results obtained by ET-AAS.

Keywords: Selenium determination; ET-AAS; k_0-INAA; Garlic; Onion; Slurry; Activated carbon

1. Introduction

In recent years, determination of selenium in trace levels has become of increasing importance in life sciences because of its dual role as an essential element at low concentration levels and as a toxic substance at higher levels as well as its cancer prevention (Ganther, 1999). Selenium is a component of enzymes such as the glutathione peroxidase enzyme (Macleod, Mcgaw, & Shand, 1996) which is one of the antioxidant for body, which catalyzes some reactions and also inhibits the toxicity of some metals such as lead, mercury, etc. and also thioredoxin reductase (Klapec et al., 2004). The biological effects of selenium may be explained from its chemical form, which shows different toxicities being exhibited for organic and inorganic compounds. Besides this, the narrow concentration range between the two contrary effects required additional knowledge of the chemical form in which this element exists in environmental and biological systems. It is well known that Keshan disease is the result of less amount of selenium dietary uptake (Klapec et al., 2004; Navarro-Alarcon & Lopez-Martinez, 2000). Daily uptake of selenium has to be controlled in foods, which depends on the geographical regions mainly in total selenium content of soil (Kos, Veber, & Hudnik, 1998). Some vegetables especially garlic and onion have accumulated higher concentration of selenium, while these plants contain in great fraction sulfur and their derivatives (Ellis & Salt, 2003; Ip, Lisk, & Stoewsand, 1992; Klapec et al., 2004). Daily uptake of selenium is given in the range of 50–200 μg day^{-1} (Camara, Cobo, Palacios, Munoz, & Donard, 1995; Robberecht & Grieken, 1982).The accurate determination of selenium is of great importance in food stuffs (Camara et al., 1995; Ip & Lisk, 1994).

Several methods to determination of selenium have been developed for many years. These include spectrophotometric, spectrofluorimetry, neutron activation analysis, electrochemical techniques and atomic absorption spectrometry. There are several spectrophotometric methods for the determination of selenium (Hoste & Gillis, 1955; Huang,

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Jie, Zhang, Yin, & Shao, 1996; Ramachandran, Kaveeshwar, & Gupta, 1993). However, these have limited sensitivity and high detection limits were needed where selenium concentration is mostly in the μg L^{-1} range or lower. Owing to the low limit of detection, selectivity, sensitivity and minimum sample quantity, the electrothermal atomic absorption spectrometry (ETAAS) is widely used for the determination of selenium in different matrices (Bulska & Pyrzynska, 1997; Dauchy, Gautier, Astruc, & Astruc, 1994; Feuerstein & Schemme, 1999; Hocquellet & Candillier, 1991; Li, Goessler, & Irgolic, 1998; Oliveira, Neto, Nobrega, Correia, & Oliveira, 2005). But some of the spectral interference problems caused the origin of matrix of iron and phosphate compounds. Volatility of selenium can be reduced by chemical modification such as palladium, nickel, magnesium and some mixtures or Zeeman background correction (Bermejo-Barrera, Moreda-Pineiro, & Bermejo-Barrera, 2002; Tsalev, Slaveykova, & Mandjukov, 1990).

A few applications have been reported making use of slurry sampling decrease the sample pre-treatment and minimize the risk of contamination and sample loss in treatment (Mendez, Alava, Lavilla, & Bendicho, 2002). It was also reported that the interferences caused by water and sediment matrices could be eliminated for the total selenium determination in using activated carbon as slurry sample introduction in graphite furnace (Kubota, Suzuki, & Okutani, 1995).

In this study, activated carbon (AC) separation/enrichment technique was improved after microwave digestion system in an analytical scheme for garlic and onion samples using slurry sample introduction for selenium analysis. An aliquot of the same garlic samples was analyzed by k_0-INAA (De Corte, 1987; De Corte et al., 1993). This multi-element technique is widely used in reference material certification, and has several advantages for direct sample measurement after irradiation with reactor neutrons (without radiochemical treatment).

2. Materials and methods

2.1. Apparatus

ATI-UNICAM 929 model atomic absorption spectrometer equipped with GF-90 graphite furnace, a selenium hollow cathode lamp which was operated in 196.0 nm wavelength, 15 mA current and 0.5 nm band-pass and deuterium background corrector, was used for measurements. In the application of AC, analyses have been done without using windows to increase the sensitivity of the lamp. Milestone Microwave Labstation MLS 1200 model system was used for the digestion procedure. Clifton model, which has stirring and heating functions, and LC 30 model ultrasonic bath were used for the sample preparation and homogenization purposes. Armfield Model FT-Vacum Freeze Drier was used for lyophilization of samples under −40 °C temperatures. TOC-Schimadzu 5000A was used for total organic carbon analysis. ATI-UNICAM, UV2-100 model spectrophotometer was used for phosphate-P and sulfate analysis. Jenway 3010 was employed for pH measurements and chloride measurements with ion selective electrode.

2.2. Reagents

All reagents used were of analytical grade. Double distilled water (Jencons Autostill 4000 X) was used through all experiments. Standards were prepared daily by appropriate dilution of Merck standards. The standard Se (IV) solution was prepared by dilution of a 1000 μg mL^{-1} atomic absorption standard (Merck, Titrisol, Darmstadt, Germany) with 0.2% HNO_3. Palladium matrix modifier (1000 μg mL^{-1}) was diluted from 10000 μg mL^{-1} palladium stock standard solution as a nitrate form. In the digestion procedures, concentrated nitric acid, hydrochloric acid, hydrogen peroxide, perchloric acid and sulfuric acid (Merck, Darmstadt, Germany) were used.

A 1000 μg mL^{-1} 3,3-diaminobezidine (DAB) solution which was used as a complexing reagent for selenium was prepared by dissolving the appropriate amount of DAB in 0.02 mol L^{-1} HCl. To elimination of calcium interference and minimization of pH, chancing after buffered 0.05 mol L^{-1} EDTA and 0.5 mol L^{-1} HCOOH solution was used. 0.5–3 mol L^{-1} HNO_3, 0.25–4 mol L^{-1} NH_3 (Merck, Darmstadt, Germany) were used for adjusting the pH.

2.3. Activated carbon (AC) preparation

Ten grams of carbon (Merck, No. 2183.1000, and Darmstadt, Germany) was purified by treating with concentrated hydrochloric acid and boiling for 3 h via stirring. After washing with cold distilled water until no chloride residue, carbon was dried at 110 °C. Then, dried carbon was treated with aqua regia [hydrochloric acid–nitric acid (3:1) (v:v)] at 24 h by stirring. The mixture was filtered by Schleicher and Schuell No. 589 blue ribbon (Germany) filter paper, and then purified carbon was washed with cold distilled water until no chloride residue and dried at 110 °C. The latest was stored in closed vessel in a desiccator. As weighing of activated carbon for every analysis is not very practical, suspension of activated carbon was followed. For this purpose, 50 mg mL^{-1} activated carbon was dissolved in demineralized water.

2.4. Materials and sampling

Garlic and onion samples were collected from Bazaar. Especially garlic samples were collected from Kastamonu Taskopru region, which is very famous for garlic production. All of the samples were peeled by hand without any cutting of the surface in order to prevent loss of selenium, while cutting on the surface activates the enzymes. Peeled samples were washed with demineralized water to remove all of the salts produced from soil, sweat, etc.

Lyophilization procedure is given as follows: peeled and washed samples were freezed with liquid nitrogen. All of the freezed samples were cut into small pieces with stainless-steel blender. Then, these samples were placed in a petri dish, very thin layer, and left to defreeze for 24 h at −20 °C. Defreezed samples were lyophilized at −40 °C with vacuum freeze drier. All samples were ground with plastic mortar to very fine powder which was kept in polyethylene bottles in the desiccator. Lyophilization procedure was used only for garlic samples. Onion samples were prepared of wet weight.

2.5. Digestion and water extraction of samples

Before the digestion, samples were released in room temperature overnight for pre-digestion with 10 mL concentrated nitric acid to prevent the foaming during digestion and to solve all of the fiber. All of the garlic and onion samples were digested with microwave assisted-wet digestion. The digestion program is given in Table 1. One and 10 g of garlic, which are lyophilized, and onion samples were used for closed and open system digestion. Some acids combinations, such as HNO_3 (10), HNO3 + HCl (10/5), $HNO_3 + H_2O_2$ (10/2), and $HNO_3 + HClO_4$ (10/1) (mL/mL), were investigated, respectively. The steps of digestion accompanied with microwave system are given in Table 1. For water extraction of garlic samples, both cold and hot water was used. Water extracts were prepared with 0.5 g lyophilized garlic samples and were stirred by a magnetic stirrer with 25 mL cold and hot water at 2 h. After digestion, separation/enrichment procedure with AC was applied on all samples.

2.6. Conditions of ETAAS measurements

The optimum AC procedure described in Fig. 1 was used and atomic signal of selenium was measured as a peak height (H) under the optimum condition, which is shown in Table 2 by ETAAS.

2.7. Conditions of k_0-INAA measurements

Lyophilized garlic samples (about 200–500 mg) were sealed into pure polyethylene ampoules (SPRONK system, Lexmond, The Netherlands). A sample and standard (Al-0.1%Au IRMM-530 disk of 6 mm in diameter and 0.2 mm high) were stacked together and irradiated for 20 h in the carousel facility (CF) of the TRIGA Mark II reactor of the JSI at a thermal neutron flux of 1.1×10^{12} cm^{-2} s^{-1}.

Table 1
Microwave assisted digestion program

Step	Time (min)	Power (Watt)
1	2	250
2	2	0
3	6	250
4	5	400
5	5	600

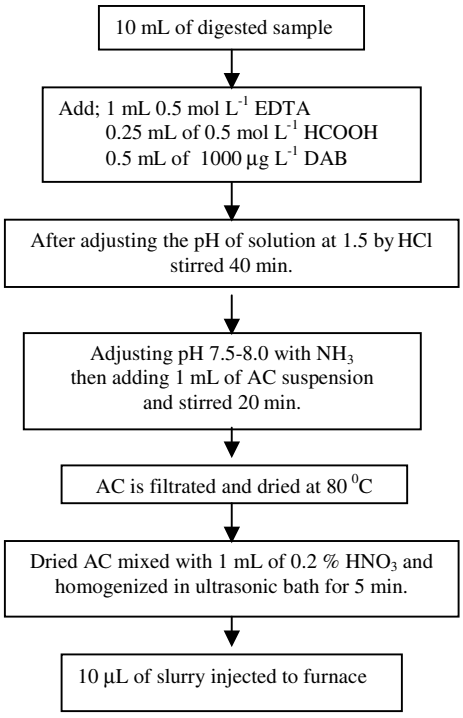

Fig. 1. An analytical scheme of the enrichment procedure.

Table 2
Optimum furnace program with activated carbon as slurry

Step	Temperature (°C)	Time (s)	Ramp (°C/s)	Gas type	Gas flow (mL/min)	Commands
1	80	10	0	Argon	100	
2	120	30	3	Argon	200	
3	900	10	10	Argon	100	RS
4	2200	3	0	Argon	0	RD, TC
5	2300	2	0	Argon	200	TC

RS: Return standbye, RD: Read, TC: Temperature control.

After irradiation, the sample and standard were transferred to clean 5 mL polyethylene mini scintillation vials for measurement. Each sample was measured three times on a calibrated coaxial HPGe detector (De Corte et al., 2001; Smodiš, Jaćimović, Jovanović, Stegnar, & Vukotić, 1988) with 40% relative efficiency, after 2–3, 8–10 and 30–35 days cooling time. For peak area evaluation, the HYPERMET-PC (Fazekas et al., 1997; HYPERMET-PC V5.0, User's Manual, 1997) program was used. For elemental concentrations and effective solid angle calculations, a software package called KAYZERO/SOLCOI® (KAYZERO/SOLCO, 1996), operated on an IBM-compatible PC, was applied.

3. Results and discussion

3.1. Determination of matrix components

Standard methods for flame atomic absorption spectrometry (FAAS), UV/VIS spectrophotometry and potentiometry techniques were used to characterize the matrix

components after water extraction and acid digestion. Matrix components were found in the ranges P: 3–8, SO_4^{2-}: 1.5–10, Fe: 7–13, Cu: 1–1.5, Mg: 10–30, Na: 5–11, K: 5–22, Ca: 60–105 in μg g^{-1} mean for garlic and onion. Artificial solution which will be representing both of the samples was used to understand the interference effects on the selenium signal by ETAAS. Artificial solution which represented garlic and onion was prepared as follows: P: 1.0, SO_4^{2-}: 1500, Fe: 2, Cu: 1, Mg: 2, Na: 5, K: 100, Ca: 40 and Cl^-: 1000 at mg L^{-1}.

3.2. Application of chemometric design

Chemometry is becoming more important not only to find optimum conditions, but also to understand the correlations and interactions due to using less chemicals, time saving, etc. (Brescia, Monfreda, Buccolieri, & Carrino, 2005; Hernandez-Caraballo, Rivas, Perez, & Marco-Parra, 2005; Izgi, Demir, & Gucer, 2000). Central composite design is used to find the optimum conditions for AC procedure by statistical design (Rigas, Panteleos, & Laoudis, 2000). A central composite design with two and three design factors at second order was applied. Two factors labeled as (X_1) AC amount and (X_2) DAB amount and three factors labeled as (X_1) Fe, Zn, Cu concentration, (X_2) EDTA amount and (X_3) HCOOH amount were checked using $b = (X' \cdot X)^{-1} \cdot X' \cdot Y$ formulation. So that, central composite design was used for comparison of the optimum conditions for AC procedure by classical optimization as detailed in 3.3. The number of experiments was calculated with $N = 2^k + 2k + 1$. Coded levels and the values of the factors of design are listed in Tables 3 and 4. The optimum condition of AC enrichment procedure was investigated with artificial solution that is detailed in Section 3.1.

3.3. Optimization of method

The method of accuracy was performed on both recovery tests and comparison of selenium amount with ETAAS and INAA. Also, the effect of many parameters such as pH, time, amount of complexing reagent and carbon was examined on the recovery of AC procedure. The selected parameters that are thought to affect the activated carbon separation/enrichment were studied in detail in our earlier works (Gucer & Yaman, 1992; Yaman & Gucer, 1995a; Yaman & Gucer, 1995b). Because of the matrix influences, the defined parameters have to be reviewed to find optimum conditions as follows. The accuracy of the results was performed by recovery tests that can be influenced by many parameters such as pH, time, amount of carbon and complexing reagents.

To find the optimum pH, the complexing of selenium with DAB was examined at the range of 1–4. The higher recovery result was seen at pH 1.5–1.8. Then, pH value of holding this complex onto the AC was investigated and the optimum pH value was found at 7.0–8.0, which is shown in Fig. 2. All of the graphs were shown with error bars. This might be related not only to adsorption process but also to co-precipitation effect on the recovery values in AC procedure (Piperaki, Berndt, & Jackwerth, 1978; Terada, Matsumoto, & Kimura, 1983; Vanderbroght & Van Grieken, 1977). The changes in the recovery value could be explained by different atomization mechanisms of selenium forms such as adsorption on the AC surface and precipitation of selenium as hydroxides especially with iron (Mizuike, 1983) on the surface.

Different amounts of DAB were used to find the recovery of optimum lowest amount of complexing reagent (DAB), so that constant amount of AC (50 mg)

Table 3
Design matrix and results of the central composite design for AC and DAB amount

No.	X_1 (AC amount)	X_2 (DAB amount)	Absorbance (peak height)
1	+1	+1	0.343
2	−1	+1	0.183
3	+1	−1	0.233
4	−1	−1	0.085
5	0	0	0.296
6	+1.414	0	0.258
7	−1.414	0	0.072
8	0	+1.414	0.322
9	0	−1.414	0.108

Table 4
Design matrix and results of the central composite design for EDTA, HCOOH and Fe, Cu, Zn concentrations

No.	X_1 (EDTA amount)	X_2 (HCOOH amount)	X_3 (Fe, Cu, Zn amount)	Absorbance (peak height)
1	+1	+1	+1	0.148
2	+1	+1	−1	0.416
3	+1	−1	+1	0.419
4	+1	−1	−1	0.437
5	−1	+1	+1	0.391
6	−1	+1	−1	0.409
7	−1	−1	+1	0.432
8	−1	−1	−1	0.424
9	+1.7	0	0	0.299
10	−1.7	0	0	0.489
11	0	+1.7	0	0.503
12	0	−1.7	0	0.492
13	0	0	+1.7	0.484
14	0	0	−1.7	0.563
15	0	0	0	0.486

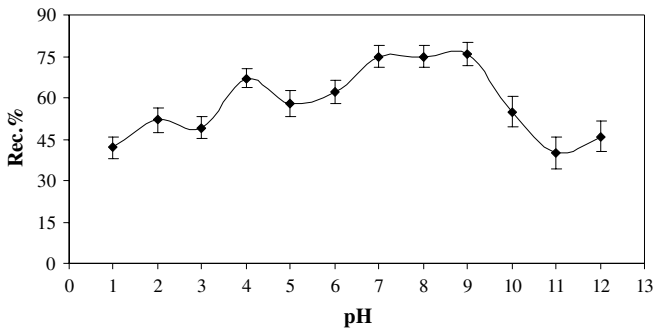

Fig. 2. The effect of pH on the recovery of sorption on the AC surface.

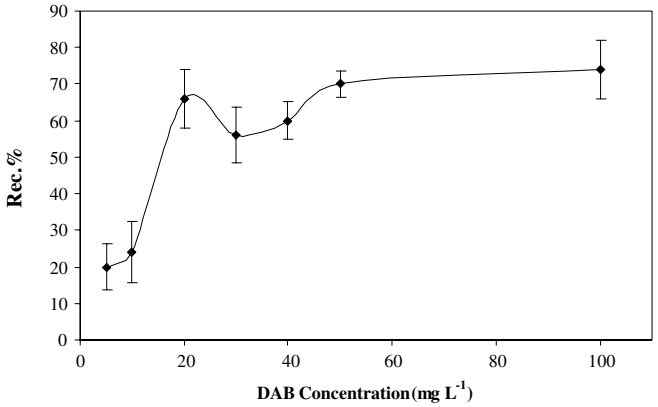

Fig. 3. The effect of complexing reagent concentration on the procedure.

and constant stirring time (70 min) were used. In these conditions, 50 mg of DAB was founded by 70–80% of recovery results, which are depicted in Fig. 3.

The contact time with DAB reagent was also studied at constant DAB amount as 50 mg, constant AC amount (50 mg) and at 60 min stirring time was founded with 95–100% recovery values.

The effect of the AC amount on the recovery was studied and 50 mg of AC was seen at 95–98% of recovery by adding optimum DAB (50 mg) and optimum contact time with DAB (60 min) at the optimum pH values 1.5 and 7.5 for complexing and adsorption on the AC, respectively. The result is depicted in Fig. 4.

The contact time with AC was also investigated and was founded 20 min at 75–85% recovery values. More than 20 min adsorption isotherm was changed till the 60 min at which point the recovery % was equal to 20 min. It was found that more than 60 min recovery % of adsorption on AC was decreased.

3.4. Effects of acids used in digestion procedure

The acids, which were used in the digestion procedure, caused interference effects on the selenium signal although 30% of signal reduction was observed with HCl due to volatile selenium compounds occurring before the atomization step (Pupishev & Obogrelova, 2000). This can be explained by boiling temperatures of Se, $SeCl_4$, and $SeOCl_2$ compounds which were given as 685, 305 and 179 °C, respectively (Volynsky, Krivan, & Tikhomirov, 1996). Before the atomization step, selenium atoms become more volatile with chloride and chloride atoms carry selenium atoms. Thirty percent of signal increasing effect was seen for H_2O_2 and $HClO_4$ acids. On the other hand, it was found that HNO_3 have varied effects on signals but this would be insignificant if the acid concentration used was up to 5%. Different oxides formation and atomization mechanism could describe these effects.

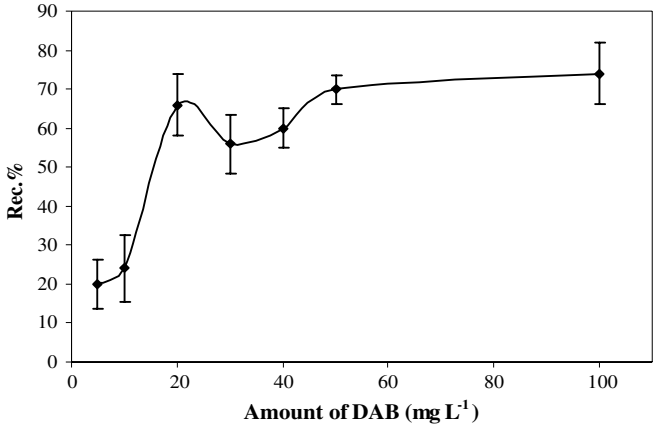

Fig. 4. The effect of activated carbon amount on the AC procedure.

After digestion of garlic and onion samples with acid mixtures such as 10 mL of HNO_3 acid and mixtures of $HNO_3 + HCl$ (10/5), $HNO_3 + H_2O_2$ (10/2), $HNO_3 + HClO_4$ (10/1) (mL/mL) for open and closed vessel, respectively, the digested solutions were spiked and analyzed by AC procedure. The results of recovery are shown in Table 5. It was found that onion sample has less matrix effect for this procedure but high matrix effects come from garlic. It can be explained by total organic carbon level (TOC) that was found to be 125 mg L^{-1} for onion and in the range of 400–8000 mg L^{-1} for garlic sample.

Table 5
Recovery results of digested onion and garlic samples after AC procedure ($n = 3$)

Sample	Addition (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Standard selenium solution	5	4.5	90
Cold water extract of garlic	20	5.0	25
Hot water extract of garlic	20	nd	nd
Artificial garlic solution	5	3.0	60
	10	6.9	69
	20	14.9	75
Open vessel digestion			
Garlic (10 mL HNO_3)	200	46.5	23
Garlic (10 mL HNO_3 + 5 mL HCl)	200	39.1	20
Garlic (10 mL HNO_3 + 2 mL H_2O_2)	200	96	48
Garlic (10 mL HNO_3), after digestion add 5 mL HCl	20	8.4	42
Garlic (10 mL HNO_3 + 0.5 mL H_2SO_4 + 0.5 mL $HClO_4$)	20	9.8	49
Onion (10 mL HNO_3 + 5 mL H_2O_2)	100	77.9	78
Closed vessel digestion			
Garlic (5 mL HNO_3)	20	6.4	32
Garlic (5 mL HNO_3 + 2 mL HCl)	20	6.5	33
Garlic (5 mL HNO_3 + 1 mL H_2O_2)	20	8.2	41
Garlic (5 mL HNO_3 + 0.5 mL $HClO_4$)	20	7.8	39
Onion (6 mL HNO_3 + 1 mL H_2O_2)	20	14.2	71

nd: Not detectable.

According to recovery results of digested samples with different acid combinations, $HNO_3 + H_2O_2$ acid mixture was selected and applied for all samples.

3.5. Comparison of experimental optimization with chemometric design

A central composite design with two design factors at second order was applied. Two factors of AC and DAB amount were checked using $b = (X' \cdot X)^{-1} \cdot X' \cdot Y$ formulation (+1 was 75 mg AC and DAB and −1 was 25 mg AC and DAB). The optimum of DAB was overlapped in a classical way but AC amount was found to be 25 mg. Three factors which were the interference effect of copper, iron and zinc on the selenium signal, EDTA amount for elimination of interference and HCOOH amount for pH adjusting were checked by the same design and formulation. (+1 was 6 mL for EDTA, 1.5 mL for HCOOH and 3 mg L^{-1} for defend elements and −1 was 2 mL for EDTA, 0.5 mL for HCOOH and 1.5 mg L^{-1} for defined elements). It was found from this serial in the case of 0.75 mg L^{-1} defined elements that the optimum EDTA and HCOOH amounts were enough to eliminate the interference effect at 2 and 0.5 mL, respectively.

3.6. Calibration graph and applications

In the optimum conditions, the enrichment/separation procedure given in Fig. 1 was applied to both standard solutions and both open and closed vessel digested samples. For quantification of selenium level in samples, the external calibration curve was used. To understand the matrix effect on the calibration, both the artificial solutions spiked with 0.5 and 50 mg L^{-1} selenium and aqueous standard solutions in the range of 20–120 mg L^{-1} selenium were investigated. From the results, peak height of signals was selected for calculations due to the good absorbance correlation by increasing concentration. Equations of calibration curves were calculated as $y = 0.0094x + 0.0024$ ($R^2 = 0.9904$) and $y = 0.0025x + 0.0147$ ($R^2 = 0.9998$) for artificial garlic and onion solution, standard selenium solutions, respectively. It could also be seen from calibration curves that there was no big difference between calibration coefficients but calibration graph of artificial solution was used for all calculations to eliminate or reduce the interference effect arising from the matrix components. It could also be explained by atomization mechanism, even if very low level of selenium in samples could be found with respect to peak height calibration versus peak area calibration due to the low detection limit. From the calibration curve, LOD (μg L^{-1}) and LOQ (μg L^{-1}) were calculated by three times standard deviation of blank solution divided to slope, 10 times standard deviation of blank solution divided to slope which were found to be 0.5–1.7 for onion and 1.3–3.3 for garlic ($n = 5$). Selenium level was found to be 0.024 μg g^{-1} for onion and 0.015 μg g^{-1} for garlic.

Table 6
Content of major and trace elements in different garlic samples determined by k_0-INAA method

Element	Lyophilized garlic[a]	Lyophilized garlic[b]	Hot water extract
Ag	<0.01	<0.01	<0.006
As	<0.01	<0.01	<0.006
Au	<0.001	<0.001	<0.0005
Ba	<0.5	<0.5	<0.3
Br	0.39 ± 0.04	<0.1	0.38 ± 0.02
Ca	116 ± 9	81 ± 9	42.1 ± 4.2
Cd	<0.05	<0.05	<0.03
Ce	<0.03	<0.03	<0.01
Co	0.0025 ± 0.0003	0.0028 ± 0.0004	0.0016 ± 0.0003
Cr	<0.05	<0.05	<0.02
Cs	<0.003	<0.003	<0.002
Eu	<0.005	<0.005	<0.004
Fe	4.97 ± 0.30	5.04 ± 0.30	1.56 ± 0.13
Ga	<0.05	<0.05	<0.02
Hf	<0.003	<0.003	<0.001
Hg	0.017 ± 0.003	0.007 ± 0.003	0.004 ± 0.001
In	<0.05	<0.05	<0.04
K	3130 ± 130	2880 ± 120	1390 ± 60
La	<0.005	<0.002	<0.001
Mo	<0.05	0.13 ± 0.03	<0.02
Na	30.3 ± 1.2	22.5 ± 1.0	13.0 ± 0.6
Nd	<0.1	<0.1	<0.04
Rb	1.16 ± 0.05	0.49 ± 0.02	0.48 ± 0.02
Sb	<0.001	<0.001	0.0030 ± 0.0002
Sc	<0.0003	<0.0003	<0.0003
Se	**<0.03**	**0.359 ± 0.015**	**<0.015**
Sm	<0.001	<0.001	<0.0005
Sn	<1	<1	<0.5
Sr	1.3 ± 0.3	0.7 ± 0.3	<0.4
Ta	<0.003	<0.003	<0.001
Tb	<0.002	<0.002	<0.001
Te	<0.03	<0.03	<0.03
Th	<0.003	<0.003	<0.001
Tm	<0.01	<0.01	<0.005
U	<0.003	<0.004	<0.002
W	<0.02	<0.02	<0.005
Yb	<0.002	<0.002	<0.001
Zn	4.50 ± 0.20	4.69 ± 0.2	1.88 ± 0.08
Zr	<1	<1	<0.5

Results are expressed in μg g^{-1}.
Hot water extract is prepared from lyophilized garlic[a] with 2 h stirring.
[a] Garlic which was obtained from Kastomonu Taskopru region of Turkey.
[b] Garlic which was obtained from Kastomonu Taskopru region of Turkey was enriched with selenium.

3.7. Comparison of ET-AAS with k_0-INAA

The data for three samples of garlic analyzed by k_0-INAA are presented in Table 6. As can be seen, 39 elements could be analyzed by this method from a single irradiation in the CF. For major elements not visible in the gamma spectra, the limit of detection is presented. Data for Se obtained by k_0-INAA are lesser than 0.03 μg g^{-1}. The data for selenium in garlic after digestion obtained by ET-AAS are 0.015 μg g^{-1}. This result agrees with the results of k_0-INAA.

Selenium concentration in garlic and onion samples was found to be 0.015 μg g^{-1} and 0.024 μg g^{-1} by AC separation/enrichment procedure, respectively. The

selenium content of garlic and onion was found to be 34–485 ng g^{-1} and 1.1–55 ng g^{-1}, respectively, by other authors (Bratakos, Zafiropoulos, Siskos, & Ioannou, 1987; Inam & Somer, 1999; Klapec et al., 2004; NDL, 2002; Smrkolj & Stibilj, 2004).

4. Conclusions

Activated carbon technique can be successfully applied for slurry analysis, even so complex matrices such as garlic and onion. It can be concluded that sample preparation might be the most important step, which can influence the application of this procedure. But special precautions are to be taken for sample preparation techniques in order to digest the whole organic content of samples. Losses caused by volatile compounds are one of the major problems in choosing digestion systems. During the separation processes, adsorption and co-precipitation can occur which increases the recovery values and complexing conditions are important to get high recovery. But some effects arise from atomization of different forms of selenium. Organic selenium compounds might be stable enough to digest and the complexing reaction with DAB cannot occur. In such cases as in garlic samples, recovery values can be reduced to zero if the sample preparation step cannot be performed properly. In the digestion procedure, HCl amount is an important factor to reduce the selenium (VI) to (IV) without any volatilization.

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