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Simultaneous determination of heavy metals in Tahini by anodic stripping voltammetry

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Abstract

Background and objective: Tahini is a regional dish prepared from sesame seeds and consumed as breakfast worldwide. It is a good source of zinc, copper, and group B vitamins. However, the product may be contaminated with toxic heavy metals. Therefore, our purpose was development of analytic method for simultaneous determination of zinc, copper, lead, and cadmium in Tahini.

Materials and methods: Our work was conducted on 37 brands of Tahini (n = 74). The samples were purchased from local market of Tehran (Iran). Concentration of heavy metals was measured by polarograph. Voltammetric analysis was carried out by using 746 VA trace analyzer by differential pulse anodic stripping Voltammeter at Hanging mercury dropping electrode.

Results and conclusion: Concentration of Zn, Cd, Pb, and Cu was calculated as 3.79 ±2.43, 1.48 ±0.08, 0.015 ±0.01, and 0.012 ±0.007 µg/100 g, respectively. Amount of Pb and Cd was lower than acceptable limit approved by CODEX in all the samples, while concentration of Cu and Zn was within the standard range. According to our investigation, Tahini can be used as a valuable food to meet the nutritional needs without any toxic effect arisen from deleterious heavy metals in the consumers.

Keywords: Cadmium; Copper; Lead; Tahini; Voltammetry; Zinc

1- Introduction

Sesame (*Sesamum indicum*) is a flowering plant which produces edible seeds in their pods. It was domesticated over 3500 years ago and has been cultivated further due to its tolerance to drought and also high oil content of the seeds with high nutritional value [1]. Majority of the seeds that is about 6.2 million tones are directly used in cooking and bakery, for oil extraction, and for preparation of Tahini (a paste made by grinding of toasted hulled sesame seeds) [2]. Tahini is of main foods consumed in Mediterranean regions followed by Caucasus, Middle East, and China. It is a source of group B vitamins, essential fatty acids, high value protein, and minerals [3].

Zinc is the second trace element in human body after iron and shows many vital roles in the body including modulation of immune system [4], involvement in learning and cognitive processes [5], wound healing [6], prevention of age-related

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macular degeneration (AMD) [7], and fertility [8]. Copper is another trace element in the body at range of 1.4-2.1 mg per kilogram body weight. It acts as co-enzyme in iron metabolism and takes part in ATP synthesis and free radical scavenging [9-12]. Copper is also necessary for proper growth [13], bone formation [14], central nervous system (CNS) function [15], and cardiovascular system function [16]. In comparison, foods may be source of toxic heavy metals either by their cross-contamination or use of inappropriate processing methods [17]. Lead and cadmium are considered as the most significant pollutant in Tahini. They may contaminate the product through the soil, air, and/or packaging. Lead can affect hematopoietic system [18], renal function [19], CNS function, and reproductive system [20]. Cadmium mostly disturbs lung function [21], kidney function [22], and bone development [23]. Concentration of heavy metals should be monitored strictly in foods and beverages to ensure that the consumers are not at risk. Several techniques such as flame atomic absorption spectrometry and inductively coupled plasma mass spectrometry (ICP-MS) have been used for analysis of trace metals [24,25]. However, differential pulse anodic stripping voltammetry (DPASV) has demonstrated a good sensitivity in determination of zinc, copper, lead, and cadmium at low quantities. Thus, we used DPASV method for analysis of above elements in the product.

2. Materials and methods

2.1. Sample size and sampling procedure

Tahini samples were collected from local markets (Tehran, Iran). In total, 37 commercial brands were collected in duplicate (n = 74), among them 32 brands were non-flavored (stated as simple in the current paper) and 5 brands were flavored. The flavored samples were prepared by addition of coffee, chocolate, date, vanilla, and cocoa. Sample size (n) was calculated according to Eq. 1 as follows:

$$n = \sigma^2(z_{1-\beta}+z_{1-\alpha})^2 / (\mu_0-\mu_1)^2 \qquad \text{Eq. 1}$$

$\sigma = 2.02$, $\alpha = 0.05$, $\beta = 0.2$, $\mu_0 = 4.61$, $\mu_1 = 3.79$

2.2. Polarograph apparatus

Trace analyzer model 746 (Metrohm, Switzerland) was used. The apparatus was equipped with three electrodes of a) hanging mercury drop electrode (HMDE) as working electrode, b) axillary electrode made of platinum, and c) Ag/AgCl electrode as reference.

2.3. Reagents

Tartaric acid, CH_3COONa, $Pb(NO_3)_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, and HNO_3 were of analytical grade and purchased from Merck (Germany). Stock solution of HNO_3 (1 g/l, 0.005 M) was prepared in the laboratory. Acetate buffer (0.2 M, pH = 4.7) containing 0.2 M tartaric acid was prepared as supporting electrolyte.

2.4. Sample preparation

For analysis, 2 g of sample was weighed and then heated until drying. After cooling down to ambient temperature, 10 ml nitric acid (65% w/v) was added to make a clear solution, and then the solution was heated again. The dried sample was transferred to a muffle furnace set at 450 °C and left for 24 h. Then, the cooled ash was washed with nitric acid (65% w/v) and filtered by Whatman paper no. 1. Final solution was made up to 25 ml with nitric acid and used for further analysis [26].

2.5. Instrumental analysis

Concentration of zinc, copper, lead, and cadmium was determined by differential pulse anodic stripping voltammetry equipped with a hanging mercury drop electrode (Model 746 VA Trace Analyzer, Metrohm, Switzerland). Analysis was done by deposition potential of -1.20 V, deposition time of 30-90 s, scan rate of 6 mv/s, pulse amplitude of 50 mv, and final potential of +0.3 v. Standard solutions of zinc, copper, lead, and cadmium were prepared at concentration of 1 g/l. At first, polarogram of the supporting electrolyte (10 ml) was recorded as blank. Then, 500 µl of each sample was added to the cell and its polarogram was recorded. Our analysis was done by standard addition method by adding 100 µl of standard solution to the samples [26].

2.6. Statistical analysis

The results were analyzed by SPSS software version 16. The means were compared by analysis of variance (ANOVA) at significance level of 0.05. Experiments were done in triplicate.

3. Results and discussion

In order to finding out the effect of additives in concentration of heavy metals in Tahini, the samples were divided to two groups. Concentrations of heavy metals in simple and flavored Tahini samples are presented in Table 1.

Table 1- Concentration of heavy metals in simple (non-flavored) and flavored Tahini samples

Samples	Zinc (µg/100g)	Copper (µg/100g)	Lead (µg/100g)	Cadmium (µg/100g)
Simple (non-flavored)				
1	1.31 ±0.71	0.48 ±0.14	0.006 ±0.041	0.007 ±0.001
2	0.83 ±0.09	0.68 ±0.11	0.003 ±0.001	0.003 ±0.001
3	3.08 ±1.70	1.63 ±0.28	0.004 ±0.000	0.003 ±0.000
4	2.76 ±0.92	2.66 ±0.21	0.048 ±0.004	0.006 ±0.001
5	1.06 ±0.12	0.48 ±0.05	0.003 ±0.001	0.007 ±0.000
6	1.10 ±0.15	0.16 ±0.02	0.030 ±0.014	0.006 ±0.001
7	2.52 ±1.04	2.75 ±0.91	0.025 ±0.002	0.019 ±0.006
8	2.23 ±1.05	1.63 ±0.82	0.014 ±0.003	0.005 ±0.001
9	0.27 ±0.17	2.71 ±1.04	0.008 ±0.000	0.005 ±0.000
10	2.77 ±0.91	2.31 ±1.04	0.008 ±0.001	0.003 ±0.000
11	1.20 ±0.13	1.05 ±0.91	0.006 ±0.001	0.003 ±0.000
12	7.43 ±0.64	2.79 ±1.09	0.045 ±0.006	0.027 ±0.008
13	3.46 ±1.02	1.23 ±0.83	0.015 ±0.001	0.012 ±0.006
14	7.99 ±0.10	2.78 ±0.36	0.015 ±0.001	0.010 ±0.005
15	6.28 ±1.03	2.01 ±0.57	0.001 ±0.001	0.008 ±0.001
16	4.70 ±1.15	1.61 ±0.80	0.029 ±0.005	0.011 ±0.008
17	4.46 ±1.03	1.11 ±0.62	0.007 ±0.003	0.003 ±0.000
18	2.37 ±0.93	0.64 ±0.25	0.027 ±0.008	0.028 ±0.006
19	7.97 ±0.14	1.08 ±0.42	0.003 ±0.001	0.006 ±0.001
20	3.65 ±1.00	0.42 ±0.05	0.004 ±0.000	0.013 ±0.004
21	5.72 ±1.02	2.03 ±0.19	0.015 ±0.008	0.010 ±0.007
22	7.90 ±0.14	2.01 ±0.64	0.012 ±0.001	0.018 ±0.001
23	1.48 ±0.32	1.65 ±0.11	0.014 ±0.001	0.028 ±0.007
24	4.11 ±1.01	2.20 ±0.17	0.019 ±0.002	0.012 ±0.006
25	6.82 ±1.06	1.65 ±0.11	0.014 ±0.009	0.015 ±0.007
26	4.48 ±1.01	2.20 ±0.17	0.007 ±0.001	0.020 ±0.012
27	7.23 ±1.06	1.89 ±0.91	0.004 ±0.001	0.010 ±0.002
28	1.96 ±0.60	1.72 ±0.61	0.033 ±0.008	0.019 ±0.007
29	4.52 ±1.02	2.57 ±1.05	0.008 ±0.001	0.018 ±0.009
30	1.39 ±0.63	0.73 ±0.31	0.004 ±0.001	0.007 ±0.001
31	2.49 ±1.07	1.97 ±0.75	0.013 ±0.003	0.015 ±0.008
32	4.56 ±1.03	0.35 ±0.11	0.001 ±0.000	0.018 ±0.006
Flavored				
33	1.06 ±0.080	0.77 ±0.31	0.03 ±0.001	0.015 ±0.001
34	0.57 ±0.270	0.31 ±0.105	0.009 ±0.003	0.009 ±0.000
35	6.45 ±1.020	0.23 ±0.20	0.007 ±0.001	0.009 ±0.003

36	4.51 ±1.108	1.61 ±0.34	0.02 ±0.008	0.011 ±0.008
37	7.67 ±0.460	0.56 ±0.13	0.02 ±0.006	0.014 ±0.008

Amount of Zn was less than permitted limit (4 mg/kg) approved by Codex ($P < 0.001$). Similar result was observed for Cu in Tahini compared to its permitted limit (2 mg/kg) determined by Codex ($P < 0.001$). Although, both minerals were within the acceptable range of Codex. In addition, Pb and Cd were also less than maximum allowed concentration of heavy metal in Tahini by Codex that is 0.01 mg/kg ($P < 0.001$) [27]. Comparison of samples revealed that concentrations of Zn, Cd, and Pb were not different significantly between simple and flavored samples ($P = 0.802$, $P = 0.954$, and $P = 0.64$, respectively); but higher amount of Cu in non-flavored samples was detected compared to flavored samples ($P = 0.022$) (Figure 1).

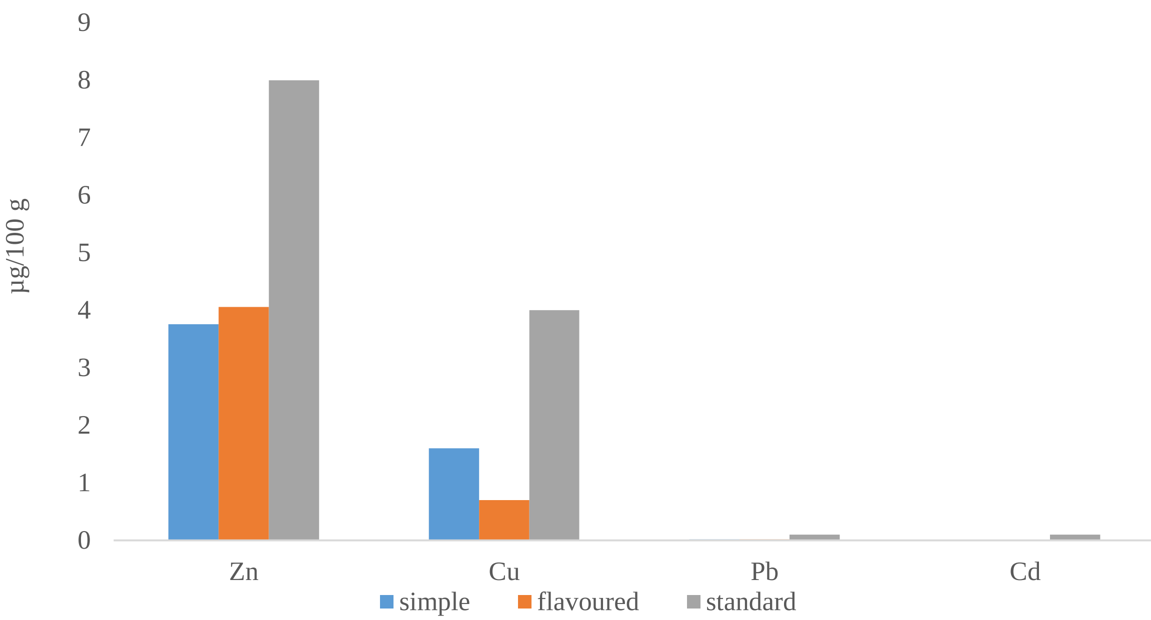

Figure 1- Heavy metals in simple and flavored Tahini compared to permitted levels determined by Codex

Comparing the results showed that there was no significant association between brands' name and concentration of elements ($P > 0.05$). For example, brand 14 and brand 9 had the highest and the lowest Zn, respectively; maximum and minimum amount of Cu was measured in brand 12 and brand 6, respectively; the highest and the lowest concentration of Pb were found in brand 4 and brand 15, respectively; the most and the least Cd-polluted samples were of brand 23 and brand 2, respectively. Several studies have been done about determination of heavy metals in sesame and its products due to their high consumption worldwide. In 2013, Park et al. studied 12 samples of sesame oil to evaluate their heavy metals. Concentration of Cd was reported as 0.109 µg/g and Pb concentration was 0.14-0.20 µg/g. The authors emphasized that products prepared from the seeds grown in contaminated areas should be monitored periodically to find out any risk arisen from high contamination load [28]. Acar in 2011 measured concentration of zinc, copper, and lead in Tahini by electro-thermal atomic absorption spectrometer. They were calculated as 35 ng/g, 42 ng/g, and 1.7 ng/g, respectively [13]. Sadat in 2011 measured 234 µg/kg and 100 µg/kg of lead in raw and peeled sesame seeds, respectively, by atomic absorption spectrophotometer. Concentration of cadmium in the samples was lower than limit of detection in her study [29]. Another study in 2011 determined concentration of heavy metals in nine vegetable oils of different species. Concentration of zinc, copper, cadmium, and lead was reported as 0.789-0.981 μg/g, 0.028-0.045 μg/g, 3.91-5.27 μg/g, and 0.014-0.022 μg/g, respectively [30]. Effect of contaminated soil on cultivated crops was studied by Hao et al. They cultivated the crops in two areas with different level of contamination. The authors concluded that sesame is very sensitive to soil contamination and the cultivated area should be monitored strictly [31]. Therefore, it is important that the soil under cultivation of sesame located far from industrial places and factories because their by-products and sewage may contaminate the farmlands. In addition, metal equipment used for sesame processing such as preparation, roasting, and squeezing are of great concerns through which heavy metals can transfer to the final product [13,32]. Thus, knowing about critical points within the food chain is important for risk assessment purposes.

4. Conclusion

Our investigation revealed that Tahini samples available in the local market could be used as a high-value food to meet nutritional needs. Fortunately, there is no concern about Pb and Cd toxicity in this regard. Given the fact that sesame seeds absorb heavy metals from soil, enrichment of farmlands by Zn and Cu is recommended. Contamination of Pb and Cd can be avoided by cultivating the plant in less polluted areas far from industrial places. Peeling the hulls can reduce contamination significantly.

5. Conflict of interest

The authors declare no conflict of interest.

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