



Determination and Evaluation of Copper, Lead, Iron and Zinc Contamination Levels in Cheese and Tahini Halva by Atomic Absorption Spectrometry

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Abstract

Copper, lead, iron and zinc contamination levels in cheese and tahini halva samples by electrothermal atomic absorption spectrometer (ETAAS) using Mo + Pt + NH₄H₂PO₄ chemical modifier mixture and flame atomic absorption spectrometer (FAAS) were determined and evaluated. Pyrolysis and atomization temperatures of Cu and Pb in a sample solution were obtained with and without modifier mixture. Optimum masses of modifier components used were 20 µg Mo, 4 µg Pt and 50 µg NH₄H₂PO₄. The mixture of Mo + Pt + NH₄H₂PO₄ was found to be preferable for the determination of Cu and Pb in samples digested in a mixture of HNO₃ plus H₂O₂. Detection limits and characteristic masses of analytes obtained by ETAAS with Mo + Pt + NH₄H₂PO₄ for a sample solution (2% m/v) were 35 ng/g and 16.4 pg for Cu, 42 ng/g and 20.2 pg for Pb, respectively. Detection limits of Fe and Zn obtained by FAAS were 3.0 ng/g for Fe and 1.7 ng/g for Zn, respectively. Recovery tests of analytes in sample solutions were studied and results found were compared with added values. Cu and Pb in white and Kasar cheese samples and tahini halva samples were analyzed by ETAAS applying Mo + Pt + NH₄H₂PO₄. Iron and Zn in samples were also determined by FAAS.

Keywords: Lead, Cheese, Halva, ETAAS with Mo + Pt + NH₄H₂PO₄ modifier mixture, FAAS

Introduction

Determination and evaluation of copper, lead, iron and zinc in foods such as cheese and tahini halva samples are very important for human daily diets, human health and contamination. Consumption of these samples in Turkey is highly important and significantly contributes to the Turkish diet. Trace amounts of Cu, Fe and Zn are essential for micro-nutrient and they have varieties of biochemical functions in all living organisms, but they can be toxic when taken in excess. However, as lead is toxic, it is non-essential metal even in trace amount (Demirel et al. 2008). Excess of these metals can lead to a wide variety of clinical effects such as deficits in psychological functions and diseases (Yüzbaşı et al. 2003).

The FAO/WHO has declared that for an average adult (60 kg body weight), the provisional tolerable daily intakes (PTDI) of Pb, Cu, Fe and Zn are 214 µg, 3 mg, 48 mg and 60 mg, respectively (Joint FAO/WHO 1999, Yüzbaşı et al. 2003, Mendil 2006). Copper, Pb, Fe and Zn contents of cheese and tahini halva samples are variable due to factors such as differences between species, geographical field, characteristics of the manufacturing practices and possible contamination from the equipment during the packaging process (Yüzbaşı et al. 2003). There are some studies for the determination of metal levels in white and Kasar cheese samples (Merdivan et al. 2004, Mendil 2006, Hayaloglu et al. 2002, Yüzbaşı et al. 2003, Karadjova et al. 2000), but there is no work for the determination of metal contents in tahini halva.

Electrothermal atomic absorption spectrometer (ETAAS) and flame atomic absorption spectrometer (FAAS) are the most widely used analytical techniques for the determinations of trace metals such as Cu, Pb, Fe and Zn in a wide range of foods such as cheese and tahini halva

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samples due to their inherent high sensitivity, selectivity and low detection limits (Tinggi et al. 1997, Mendil 2006, Karadjova et al. 2000, Yüzbaşı et al. 2003). However, interferences arising from high background signals, volatilization of analytes together with organic compounds and high concentrations of inorganic acids or halides in the sample matrix may affect the direct determinations of analytes, especially with ETAAS. Platform atomization, chemical matrix modification, integrated absorbance and a powerful background correction technique have been used to overcome these problems. Different permanent modifiers (W-Rh, W-Ir and W-Ru) (Lima et al. 2002) and other suitable modifiers, such as Mo + Pt + TA and Ni + Pd + NH₄H₂PO₄ (Acar et al. 1999, Acar 2001) have been used for the determination of Cu and Pb in various samples in order to stabilize analytes up to higher possible pyrolysis temperatures and to reduce such interferences in sample matrix before atomization steps.

Aim and Objective of This Research Work

The objective of this study was to analyze Cu and Pb in white and Kasar cheese and tahini halva samples by ETAAS using Mo + Pt + NH₄H₂PO₄ mixture, and Fe and Zn by FAAS. The effects of Mo + Pt + NH₄H₂PO₄ mixture on pyrolysis and atomization temperatures of Cu and Pb in sample solutions were studied to reduce interferences from organic substances and background levels in such samples. The Mo + Pt + NH₄H₂PO₄ proposed was applied to the determination of Cu and Pb in such real samples. The results of analytes found in samples were compared with the results reported in previous studies, Turkish standards, Turkish food codex and the FAO/WHO limits.

Material and Methods

REAGENTS:-All acids and reagents used were of analytical reagents grade. All solutions were prepared by dissolving analytical grade reagents in ultra pure water (resistivity 18 MΩ/cm) obtained from Ultra pure water system (Nanopure Infinity, Barnstead, P/N-1161, Dubuque, USA). Nitric acid (65% m/m), HCl (37% m/m) and H₂O₂ (30% m/m) obtained from Merck (Darmstadt, Germany) were used. All solutions prepared were stored in high density polypropylene bottles. Plastic bottles, autosampler cups and pipettes, and glassware materials were cleaned by soaking in HNO₃ (20% v/v) for two days and rinsing six times with ultra pure water and dried. Autosampler washing solution containing HNO₃ (0.2% v/v) plus triton X-100 (0.1% v/v) was used to avoid clogging of the autosampler pipette and to improve dispersion of sample solution onto the platform (Lima et al. 2000).

Platinum (VI) standard solution (2.0 g/l) was prepared by dissolving ammonium hexachloro-platinate (Aldrich) in HCl (15% v/v) and diluting to 100 ml. Mo (VI) (0.4% m/v)

solution was prepared from H₂MoO₄ (Merck) by dissolving in ammonia solution (1% v/v). NH₄H₂PO₄ (4% m/v) solution was prepared by dissolving 4.0 g of NH₄H₂PO₄ (Merck, 99.99% pure) in a sufficient volume of ultra pure water, transferring into a 100-ml volumetric flask and diluting to the mark with ultra pure water. All modifier solutions were diluted as required.

Stock standard solutions of Cu, Pb, Fe and Zn (1.0 g/l each) obtained from BDH chemicals (Poole, UK) were used. Working standard solutions of analytes were freshly prepared by successive dilution of the stock standard solutions to the desired concentrations in nitric acid (0.2% v/v) solutions immediately before use.

SAMPLING:-Cheese and halva samples were purchased from different markets in Ankara at different dates. The samples were taken to the laboratory. After homogenization with a stainless blender, the samples were weighed and transferred into poly-ethylene storage containers until decomposition.

DIGESTION OF SAMPLES:-A portion (2.0 g - 4.0 g) of white or Kasar cheese or tahini halva sample dried at 110 °C for 4 h was accurately weighed into a teflon digestion bomb. A mixture of 6 ml of HNO₃ (65% m/m) plus H₂O₂ (30% m/m) (2:1 v/v) and 2 ml ultra pure water were added to the sample and left overnight at laboratory temperature in order to dissolve the sample without heating. The bomb closed with a cover was placed inside a Milestone ethos microwave oven and digested according to the procedure described in previous works (Acar 2004, Lima et al. 2002). Steps of the microwave program applied were the heating from laboratory temperature to 120°C in 20 min and holding at this temperature for 10 min (up to 800 W); heating from 120°C to 160°C for 10 min and waiting for 20 min (up to 800 W) and cooling to laboratory temperature. After digestion, the bomb opened was placed on a hot plate and gently heated at 100°C to evaporate sample volume nearly to 4 ml. When the residue was observed, digestion procedure given above was repeated. After cooling, the final solution was transferred into a 50 ml volumetric flask by washing interior surface of the bomb with a sufficient volume of HNO₃ (0.2% v/v) twice and diluted up to the mark with ultra pure water. The aqueous standard solutions were added into the some samples before digestion in order to control the possible loss of analyte, some interferences of sample matrices on analytes during measurements and to obtain recovery test results. Three equal amounts of a white cheese or a halva sample were accurately weighed into teflon digestion bombs, respectively. One ml of Cu and Pb (1 mg/l each), 1 ml of Fe (25 mg/l) and 1 ml of Zn (10 mg/l) aqueous standard solutions were added into first parts of white cheese or halva sample before digestion. Two ml of Cu, Pb, Fe and Zn aqueous standard solutions at concentrations given above were added into the second parts. Aqueous standard solutions were not added into the third parts. Digestion

procedure given above was repeated to solve the samples. After dissolving, the sample solution was transferred into a 50 ml volumetric flask and diluted to the mark with ultra pure water. Blank solutions were carried out through the digestion procedure in order to check the possible analyte contaminations in the reagents used for the solution preparation.

INSTRUMENTATION:-A Hitachi Model (Japan) 180/78 graphite furnace and flame (Hitachi 180/080) atomic absorption spectrometer equipped with a Zeeman effected background corrector and an automatic data processing unit (180/205) was used for all absorption measurements of analytes. Hitachi graphite platforms (P/N-190/6008) inserted into pyrolytically coated graphite tubes (P/N-190/6007) and integrated (peak area) mode were used for atomization throughout. Single element hollow cathode lamps of Cu (7.5 mA and 324.8 nm), Pb (10 mA and 283.3 nm), Fe (12.5 mA and 248.3 nm) and Zn (10 mA and 213.9 nm) were used as radiation sources. The slit width was 1.3 nm for all elements. Instrumental parameters and operating conditions recommended by the manufacturer for the analytes were used, unless otherwise stated. Argon (99.98%, w/w) was used as a carrier gas during all stages except for atomization in ETAAS. A 20 μ l volume of calibration or sample solution together with modifier solutions was injected into the platform by an autosampler (P/N-170/126). Iron and zinc in samples were determined by FAAS using air-asetilene flame. A Milestone Ethos microwave oven (MLS Ethos 1600, Italy), equipped with temperature and pressure sensor, Teflon digestion bombs and vessels, was used to dissolve the samples.

OPTIMIZATION PROCEDURE:-Sample solutions were diluted with the mixture of nitric acid (0.2% v/v) plus triton X-100 (0.1% v/v) until the absorbance values of analytes were below 0.20 absorbance units and they were used to obtain optimum parameters for ETAAS determinations with modifiers. One ml of sample solution diluted was mixed with 1 ml of modifier solution (2.0 g/l Mo, 0.4 g/l Pt, 5.0 g/l $\text{NH}_4\text{H}_2\text{PO}_4$, 2.0 g/l Mo + 0.4 g/l Pt, 2.0 g/l Mo + 0.4 g/l Pt + 5.0 g/l $\text{NH}_4\text{H}_2\text{PO}_4$) and injected into the platform. The maximum absorbance values of analytes were obtained with Mo + Pt + $\text{NH}_4\text{H}_2\text{PO}_4$ by changing the heating temperatures, ramp and hold times in preliminary studies. The optimized graphite furnace heating temperature program for the determination of Cu and Pb by ETAAS with Mo + Pt + $\text{NH}_4\text{H}_2\text{PO}_4$ was given in Table 1. The optimized modifier masses of mixed modifier components for Pb obtained from our previous works (Acar et al. 1999, Acar 2001) as 20 μ g Mo, 4 μ g Pt and 50 μ g $\text{NH}_4\text{H}_2\text{PO}_4$ were used. The pyrolysis and atomization temperature curves of Cu and Pb in sample solutions with or without of modifiers were then plotted by using absorbance versus pyrolysis and atomization temperature and given in Figure 1.

Results and Discussion

THERMAL STABILIZATION STUDIES:-The optimum parameters of heating program for analytes were studied by using the sample solution together with Mo + Pt + $\text{NH}_4\text{H}_2\text{PO}_4$ mixture and given in Table 1. The main goal of using a modifier in ETAAS is to stabilize analyte elements upto higher possible pyrolysis temperatures and to volatilize matrix components such as organic compounds in the sample solution. The pyrolysis and atomization temperature curves of Cu and Pb in the white cheese and tahini halva sample solutions with and without of modifiers were obtained by using optimum parameters of heating program (Table 1) and were given in Figure 1 as an example. As can be seen in Fig. 1, the highest absorbance values and pyrolysis temperatures of analytes were obtained with Mo + Pt + $\text{NH}_4\text{H}_2\text{PO}_4$ in sample solutions (1250°C for Cu and Pb) and they were in agreement with previous studies for Pb (Tsalev and Slaveykova 1992, Acar et al. 1999, Acar 2001). The addition of $\text{NH}_4\text{H}_2\text{PO}_4$ and nitric acid (0.2% v/v) plus triton X-100 (0.1% v/v) together with Mo + Pt has an additional effect on the pyrolysis temperatures of analytes. In general, NO_3^- , PO_4^{3-} , NH_4^+ and triton X-100 were provided to eliminate interferences in samples and to be efficient in reducing the modifiers to reactive metallic forms at higher temperatures (Acar 2001).

ANALYTICAL CHARACTERISTICS:-The determinations of Cu, Pb, Fe and Zn in sample solutions were performed with the calibration graphs on the base of single element solutions in nitric acid (0.2% v/v) plus triton X-100 (0.1% v/v). Calibrations against aqueous standard solutions were performed for analytes by using optimum parameters such as furnace temperature program, mass ratios of the Mo + Pt + $\text{NH}_4\text{H}_2\text{PO}_4$ modifier mixture and operating conditions. Calibration ranges of working standard solutions were 5 - 80 μ g/l for Cu and Pb, 0.2 - 4.0 mg/l for Fe and 0.05 - 1.0 mg/l for Zn, respectively. Calibration graphs of all analytes obtained were linear and correlation coefficients (r) were about > 0.99.

Limits of detection (LOD) and characteristic mass (m_0) values for Cu and Pb in the presence of the Mo + Pt + $\text{NH}_4\text{H}_2\text{PO}_4$ by ETAAS based on integrated absorbance measurements were obtained and calculated from 20 consecutive measurements of the sample solution (2% m/v) (Barrera et al. 1993). They were 35 ng/g and 16.4 pg for Cu, 42 ng/g and 20.2 pg for Pb, respectively. LOD values for Fe and Zn obtained by FAAS were 3.0 ng/g for Fe and 1.7 ng/g for Zn, respectively.

Since an available standard reference material was not found to provide the validation of the method used, aqueous standard solutions of analytes were added into some samples before digestion in order to control the possible loss of analyte during digestion and measurement, and to obtain recovery tests. The recovery test results carried out by ETAAS with Mo + Pt + $\text{NH}_4\text{H}_2\text{PO}_4$ and by FAAS were given in Table 2. As can be seen in Table 2, percent recoveries of analytes obtained were about 95-102%. Mass loss of analyte and such interferences in the

digestion procedures and measurements were not observed. As a result of explanations mentioned above, Mo + Pt + NH₄H₂PO₄ mixture in nitric acid (0.2% v/v) + triton X-100 (0.1% v/v) diluent was applied for determinations of Cu and Pb in white and Kasar cheeses and tahini halva samples.

ANALYSIS OF SAMPLES:-Copper, Pb, Fe and Zn in white and Kasar cheeses and tahini halva samples digested by HNO₃-H₂O₂ mixture were determined by ETAAS with Mo + Pt + NH₄H₂PO₄ modifier mixture and heating program (Table 1), and by FAAS. The results of analytes found in samples were given in Tables 3 and 4. The results were presented as the average ± confidence interval ($t_{\text{student}}=2.57$, n= 6 replicates of sample where each one was measured six times at 95% confidence level). As can be seen in Table 3, mean and (range) of analytes found in white cheese samples are 0.67 (0.16 – 0.96) mg/kg for Cu, 0.17 (0.11 – 0.22) mg/kg for Pb, 5.70 (3.65 – 8.63) for Fe and 11.7 (7.56 – 17.3) for Zn, respectively. Mean and (range) of analytes in Kasar cheese samples are 0.19 (0.13 – 0.26) mg/kg for Cu, 0.26 (0.18 – 0.31) mg/kg for Pb, 8.49 (5.74 – 10.3) mg/kg for Fe and 13.5 (11.4 – 15.3) mg/kg for Zn, respectively. As can be seen in Table 4, the mean and (range) of analytes found in tahini halva samples are 5.32 (2.18 – 7.93) mg/kg for Cu, 0.17 (0.10 – 0.24) mg/kg for Pb, 9.95 (7.36 – 12.6) mg/kg for Fe and 10.6 (8.32 – 13.6) mg/kg for Zn, respectively.

The maximum concentration values of analytes found in samples were compared and evaluated with literature values. The maximum concentration values of Cu found in white and Kasar cheeses are lower than the limits of FAO/WHO (3 mg/kg Cu) and Turkish standard (1.0 mg/kg Cu) (TS591 2006). The concentration ranges of Cu in Kasar cheeses are in agreement with average copper concentration values reported as 0.10 – 0.27 mg/kg in the literature (Mendil 2006). The copper content found in cheese samples is in agreement with Kasar cheese reported as 0.7 ± 0.2 mg/kg in the literature (Yüzbaşı et al. 2003). The maximum lead concentrations found in white and Kasar cheese samples are 0.22 and 0.31 mg/kg, respectively (Table 3). These values are higher than white cheese reported as 0.05 mg/kg Pb in the Turkish standard (TS591 2006), but they are lower than the limit of 0.5 mg/kg Pb accepted by Germany for hard cheese samples (International Dairy Federation 1992). The maximum lead concentration found in Kayseri Comlek cheese is lower than the literature reported as 1.2 mg/kg (Mendil 2006). In the literature, lead concentrations have been reported as 0.010 – 0.422 mg/kg (Yüzbaşı, et al. 2003) and 1.8 - 8.3 µg/100g of Pb (Alberti-Fidanza et al. 2002) in cheese. The maximum concentration levels of Cu and Pb found in tahini halva (Table 4) are lower than tahini halva reported in Turkish standard and Turkish food codex regulation as 10 mg/kg Cu and 0.3 mg/kg Pb, respectively (TS 2590 2006, TKB 2002).

The iron values of the cheese samples found are varied from 3.65 to 8.63 mg/kg for white cheese and from

5.74 to 10.3 mg/kg for Kasar cheese samples. These concentrations are in the range of the values reported by Yüzbaşı et al. (Yüzbaşı, et al. 2003) and Park (Park 2000) as 1-14 mg/kg for white cheese and 7.68-17.8 mg/kg for Kasar cheese samples, respectively. Maximum value of Fe found in halva samples is 12.6 mg/kg and it is lower than Turkish standard (TS 2590 2006) given as 40 mg/kg. Iron values found in samples are also lower than Joint FAO/WHO limit given as 48 mg/kg.

Maximum Zn values found in white and Kasar cheese and tahini halva samples are 17.3, 15.3 and 13.6 mg/kg, respectively. These values are lower than the values reported in FAO/WHO (60 mg) and in the literature (Yüzbaşı et al 2003) given as 63.0 mg/kg and they are in agreement with the values given in the previous work (Mendil 2006).

The significant differences in lead, copper, iron and zinc contents of samples come from different cheese and halva producers, some contaminations occurred during production and/or manufacturing of samples depending on the equipment used. Therefore, further research is necessary to find out the exact source of contaminations (Yüzbaşı et al. 2003). The consumption of average amounts of white and Kasar cheese and tahini halva samples can not be posed a health risk for the consumer since the FAO/WHO PTDI of Pb, Cu, Fe and Zn are 214 µg/day, 3, 48 and 60 mg/day for an average body weight of 60 kg (Joint FAO/WHO Expert committee on Food additives 1999), respectively.

Conclusion

Lead, copper, iron and zinc in cheese and tahini halva samples by ETAAS using Mo + Pt + NH₄H₂PO₄ modifier mixture and by FAAS were determined and evaluated. Recovery tests for analytes in samples were performed for the accuracy of the method. Chemical interferences from organic and inorganic compounds on analytes in the sample matrix are minimized by using the Mo + Pt + NH₄H₂PO₄ and digestion of the samples by HNO₃ + H₂O₂ mixture. Mo + Pt + NH₄H₂PO₄ can be applied for the determination of analytes in various matrixes such as food and biological samples. The contents of Cu, Pb, Fe and Zn in such samples are generally within safe limits when they are compared with similar samples given in Turkish standards, Turkish food codex and FAO/ WHO results. From the results found, it is deduced that cheese and tahini halva samples are not significant contributors to heavy metal intake. The results obtained may be used to test the chemical quality of such samples and to assess the possible risk associated with their consumption by humans.

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Table 1. Heating program for the determinations of Cu and Pb in samples with Mo + Pt + NH₄H₂PO₄

Step	Temperature (°C)		Time (s)		Ar flow rate, (ml/min)
	Cu	Pb	Ramp	Hold	
Dry-1	50-120		30	-	250
Dry-2	120-300		15	15	250
Pyrolysis	300-1250		30	20	250
Atomization	2700	2000	0	5	0
Cleaning	2800	2650	-	3	250

Table 2. Recovery tests for Cu, Pb, Fe and Zn in samples

Element	Concentrations, µg/l				
	Added	White Cheese		Havla	
		Found ^a	Recovery, %	Found ^a	Recovery, %
Cu (µg/l)	0.0	28.9 ± 1.0	0.0	18.7 ± 0.7	0.0
	20	46.9 ± 1.7	96	37.7 ± 1.6	97
	40	70.1 ± 2.9	102	58.3 ± 2.3	99
Pb (µg/l)	0.0	24.6 ± 0.9	0.0	22.3 ± 1.1	0.0
	20	43.5 ± 1.6	98	40.2 ± 1.4	95
	40	63.8 ± 2.8	99	60.6 ± 2.5	97
Fe (mg/l)	0.0	0.28 ± 0.01	0.0	0.24 ± 0.01	0.0
	0.5	0.76 ± 0.02	97	0.72 ± 0.02	97
	1.0	1.30 ± 0.03	102	1.20 ± 0.03	97
Zn (mg/l)	0.0	0.21 ± 0.01	0.0	0.17 ± 0.01	0.0
	0.2	0.40 ± 0.01	98	0.35 ± 0.01	95
	0.4	0.60 ± 0.02	98	0.58 ± 0.02	102

^a Mean of six replicate measurements with 95 % confidence level, $\bar{X} \pm ts / \sqrt{n}$.

Table 3. Results of Cu, Pb, Fe and Zn in cheese samples

Sample No	Concentrations ^a , wet weight, mg/kg			
	Cu	Pb	Fe	Zn
White cheese				
1	0.91 ± 0.06	0.18 ± 0.02	4.66 ± 0.11	11.6 ± 0.17
2	0.85 ± 0.04	0.16 ± 0.01	5.44 ± 0.12	10.4 ± 0.15
3	0.81 ± 0.03	0.18 ± 0.01	3.96 ± 0.07	14.8 ± 0.22
4	0.66 ± 0.03	0.15 ± 0.01	7.41 ± 0.16	16.3 ± 0.25
5	0.79 ± 0.04	0.13 ± 0.01	4.71 ± 0.10	10.2 ± 0.17
6	0.96 ± 0.05	0.16 ± 0.01	5.74 ± 0.09	12.7 ± 0.26
7	0.62 ± 0.03	0.14 ± 0.01	8.63 ± 0.17	8.96 ± 0.16
8	0.44 ± 0.02	0.19 ± 0.01	6.86 ± 0.17	11.7 ± 0.18
9	0.16 ± 0.02	0.11 ± 0.01	4.69 ± 0.11	12.9 ± 0.16
10	0.92 ± 0.04	0.16 ± 0.01	5.53 ± 0.09	10.6 ± 0.19
11	0.83 ± 0.03	0.18 ± 0.02	4.38 ± 0.13	12.1 ± 0.23
12	0.66 ± 0.03	0.15 ± 0.01	6.17 ± 0.15	10.3 ± 0.18
13	0.74 ± 0.03	0.17 ± 0.01	5.45 ± 0.14	8.92 ± 0.15
14	0.53 ± 0.02	0.21 ± 0.02	5.18 ± 0.10	10.9 ± 0.17
15	0.42 ± 0.02	0.19 ± 0.02	6.28 ± 0.15	7.56 ± 0.11
16	0.54 ± 0.02	0.17 ± 0.01	7.13 ± 0.13	14.8 ± 0.24
17	0.75 ± 0.03	0.20 ± 0.02	4.74 ± 0.08	9.72 ± 0.15
18	0.69 ± 0.03	0.17 ± 0.01	6.73 ± 0.12	11.6 ± 0.18
19	0.78 ± 0.04	0.18 ± 0.01	7.36 ± 0.13	8.41 ± 0.12
20	0.53 ± 0.02	0.16 ± 0.01	5.77 ± 0.12	17.3 ± 0.21
21	0.41 ± 0.02	0.22 ± 0.01	4.86 ± 0.07	15.4 ± 0.17
22	0.63 ± 0.03	0.19 ± 0.01	3.65 ± 0.08	10.2 ± 0.12
Mean ± SD	0.67 ± 0.19	0.17 ± 0.03	5.70 ± 1.23	11.7 ± 2.57
(range)	(0.16 – 0.96)	(0.11 – 0.22)	(3.65 – 8.63)	(7.56 – 17.3)
Kasar cheese	Concentrations ^{a,b} , wet weight, mg/kg			
Van oltu (N=4)	0.15 ± 0.02	0.18 ± 0.02	10.3 ± 1.1	13.2 ± 1.7
Tokat (N=5)	0.13 ± 0.01	0.24 ± 0.03	5.74 ± 0.3	14.2 ± 1.3
Kars (N=4)	0.26 ± 0.04	0.29 ± 0.02	8.36 ± 0.7	15.3 ± 1.8
Kayseri comlek (N=4)	0.21 ± 0.03	0.31 ± 0.03	9.54 ± 0.8	11.4 ± 1.3
Mean ± SD (range)	0.19 ± 0.06	0.26 ± 0.06	8.49 ± 2.0	13.5 ± 1.7
	(0.13 – 0.26)	(0.18 – 0.31)	(5.74 – 10.3)	(11.4 – 15.3)

^a Mean of six replicate measurements with 95% confidence level, $\bar{X} \pm ts / \sqrt{n}$.

^b Mean ± SD was obtained from parallel studies of the same sample (N).

Table 4. Results of analytes in tahini halva samples

Sample No	Concentrations ^a , wet weight, mg/kg			
	Cu	Pb	Fe	Zn
1	5.44 ± 0.19	0.24 ± 0.01	9.24 ± 0.16	11.8 ± 0.14
2	7.93 ± 0.34	0.23 ± 0.01	11.6 ± 0.23	13.6 ± 0.19
3	4.72 ± 0.21	0.20 ± 0.01	8.72 ± 0.14	10.9 ± 0.15
4	6.13 ± 0.28	0.15 ± 0.01	12.6 ± 0.19	12.1 ± 0.18
5	4.81 ± 0.24	0.18 ± 0.01	9.53 ± 0.12	9.78 ± 0.13
6	2.30 ± 0.11	0.24 ± 0.01	8.78 ± 0.15	10.6 ± 0.15
7	3.38 ± 0.16	0.14 ± 0.01	7.36 ± 0.16	11.9 ± 0.14
8	2.57 ± 0.13	0.11 ± 0.01	7.94 ± 0.13	12.6 ± 0.18
9	2.18 ± 0.09	0.10 ± 0.01	8.46 ± 0.17	10.2 ± 0.16
10	7.62 ± 0.36	0.24 ± 0.01	10.9 ± 0.21	8.91 ± 0.13
11	7.27 ± 0.32	0.22 ± 0.01	13.4 ± 0.18	9.26 ± 0.14
12	6.24 ± 0.29	0.11 ± 0.01	10.2 ± 0.14	10.7 ± 0.16
13	5.63 ± 0.27	0.14 ± 0.01	9.17 ± 0.13	11.4 ± 0.15
14	3.23 ± 0.16	0.13 ± 0.01	7.88 ± 0.11	12.1 ± 0.18
15	4.82 ± 0.21	0.17 ± 0.01	10.3 ± 0.15	9.62 ± 0.17
16	7.18 ± 0.30	0.12 ± 0.01	11.2 ± 0.12	8.41 ± 0.13
17	6.06 ± 0.26	0.16 ± 0.01	10.8 ± 0.09	12.9 ± 0.19
18	7.83 ± 0.32	0.13 ± 0.01	12.4 ± 0.11	8.32 ± 0.12
19	7.07 ± 0.27	0.15 ± 0.01	10.5 ± 0.12	9.46 ± 0.14
20	2.64 ± 0.11	0.19 ± 0.01	7.68 ± 0.08	8.41 ± 0.09
21	3.26 ± 0.16	0.13 ± 0.01	8.41 ± 0.14	11.4 ± 0.17
22	6.12 ± 0.25	0.23 ± 0.01	9.74 ± 0.16	10.9 ± 0.18
23	7.04 ± 0.32	0.21 ± 0.01	11.7 ± 0.17	8.91 ± 0.15
24	6.33 ± 0.31	0.19 ± 0.01	10.4 ± 0.12	11.3 ± 0.21
Mean ±SD	5.32 ± 1.85	0.17 ± 0.05	9.95 ± 1.63	10.6 ± 1.49
(Range)	(2.18 – 7.93)	(0.10 – 0.24)	(7.36 – 12.6)	(8.32 – 13.6)

^a Mean of six replicate measurements with 95% confidence level, $\bar{X} \pm ts / \sqrt{n}$.

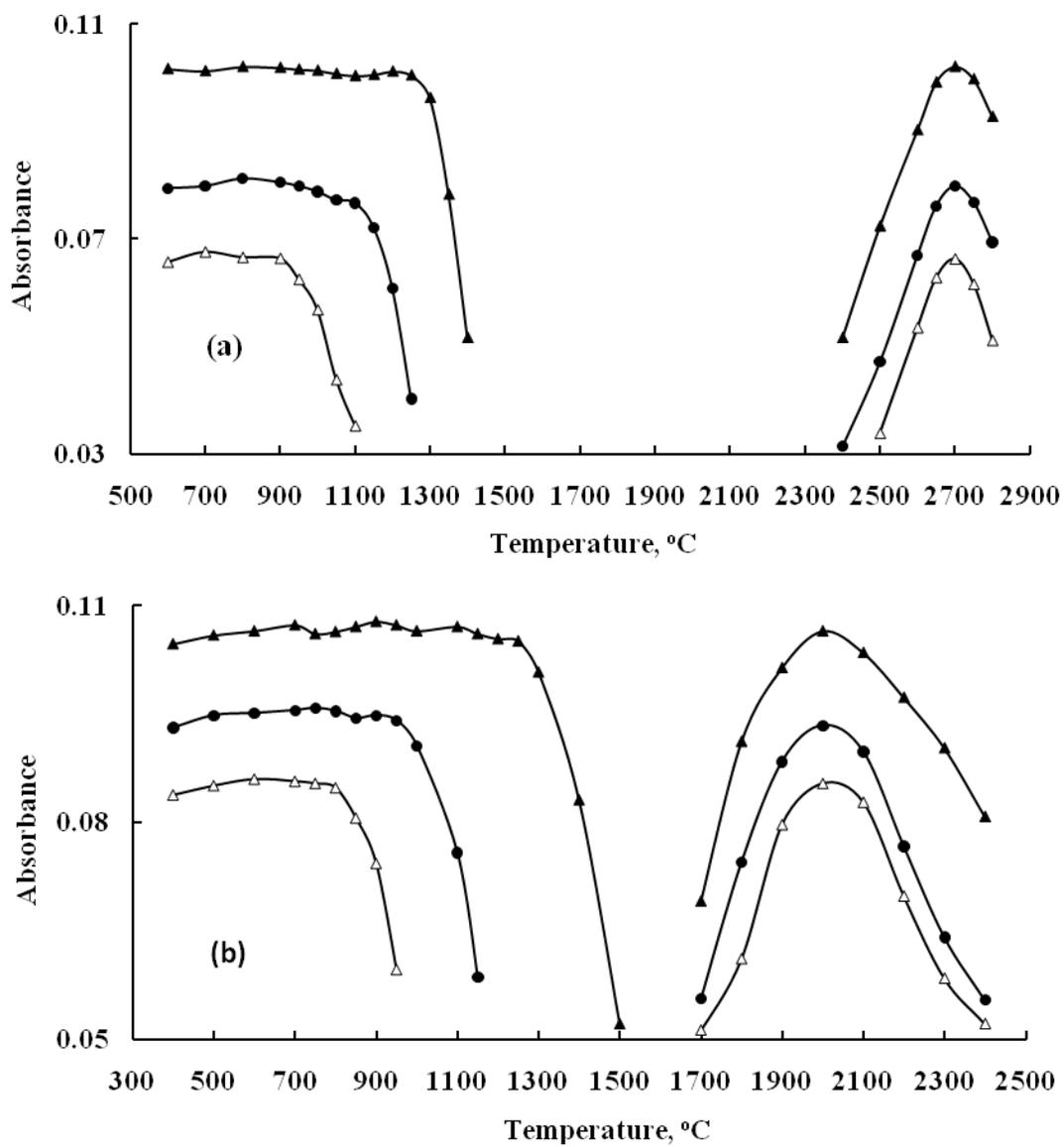


Fig. 1. Pyrolysis and atomization curves for (a) Cu in white cheese and (b) Pb in tahini halva sample solutions (Dilution ratio is 4 for Pb and Cu) with and without of the modifiers: without (Δ); 20 μg Mo (\bullet); 20 μg Mo + 4 μg Pt + 50 μg $\text{NH}_4\text{H}_2\text{PO}_4$ (\blacktriangle).