PAPER DETAILS

TITLE: Determination of 12 heavy metals in hennas by microwave induced plasma optical emission

spectrometry

AUTHORS: Nil OZBEK

PAGES: 857-868

ORIGINAL PDF URL: https://dergipark.org.tr/tr/download/article-file/501975



Elemental analysis of henna samples by MP AES



¹ Department of Chemistry, Science and Letters Faculty, Istanbul Technical University, Istanbul, Turkey.

Abstract : In this study, a new methodology using microwave-induced plasma atomic emission spectrometry (MP AES) after microwave assisted digestion been developed to determine aluminum, boron, cadmium, cobalt, chromium, copper, iron, lead, manganese, molybdenum, nickel, and tin concentrations in 18 commercial henna samples purchased from markets in Turkey. For the elemental determination, 0.100 g henna sample weighed and digested with 10 mL of $HNO_3+H_2O_2$ (3:1) mixture in a microwave digestion system. The analytes in certified reference material bush branches and the leaves were determined in the uncertainty limits of the certified values as well as the analytes added to the henna sample prior the digestion were recovered quantitatively (95-105%). Finally found results in henna samples were compared with several regulations from different countries as well as other published results.

Keywords: Microwave Induced Plasma Optical Emission Spectrometry, henna, Lawsonia inermis.

Submitted: May 15, 2018. Accepted: July 03, 2018.

Cite this: Ozbek N. Elemental analysis of henna samples by MP AES. JOTCSA. 2018; 5(2):857-66.

DOI: <u>http://dx.doi.org/10.18596/jotcsa.423820</u>.

Correponding Author: E-mail: nil.ozbek@itu.edu.tr

INTRODUCTION

Henna is a dye prepared from the *Lawsonia inermis*, plant, which is found in hot climates such as Egypt, India, Africa, and Morocco. Originally, henna was used in Egypt. It is well documented that Cleopatra used henna for cosmetic purposes. It is mainly used for dying the skin, hair, and nails, and as a component for some cosmetic products (1). Since it is believed to create healthy and beautiful hair, it is also used as a common hair product, as a natural component for shampoos and conditioners (2). Henna is also applied as a temporary tattoo on hands and feet for cosmetic purposes. Since it is not permanent and is painless, cheap and carries no risk of HIV or hepatitis infections, it is highly popular among children and young adults (1, 3).

Lawsone, primarily concentrated in the petioles of the leaves of *Lawsonia inermis*, causes staining or dyeing. However, they must be crushed in order to release the lawsone molecules contained within the leaf. Once released, the lawsone gradually binds to the outer layer of the proteins in the skin or hair, thus staining or dyeing it. Its characteristic staining properties are caused by the compound 2-hydroxy-1,4-napthoquinone, which is also known as hennotannic acid. Leaves of henna contain this compound up to 5% by weight. Since hennotannic acid does not dissolve in water, henna leaves are mixed with a mild acidic agent (i.e. lemon juice, and strong tea, etc.) to release it from the plant. In order to enhance the scent of henna paste, various oils and herbs may also be added. One day after mixing, the activation of dye is completed. But after three days, it loses staining capabilities. The lawsone dye does not chemically alter the skin and hair so there is no permanent change. Since the dye molecules, 2-hydroxy-1,4-napthoquinone, are about the same size as amino acid molecules, they migrate from the outermost layer of the skin or hair.

Natural henna, while being totally organic and natural, is altered by additives such as pphenyldiamine (PPD), eucalyptus oil, black tea, vinegar, lemon oil, clove oil, mustard oil or coffee powder to obtain different colors in the applications (4, 5). Natural henna is relatively safe but these additions may cause allergic reactions; moreover, heavy metal concentrations of these enhanced types of hennas are reportedly high (6). In a previous study, heavy metals such as chromium, cobalt, nickel and lead were found in black henna tattoo samples (4). Moreover, as an allergic reaction to cobalt and lead in henna, contact dermatitis were observed in a patient (7).

Some non-essential heavy metals like cadmium, mercury and lead, can damage biological structures and cause health problems even at the lowest concentrations (8). These metals can have toxic effects by ingestion, inhalation, and by skin exposure (9). The Canadian Government determined heavy metal impurity concentrations in cosmetic products as 5 ppm for antimony, 3 ppm for arsenic, 3 ppm for cadmium, 10 ppm for lead and 1 ppm for mercury (10). Heavy metal concentrations in cosmetic products in Germany are also limited to 0.5 ppm for antimony, 0.5 ppm for arsenic, 0.1 ppm for cadmium, 2.0 ppm for lead and 0.1 ppm for mercury (11).U.S. Food and Drug Administration (FDA) limited lead and arsenic content of henna (as a color additive for cosmetic products) as not more than 20 ppm and 3 ppm, respectively (12). In this context, levels of different elements should be determined in henna samples. Till now, potential stripping analysis (PSA) (13), graphite furnace and flame atomic absorption spectrometry (GFAAS and FAAS) (14-17) and inductively coupled plasma atomic emission and mass spectrometry (ICP-AES and ICP-MS) (2, 4, 18) have been used for determination of different elements in henna samples (Table 1).

Sample	Method	Elements (Ranges)	Ref
Henna (3 Samples)	PSA	Pb (8.52-19.61 μg g ⁻¹)	(13)
		Zn (<lod-490 g⁻¹)<="" td="" µg=""><td></td></lod-490>	
Henna (7 Samples)	GFAAS	Pb (2.20-19.9 μg g ⁻¹)	(16)
Henna (15 samples)	FAAS	Ni (2940-3900 μg g ⁻¹)	(15)
		Co (2960-3540 µg g ⁻¹)	
Henna (4 Samples)	ICP-AES	AI (610-3293 μg g ⁻¹)	(18)
		Cr (33-86 μg g ⁻¹)	
		Cu (7.0-21 µg g ⁻¹)	
		Fe (750-2404 µg g ⁻¹)	
		Mn (65-120 μα α ⁻¹)	
		Ni ($<$ LOD-8.0 µg g ⁻¹)	
Henna (20 Samples)	GFAAS	Pb (1.29-16.48 µg g ⁻¹)	(14)
Henna (12 Samples)	ICP-AES	Pb (2.29-65.98 µg g ⁻¹)	(2)
Henna (5 Samples)	ICP-MS	Cr (35.0-76.9 µg g ⁻¹)	(4)
		Co (0.44-3.11 µg g ⁻¹)	
		Ni $(1.13-2.20 \text{ µg g}^{-1})$	
		Pb $(1.59-17.7 \ \mu g \ q^{-1})$	

Table 1: Available methods for determination of different elements in henna samples.

Microwave Induced Plasma Atomic Emission Spectrometry (MP AES) is a plasma technique which uses 2.45 GHz microwave magnetic field and nitrogen gas to sustain the plasma (Figure 1). In this technique, since nitrogen generator is used, flammable and toxic gasses are not required. Nitrogen plasma have relatively higher temperature than the flame of AA, which makes possible to determine refractive and carbide forming elements. This technique has recently become commercialized, so the number of papers regarding the applications of MP AES on different samples are relatively low when compared to the AAS and ICP techniques (19, 20). It was recently used for different elemental determination in various matrices, *i.e.* gasoline and ethanol fuel (21), diesel and biodiesel (22), animal feed and fertilizer (23), steel (24), wine (25), cheese (26), leather and fur (27), maize seed (28), vinegar (29), bread (30) and tarhana (sundried food made of curd, tomato and flour) (31) and geological samples (32). Total dissolved salt (TDS) content limitation of the sample is the only drawback of the method. When TDS of the solution is above 4%, with the aspiration of sample, a critical damage to the torch may occur due to the accumulation of salt residues.



Figure 1: Schematic of Microwave Induced Plasma Atomic Emission Instrument.

In this paper, a novel and easy method were developed for the determination of aluminum, boron, cadmium, chromium, cobalt, copper, iron, manganese, molybdenum, nickel, lead and tin concentrations in 18 commercial henna samples sold in Turkey by MP AES.

MATERIALS AND METHODS

Instrumental

An Agilent 4200 Microwave Induced Plasma Atomic Emission Spectrometer (MP OES) (Agilent Technologies, Melbourne, Australia) equipped with an Inert One Neb nebulizer and a double-pass glass cyclonic spray chamber (Agilent Technologies, Melbourne, Australia) were used throughout this study. Nitrogen was extracted from the air using an F-DGSi, Thyster 8/1 LV, (Innovative Gas System Co., Evry, France), dual flow *nitrogen* generator. The sample and waste tubings were orange/green and blue/blue solvent resistant, respectively (Agilent Technologies, Melbourne, Australia). Before every sample reading, 10 seconds of uptake time and 20 seconds of torch stabilization time were set, whereas for the emission measurement of each sample, 5 seconds read time with 3 replicates were applied. The torch alignment and wavelength calibration were optimized using a wavelength calibration solution (Agilent Technologies, Melbourne, Australia). The instrumental parameters for MP AES are given in Table 2. Samples were weighed using a Model XR 205SM-DR Precisa 5-digits balance with 0.01 mg readability. For digestion procedure, microwave-assisted Topwave digestion system (Analytik Jena, Berlin, Germany) equipped with pressure controlled Teflon vessels (50 mL) were used.

	AI	В	Cd	Со	Cr	Cu
Wavelength, nm	396.15	249.77	228.80	340.51	425.43	324.75
Ion Type	I	I	Ι	Ι	Ι	Ι
Viewing Position	0.00	0.00	0.00	0.00	0.00	0.00
Nebulizer Flow, L min ⁻¹ Background	0.85	0.40	0.45	0.65	0.95	0.75
Correction Uptake Time,	Auto	Auto	Auto	Auto	Auto	Auto
sec	15.00	15.00	15.00	15.00	15.00	15.00
Time, sec	20.00	20.00	20.00	20.00	20.00	20.00
LOD, µg L ⁻¹	1.58	1.14	3.56	4.39	1.19	0.30
LOQ, µg L ⁻¹	5.28	3.79	11.8	14.6	3.98	0.99
Regression Coefficient, r ² Calibration Curve Equation	0.999 44476.694C- 1767.305	0.998 17404.721C- 1060.608	0.999 23016.624C +86.113	0.999 34681.460C+ 144.598	0.999 50288.135C +12.838	0.999 137723.124C -23.418
Linearity, mg L ⁻¹	LOQ-10	LOQ -10	LOQ -5	LOQ -10	LOQ -10	LOQ -10
	Fe	Mn	Мо	Ni	Pb	Sn
Wavelength, nm	371.99	403.08	379.83	352.45	405.78	317.51
Ion Type	Ι	Ι	I	Ι	Ι	I
Viewing Position	0.00	0.00	0.00	0.00	0.00	0.00
L min ⁻¹ Background	0.80	0.75	0.80	0.30	0.65	0.90
Correction	Auto	Auto	Auto	Auto	Auto	Auto
sec Stabilization	15.00	15.00	15.00	15.00	15.00	15.00
Time, sec	20.00	20.00	20.00	20.00	20.00	20.00
LOD, µg L ⁻¹	3.51	0.333	0.987	8.43	2.43	7.71
LOQ, µg L ⁻¹ Regression	11.71	1.11	3.29	28.1	8.11	25.7
Coefficient, r ² Calibration Curve Equation	0.999 11874.461C- 9.994	0.999 50176.156C+ 17.206	0.999 40646.008C- 64.484	0.998 7945.255C+8 6.744	0.999 8314.895C+ 51.168	0.998 3652.684C+ 146.860
Linearity, mg L ⁻¹	LOQ -10	LOQ -10	LOQ -10	LOQ -10	LOQ -10	LOQ -10

Table 2: Optimized instrumental parameters and figures of merit for the method.

*C: concentration, mg L⁻¹.

Reagents and Solutions

For the preparation of the solutions, the water with 18.2 M Ω cm resistivity obtained from a TKA reverse osmosis and a deionizer system (TKA Wasseraufbereitungsstandards, system GmbH, Niederelbert Germany) were used. The calibration standards were prepared from a mixed standard which included 1000 mg L⁻¹ of Al, B, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Sn (Carlo Erba, Radona, Italy) daily. For accuracy tests, certified reference material, bush branches and leaves CRM from the China National Analysis Center for Iron and Steel (Beijing, China) were used.

Procedure

Before starting the experiments, eighteen henna samples were bought from different locations in Istanbul. They and the certified reference materials were stored in polyethylene bags and kept at room temperature. Prior to the analysis, the samples were dried at 50 °C in an airventilated oven for 12 h. The samples were allowed to cool over silica gel and stored in tightly closed folding polyethylene cups. All the samples were ground manually in an agate mortar. A topwave microwave-assisted digestion system (Analytik Jena, Berlin, Germany) equipped with pressure controlled Teflon vessels (50 mL) were used for the sample digestion. Each sample was weighed around 0.1 g with 0.1 mg sensitivity and

50

underwent microwave-assisted digestion using 10 mL of $HNO_3+H_2O_2$ (3:1) mixture. After the microwave digestion program, the digested samples were allowed to cool down and then completed to 10 mL. The microwaveassisted digestion program is shown in Table 3.

Temperature (°C)	Pressure (bar)	Ramp (min)	Time (min)	Power (%)
180	60	36	5	90
180	60	1	15	90
50	50	10	10	0
50	50	10	10	0

10

10

0

50

Table 3: The microwave-assisted dig	ligestion programme	for the digestion of	henna samples
-------------------------------------	---------------------	----------------------	---------------

RESULTS AND DISCUSSION

Instrumental Optimization

The main limitation of this technique is the total dissolved salt (TDS) concentration of the samples. In case of excess salt concentration in the sample, the accumulation of salts may cause blockages of the torch and the nebulizer. For the 4200 MP AES system, the limiting TDS concentration is 4%. This problem can be avoided using diluted solutions. However, while the dilution of the sample reduces the TDS concentration and the risk of damaging the torch and nebulizer, diluting the sample too much may cause the concentration of the analyte falling under LOD. Therefore, selecting the appropriate emission wavelength and optimum dilution factor is an important step for this analysis.

First of all, optimum wavelengths were selected for highest sensitivity and lowest spectral interference. After several experiments 396.15 nm, 249.77 nm, 228.80 nm, 340.51 nm, 425.43 nm, 324.75 nm, 371.99 nm, 405.78 nm, 403.08 nm, 379.83 nm, 352.45 nm, and 317.51 nm were selected

most appropriate wavelengths for as aluminum, boron, cadmium, cobalt, chromium, copper, iron, lead, manganese, molybdenum, nickel, and tin respectively. Then, automatic optimization for nebulizer pressure and viewing position were done by the instrument for the highest sensitivity (Table 1). Finally, the dilution factor was determined. It is important to determine the optimum dilution factor in order to prevent defections at the torch and stay above LOD for all the analytes. After several tries, it was decided to dilute all samples to 10 mL in order to stay in the linear range of all elements and generally above LOD. Some further dilution were needed for some samples in order to determine aluminum and iron. With this dilution factors, samples did not cause any damage to the torch during the whole study.

Figures of Merit

Limit of detection and quantification (LOD and LOQ) were calculated as figures of merit for the method. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as 3 and 10 times the standard deviation (σ) for 10 repetitive aspiration of a blank used for the digestion of samples were divided by the slope of linear calibration graph (3 σ and 10 σ /slope of calibration graph), respectively. The figures of merit are given in Table 1.

In order to test the accuracy of the method, the analytes in a certified reference material (CRM) were determined. Since henna CRM could not be found, a plant based CRM, NCS DC 73349-bush branches and leaves were used. As can be seen from Table 4, the accuracy test showed that there were no systematical errors (due to the balance, pipettes, flasks, and impurities of the reagents etc.).

	Certified Value (µg g⁻¹±SD)	Found Value (µg g⁻¹±SD)
Al	2000±300	1995±80
В	38±6	35.2±8
Cd	(0.38)	0.40 ± 0.01
Со	0.41±0.05	0.39 ± 0.06
Cr	2.6±0.2	2.8±0.1
Cu	6.6±0.8	7.2±0.1
Fe	1070±57	999±32
Mn	61±5	64±5
Мо	0.28±0.05	0.22±0.5
Ni	1.7±0.3	2.0±0.1
Pb	47±3	43±3
Sn	(0.27)	0.17±0.11

Tuble 4. Accuracy (coto for citier (NCO DC 75545 busin branches and icaves) (in 4

*Data enclosed in the brackets show unceritifed values, given as reference only in the certificate.

In order to validate the results, recovery tests were conducted also. In order to find out if there is any analyte lost in digestion step, analytes were added to henna samples prior the digestion step. As can be seen from Table 5, added elements were completely recovered. This shows that the sensitivity (emission intensities) were not influenced from the sample matrix and there is no analyte loss during sample preparation step. The obtained recoveries were between 95 to 105 %, which allows us to use linear calibration technique without needing standard addition technique.

Fable 5: Recoveries of a	nalytes added to a	henna sample prior to	o the digestion step.
--------------------------	--------------------	-----------------------	-----------------------

	Addition	Recovery (%)
AI	0.1 mg g ⁻¹	95.7
В	10 µg g ⁻¹	97.3
Cr	10 µg g ⁻¹	96.7
Cu	10 µg g ⁻¹	98.4
Fe	1 mg g ⁻¹	96.4
Mn	10 µg g ⁻¹	101.2
Ni	10 µg g ⁻¹	97.3
Pb	10 µg g ⁻¹	95.6

Finally, in Table 6, the concentrations of aluminum, boron, cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, lead, and tin in the henna samples are given. As can be seen from the table, Cd, Co, Mo and Sn concentrations are under their respective LOD values (0.356 µg g^{-1} for Cd, 0.439 µg g^{-1} for Co, 0.0333 µg g^{-1} for Mo and 0.771 μ g g⁻¹ for Sn). After all the optimizations, there is no accumulation of deposits in the torch during the whole analysis. Repeatability of the results were checked by the RSDs of the emissions, which were below 10% for all the analytes on the same day. In 18 different henna samples bought from Turkey, Fe (0.26-3.17 mg g^{-1}) and AI (0.122-5.22 mg g^{-1}) were the most abundant elements. On basis of the overall mean levels, the mean heavy metal levels were in the following order Fe (0.26-3.17 mg q⁻¹) >AI (0.122-5.22 mg q⁻¹)>Mn (15.5-188 μg g⁻¹)>B (4.5-71.6 μg g⁻¹)>Cr (0.70-54.4 μg g⁻¹) ¹)>Ni (6.50-25.2 μg g⁻¹)>Cu (2.70-67.6 μg g⁻ ¹)>Pb (6.50-17.4 μ g g⁻¹) which were similar with previous studies. Found concentrations were below the limits regulated by the FDA (12) and Canadian Government (10), except values for Canadian for some lead Government. Lead values also exceeded the limits regulated by Germany (11).

CONCLUSION

In this study, MP AES was used to analyze henna samples after wet digestion procedure. Various elements were determined (aluminum, boron, cadmium, cobalt, chromium, copper, iron, lead, manganese, molybdenum, nickel, and tin) in henna samples. This technique offers multiple benefits over other methods, such as fast sequential determination of multiple elements with lower detection limits when compared to FAAS. Since there is no need to change and optimize lamps, there is no need of a complicated procedure for optimization. Each element was optimized by the software automatically in a few minutes. Sample consumption is also very low when compared to AAS methods (around 2 mL for 10 elements). Moreover, since there is no use of flammable gases and nitrogen is extracted from air by a nitrogen generator, this method is safer and has low running costs when compared to other emission techniques. To conclude, а fast. practical, and environmentally friendly and also a safe procedure was developed. Determined concentration values of 18 henna samples were below regulated limits except lead concentrations. With this study, it is proved that MP AES can be use to determine elemental values in cosmetic industry.

Ozbek N. JOTCSA. 2018; 5(2):857-68.

Duand	Place of Origin		Expected		Р	C.	C ++	
вгапо	Place of Origin	Color of Henna	Color Effect	AI	В	Cr	Cu	r
				mg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	mg g
BRAND 1	Iran	Green	ND	0.122 ± 0.001	<lod< td=""><td><lod< td=""><td>2.70±0.162</td><td>0.24±0.01</td></lod<></td></lod<>	<lod< td=""><td>2.70±0.162</td><td>0.24±0.01</td></lod<>	2.70±0.162	0.24±0.01
BRAND 2	Iran	Green	ND	0.743±0.035	14.2 ± 0.712	44.4±1.61	11.8±0.85	1.31±0.07
BRAND 3	Iran	Green	ND	1.25 ± 0.063	18.2±0.861	0.70±0.042	11.9±0.65	2.61±0.13
BRAND 4	India	Green	ND	1.22 ± 0.061	18.4 ± 0.744	8.20 ± 0.511	9.50 ± 0.431	2.21±0.14
BRAND 5	India	Green	ND	1.59 ± 0.081	20.4±0.853	3.70±0.213	9.80±0.588	3.17±0.17
BRAND 6	India	Brown	Chestnut	0.541±0.027	19.3±0.852	23.6±1.23	6.80±0.421	1.05 ± 0.05
BRAND 6	India	Brown	Brown	0.283 ± 0.015	17.2±0.657	19.2±1.101	6.70 ± 0.561	0.80±0.04
BRAND 7	India	Brown	Burgundy	0.354 ± 0.018	10.1±0.641	34.7±1.53	6.70±0.402	0.75±0.05
BRAND 7	India	Green	Yellow	0.211 ± 0.010	15.3±0.665	9.70±0.352	4.90±0.321	0.44±0.03
BRAND 8	ND	Green	ND	0.311 ± 0.016	4.50±0.151	2.40±0.151	67.6±3.21	0.26±0.01
BRAND 9	Turkey	Green	ND	1.29 ± 0.065	20.5±1.04	6.30±0.323	10.1 ± 0.511	2.67±0.16
BRAND 10	Saudi Arabia	Brown	ND	1.11 ± 0.055	15.0±0.644	54.4±2.14	14.0±0.75	2.06±0.12
BRAND 11	ND	Black	Black	5.22±0.261	6.80±0.457	2.20±0.112	3.60±0.231	1.70 ± 0.32
BRAND 12	India	Light Brown	Orange	0.721±0.036	71.6±2.89	8.30±0.432	10.9±0.652	1.80 ± 0.23
BRAND 12	India	Light Brown	Burgundy	0.258 ± 0.013	15.1±0.862	2.30 ± 0.112	4.20±0.342	0.74±0.04
BRAND 12	India	Dark Brown	Purple	0.434±0.022	5.20±0.455	3.50 ± 0.164	5.30±0.317	0.86±0.06
BRAND 12	India	Dark Brown	Brown	0.440 ± 0.022	8.90±0.546	2.10 ± 0.142	9.40±0.452	9.59±0.64
BRAND 12	India	Black	Black	0.561 ± 0.028	10.6±0.649	<lod< td=""><td>6.70±0.328</td><td>1.23 ± 0.05</td></lod<>	6.70±0.328	1.23 ± 0.05

Table 6: Metal concentrations in various kinds of henna samples determined by MP AES (Mean Value

*ND: Not Defined. *Cd, Co, Mo and Sn concentrations are under their respective LOD values.

865

ACKNOWLEDGMENTS

We are grateful to Agilent Technologies and SEM, Agilent Authorized Distributor in Turkey for providing MP AES 4200 spectrometer. I am very thankful to Hande TINAS for her help during the study.

REFERENCES

1. El Habr C, Mégarbané H. Temporary henna tattoos and hypertrichosis: A case report and review of the literature. J Dermatol Case Rep. 2015;9(2):36-8.

2. Jallad KN, Espada-Jallad C. Lead exposure from the use of Lawsonia inermis (Henna) in temporary paint-on-tattooing and hair dying. Sci Total Environ. 2008;397(1):244-50.

3. Onder M. Temporary holiday "tattoos" may cause lifelong allergic contact dermatitis when henna is mixed with PPD. J Cosmet Dermatol. 2003;2(3-4):126-30.

4. Aktas Sukuroglu A, Battal D, Burgaz S. Monitoring of Lawsone, p-phenylenediamine and heavy metals in commercial temporary black henna tattoos sold in Turkey. Contact Dermatitis. 2017;76(2):89-95.

5. Neri I, Guareschi E, Savoia F, Patrizi A. Childhood allergic contact dermatitis from henna tattoo. Pediatr Dermatol. 2002;19(6):503-5.

6. Ortiz G, Terron M, Bellido J. Contact allergy to henna. Int Arch Allergy Immunol. 1997;114(3):298-9.

7. Kang IJ, Lee MH. Quantification of paraphenylenediamine and heavy metals in henna dye. Contact Dermatitis. 2006;55(1):26-9.

8. Oymak T, Ulusoy Hİ, Hastaoglu E, Yılmaz V, and Yıldırım Ş. Some Heavy Metal Contents of Various Slaughtered Cattle Tissues in Sivas-Turkey. JOTCSA 2017;4(3):721-8.

9. Elaziz MMA, Khalifa MA, Ghariani RA, Mohamed HDA, Ashtewi MAS. Chemical and Physical Investigations of Arabian Eye Kohl Brands as Cosmetic in Libya. J Turkish Chem Soc Sect A Chem. 2017;4(1):463-76.

10. Guidance on Heavy Metal Impurities in Cosmetics, (2012).

11. Bund B. Technically avoidable heavy metal contents in cosmetic products. J Verbrauch Lebensm. 2017;12(1):51-3.

12. U. S. Food and Drug Administration. FDA's Testing of Cosmetics for Arsenic, Cadmium,

Chromium, Cobalt, Lead, Mercury, and Nickel Content 2018 [cited 2018 20.06.2018]. Available from:

https://www.fda.gov/cosmetics/productsingredient s/potentialcontaminants/ucm452836.htm#S1FP.

13. Kaličanin B, Velimirović D. A Study of the Possible Harmful Effects of Cosmetic Beauty Products on Human Health. Biol Trace Elem Res. 2016;170(2):476-84.

14. AI-Saleh IA, Coate L. Lead exposure in Saudi Arabia from the use of traditional cosmetics and medical remedies. Environ Geochem Health. 1995;17(1):29-31.

15. Kang IJ, Lee MH. Quantification of paraphenylenediamine and heavy metals in henna dye. Contact Dermatitis. 2006;55(1):26-9.

16. Lekouch N, Sedki A, Nejmeddine A, Gamon S. Lead and traditional Moroccan pharmacopoeia. Sci Total Environ. 2001;280(1):39-43.

17. Ozbek N, Akman S. Determination of lead, cadmium and nickel in hennas and other hair dyes sold in Turkey. Regul Toxicol Pharm. 2016;79:49-53.

18. Ghanjaoui M, Cervera M, El Rhazi M, de la Guardia M. Assessment Of Trace Elements In Traditional Moroccan Cosmetics By Inductively Coupled Plasma Atomic Emission Spectroscopy. International Journal of Scientific & Technology Research. 2014;3(10):104-12.

19. Jankowski KJ, Reszke E. Microwave Induced Plasma Analytical Spectrometry: Royal Society of Chemistry; 2010.

20. Akbiyik D, Özbek N, Akman S. Determination of Ca, Mg, and Mn in Tea Samples with Microwave Plasma Atomic Emission Spectrometry. J Turkish Chem Soc Sect A Chem. 2014;1(1):7.

21. Donati GL, Amais RS, Schiavo D, Nobrega JA. Determination of Cr, Ni, Pb and V in gasoline and ethanol fuel by microwave plasma optical emission spectrometry. J Anal Atom Spec. 2013;28(5):755-9.

22. Amais RS, Donati GL, Schiavo D, Nóbrega JA. A simple dilute-and-shoot procedure for Si determination in diesel and biodiesel by microwave-induced plasma optical emission spectrometry. Microchem J. 2013;106(0):318-22.

23. Li W, Simmons P, Shrader D, Herrman TJ, Dai SY. Microwave plasma-atomic emission spectroscopy as a tool for the determination of copper, iron, manganese and zinc in animal feed and fertilizer. Talanta. 2013;112:43-8.

24. Hettipathirana TD. Determination of boron in high-temperature alloy steel using non-linear interelement correction and microwave plasma-atomic emission spectrometry. J Anal At Spectrom. 2013;28(8):1242-6. 25. Ozbek N, Akman S. Determination of boron in Turkish wines by microwave plasma atomic emission spectrometry. LWT. 2015;61(2):532-5.

26. Ozbek N, Akman S. Microwave plasma atomic emission spectrometric determination of Ca, K and Mg in various cheese varieties. Food Chem. 2016;192:295-8.

27. Zhao Y, Li Z, Ross A, Huang Z, Chang W, Ouyang K, et al. Determination of heavy metals in leather and fur by microwave plasma-atomic emission spectrometry. Spectrochim Acta B. 2015;112:6-9.

28. Heredia JZ, Cina M, Savio M, Gil RA, Camiña JM. Ultrasound-assisted pretreatment for multielement determination in maize seed samples by microwave plasma atomic emission spectrometry (MPAES). Microchem J. 2016;129:78-82.

29. Ozbek N, Koca M, Akman S. A Practical Method for the Determination of Al, B, Co, Cr, Cu, Fe, Mg, Mn, Pb, and Zn in Different Types of Vinegars by Microwave Induced Plasma Optical Emission Spectrometry. Food Anal Meth. 2016:1-5.

30. Ozbek N, Akman S. Method development for the determination of calcium, copper, magnesium, manganese, iron, potassium, phosphorus and zinc in different types of breads by microwave induced plasma-atomic emission spectrometry. Food Chem. 2016;200:245-8.

31. Ozbek N, Ozcan M. Elemental Analysis of Tarhana by Microwave Induced Plasma Atomic Emission Spectrometry. Anal Lett. 2017;50(13):2139-46.

32. Niedzielski P, Kozak L, Wachelka M, Jakubowski K, Wybieralska J. The microwave induced plasma with optical emission spectrometry (MIP–OES) in 23 elements determination in geological samples. Talanta. 2015;132:591-9.