Determination of Lead and Cadmium Concentration in Different Samples of Tea and Coffee Circulating in the Libyan Market

EzuldeenMohammad Abraheem[1*], Abdunnaser Mohamed Etorki[2], Aborawi M. Elgornazi[3], Sabreen Atrabelse[4]

[1, 3, 4]Chemistry Department, Faculty of Education, University of Tripoli-Libya

[2]Department of chemistry, Faculty of science, University of Tripoli, PO-BOX-13203, Tripoli, Libya
* Corresponding author: *E.pashloa[at]uot.edu.ly*

Abstract: ***The study focused on determining the levels of lead and cadmium in some samples of the best-selling and popular tea and coffee among people in Tripoli city-Libya during the years 2018-2019. Atomic Absorption Spectroscopy (AAS) has been used to determine the concentrate of cadmium and lead ions in different 17 tea samples, and 11 coffee samples. The mean values of cadmium and lead in (mg/kg) in tea samples as follows: The highest value for cadmium was found in Libton tea sample 0.260 ± 0.017, while the lowest value was found in Alkoozi red tea and Alfrdous tea samples 0.037 ± 0.006, with the overall mean was 0.119 ± 0.054. The highest value for lead was found in Alkoozi green tea sample 2.153 ± 0.012, while the lowest value was found in Alzahra tea sample 0.187 ± 0.002, with the overall mean was 1.118 ± 0.612. The results show that there are no significant differences in the values of lead in all coffee samples, which ranged from 1.23 to 1.62 mg/kg with the overall mean was 1.277 ± 0.358, except Sheikh Hbahanbelend coffee sample 0.271± 0.002 mg/kg. While the cadmium concentration in coffee samples ranged from 0.022 to 0.064 mg/kg, with the mean value 0.0514±0.0012. From these results can be noticed that coffee samples have about 11 times higher concentration of cadmium than tea, whereas the concentration of lead in tea is about 22 times higher than that in coffee samples.***

Keywords: Lead**;** Cadmium**;** Coffee**;** Tea**;** determination

1. Introduction

Coffee beans are one of the most exceedingly traded products in the world. More than 100 different plant kinds of the Coffee genus are present in the world. Regardless of the great variety, only two kinds have considerable economic value in the world coffee market: Coffea arabica L. and Coffee canephor Pierre ex A. Formerly known as arabica coffee and robusta coffee or conilon, respectively (**Pigozzi et al., 2018).** The Teaplant is evergreen plantwith three races (C. sinensis, C. assamica and C. cambodiensis). Tea plant grows in more than 36 countries spread over all continents (**Jeszka-Skowron** et al., 2015). Tea plant grows best in tropical and subtropical areas with adequate rainfall, good drainage and acid soils. Tea leaf comprises of two leaves and the terminal apical bud of a growing shoot of a tea bush. Made teas are classified into six main types such as white, green, oolong, black, compressed and flavored based on their respective manufacturing techniques (**The United Kingdom Tea Council Ltd, 2015**). China is the leading producer of tea in the world, with 1, 726, 023 tons produced in 2011. Other countries producing large quantities of tea include India, Kenya, and Sri Lanka (**FAOSTAT 2014).**

Numerous elements that are existed in food at major, minor and trace levels are considered to be important to human well-being; however, the uncontrolled intake of these elements can cause severe health complications. The ideal amount desired for this purpose widely varies relying on the kind of element and the sex and age of the consumers. The human body needs both non-metallic and metallic elements for healthy growth, development and adequate working. Thus, the determination of these elements in food, plant beverages, water, and soil are of most importance and is presently the subject of studies by numerous researchers **Pigozzi et al., 2018).** Most often, people drink 1–3 cups of coffee a day (**Bartkowicz**., 2015**; Kwiatkowska**., 2017). However, one should not drink more than 5 cups (1 cup = 150 ml = 80 mg caffeine) a day due to its possible negative effect on the cardiovascular system (increased LDL-chol and total cholesterol levels due to diterpenoid alcohols), problems falling asleep (caffeine), pregnancy (caffeine intake of > 300 mg per day proved negative effect on the duration of pregnancy and weight at birth) and increased secretion of gastric acid and bile, which exacerbates peptic ulcer disease and hyperacidity (**EFSA., 2015; Gökcen., 2017; Poole** et al., 2017). Apart from antioxidants and other bioactive compounds, coffee contains carbohydrates, lipids, nitrogen compounds, vitamins and minerals, including toxic elements such as cadmium (Cd) and lead (Pb) (**Gökcen., 2017; Pigozzi et al., 2018).** Although, according to available literature and own studies, the content of Cd and Pb in food products normally does not exceed acceptable standard levels, due to the fact that these metals are capable of accumulating in tissues and have a long half-life: 5–30 years for Cd and from 30 days (in soft tissue) to 10 years (in bones) for Pb (**Winiarska-Mieczan**., 2017) Elemental analysis of a tea sample requires destruction of the organic fraction of the sample, leaving the heavy metals either in solution or in a form that is readily dissolved. Unfortunately, because of a large number of analytic and a variety of sample types, there is no universal sample preparation technique that meets all of the diverse requirements. Among the strategies for sample preparation, dilution, acid digestion and extraction are the most commonly considered (**Pigozzi** et al., 2018**; Winiarska-Mieczan et al., 2019).** Microwave digestion, wet digestion and dry ashing are commonly utilized for the total decomposition of organic matter in samples (**Pigozzi** et al., 2018**; Winiarska-Mieczan et al., 2018; Sultana et al., 2017).** Apart from these techniques, ultrasound-assisted solubilization/extraction sample preparation procedures were reported to be used for green and black tea samples (**Issa et al., 2018).**

Recently, food safety has become one of the most important hygienic problems, which has become more relevant in the Libyan. This is due to the fact that more and more food raw materials and food products (sometimes of dubious origin and quality) are coming to our consumer market from abroad, changing production technologies, storage and sales conditions. All new chemicals are added to food, the quantity of which is increasing. Contaminated food and raw materials are more at risk due to adverse environmental conditions. According to sanitary and epidemiological norms and rules, the Ministry of Health of the Libyan and another country defines food safety criteria mainly according to the following elements: mercury, cadmium, lead, arsenic. These heavy metals accumulate in the human body and plants as a result of various processes that cause negative effects. Heavy metals such as Zn, Cd, Pb, Cu are transported and separated into cells and body tissues by binding to proteins, nucleic acids destroy these macromolecules and disrupt their cellular functions (**Maharramov** et al., 2019**; Maharramova., 2021).**

2. Experimental Methods

2.1 Sample collection

All samples of tea and coffee were collected from different markets and mills in the Tripoli city-Libya.

2.1.1 Lead and cadmium content

Accurately 1.0 g of dry samples of tea and coffee were weighed in a container and then covered with its lid.5.0 mL of nitric acid (65%) was added and the mixture was allowed to stand at room temperature until the initial reaction had subsided and then 2.0 mL of peroxide (30 vol.) was also added. The mixture was then transferred to a Milestone microwave unit after the vessel was sealed inside the rotor, and the microwave program was then started by adjusting the time and wattage. This solution was filtered into a 100.0 mL volumetric flask and supplemented to the mark with deionized water, and transferred to a polyethylene container. The Lead, and cadmium concentrations were measured using an atomic absorption spectrometer (Shimadzu AA 6701 F; A. A Spectrophotometer; Shimadzu Ltd, Japan) equipped with a hollow cathode lamp.

3. Results and Discussion

In this study, the concentration of lead and cadmium was estimated in some samples of tea and coffee in the Libyan market. The results of the study ware as follows:

Table 1: Estimation of the concentration of some Pb and Cd in some samples of tea and coffee in the Libyan market

Samples	*Lead concentration / mg/kg*	*Cadmium concentration / mg/kg*
Alfrdous tea	0.224 ± 0.006	0.037 ± 0.006
Alarosa tea	1.248 ± 0.006	0.167 ±0.015
Alezdehar tea	2.130± 0.017	0.120± 0.010
Assam tea	0.567 ± 0.015	0.157 ± 0.012
Alzahra tea	0.187 ± 0.002	0.037 ± 0.006
Alkoozi red tea	1.267 ± 0.015	0.150 ±0.005
Ahmad red tea	1.240± 0.020	0.057 ± 0.001
tamween tea	1.132 ± 0.003	0.092 ± 0.002
Alkoozi green tea	2.153 ± 0.012	0.129 ± 0.004
Nabet tea	1.273 ± 0.012	0.110 ±0.01
Ajwad tea	1.097 ± 0.021	0.079 ± 0.002
Libton tea	0.194 ± 0.014	0.260 ± 0.017
Alqafela tea	1.542 ± 0.008	0.157 ± 0.003
Ahmad green tea	1.720 ± 0.006	0.122 ± 0.001
Alrabea tea	1.343 ±0.016	0.105 ± 0.030
Alrahela tea	0.482± 0.003	0.129 ± 0.003
Ali anwar tea	1.210 ± 0.026	0.123 ± 0.003
Sheikh Hbahanbelend coffee	0.271± 0.002	0.047 ± 0.002
Brazilian habahan coffee	1.620 ± 0.020	0.055 ± 0.002
Pure Indian coffee	1.530 ± 0.010	0.022 ± 0.001
Pure Brazilian coffee	1.288 ± 0.002	0.051 ± 0.002
Pure Syrian coffee	1.343 ± 0.012	0.064 ± 0.002
Pure alasala mix coffee	1.283 ± 0.015	0.056 ±0.002
Dubai coffee	1.283 ± 0.025	0.063 ± 0.001
Yeman coffee	1.430± 0.010	0.064 ± 0.002
Habahan Syrian coffee	1.230 ± 0.010	0.038 ± 0.001
Alasalahabahan mix coffee	1.257 ± 0.012	0.054 ± 0.001
Pure Indian coffee	1.520 ± 0.010	0.052 ± 0.000

All values are expressed as mean ±SD

Table 1 shows that the lowest value of cadmium in coffee sample was appeared in Pure Indian coffee (0.022 ± 0.00), and the highest value for Lipton tea (0.260 ± 0.017), Ferdous tea (0.037 ± 0.006), flower tea 0.037 ± 0.006, Pure Brazilian coffee (0.051 ± 0.002), Brazilian coffee Habhan (0.055± 0.002), Sheikh Habhan blend coffee 0.047 ± 0.002, Al Asala Mixture Habban coffee 0.054 ± 0.001, Al Asala Mixture pure coffee 0.056 ± 0.002 Ahmad tea (red) 0.057± 0.001, Habahan Syrian coffee 0.038± 0.001, pure Indian coffee (0.0544 ±0.00), which had the value less than the permissible quantity. These results clearly show that these popularly consumed materials contained levels of cadmium much higher than the normal permissible level, which is 0.06 ppm according to FAO. Table 1 shows the levels of lead in the research samples, which are the best-selling and popular among people, and it is clear that the lowest concentration of Alzahra tea and Lipton tea ranges between 0.187 ± 0.002, and 0.194 ± 0.014 mg/kg, respectively. While the highest concentrations were found in Alezdehar tea and Alkoozi green tea (green) with a range between 2.130 ± 0.017 and 2.153 ± 0.012 mg/kg, respectively. These results clearly show that these popularly consumed materials contained levels of lead much higher than the normal permissible level in foodstuffs, which is 0.05 ppm according to FAO. As for Alarosa tea 1.248 ± 0.006, Nabet tea 1.273 ± 0.012, Alrabea tea 1.343 ± 0.016, pure Indian coffee 1.530 ± 0.010, pure Brazilian coffee 1.288 ± 0.002, and Brazilian coffee 1.620 ± 0.020, Alqafela tea 1.542 ± 0.008, Ahmad tea (green) 1.720 ± 0.006, Alkoozi tea (red) 1.267 ± 0.015, AlasalaHabahan mix coffee 1.257 ± 0.012, pure Syrian coffee 1.343 ± 0.012, Pure alasala mix coffee 1.283 ± 0.015, Ajwad tea 1.097 ± 0.027, Dubai coffee 1.283 ± 0.025, Tamween tea 1.132 ± 0.002, Yemen coffee 1.430 ± 0.01, Syrian Haban coffee 1.230 ± 0.010, Ali Anwar tea 1.210 ± 0.026, pure Indian coffee 1.520 ± 0.010, and Ahmad red tea 1.240 ± 0.020 contained levels higher than the internationally permitted concentrations. This study shows that there are accumulations of lead in the research samples, especially flowering tea and alokozay tea (green), which exceed the permissible limits according to (FWO), and here it is likely that the harmful elements that are released to the atmosphere or spread over the surface of the earth are the ones that occur an imbalance in the ecosystem, which is either gaseous in the form of harmful gases emitted by car exhaust, or factories, especially oil refineries. This study has found that both in dry grains and infusions of Ethiopian coffee (n = 3), the level of Cd and Pb was lower than LOD. Studies in Brazil demonstrated that the level of Cd in roasted ground coffee (n = 15) was < 0.025 μg g−1, whereas the level of Pb ranged from 0.14 to 2.59 μg g−1 (Pigozzi et al., 2018). In as many as 8 samples, the level of Pb exceeded the maximum limit accepted by Brazilian legislation 0.5 μg g−1 (Pigozzi et al., 2018). According to other Brazilian studies (Issa et al., 2018), ground coffees contained 0.03–0.1 mg Cd and 0.025–1.58 mg Pb per 1 kg. The same authors found that the coffees were not safe in terms of the content of Pb; in 75% of 50 analyzed samples, it contained more Pb than acceptable in Brazil, whereas, in 86% of samples, it exceeded the limit in the European Union (0.2 μg kg−1). In addition, (da Silva et l., 2017). found that in coffee grains, the average content of Cd < 0.1 μg g−1, whereas that of Pb < 2.6 μg g−1. Turkish studies showed that green coffee grains contained on average 0.005 μg g−1 Cd (0.003–0.006 μg g−1) and 0.12 μg g−1 Pb (0.06–0.3 μg g−1) (Şemen et al., 2017). Those authors recount that up to 84% of Cd and up to 82.6% of Pb pass into the infusion, which is dependent on the coffee brewing method only (Turkish method—cooking—leaches more minerals, including toxic elements—except for Pb, than pouring with boiling water as practiced in Poland), but it is not dependent on the type of coffee. Studies by Anderson et al. (Anderson et al., 2017). As for the tea samples, the level of lead and cadmium in this study was lower than the results obtained from the study conducted in Iran (Behrooz et al., 2018). And an approach to the results obtained from the study conducted in Bangladesh (Harunur et al., 2016).

4. Conclusion

Tea and coffee are the most widely traded beverages in the Middle East and North Africa, and therefore it is necessary to conduct periodic detection for the presence of heavy metals. The results of this study clearly showed that the concentration of lead and cadmium in tea and coffee samples is higher than the permissible limit, which is a very dangerous indicator of the health of consumer.

References

[1] **M. T. Pigozzi, F. R. Passos and F. Q. Mendes. (2018**). Quality of Commercial Coffees: Heavy Metal and Ash Contents. Journal of food quality, 2018 (2018) 7.

[2] **Jeszka-Skowron, M., Krawczyk, M., Zgola-Grześkowiak, A. (2015**). Determination of antioxidant activity, ruin, quercetin, phenolic acids and trace elements in tea infusions: Influence of citric acid addition on extraction of metals. Journal of Food Composition and Analysis, vol.40, p.70-77.

[3] **The United Kingdom Tea Council Ltd, (2015).** [online]. Available at: http: //www.tea. uk/ (accessed 29.07.15).

[4] **China is the leading producer of tea in the world. (2014**). with 1, 726, 023 tons produced in 2011 (FAOSTAT 2014). Other countries producing large quantities of tea include India, Kenya, and Sri Lanka (FAOSTAT 2014).

[5] **Bartkowicz J. (2015).** The selected behaviors of consumers in the market for natural coffee. Handel Wewn 355: 45–57

[6] **Kwiatkowska K, Winiarska-Mieczan A, Kwiecień M, Klebaniuk R, Krusiński R, Rusinek-Prystupa E, Sembratowicz I, Kamińska E, Danek-Majewska A, Cholewińska E (2017).** Analysis of coffee consumption among primary school teachers. ProbeHigh Epidemiol 98: 285–289

[7] **EFSA (2015).** Scientific opinion on the safety of caffeine. EFSA J 13 (5): 4102.

[8] **Gökcen BB, Şanlier N. (2017).** Coffee consumption and disease correlations. Crit Rev Food Sci Nutr 59: 336–348.

[9] **Poole R, Kennedy OJ, Roderick P, Fallowfield JA, Hayes PC, Parkes J. (2017).** Coffee consumption and health: umbrella review of meta-analyses of multiple health outcomes. BMJ 359: j5024.

[10] **Winiarska-Mieczan A, Grela ER. (2017).** Content of cadmium and lead in raw, fried and baked commercial frozen fishery products consumed in Poland. J Sci Food Agric 97: 2969–2974.

[11] **Winiarska-Mieczan A, Kwiatkowska K, Kwiecień M, Baranowska-Wójcik E, Wójcik G, Krusiński R. (2019).** Analysis of the intake of sodium with cereal products by the population of Poland. Food AddictContac Part A 36: 884–892.

[12] **Winiarska-Mieczan A, Florek M, Kwiecień M, Kwiatkowska K, Krusiński R (2018).** Cadmium and lead content in chosen commercial fishery products consumed in Poland and risk estimations on fish consumption. Biol Trace Elem Res 182: 371–380

[13] **Sultana MS, Rana S, Yamazaki S, Aono T, Yoshida S. (2017).** Health risk assessment for carcinogenic and noncarcinogenic heavy metal exposures from vegetables and fruits of Banglaesh. Cog Environ Sci 3: 1291107

[14] **Issa AB, Yasin K, Loutfy N, Ahmed MT. (2018).** Risk assessment of heavy metals associated with food consumption in Egypt: a pilot study. J Clin Exp Toxicon 2: 15–24

[15] **M. A. Maharramov, S. I. Maharramova, I. G. Kazimova. (2019**). Safety of raw materials and food products, 270 (2019)

[16] **S. I. Maharramova. (2021).** Determination of heavy metals content in tea leaves and products of their processing by method of inversion voltammetry, E3S Web of Conferences 254, 02027 (2021)

[17] **Da Silva SA, Mendes FQ, Reis MR, Passos FR, de Carvalho AMX, de Oliveira Rocha KR, Pinto FG. (2017).** Determination of heavy metals in the roasted and ground coffee beans and brew. Afr J Agric Res.2017; 12: 221–228. doi: 10.5897/AJAR2016.11832.

[18] **Şemen S, Mercan S, Yayla M, Açıkkol M. (2017).** Elemental composition of green coffee and its contribution to dietary intake. Food Chem 215: 92–100.

[19] **Anderson GL, Garnick L, Fung MS, Gaffney SH. (2017).** A pilot study to assess lead exposure from routine consumption of coffee and tea from ceramic mugs: comparison to California Safe Harbor Levels. Int J Food Contam 4: 4.

[20] **Behrooz Jannat, Naficeh Sadeghi, Mohammad Reza Oveisi, Masoomeh Behzad, Manan Hjimahmoodi and Morteza Ebrahimi (2018).** Determination of trace elements and heavy metals content of green and black tea varieties consumed in Iran. African Journal of Biotechnology. Vol.17 (51), pp.1436-1444, 19 December, 2018

[21] **Md. Harunur Rashid, ZeenathFardous, M. Alamgir Zaman Chowdhury, Md. KhorshedAlam, Md. Latiful Bari, Mohammed Moniruzzaman, Siew Hua Gan. (2016).** Determination of heavy metals in the soils of tea plantations and in fresh and processed tea leaves: an evaluation of six digestion methods. Chemistry Central Journal volume 10, Article number: 7 (2016)