Flame Atomic Absorption Spectrophotometry Analysis of Heavy Metals in Some Food Additives Available in Baghdad Markets, Iraq

Wasan Abdulwahid Jasim[1], Jassim Dawood Salman[2], Jasim Mohammed Shamar Jamur[3]

[1]Assistant Lecturer, [2]Assistant Professor, [3]Dr. Lecturer, Department of Chemistry, College of Education for Pure Science (Ibn Al- Haitham), University of Baghdad, Iraq

Abstract

Flame atomic absorption spectrophotometer (FAAS) was used in this study to determine the concentrations of heavy metals such as Ca, Fe, Mn, Cd, Co, Cr, Ni, Cu, Pb and Zn in some food additives of Iraq. The order of metal contents in food additives was found to be Ca > Mn > Fe > Cu > Zn > Pb > Cr > Ni > Co > Cd. The concentration level of each metal was compared with that recommended by food agriculture organisation (FAO) and world health organisation (WHO). Calibration curves were linear for all standard solutions of heavy metals in the range starting from 0.02-0.4 mg/kg for Cd to 11-100 mg/kg for Ca. The correlation coefficients values (R^2) of calibrations were investigated and ranged from 0.9971 for Cr to 0.9999 for Ca. The limit of detection (LOD) and limit of quantification (LOQ) were found to be in highest value for Ca (1.6569 mg/kg and 5.5232 mg/kg), while they were found to be in lowest values for Cd (0.0150 mg/kg and 0.0499 mg/kg).

Keywords: *Heavy metals, Food additives, Flame atomic absorption spectrophotometer*

Introduction

Several elements are important for a wide range of biological processes due to their conjugation with proteins to form metalloproteins which are an important component in the enzymatic systems(1,2). Despite the importance of some metals including Cr, Al and Ni for plants, they can be toxic with high concentrations(3). Furthermore, some heavy metals such as Pb and As in food are a major health problem due to their carcinogenic effects(4). In addition, the presence of metals in soils during wastewater are environmental problem, and the main cause of the agricultural pollution(5).

The last three decades have seen increasing the production of spices about 3.5% per year, and play a key role in the history of civilisation around the world(6,7). Although spices are essential, there is increasing concern that some of them are being disadvantaged. This attributed to the accumulation of toxic trace elements(8).

Corresponding author:
Jasim jamur,
E-mail: jasimphduk@gmail.com

In addition, the spices may be contaminated with trace and heavy metals, and this could led to health problems(9). Therefore, researches have shown an increased interest in examine the effect of metals on air, water and food and their impact on human consumption. Concentrations of trace and heavy metals in spices are an important components in the healthcare systems due to their medicinal effective on human health(8). Some metals such as lead (Pb), arsenic (As), nickel (Ni) and cadmium (Cd) can be extremely harmful to human beings even in trace levels(10). However, spices are one of the most widely used groups of antibacterial, antioxidant and anti-diabetic agents(11).

A number of studies have been made to investigate the concentration of metals in spices(12). On the other hand, information about the efficacy of heavy metals and safety of spices are limited(13). The heavy metals in food need to be monitored in order to protect human and animals from the hazards of these metal ions; WHO has determined the maximum level for each toxic element in foodstuffs(8). Several analytical methods have been used to determine the metal concentrations in spice samples of different countries. Krejpcio and co-workers have shown the quantification analysis of some heavy metals such as Cd, Pb, Cu and Zn in popular spices used in Polish market using atomic absorption spectrophotometer (AAS)[11]. In the study by Nkansah and Amoako, AAS has been successfully used to monitor the concentration levels of heavy metals including Ni, Fe, Cu, Co, Pb and Zn in many different types of spices in Ghana[9]. The quantification analysis of some toxic metals such as As, Pb, Cd and Ni in a number of common spices in Pakistan using AAS method were carried out by Baig *et al*[8]. In a study conducted by Karadas and Kara, it was shown that geometric methods such as principal component analysis (PCA) and cluster analysis (CA) can be used to analyse the trace metal concentrations such as Co, Mn, Fe, Mg, Cr, Cu, Ca, Cd, Ba, As and Sr in some spices in Turkey[15].

The experimental work presented here provides the levels of heavy metals in some food additive available in the local markets of Baghdad, Iraq. This study therefore set out to assess the effect of some heavy metals such as Ca, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in some popular food additive in Iraq such as qayima, dolma, kubba, seven, pizza, biryani, judur, chicken, kubsa, burger and sumac using FAAS technique. Both qualitative and quantitative methods were used in this investigation.

Materials and Method

Apparatus

Flam atomic absorption spectroscopy (FAAS) model AA-7000 Shimadzu was used as instrumental detection system using hollow cathode lamps. Absorbance measurements of blank (solvent) were recorded using deuterium lamp. Air/ acetylene burner head was used as a carrier gas for all samples. The wavelength used for each metal was: Ca (422.7 nm), Fe (248.3 nm), Mn (279.5 nm), Cd (228.8 nm), Co (240.7 nm), Cr (357.9 nm), Ni (232 nm), Cu (324.8 nm), Pb (283.3 nm) and Zn (213.9 nm).

Chemicals

All chemicals were used without any further purification and all solutions were prepared by deionised water. Nitric acid (65 %) was supplied by Riedel-de Haen. Standard solution of each metal that used for the calibration curve was prepared by stock solution (1000 mg/ L) supplied by Aldrich. Deionised water was provided by Daihan Labtech CO., LTD (Model WD-2008F) with a volts of 220V 50 Hz.

Preparation of samples

Eleven samples of food additives such as qayima, dolma, kubba, seven, pizza, biryani, judur, chicken, kubsa, burger and sumac that used in the study were collected by the local markets of Baghdad, Iraq. One gram of each sample was weighed and digested by mixing with 2 ml of concentrated nitric acid and heated for 1 hour. Then, the produced samples were cooled at room temperature. After digestion, the samples were filtered and diluted to 25 ml with deionised water.

Analysis of sample

All prepared sample solutions were analysed by FAAS method to determine the concentrations of heavy metals such as Ca, Fe, Mn, Cd, Co, Cr, Ni, Cu, Pb and Zn that used in this study. Blank solution was also measured before the sample analysis using the same conditions.

Quantification

For quantification, calibration curves of five different concentrations of each standard solution were applied. All calibrations curves showed a good linear correlation between the concentrations of standard solutions and absorbance. Some statistical analysis including the standard deviation (S.D.), standard error of the mean (S.E.M.) and correlation of coefficients (R^2) were done in order to check the validation of FAAS method. All R^2 were found to be ≥ 0.997. The limit of detection (LOD) and the limit of quantification (LOQ) were also determined by considering standard deviation to the slope:

STEYX means the standard deviation of the y-value and x-value.

Results and Discussion

FAAS has been used to determine many heavy metals such as Ca, Fe, Mn, Cd, Co, Cr, Ni, Cu, Pb and Zn in some food additives such as qayima, dolma, kubba, seven, pizza, biryani, judur, chicken, kubsa, burger and sumac. The results obtained from the analysis are presented in Table 1. The samples were prepared in the same solvent used for the analysis. The wavelength was set for each element (see the material and method section). It can be seen from the date in Table 1 that the level of Ca in all samples is higher than levels observed of other metals. Interestingly, the samples of qayima and judur did not detect any value of Cr and Co. The results of the study are in agreement with those obtained by WHO. Therefore, there was no evidence that the levels of heavy metals concentrations in these food additives has an influence on human consumption.

Table 1: Contents of heavy metals in different food additives in mg/kg

Heavy metals Food additives	Ca	Fe	Mn	Cd	Co	Cr	Ni	Cu	Pb	Zn
Qayima	45.840	6.657	6.519	0.009	0.018	0.000	0.028	0.291	0.024	1.106
Dolma	48.146	5.785	7.146	0.005	0.018	0.030	0.028	2.148	0.048	1.056
Kubba	40.089	3.133	6.188	0.007	0.016	0.008	0.024	1.442	0.072	0.836
Seven	47.985	6.184	6.362	0.005	0.015	0.015	0.046	3.047	0.167	1.182
Pizza	47.725	5.134	6.559	0.015	0.034	0.060	0.055	0.402	0.127	0.842
Biryani	62.550	5.889	7.611	0.023	0.015	0.067	0.041	0.334	0.270	1.360
Judur	37.324	6.683	4.710	0.012	0.000	0.104	0.009	0.273	0.040	0.928
Chicken	45.555	6.562	5.930	0.006	0.023	0.052	0.047	2.414	0.095	0.970
Kubsa	56.055	6.167	5.888	0.005	0.030	0.074	0.043	1.101	0.048	0.993
Burger	69.058	6.258	4.843	0.008	0.033	0.037	0.110	0.855	0.087	0.575
Sumac	7.896	3.329	1.319	0.016	0.018	0.134	0.129	1.668	0.024	1.031

The results obtained from the Figure 1, it can see that the burger recorded the highest level of Ca (69.058 mg/kg), whereas the lowest level was found in sumac (7.896 mg/kg). From the data in Figure 1, it can see that the study resulted the concentration levels of Fe in the samples and found to be between 3.133 mg/kg in kubba and 6.683 mg/kg in judur. These values are lowest than that of determined by FAO and WHO, 2009 (20 mg/kg). Compared to permissible limit of FAO and WHO, 1984 (2 mg/kg), there was the higher Mn content in all food additives samples (> 4 mg/kg) except sumac, Figure 1.

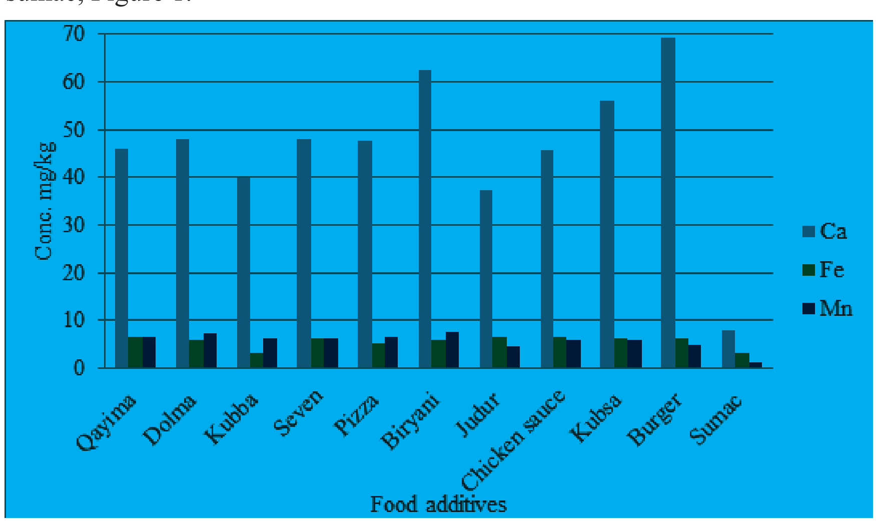

Figure 1:Levels of Ca, Fe and Mn in different food additives

As can be seen from the Figure 2, the concentrations of cadmium in all food additives were lower than that determined by FAO and WHO, 1984 (0.2 mg/kg). They found to be in the range from 0.005 mg/kg in dolma to 0.023 mg/kg in biryani. As shown in Figure 2, the concentrations of "Co" in all samples were under the permissible limit of FAO and WHO, 1984 (0.4 mg/kg). They were in the range of 0.015- 0.034 mg/kg in seven, biryani and pizaa, whereas judur sample did not show any content of Co. Only trace amounts of Cr were detected in the food additives samples, however, FAO/WHO (2009) suggested that the concentration of Cr should be zero in these samples. When Cr was found from 0.008 mg/kg in kubaa to 0.134 mg/kg in sumac, no amount in qayima was detected. The results also shows that the greatest value of Ni was in sumac (0.129 mg/kg), while the lowest value was in judur (0.009 mg/kg). This data can be compared with that determined by FAO and WHO, 1984 (1.63 mg/kg). As shown the maximum obtained values were too far from the permissible limit of FAO and WHO, therefore, the selective food additives in this study appeared to be unaffected by these levels of Ni.

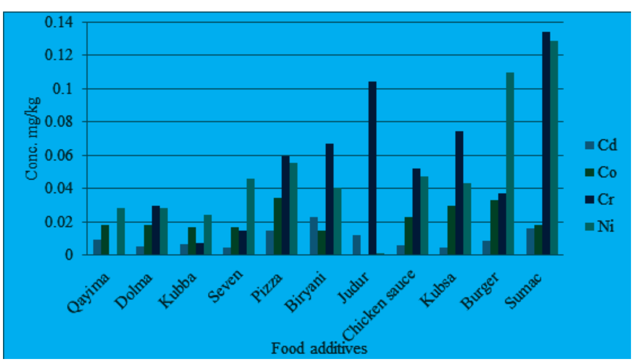

Figure 2: Levels of Cd, Co, Cr and Ni in different food additives

It can be seen from the Figure 3 that the food additives samples reported significantly high concentrations of copper compared to those of some heavy metals such as Cd, Co, Cr, Ni and Pb. It found to be between 0.273 mg/kg in judur and 3.047 mg/kg in seven. However, these observed concentrations were in general under the maximum limit of FAO and WHO, 1984 (3.00 mg/kg). From the data in this Figure, it is apparent that the Pb levels in food additives were higher than those of Cd and Co and lower than other metals. The range of concentrations were found from 0.024 mg/kg in both qayima and sumac to 0.270 mg/kg in biryani. This results indicated there was no evidence that Pb has an influence on human health due to their levels were under the permissible limit of FAO and WHO, 1984 (5.00 mg/kg). The results also shows that the levels of Zn ranged from 0.575 mg/kg in burger to 1.360 mg/kg in biryani. Therefore, they were too far from the maximum level that recommended by FAO and WHO, 2009 (50 mg/kg).

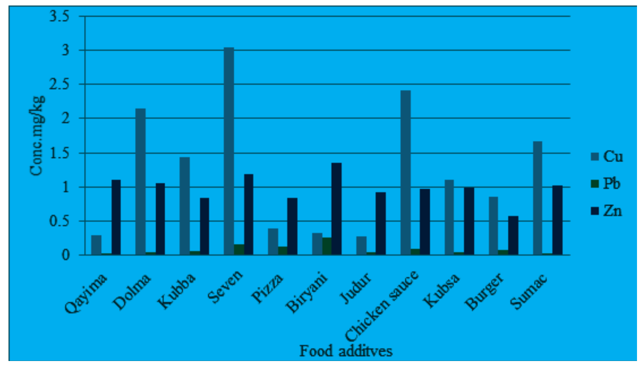

Figure 3: Levels of Cu, Pb and Zn in different food additives

Calibration curves

Correlation analysis of five different concentrations including the blank of each metal were tested to predict the linearity. Calibration ranges of standard solutions are set out in Table 2. From the Figure 4, it can see that all calibrations showed a good linearity over the range of concentrations. The LOD and LOQ of Ca is expected to be higher than others, whereas for Cd they were found to be lower than others . Other values of LOD and LOQ were listed in Table 2. Standard deviation (S.D.) and standard error of the mean (S.E.M.) were calculated by the equations:

$$S = \sqrt{\frac{\sum_{i=1}^{n}(xi - \bar{x})2}{n-1}}$$

$$\text{S.E.M.} = \frac{s}{\sqrt{n}}$$

Where *S* is standard deviation, *n* is number of values in the sample, *xi* is data value. x^{-} sample mean, S.E.M. is standard error of the mean and *s* is size of the sample. The results of the mean, S.D. and S.E.M. are summarised in Table 2.

Table 2: Data of linear regression, sensitivity and precision of the FAAS method of the FAAS method

Metal	Calibration Range (mg/kg)	Corr. R2	LOD (mg/kg)	LOQ (mg/kg)	S.D.	S.E.M.
Ca	11-100	0.9999	1.6569	5.5232	15.7482	4.7482
Fe	0.5-10	0.9992	0.3813	1.2825	1.2603	0.3800
Mn	0.4-7.0	0.9991	0.2975	0.9959	1.6972	0.5117
Cd	0.02-0.4	0.9993	0.0150	0.0499	0.0057	0.0017
Co	0.4-4.0	0.9991	0.1696	0.5654	0.0096	0.0029
Cr	0.1-2.0	0.9971	0.1505	0.5019	0.0412	0.0124
Ni	0.1-2.0	0.9997	0.0518	0.1727	0.0372	0.0112
Cu	0.3-4.0	0.9987	0.1974	0.6581	0.9595	0.2894
Pb	2.5-10	0.9988	0.4823	1.5951	0.0741	0.0223
Zn	0.1-1.0	0.9997	0.0209	0.0698	0.2038	0.0614

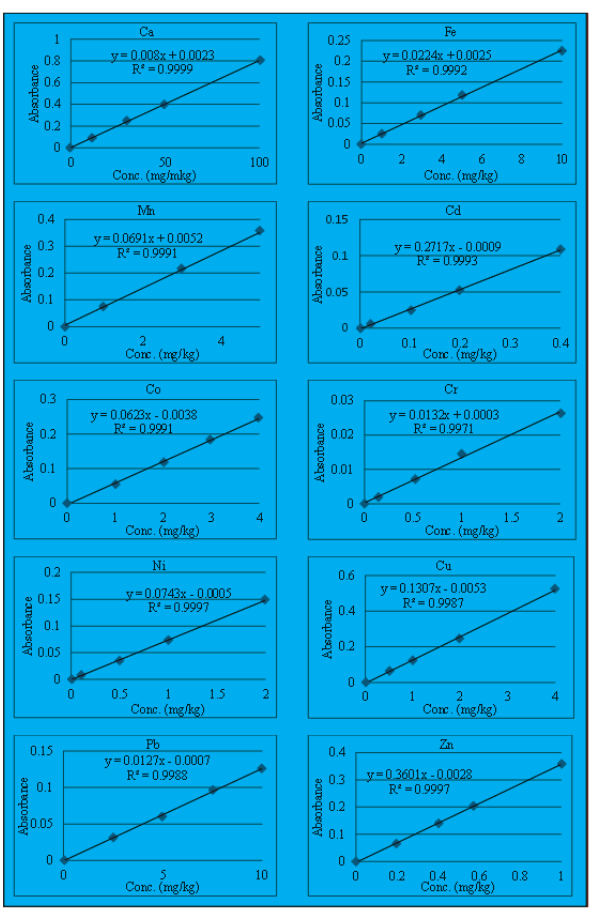

Figure 4. Calibration curves for the standard solutions of heavy metals by FAAS

CONCLUSION

The present study was designed to determine the levels of some heavy metals in different samples of food additives available at local markets in Baghdad, Iraq using FAAS technique. This has shown that the method is simple, fast and sensitive. The obtained concentrations of metals were acceptable with that recommended by FAO and WHO. The study has shown that highest correlation coefficient (R^2) of calibrations was found to be for Ca (0.9999), while the lowest was found to be for Cr (0.9971). The LOD and LOQ for Cd were found to be lower than others (0.0150 mg/kg and 0.0499 mg/kg) followed by Zn (0.0209 mg/kg and 0.0698 mg/kg). This could attributed to that the Cd and Zn are sensitive enough even at low concentrations.

For recommendations, the findings of this study have several important applications for future work. The method can be applied for determination of other metals in different samples of foodstuffs. Further research should also focus on determining the toxic and carcinogenic heavy metals in food additives and how can be able to reduce their effects by reducing their amounts.

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Ethical Clearance: The Research Ethical Committee at scientific research by ethical approval of both environmental and health and higher education and scientific research ministries in Iraq

Conflict of Interest: The authors declare that they have no conflict of interest.

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References

1. Khan N, Choi JY, Nho EY, Jamila N, Habte G, Hong JH, et al. Determination of minor and trace elements in aromatic spices by micro-wave assisted digestion and inductively coupled plasma-mass spectrometry. Food Chemistry. 2014;158:200–206.
2. Fraga CG. Relevance, essentiality and toxicity of trace elements in human health. Molecular Aspects of Medicine. 2005;26(4–5 SPEC. ISS.):235–244.
3. Smichowski P, Londonio A. The role of analytical techniques in the determination of metals and metalloids in dietary supplements: A review. Microchemical Journal. 2018;136:113–120.
4. Haque N, Islam MMT, Hassan T. Determination of Heavy Metal Contents in Frequently Consumed Fast Foods of Bangladesh. Proceedings of the National Academy of Sciences, India Section B: Biological Sciences. 2019; 89(2):543–549.
5. Uddin J, Abdul A. Heavy metal contamination in water , soil , and vegetables of the industrial areas in Dhaka , Bangladesh. 2010;166(1–4):347–357.
6. Shim J, Cho T, Leem D, Cho Y, Lee C. Heavy metals in spices commonly consumed in Republic of Korea. Food Additives & Contaminants: Part B. 2019;12(1):52–58.
7. Olusakin O P, Olaoluwa J D. Evaluation of Effects of Heavy Metal Contents of Some Common Spices Available in Odo-Ori Market, Iwo, Nigeria. Journal of Environmental Analytical Chemistry. 2016;03(01):3–6.
8. Baig JA. Evaluation of Arsenic , Cadmium , Nickel and Lead in Common Spices in Pakistan. 2019;187(2):586–595.
9. Nkansah M, Amoako C. Heavy metal content of some common spices available in markets in the Kumasi metropolis of Ghana. American Journal of Scientific and Industrial Research. 2010;1(2):158–163.
10. Divrikli U, Horzum N, Soylak M, Elci L. Trace heavy metal contents of some spices and herbal plants from western Anatolia, Turkey. International Journal of Food Science and Technology. 2006;41(6):712–716.
11. Krejpcio Z, Król E, Sionkowski S. Evaluation of heavy metals contents in spices and herbs available on the Polish market. Polish Journal of Environmental Studies. 2007;16(1):97–100.
12. Inam F, Deo S, Narkhede N. Analysis of minerals and heavy metals in some spices collected from local market. IOSR Journal of Pharmacy and Biological Sciences (IOSR-JPBS). 2013;8(2):40–43.
13. Ibrahim GI, Hassan LM, Baban SO. Effect of Heavy Metal Content of some Common Spices Available in Local Markets in Erbil City on Human Consumption. Rafidain Journal of Science. 2012; 23(3): 106–114.
14. Karadaş C, Kara D. Chemometric approach to evaluate trace metal concentrations in some spices and herbs. Food Chemistry. 2012;130(1):196–202.