

## SHORT COMMUNICATION / COMUNICACIÓN BREVE

### INVESTIGATION OF METALS RELEASED FROM IMPORTED COOKWARE COLLECTED FROM A LOCAL MARKET IN RIYADH, SAUDI ARABIA

Investigación sobre la liberación de metales de utensilios de cocina importados, recolectados en un mercado local de Riad, Arabia Saudita

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*(Received: March 2019; accepted: March 2020)*

Key words: ICP-OES, cookware, heavy metals.

#### ABSTRACT

Monitoring the presence of heavy metals in cookware intended for use by both humans and animals is of interest, because of their toxic effects. In this report, a study has been conducted to determine the heavy metals released from 46 items of metallic cookware purchased from a local market in Riyadh. Mn, Fe, Cu, Cr, As, Zn, Ni, Al, Cd and Pb, were analyzed using an inductively coupled plasma-optical emission spectrometer. The order of concentration of essential and toxic elements in all samples showed the following trend: Mn > Al > Pb = As > Fe > Zn > Cu = Ni = Cd > Cr. This study highlighted the importance of the metal release monitoring from cooking utensils in order to protect people from the dangers posed by toxic metals.

Palabras clave: ICP-OES, utensilios de cocina metálicos, metales pesados.

#### RESUMEN

El monitoreo de la presencia de metales pesados en utensilios de cocina destinados a ser utilizados tanto por humanos como por animales es de interés debido a sus efectos tóxicos. En este informe se realizó un estudio para determinar los metales pesados liberados de 46 utensilios de cocina metálicos comprados en un mercado local en Riad. Se analizaron Mn, Fe, Cu, Cr, As, Zn, Ni, Al, Cd y Pb usando un espectrómetro de emisión de plasma óptico acoplado inductivamente. El orden de concentración de elementos esenciales y tóxicos en todas las muestras mostró la siguiente tendencia: Mn > Al > Pb = As > Fe > Zn > Cu = Ni = Cd > Cr. Esta investigación destacó la importancia del monitoreo de la liberación de metales de los utensilios de cocina para proteger a las personas de los peligros que representan los metales tóxicos.

## INTRODUCTION

People have, over a period of time that predates historical record, constantly ground and stewed foods using various grinding techniques and cookware (Street et al. 2020). These varied in type and sophistication by both geographical location and technological means. The customs and traditions of the society have significantly contributed to the shape and functionality of the utensils and equipment that were used in the milling and cooking processes, as have the culture, level of urbanization and typical lifestyle. Food contamination by heavy metals is a prevalent concern in public health, as food is the principal source of nutrition for humans (Pennington. 2000, Jigam et al. 2011). Zinc is relatively harmless. Only exposure to high doses has toxic effects, making acute zinc intoxication a rare event (Plum et al. 2010). Copper surfeit can affect different organ systems leading to diseases such as diabetes, cardiovascular system illnesses, Alzheimer disease, angiogenesis, and some forms of cancer (Finney et al. 2009). Nickel contact can cause a variety of side effects on human health, such as allergy, cardiovascular and kidney diseases and lung fibrosis, (Genchi et al. 2020). The toxicity of Al to humans is mainly related to neurotoxicity and the development of neurodegenerative diseases (Verstraeten et al. 2008). Lead may disturb physiological functions and induce numerous adverse effects such as chronic obstructive pulmonary disease, asthma, lung cancer and cardiovascular diseases (Boskabady et al. 2018). Chromium (Cr) usually exists in the environment in different multi oxidation states. Cr (VI) has toxic, genotoxic, mutagenic and carcinogenic effects, causing skin lesions, ulceration, nasal septum and lung carcinoma (Yoshinaga et al. 2018). Chronic ingestion of arsenic has been associated with various health effects including skin lesions, diabetes mellitus, bronchitis, cardiovascular disease, and haematological effects (Sinha and Prasad 2020). Over exposure to cadmium can lead may cause lung, liver, skeletal and renal problems, and cancer (Djordjevic et al. 2019). Continuous exposure to manganese can lead to Parkinson's disease (Hernández-Pellón et al. 2017). Nowadays, awareness about food safety is increasing in most parts of the world. Many of the heavy metals are probably the most harmful and insidious contaminants because of their biological non-degradable nature and their potential to cause adverse effects in human beings, at a certain level of exposure and absorption (Alabdula'aly et al. 2009). Therefore, monitoring the presence of heavy metals in metallic cookware intended for use by both humans

and animals is of interest and requires particular attention, because of their toxic effects. The overall objective of this work is to build up a nation-wide baseline data regarding heavy metals as well as concentration in metallic cookware in Saudi Arabia This study aims to determine the metal released from a variety of common cookware, purchased from Riyadh local market.

## MATERIALS AND METHODS

### Sample collection and preparation

A total of 46 different types of samples of metallic (aluminium) cookware for human use were collected from the local market of Riyadh city and transported to the environmental research laboratory at Al-Imam Mohammad Ibn Saud Islamic University for elemental analysis. The aluminium pots were firstly washed with distilled water many times to remove any possible contamination. Afterward, 0.9. liters of distilled water were added to the aluminium cookware pots, then allowed to boil for 30 minutes at 100 °C in order to allow prolonged contact to take place between the distilled water and the cookware wall, finally, 15 mL of the remaining water was taken for elemental analysis.

### Chemicals and reagents

All the standard stock solutions of heavy metals were certified reference materials that were purchased from Agilent Technologies (USA). HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> were heavy metal analysis grade and purchased from Wako Chemical Co. (USA). Reagent water, toluene, and acetone were of analytical reagent grade purchased from J.T. Baker (USA).

### Spectrometric analysis

The measurements were performed using a Genesis ICP optical emission spectrometer (Spectro Analytical Instruments, Kleve, Germany) with axial plasma observation. The instrument includes a Paschen-Runge mount spectrometer, constructed employing the optimized Rowland circle alignment (ORCA) technique. It consists of two hollow section cast shells, designed for direct thermal stabilization and small volume. 15 pre-aligned linear CCD detectors are installed on the outside of the optics body, which allow fast, simultaneous spectrum capture of the wavelength range between 175 nm and 777 nm. For UV access (< 200 nm), the optical system was purged with argon. The purge rate during normal operation is 0.5 L/min. To enable the method, intelligent calibration logic (ICAL) transfer between

individual instruments, was used to normalize the wavelength and the intensity scale of the optical system to a reference optic (“optic master”). Stability of the forward power in the case of rapidly changing sample loads was achieved through the use of an air-cooled ICP-generator, based on a free running 27.12 MHz system. All ICP operating parameters were software controlled. The ICP-OES instrument was initialized and allowed to achieve thermal equilibrium over 30 min. ICP-OES determinations of elements concentration were performed using the emission lines 228.802, 267.716, 324.752, 238.204, 285.213, 259.372, 231.604, 220.353, 213.857, 189.641, 196.090, 384.401 and 311.071  $\lambda$  (nm) for the elements Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, As and Al respectively.

### Quality control

An adequate quality control method and vigilance were carried out in order to get reliable results. Throughout the experiments, all glass ware and equipment were cautiously washed beginning with acetone followed by 5 % HNO<sub>3</sub> and ending with repeated rinsing distilled water to prevent contamination. Reagent blank determinations were used to correct the readings. The lower detection limit values of the elements were found to be 0.001 mg/L for Cr, 0.001 mg/L for Cu, 0.0001 mg/L for Zn, 0.002 mg/L for Fe, 0.0001 mg/L for Mn, 0.0001 mg/L for Cd, 0.001 mg/L for Al, 0.001 mg/L for Ni, 0.01 mg/L for Se, 0.004 for Pb and 0.01 mg/L for As in this study. Samples were measured tow time and the recovery values were nearly quantitative (95 %) for digestion method. The relative standard deviations were less than 10 % for all investigated elements. Multi-element solution standards obtained from Agilent technology were used to calibrate and for quantitative sample results.

## RESULTS AND DISCUSSION

Determination of metals released from imported cookware is very important, since several elements play major roles in various metabolic processes in the human body. Moreover, some of these elements are toxic if consumed in excessive quantities (Baran et al. 2019). In this study, 10 elements (i.e. Mn, Fe, Cu, Cr, Zn, Ni, Al, Pb, As and Cd) in 46 items of cookware collected from a local market in Riyadh were investigated using an inductively coupled plasma-optical emission spectrometer (ICP-OES), as shown in (Table I and Table II).

**TABLE I.** STATISTICAL SUMMARY OF Cd, Cr, Cu, Fe AND Mn CONCENTRATION RELEASED FROM IMPORTED METALLIC COOKWARE (mg/L).

Sample	Cd	Cr	Cu	Fe	Mn
1	LDL	0.001	0.009	0.071	0.053
2	LDL	0.001	0.008	0.041	0.085
3	LDL	LDL	0.004	0.008	0.002
4	LDL	0.003	0.009	0.142	0.393
5	LDL	0.001	0.008	0.02	0.029
6	LDL	0.001	0.005	0.005	LDL
7	LDL	0.004	0.111	0.186	0.116
8	LDL	LDL	0.013	0.005	0.01
9	LDL	LDL	0.003	0.002	0.001
10	LDL	LDL	0.004	0.012	LDL
11	LDL	LDL	0.006	0.003	0.001
12	LDL	LDL	0.004	0.008	0.001
13	LDL	0.001	0.005	0.036	LDL
14	0.007	0.001	0.011	0.009	0.052
15	LDL	LDL	0.003	0.016	0.024
16	LDL	0.001	0.004	0.004	0.003
17	LDL	0.002	0.004	0.115	0.003
18	LDL	0.001	0.012	0.073	0.126
19	LDL	0.001	0.006	0.022	0.106
20	LDL	LDL	0.004	0.008	LDL
21	LDL	LDL	0.003	0.023	0.045
22	LDL	0.001	0.005	0.018	0.02
23	LDL	LDL	0.001	0.003	0.001
24	LDL	0.001	0.004	0.018	0.054
25	0.093	0.017	0.175	0.574	0.357
26	LDL	0.001	0.002	0.004	0.002
27	0.002	0.002	0.006	0.014	0.082
28	LDL	LDL	LDL	0.02	0.001
29	LDL	0.001	0.001	0.013	0.002
30	LDL	0.001	0.006	0.047	0.392
31	0.213	0.007	0.137	0.208	0.303
32	LDL	0.001	0.002	0.019	0.004
33	LDL	0.001	0.004	0.164	0.505
34	LDL	0.001	0.003	0.037	0.005
35	LDL	LDL	0.005	0.116	0.134
36	LDL	LDL	0.001	0.009	0.054
37	LDL	LDL	0.002	0.013	0.004
38	LDL	0.001	0.003	0.015	0.004
40	LDL	0.001	0.009	0.142	0.004
41	0.001	0.001	0.006	0.017	0.096
42	LDL	0.001	0.005	0.065	0.104
43	LDL	0.001	0.004	0.12	0.071
44	LDL	0.001	0.006	0.02	0.022
45	LDL	LDL	0.001	0.018	0.004
46	LDL	0.001	0.001	0.065	0.004
Min	0.001	0.001	0.001	0.002	0.001
Max	0.213	0.017	0.175	0.574	0.505
Average	0.007	0.001	0.014	0.057	0.073
Std	0.034	0.003	0.035	0.096	0.122

Where: LDL = Lower than detection limit, Min = Minimum, Max = Maximum, Avg = Average and Std = Standard deviation.

**TABLE II.** STATISTICAL SUMMARY OF Ni, Zn, Al, Pb AND As CONCENTRATION RELEASED FROM IMPORTED METALLIC COOKWARE (mg/L).

Sample	Ni	Zn	Al g	Pb	As
1	LDL	LDL	0.103	LDL	LDL
2	0.009	LDL	0.012	LDL	LDL
3	LDL	LDL	0.999	LDL	LDL
4	0.004	LDL	0.055	LDL	LDL
5	0.003	LDL	0.031	LDL	LDL
6	LDL	LDL	0.027	LDL	LDL
7	0.016	LDL	0.049	LDL	LDL
8	0.073	LDL	0.007	LDL	LDL
9	LDL	LDL	0.014	LDL	LDL
10	LDL	LDL	0.255	LDL	LDL
11	LDL	LDL	0.203	LDL	LDL
12	LDL	0.034	0.629	LDL	LDL
13	LDL	0.032	0.013	LDL	LDL
14	LDL	0.042	0.012	LDL	0.012
15	LDL	0.041	0.351	LDL	LDL
16	LDL	0.035	0.055	0.099	0.114
17	LDL	0.03	0.011	0.138	0.137
18	LDL	0.048	0.069	0.134	0.137
19	0.005	0.039	0.010	0.112	0.116
20	LDL	0.026	1.910	0.112	0.122
21	LDL	0.034	0.437	0.129	0.119
22	0.072	0.048	0.019	0.123	0.125
23	LDL	0.029	0.038	0.125	0.124
24	0.003	0.041	0.07	0.105	0.098
25	0.035	0.239	0.062	0.134	0.128
26	LDL	0.032	0.210	0.114	0.109
27	LDL	0.037	0.012	0.119	0.122
28	LDL	0.031	0.659	0.120	0.110
29	LDL	0.032	0.959	0.123	0.122
30	0.004	0.025	0.074	0.128	0.131
31	0.031	0.314	0.047	0.108	0.108
32	LDL	0.04	0.046	0.114	0.123
33	0.056	0.045	0.044	0.146	0.141
34	LDL	0.042	0.579	0.138	0.142
35	0.002	0.068	0.068	0.155	0.146
36	LDL	0.028	0.063	0.148	0.148
37	LDL	0.035	0.109	0.155	0.151
38	LDL	0.038	0.813	0.133	0.132
40	LDL	0.035	0.017	0.152	0.139
41	LDL	0.05	0.024	0.132	0.131
42	0.007	0.064	0.038	0.146	0.138
43	0.003	0.042	0.079	0.138	0.133
44	0.051	0.046	0.031	0.14	0.132
45	LDL	0.035	0.038	0.141	0.133
46	0.005	0.043	0.657	0.184	0.164
Min	0.002	0.03	0.01	0.099	0.012
Max	0.073	0.314	1.910	0.184	0.164
Average	0.008	0.040	0.222	0.088	0.086
Std	0.019	0.055	0.374	0.064	0.062

Where: LDL = Lower than detection limit, Min = Minimum, Max = Maximum, Avg = Average and Std = Standard deviation.

Iron was detected in all measured samples and ranged from 0.002 to 0.574 mg/L and an average value of 0.057 mg/L. Iron is an important element for human beings and animals (Shukla et al. 2018), and is an essential component of hemoglobin (Balarabe et al. 2019). It facilitates the oxidation of carbohydrates, proteins and fats to control body weight, which is an extremely important factor in diabetes; furthermore, an iron deficiency can induce anaemia (Zhang et al. 2018).

Manganese is essential in many biological processes such as, blood sugar regulation and bone growth, as well as being a cellular antioxidant (Pfalzer and Bowman 2017). Manganese was detected in 91.30 % of the samples, within a range of 0.001 to 0.505 mg/L, with an average value of 0.073 mg/L. Cu was detected in 97.82 % of the samples and found to be in the range of 0.001 to 0.175 mg/L, with an average value of 0.014 mg/L. Copper has numerous functions in the human body, and they are essential nutrients that play important roles in the production of hemoglobin for human health; however, an excessive intake of copper has been reported to be toxic (Ahmed et al. 2005).

Chromium is important to make use of glucose as reported by Yagi et al. (2013). Chromium was detected in 67.39 % of the samples, The Cr concentration varied from 0.001 to 0.017 mg/L, with an average value of 0.002 mg/L.

Cadmium was detected in 10.86 % of the 46 samples. Cadmium is an extremely toxic metal found naturally in the soil, but also spread in the environment due to human activity. Over exposure to cadmium can lead to lung, liver, skeletal and renal problems and cancer (Djordjevic et al. 2019).

Zinc was detected in 76.08 % of the samples and the concentrations varied from 0.03 to 0.017 mg/L with an average value of 0.001 mg/L. Zinc has essential function in carbohydrate and cholesterol metabolism (Ahmed et al. 2005). Acute zinc poisoning is a rare event, except in very high doses (Plum et al. 2010).

Nickel was detected in 63.043 % of the samples and the concentrations varied from 0.002 to 0.213 mg/L with an average value of 0.007 mg/L. Trace amounts of nickel may be beneficial as an activator of some enzyme systems, but its toxicity at higher levels is more prominent (Fangkun 2011).

The arsenic content of the samples was detected in 69.56 % of the samples and found to be in the range from 0.012 to 0.505 mg/L with an average value of 0.073 mg/L. Arsenic is a naturally occurring element that can be toxic to humans, animals and plants;

however, its toxicity varies, depending on what form it is (Hare et al. 2019).

Aluminum concentration was analyzed in all samples and ranged from 0.01 to 0.175 mg/L, with an average of 0.014 mg/L. The toxicity of Al to humans is mainly related to neurotoxicity and the development of neurodegenerative diseases (Christopher 2012). Lead was detected in 69.56 % of the samples. Its concentration ranged from 0.099 to 0.574 mg/L with an average of 0.057 mg/L. Lead is a naturally occurring element, and is a common industrial metal that has become widespread. Lead contamination varies and manifests itself in other ways than in green plants (Ahmad et al. 2019). Lead has severe health effects even at relatively low levels in the body, and can cross the placenta and damage developing foetal nervous systems (Khan and Khan 2017). Lead causes both acute and chronic poisoning; it has adverse effects on the kidneys, liver, heart and both the vascular and immune systems (Zhang 2001).

## CONCLUSIONS

The elemental measurement for metallic cookware is very important from the perspective of food safety. The average concentrations of measured Ni, Zn, Al, Pb, As, Cd, Cr, Cu, Fe and Mn released from metallic cookware are comparatively normal. This implies that the metallic cookware under investigation are free of metals contamination and without possibility of metallic poisoning. The outcome of this work highlights the concept of safety for food security by analyzing with the highest quality standards the metallic cookware and, thus, expanding public awareness.

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