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Leaching of Some Essential and Non-Essential Heavy Metals from Modern Glazed Ceramic Crockeries Imported into Qatar from China, India and Spain

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Abstract

In this study, the leaching potential of ceramic crockeries available in Qatar market has been evaluated using inductively coupled plasma mass spectrometry (ICP-MS). Ceramic crockeries decorated with glaze matter containing various essential (Zinc, Iron, and Barium, etc.) and non-essential heavy metals (lead and cadmium) can adulterate the foodstuff and/or can release deadly metals into the food substance. Chines, Indian, and Spanish ceramic crockeries were randomly selected from the products available in the local Qatari market and analyzed to determine the level of leachable essential and non-essential heavy metals. Leaching studies were performed according to the ASTM 738-94 standard test methods for specific metals leaching into 4% acetic acid solutions over 24 hours exposure time. ASTM 738-94 is a precise and standard method and particularly designed for the determination of some heavy metals extracted by acetic acid from the glazed ceramic surface. Results show that all the ceramic crockeries contain both leachable essential and non-essential heavy metals. However, the concentration of these heavy metals is not potentially high to cause any adverse effect on human health.

Keywords: Heavy metals; Ceramic ware; Acetic acid; Lead; Cadmium; ICP-MS; Leaching

Introduction

The design requirements of ceramic crockeries are occasionally mandated for the use of decorative borosilicate enamels. However, these contain some essential and non-essential heavy metals, which may leach out from the crockeries to foodstuff and/or beverages. Moreover, it is quite difficult to eliminate the metals from the pigments used for decoration; a number of metals leached out should not surpass a certain level to avoid health threat. Toxic metals e.g., Lead and Cadmium along with those of barium, zinc, cobalt, and iron, etc. are widely contained in glazing and coloring materials. These are widely used in a variety of products, especially in ceramics, due to various aesthetic attributes. In order to have permissible levels of these metals, decorators, third-party laboratories and other related authorities should follow extremely accurate testing protocols to estimate the minute levels of leaching metals in parts-per-million (ppm). In this connection, national institute of hygiene and the ceramic standard in Poland recommends the limit of Cd and Pb in mg/dm^3 measured by extraction and subsequent atomic absorption spectrometry [1,2]. Furthermore, according to Food and Drug Administration (FDA), the limit for Pb and Cd leachable from ceramic is 7 mg/kg and 0.5 mg/kg, respectively [3]. However, any glazed ceramic crockeries can become poisonous if it is not fired properly. Moreover, intense exposure to the heavy metals prompts sickness, anorexia, spewing, gastrointestinal irregularities and dermatitis problems [4-7]. Heavy metals are risky in light of the fact that they tend to accumulate in the living systems. This bioaccumulation implies an increase in the deposition of a chemical compound in a natural living being, which tend to have potentially failed organs as the time passes on. Basically, heavy metals refer to chemical elements with relatively high densities or with a specific gravity that is at least 5 times higher than the specific gravity of water such as As, Cd, Fe, Pb and Hg [4,8]. Therefore, the elements that are of concern in this study include Pb, Cd, Zn, Fe, Cu, Cr, Mn, and Ba.

Ceramic crockeries are widely used in many countries around the world for foodstuff. The literature survey has suggested that little attempt has been made to determine the leach out of heavy metals from glazed food and drinking products daily used not only in a specific Arab country but all over the world. Moreover, the survey demonstrated that no study has yet been carried out in Qatar to determine the leachability of different heavy metals from ceramic crockeries. Therefore, in this work, the leaching of essential and non-essential heavy metals into 4% acetic acid solution at different temperatures according to ASTM standard method (ASTM 738.81) was studied. This further enabled a simultaneous determination of Pb, Cd, Zn, Fe, Cu, Cr, Mn, and Ba by using inductively coupled plasma mass spectrometry (ICP-MS). The ceramic crockeries collected from local Qatari market were imported from China (C_{china}), Spain (S_{spain}) and India (I_{india}).

Experimental

Fancy ceramic crockeries including bowls, teacups, saucers and dinner plates imported from China, Spain, and India, were collected from local market in Qatar. Samples from each country have been selected randomly and washed with detergent, rinsed with deionized water and conditioned at room temperature. Leachable heavy metals were collected by dipping each sample into 4% acetic acid solution at different temperatures. In a typical procedure, 2 set of samples from each country were dipped into the acid solution. After 24 hours, acid

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solution was decanted, and aliquots were taken for analysis. Heavy metals were analyzed according to FDA by Inductively Coupled Plasma Mass Spectrometry ICP-MS (Perkin Elmer NexION 300D). Figure 1 shows a schematic diagram of the experimental procedure.

Results and Discussion

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique was used for elemental determinations. Inductively Coupled Plasma Mass Spectrometry is a very powerful instrument for the qualitative/qualitative analysis of heavy metals. It is a type of mass spectrometry which is capable of detecting metals at concentrations as low as one part in 10^{15} (part per quadrillion, ppq).

Mainly this technique was commercially introduced in 1983 and has become popular in many types of analytical laboratories due to the higher throughput and detection limits compared to other conventional spectroscopy techniques. In this connection, the detection limits of the ICP-MS, Perkin Elmer NexION 300D, instrument used for multi-elements analysis are given in Table 1.

In recent centuries, the industrial use of Pb has been considerably reduced from paints and ceramic products [9]. Despite the reduction of Pb from the paints and ceramics, human exposure to Pb remains a serious health problem [10]. Lead is the most systemic toxicant that seriously affects the kidneys, liver, central nervous system, hematopoietic system, endocrine system, and reproductive system [10]. Results of the acetic acid leaching analysis at 35°C, 45°C and 65°C are given in Tables 2-4, respectively.

Metals	Pb	Cd	Zn	Fe	Cu	Cr	Mn	Ba
(µg/l)	0.0004	0.01	0.10	0.10	0.009	0.01	0.03	0.002

Table 1: Perkin Elmer NexION 300a (ICP-MS) Minimum detection limit for multi-element analysis for metals of interest in the leaching studies (ppb, µg/l).

Metals *(µg/l)*	C_1	C_2	I_1	I_2	Sp_1	Sp_2
Pb^{206}	17.991	37.034	10.449	15.317	ND	ND
Cd^{111}	ND	ND	ND	ND	ND	ND
Zn^{66}	136.038	236.480	297.092	195.003	122.992	32.064
Fe^{56}	111.185	203.459	120.125	134.003	142.157	87.256
Cu^{63}	28.234	96.753	43.590	67.830	45.683	79.575
Cr^{53}	26.565	10.982	ND	ND	ND	ND
Mn^{55}	ND	18.768	15.477	72.012	ND	20.018
Ba^{137}	30.031	24.979	36.449	15.016	12.324	14.577

Table 2: Metal released into 4% acetic acid leachate solution in ppb (µg/l) from modern DOHA ceramic samples after a contact period of 24 hours at 35°C ND means "Not Detected".

Metals *(µg/l)*	C_1	C_2	I_1	I_2	Sp_1	Sp_2
Pb^{206}	20.324	23.401	12.585	23.657	ND	ND
Cd^{111}	ND	ND	ND	ND	ND	ND
Zn^{66}	443.973	249.452	314.773	184.013	174.968	28.946
Fe^{56}	118.447	302.459	127.042	182.041	174.737	137.609
Cu^{63}	236.253	288.166	341.542	382.211	264.164	202.539
Cr^{53}	124.253	89.563	115.579	67.457	24.188	112.151
Mn^{55}	ND	ND	212.075	314.991	88.186	28.795
Ba^{137}	130.033	238.449	236.141	183.364	293.875	257.994

Table 3: Metal released into 4% acetic acid leachate solution in ppb (µg/l) from modern DOHA ceramic samples after a contact period of 24 hours at 45°C ND means "Not Detected".

As can be seen in Tables 2-4, Pb and Cd are not detected in Spanish imported crockeries at 35°C, 45°C, and 65°C. However, Pb which is one of the most poisonous metals, and was detected in both Chinese and Indian imported crockeries. Moreover, the amount of Pb is at a higher level for the Chinese sample (i.e., C_1 and C_2) compared to the Indian samples (i.e., I_1 and I_2) at 35°C and 45°C. However, the amount is not high enough to cause any adverse effect on human health. Interestingly, Pb was not detected from the Chinese sample (i.e., C_1 and C_2) at 65°C. In general, the higher the temperature, the higher the leaching of lead and other heavy metals as in most cases of diffusion-controlled and ion-exchange processes. However, the results as shown on comparing the general results of Tables 3 and 4, shows that the leaching at a temperature of 65°C was less than that at 45°C. This might be attributed to the formation of complexed compounds of heavy metals oxides and hydrides, which possess a lower solubility and hence not decanted with the aliquot to be analyzed. The work of Norita et al. has shown a similar trend for leaching of lead in 4% acetic acid, at which the leaching of lead has a minimum at temperature over the range of 50-70°C, with a general trend of increased leaching of lead over the range of 30-10°C [11-13].

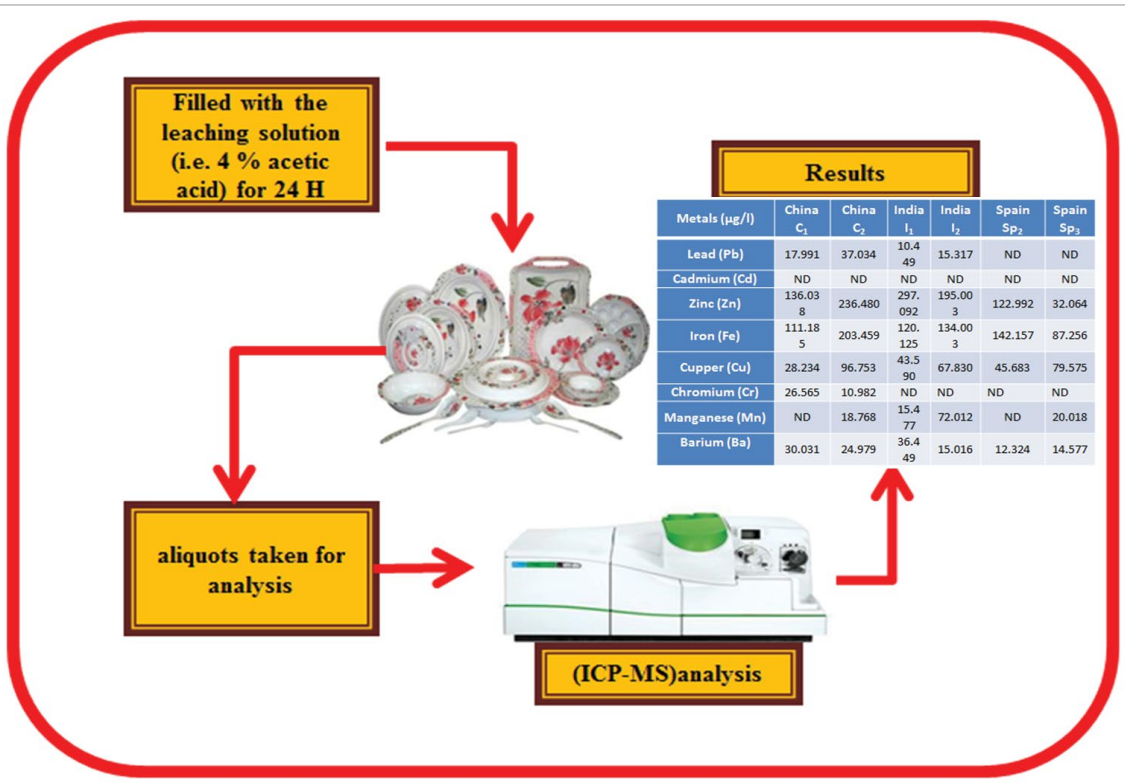
Cd is a heavy metal of considerable ecological and industrial concern. It is extensively available in the earth's crust. Cd is frequently used in the production of alloys, pigments, and ceramics. The possible exposure to Cd is via ingestion of contaminated food and smoking, smoking being a major contributor. Extensive exposure to Cd seriously affects the blood vessels, pulmonary function and chest radiographs that are consistent with emphysema [5,6]. The analysis shows that Cd was no released from all the samples at 35°C, 45°C and 65°C, respectively.

It is noteworthy to mention that some of the heavy metals (i.e., Fe, Cu, and Zn) are essential for living beings [14-16]. These essential heavy metals are an integral part of several enzymes and also participate in redox reactions in living cells. However, all these essential heavy metals are toxic at high concentrations and can be damaging to the organism.

The amounts of essential heavy metals (i.e., Zn, Fe and Cu) are significantly higher compared to the level of Pb leached from all the samples at 35°, 45° and 65°C, respectively. Chromium (Cr) belongs to the transition element with oxidation states ranging from chromium (II) to chromium (VI) [Cr(III)]. Cr is considered an essential nutrient that plays a role in glucose, fat and protein metabolism by potentiating the action of insulin. On the other hand, chromium (VI) is mainly toxic to organism and well-known to cause numerous health effects; especially it can modify genetic materials and cause cancer. The results show that Cr was released only from Chines samples (i.e., C_1 and C_2) in the range of 11~30 *µg/l* at 35°C while significantly high level of Cr was leached from all the samples at 45° and 65°C. On the other hand, Mn was found to be leached slightly even not detected from C_1 and Sp_1 samples

Metals *(µg/l)*	C_1	C_2	I_1	I_2	Sp_1	Sp_2
Pb^{206}	ND	ND	18.140	12.908	ND	ND
Cd^{111}	ND	ND	ND	ND	ND	ND
Zn^{66}	253.268	124.360	172.093	152.070	115.042	43.053
Fe^{56}	98.058	329.294	206.683	164.142	213.020	118.921
Cu^{63}	173.611	207.027	195.892	213.728	194.961	172.367
Cr^{53}	112.736	54.066	89.517	51.972	103.826	192.573
Mn^{55}	ND	ND	179.982	169.035	198.874	28.990
Ba^{137}	63.842	121.743	80.876	115.805	142.033	106.241

Table 4: Metal released into 4% acetic acid leachate solution in ppb (µg/l) from modern DOHA ceramic samples after a contact period of 24 hours at 65°C ND means "Not Detected".



Metals (µg/l)	China C_1	China C_2	India I_1	India I_2	Spain Sp_2	Spain Sp_3
Lead (Pb)	17.991	37.034	10.449	15.317	ND	ND
Cadmium (Cd)	ND	ND	ND	ND	ND	ND
Zinc (Zn)	136.038	236.480	297.092	195.003	122.992	32.064
Iron (Fe)	111.185	203.459	120.125	134.003	142.157	87.256
Cupper (Cu)	28.234	96.753	43.590	67.830	45.683	79.575
Chromium (Cr)	26.565	10.982	ND	ND	ND	ND
Manganese (Mn)	ND	18.768	15.477	72.012	ND	20.018
Barium (Ba)	30.031	24.979	36.449	15.016	12.324	14.577

Figure 1: Schematic diagram of the experimental procedure adopted in this study.

at 35°C. The concentration of Mn leached from Indian and Spanish samples were ranges 100~300 *µg/l* at 45° and 65°C, respectively. In case of Barium, the amount leached in all the samples at 35°C. Moreover, as temperature increased, the amount of Ba leaching increased, with overall range of 10-300 *µg/l*.

Conclusions

From the leaching potential, conducted with various crockeries available in Qatar market, it was fond that all the ceramic crockeries contain both leachable essential and non-essential heavy metals. However, the concentrations of these heavy metals are not potentially high to cause any adverse effect on human health. But it is concluded that the relevant regulatory agencies in the countries should come forward to enact necessary regulations to minimize the exposure of public to toxic heavy metals leaching into the foodstuff from crockeries.

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