Int. J. Electrochem. Sci., 10 **(2015)** 3792 - 3802

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Stainless Steel as a Source of Potential Hazard due to Metal Leaching into Beverages

Ghada Bassioni[1,*], *Ali Korin*[2], *Alaa El-Din Salama*[2]

[1] Chemistry Department, Faculty of Engineering, Ain Shams University, P. O. Box 11517, Cairo, Egypt.
[2] Food Science and Technology Department, Faculty of Agriculture, Al-Azhar University, Cairo, Egypt
[*]E-mail: ghada_bassioni@eng.asu.edu.eg

Received: 26 December 2014 / *Accepted:* 28 February 2015 / *Published:* 23 March 2015

Stainless steel is a widely used material in cookware. Stainless steel is readily attacked by organic acids, particularly at storage time. Hence iron, chromium, and nickel are investigated on their leaching potential from the cookware into food. Toxicological studies reveal that increased doses of metals such as Ni and Cr can cause adverse reaction such as dermatitis. In this study the effect of different pH and various periods of storage times for four types of juices (lemon, orange, mango and strawberry) are examined on the leaching of metals from new stainless steel cookware. One type of stainless steel grade 201 is chosen from the local market. Samples are analyzed by Atomic absorption spectroscopy for Ni, Cr and Fe, Weight loss (WL) and electrochemical polarization measurements as well as environmental scanning electron microscopy (ESEM). Surprisingly, the human intake of Ni, Cr and Fe after 5 days of lemon juice storage is found to be 3.96, 0.48, and 36.57 mg/person, respectively. This metal intake is higher than the permissible limit set by the world health organization WHO. Stainless steel utensils have been considered as an ignored source of nickel, chromium and iron, where the contribution is dependent on stainless steel grade and period stored.

Keywords: stainless steel, cookware, leaching, toxicity

1. INTRODUCTION

Stainless steel is an iron-based alloy containing at least 10.5 % chromium and maximum of 1.2 % carbon. Other alloying elements may be added during melting such as nickel, molybdenum, columbium or titanium that serve to change certain properties. Stainless steel cookware account for 43% of cookware [1, 2].

Actually, most of the stainless steel used in cookware contains around 18% of chromium that give optimum corrosion resistance. In addition to nickel with a percentage of around 8-10%, both Cr and Ni enhance the corrosion resistance, and durability [3].

The world health organization (WHO) reported in 1989 that Provisional Tolerance Weekly Intake (PTWI) is 1.0 and 45 mg/kg bw/week for Ni and Fe, respectively. For Cr WHO (1993) has set a maximum of 0.05 mg/l in drinking water

However, food standard regulation and tables of food composition are of limited assistance to the toxicologist investigating dietary intake of metals by individuals. So that during the cooking and the storage of food in metallic cookware significant quantities of toxic elements may leach out and increase the uptake of metal above the admissible daily intake (ADI) values even in well regulated and hygienic household [4].

The release of appreciable quantities of metals such as Cr, Ni and Fe and consequent excessive intake of these metals cause health hazards. It has been reported that chromium and nickel are released from stainless steel pans, bowls and tumblers using 0.1 N acetic acid, tartaric acid, lactic acid and some Indian juices and boiling for different periods of time and stored for 10 min to 1 hour. The results were 60-130, 20-70 μg/L for chromium and nickel, respectively in acid solution and 170-560, 120-200 μg/L for chromium and nickel, respectively in Indian juice [5].

In the study of Bost et al. in alkaline solution (5% of sodium carbonate) of a pH of 11.50 the concentration of chromium, nickel and iron are found to be 5-12, 5-310 and 5-310 μ/L, respectively. [6].

At low pH for stainless steel pans (19% Cr and 9% Ni) containing apricot, lemon, rhubarb, marmalade, metal leaching is found to be negligible. [7].

In this study, leaching of Cr, Ni and Fe from stainless steel cookware in some fruit juice is evaluated during storage at different periods of time. The fruit juices are prepared using typical household recipes. The results obtained from this study will be of great benefit to the consumer and regulatory agencies for laying down consumer protection standards to those types of juice that are stored in stainless steel. This study focuses on selected juices (lemon, orange, mango and strawberry) since they are assumed to be aggressive to stainless steel due to their low pH that ranges from 2.8 to 4.35.

Chromium is an essential nutrient to stimulate protein, carbohydrate, and lipids metabolism and is known for its protective action towards diabetes and arteriosclerosis in humans [8].Chromium (III) in oxidation state is known to be less harmful but Cr (VI) entangled in digestive system causes cancers, especially increased risk lung cancer [9]; its LD_{50} for rats is 20 - 50 mg of Cr (VI) 185 - 615 per kg of body weight, respectively [10].

Nickel a is metal frequently responsible of allergic skin reactions and has been reported to be the most common cause of allergic contact dermatitis. The general population (approximately 8 - 10% of women and 1.2% of men) demonstrate a sensitivity to nickel. Many studies have also demonstrated skin effects in sensitive human results from ingested nickel. Several studies have shown that oral exposure may be worsening of eczema in nickel sensitive individuals. Nickel compound have been well established as carcinogenic in animal species and many modes of human exposure but the mechanism is still not fully understood. Not all nickel compounds are equally carcinogenic, so the carcinogenic potency is directly related to their ability to enter cells [11].

Iron is essential to life and health but toxic in excess causing organ damage [12]. A study estimates iron increase in daily iron intake using iron pots to be 14.5 and 7.4 mg for adults and child, respectively. [13]. The impact factor of the various food components on the amount of iron leached from iron pots during cooking is largely unknown, except for an effect of pH and moisture content of the raw food [14].

This study aims to access the factors affecting the leaching of Cr, Ni and Fe from stainless steel cookware during storage of different fruit juice.

Lemon juice (citrus limon L.) is also a rich source of nutrients, including flavonoids, citric acid, minerals (e.g. potassium) and ascorbic acid (vitamin C) which provide numerous health promoting characteristics. Lemon juice has particularly high concentration of citric acid, which can constitute as much 8% of dry weight of these fruits (about 97 g/L in the juice) [15].

Mango fruit is one of the nutritionally rich fruits with unique flavor, fragrance and taste that promotes health benefits to humans because it is a rich source of carotenoids and provides high contents of ascorbic acid and phenolic compounds [16]

Orange juice provides a variety of vitamin and minerals. It is healthy and naturally sweet with any sugar. A cup serving of raw fresh orange juice, amounting to 248 g has 124 mg of vitamin C (> 100% RDI) and has 20.8 g sugar. It also supplies potassium, thiamin and folate [17].

Strawberries are a common and important fruit in the Mediterranean diet because of their high content of essential nutrients and beneficial phytochemicals, which seem to have relevant biological activity in human health. Among these phytochemicals, anthocyanin and ellagitannins are the major antioxidant compounds [18].

2. EXPERIMENTAL

2.1. Materials

2.1.1. Cookware and lacquer

Stainless steel cookware is purchased from the local market, Egyptian origin. The bulk composition of the stainless steel is given in table 1 [19]. The utensils are cut into square shaped coupons of dimensions (5.0×5.0×0.3) cm. The utensils two surfaces are treated as a matt interior surface of roughness of 430-450 πm (measured with a surface roughness tester model TR 100, China) and a glossy external one. The glossy surface is covered with a commercial lacquer that is used in covering the metal packages food contact according to Herting [9].

Table 1. Chemical composition of stainless steel grade 201 (WT %).

C	Cr	Ni	S	P	Si	Mn	N	Fe
0.15 max	16.0-18.	3.50-5.5	0.03 max	0.060 max	1.00 max	6.50-7.5	0.25 max	Balance

AISI and ACI standard composition ranges for wrought and cast chromium – nickel stainless steel American Iron and Steel Institute.

2.1.2 Preparation of test solution (Fruit juice)

Mango, strawberry, lemon and orange juices are prepared from fruit, deionized water and sugar:

Lemon juice: 20 ml. lemon + 300 ml. deionized water + 60 gm sugar (pH 2.63)
Orange juice: 300 ml orange (pH 3.60)
Mango juice: 104.26 gm mango + 200 ml. deionized water + 60 gm sugar (pH 4.43)
Strawberry juice: 110gm strawberry + 200 ml. deionized water + 60 gm sugar (pH 3.64)

The coupons are immersed for different storage periods at refrigerator temperature for 1 - 5 days.

2.2. Methods

2.2.1 (Weight loss)

The stainless steel coupons are cleaned by water, dried and weight using a four digits balance, and reweight again after the test. Juice solutions have been stored at various periods of 1 - 5 days .The pH of the juice is also measured before the experiment. The reading is recorded to the nearest 0.001 mg on an electronic weighing balance. Corrosion rate in mm year^{-1} is calculated using the following equation:

$$\text{Corrosion Rate} = \frac{87.6\,W}{D.A.T}\ \text{mm/Y}$$

where, W= weight loss in mg,
A = Total surface area of sample in cm^2
T = Exposure time in hours, in various media.
D = density of stainless steel in g/cm^3 (7.81 g/cm^3)

2.2.2 Atomic Absorption Spectroscopy

The total metal concentration of leaching from stainless steel is analyzed by Atomic Absorption Spectroscopy (AAnalyst 400). This instrument is used to analyze concentrations of chromium, nickel, iron and manganese using graphite furnace with a detection limit of 0.19, 3.6, and 0.18 pg for chromium, nickel, and iron, respectively. The relative analytical error is 2%. Quality control tests are performed throughout the experiment by analyzing samples with a known concentration at regular intervals. After preparation, the samples are subjected to dry digestion in pre-heated porcelain crucibles and later in a muffle furnace at 500 °C – 550 °C between 3 - 4 hours. This is followed by cooling in a desiccator and subsequently digested with 5 ml of 5 M HNO_3 prepared solution to dissolve the ash. The dissolved ash solutions are steam heated to remove any adhered metal, cooled and individually filtered through a Whatmann filter paper into a 25 ml standard flask and made up to the mark with distilled water. The extracts are transferred quantitatively into pre-heated plastic sample bottles, tightly closed and kept in a refrigerator at a temperature around 4 °C before analyses are done. The maximum absorbance is obtained by adjusting the cathode lamps at specific slit widths and definite wavelengths as follows: 4.25.4, 372.0 and 341.5 nm for chromium, iron and nickel, respectively and at a slit setting of 0.2 nm.

2.2.3 Surface analysis

Environmental Scanning Electron Microscopy (ESEM) and-Energy Dispersive X-Ray Analysis (EDAX) measurements examined the surface morphology of the stainless steel samples before and after immersion in fruit juices. This test gives an indication about leaching of the metals compared to the initial condition.

2.2.4 Electrochemical (polarization) measurements

Measurements were obtained using a IVIUMSTAT potentiostat-galvanostat operated under computer control combined with easy corrosion program (IVIUMSTAT soft). All potentials were measured against SCE. The Potentiodynamic current-potential curves are recorded by changing the electrode potential automatically with a scan rate of 2 mVs^{-1} from a low potential of -800 to -300 mV (SCE). Before each run, the working electrode is immersed in the test solution for 30 min to reach steady state. Before the measurements, the working electrode is degreased with acetone and rinsed with distilled water. The stainless steel cookware is cut into circular disks of 1.4 cm diameter and an exposed area of 1 cm^2. The stainless steel coupon (as the working electrode) is fitted into a thermo stated sample holder cell. The reference electrode is SCE and the auxiliary electrode is Platinum. All electrochemical experiments are performed in aerated solutions at 25°C. After performing open circuit potential for 1 h, polarization measurements are done to obtain corrosion current density from Tafel method.

3. RESULTS AND DISCUSSION

Some assumptions are made: Assuming a family of three persons using a stainless steel utensil of medium size with a diameter of 10 cm and height of 14 cm, the internal area of the stainless steel utensil exposed to leaching is about 520 cm^2. The metals intake per person is equivalent to: $\frac{concentrate\ of\ metals}{Area\ of\ sample}$ x Internal Area / Number of personnel [20, 21].

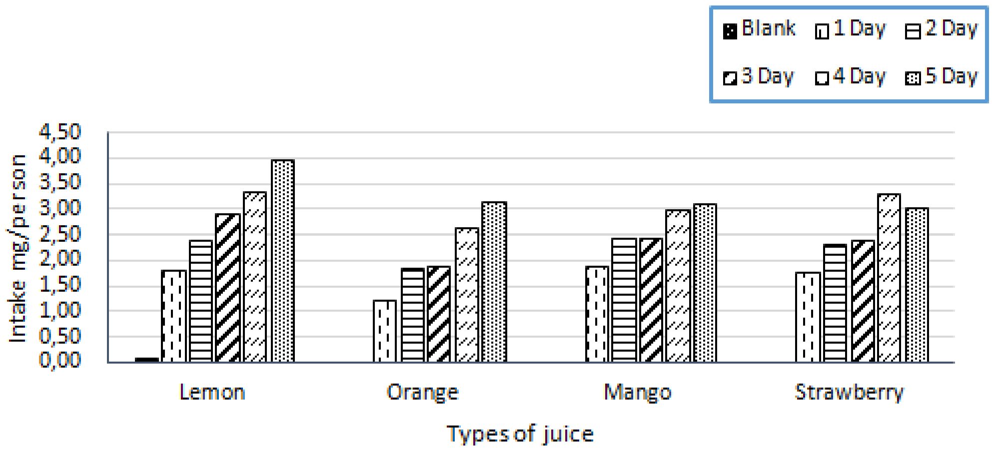

Figure 1. Comparison of Nickel intake in mg/ person from stainless steel samples in different juices during various storage periods.

Figure (1) shows the nickel intake in mg/person for different types of juices at different storage time. In case of lemon, orange, mango and strawberry juices it is found that there is a liner increase in Ni leaching from the first day to the fifth day for all samples compared to the blank sample.

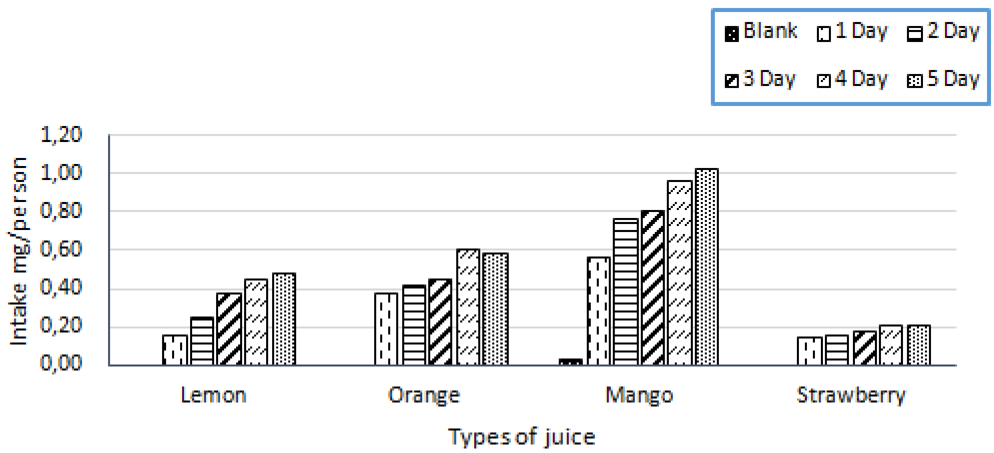

Figure 2. Comparison of Chromium intake in mg/ person from stainless steel samples in different juices during various storage periods.

In the first day, the intake of nickel in presence of lemon juice is found to be 1.817 mg/person and increased until it reaches 3.96 mg/person on the fifth day as the highest value that is attributed to the pH value of 2.63. As for the orange juice the percentage intake is 66.58, 96.87, 72.06 and 84.13% for the second day, the third, fourth and fifth day, respectively. In the case of the mango juice the nickel intake is 1.885 mg/person on day 1 that increases by 77.05% on the second day following an increase until it reaches 96.14% on the fifth day.

For the strawberry juice the intake value increases to 1.7, 2.252, 2.353, 3.235 and 3.01 mg/ kg for first, second, third, fourth and fifth day, respectively.

Figure (2) shows the chromium intake in mg/ person for different types of juices at different storage time. In case of lemon juice, an increase of chromium intake is seen starting from 0.0070 mg/person in the blank sample that increases to 0.481 mg/person on the fifth day. The percentage of chromium intake increased from 60.75% on the second day to reach 93.34% on day 5. For orange juice, the intake of chromium in the blank sample is 0.0193 mg/person and increases on the fifth day to 5.922 mg/person.

Figure 3. Comparison of Iron intake in mg/ person from stainless steel samples in different juices during various storage periods.

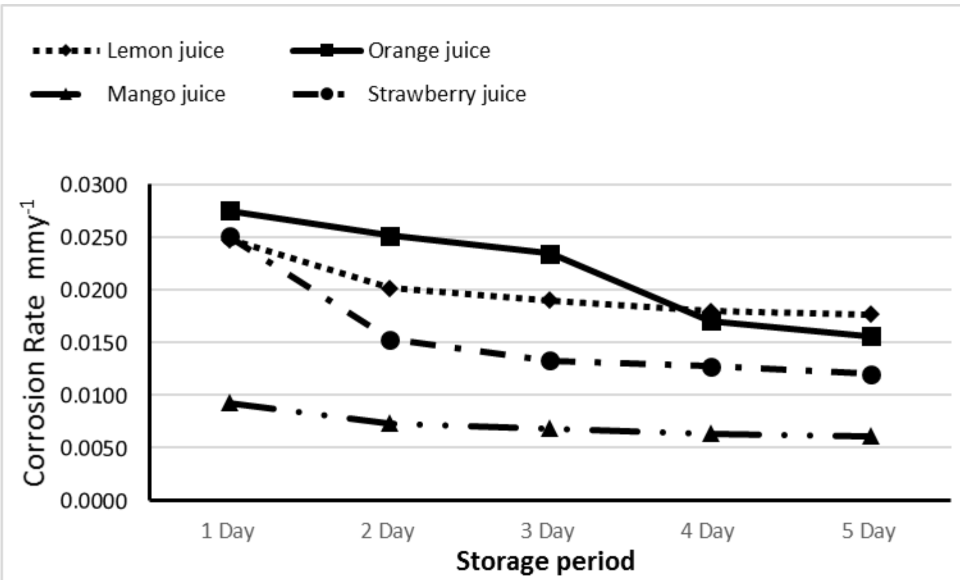

Figure 4. Corrosion rate of the stainless steel cookware samples in different juices for various storage periods.

The highest percentage of chromium leaching and consequently reflected in human intake is in mango juice which increases the content of the element chromium naturally found in mango of 0.03 mg/L. The chromium leaching in strawberry juice is less than in the rest of the juices where the intake in the blank sample is 0.0056 mg/ person and becomes on the fifth day to 0.213 mg/person. Figure (3) shows the iron intake in mg/person in different types of juices under investigation at various storage periods. The quantity of iron leaching is found to be higher than for chromium and nickel. Iron intake in mg/ person is found to be 36.57 in lemon juice after 5 days storage time as compared to 0.785 in the blank sample. As for the orange juice increased intake of iron is found with a 70.08% increase in the second day and further increases by 86.71, 92.57, 101.4 % for the third, fourth, and fifth day, respectively. Therefore, leaching of iron in the mango and strawberry juices is of 23.24 fold and 26.07 fold, respectively.

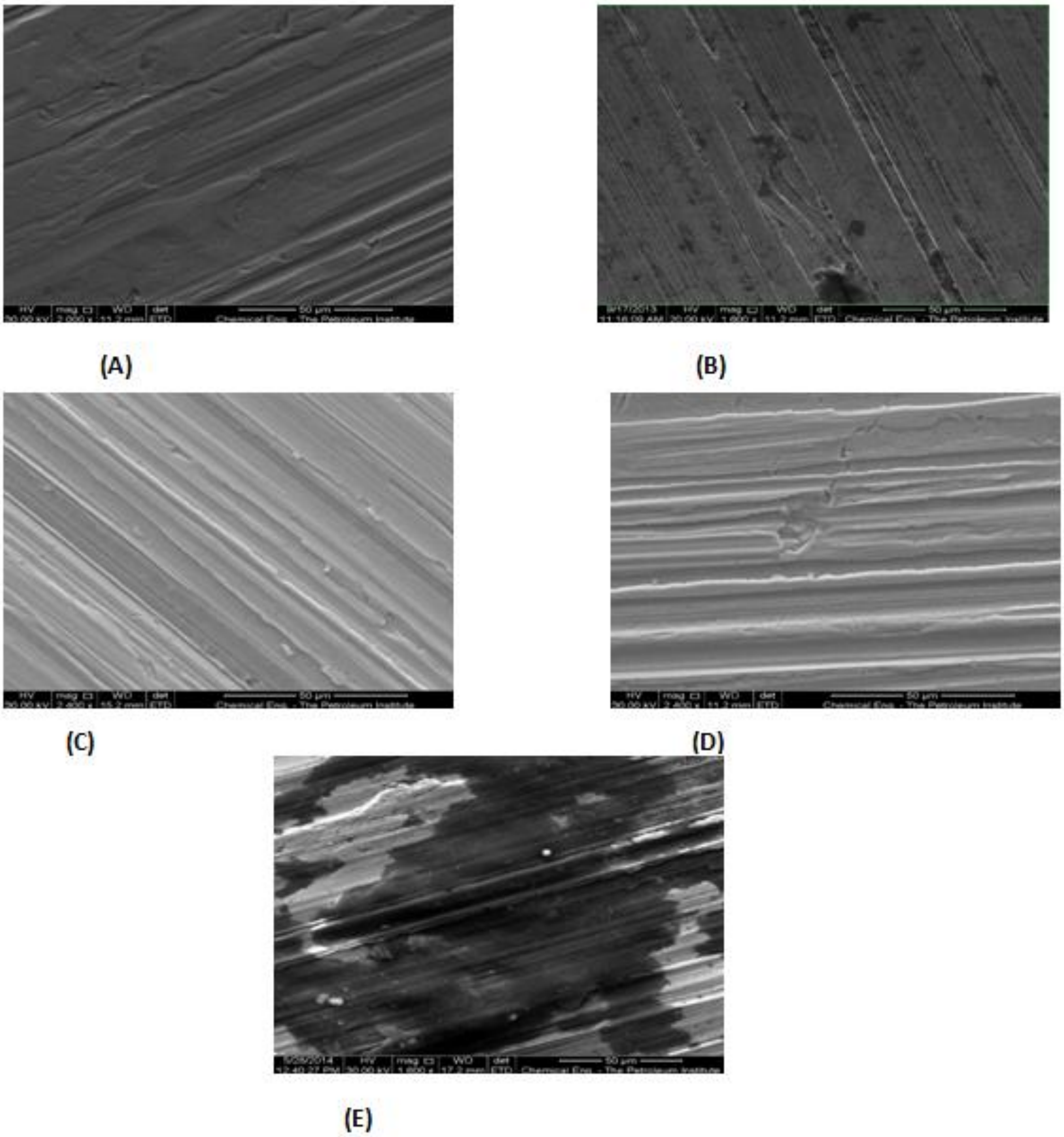

Figure 5. (A) ESEM images of stainless steel grade 201 without treatment (blank), B-E ESEM images of stainless steel sample after 5 days of exposure to juices at refrigerator temperature (B) lemon juice, (C) orange juice, (D) Mango juice, (E) strawberry juice.

Figure (4) shows the variation of corrosion rate in stainless steel cookware in different juices for various storage periods. It shows a relatively low corrosion rate in mango juice; the corrosion rate is on the first day 0.0093 mm/y and decreases gradually until it reaches 0.0061 mm/ y. While in orange and lemon juices the corrosion rate is on the first day 0.0275 and 0.0248 mm/ y, respectively, the corrosion in the orange and lemon medium is very substantial because citric acid (80 and 90% of the total acids) is recognized as an oxidizing agent. An autocatalytic mechanism has generally been proposed to explain the high rates of corrosion in acids with primary displacement of H^+ ions from solution; followed by acid reduction rather than hydrogen evolution as acid reduction leads to a manifest decrease in free energy. [22]

Figure (5) shows environmental scanning electron micrographs of stainless steel grade 201 with and without treatment. Figure (5A) is the blank sample without treatment, while Figure (5B) shows the stainless steel coupon that has been immersed in lemon juice for 5 days. Pitting corrosion is observed on some parts. Figure (5C) shows the stainless steel coupon after immersion in orange juice for 5 days. The figure shows that the damage caused is nearly homogenous throughout the sample. Leaching of the metal after 5 days exposure to Mango juice is reflected in Figure (5D). Significant damage is observed on the metal's surface indicating pitting corrosion. The effect of strawberry juice on metal leaching can be clearly seen in Figure (5E). In Figure (6) the polarization curves are represented. The purpose for using this method is to detect any small changes in stainless steel leaching. However, it does not reflect the natural tendency of stainless steel dissolution as the weight loss method. The electrochemical parameters of stainless steel in fruit juices solution are listed in Table (2). It is shown that values of current density (I_{corr}) are in general less than 0.60 μA/cm^2.

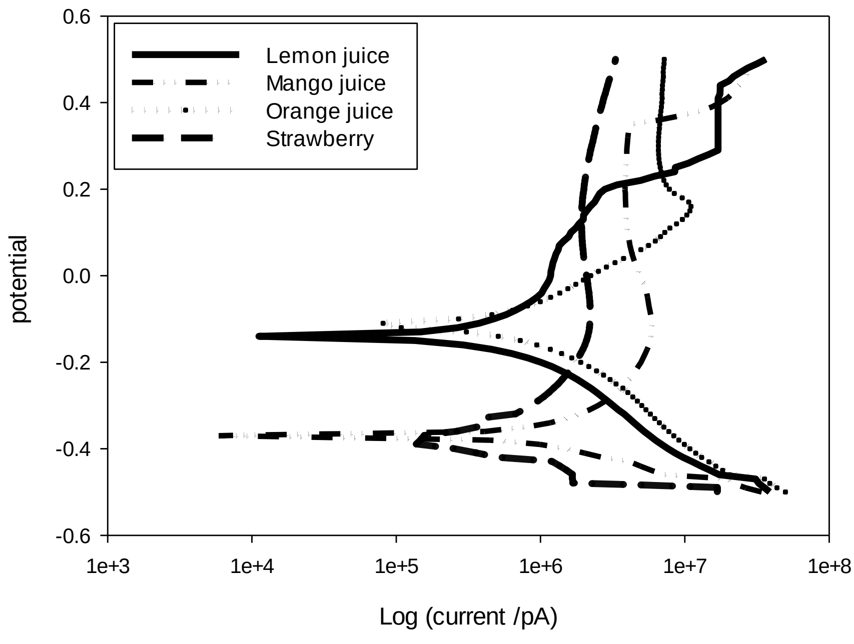

Figure 6. Polarization curves of the stainless steel sheets grade 201 in different fruit juices.

All experiments are performed in freshly prepared fruit aerated solutions at 25°C. After running open circuit potential measurements for an hour to attain equilibrium (not shown), Tafel plots are obtained (Figure 6). From Tafel results the order of corrosion rate from stainless steel alloy in fruit juices appeared to be: Mango < Strawberry < Lemon < Orange which lies in perfect agreement to the results obtained for the corrosion rates in Figure (4).

Table 2. Electrochemical parameters for stainless steel dissolution in different media from fruit juices.

Fruit juices	$-E_{corr}$ (mV)	$I_{corr.}$ ($\mu A\ cm^{-2}$)	β_a $V.dec^{-1}$	$-\beta_c$ $V.dec^{-1}$	Corrosion Rate (mmy^{-1})
Mango	356.1	0.2312	2.054	0.068	0.0017
Strawberry	123.4	0.4271	1.484	0.303	0.0320
Lemon	154.6	0.4528	0.246	0.259	0.0034
Orange	147.5	0.5912	16.03	0.044	0.0044

4. CONCLUSION

The results of the present work clearly indicate that stainless steel utensils in stored juice (lemon, orange, mango and strawberry) contribute significantly to the total daily intake of nickel, chromium and iron increasing the concentration of metals. The amount of Cr, Ni and Fe leaching from stainless steel cookware into food depends on the pH and exposure time. Increasing the storage period enhances the leaching of metals in all the fruit juices under investigation. The obtained results necessitate increased societal awareness towards the use of stainless steel with highly corrosive juices and accompanied possible health hazards.

ACKNOWLEDGEMENT
In memory of Prof. Dr. Hassan Abdeldayem, the authors wish to thank him for his support and extended care throughout his life and as a co-supervisor in the beginning of his work. A special thanks to Ms. Sabana Khadar for conducting the ESEM measurements at The Center for Applied and Environmental Chemistry at The Petroleum Institute in Abu Dhabi, UAE.

References

1. I. M, Bernstein, Handbook of stainless steels, New York, NY: McGraw-Hill, 1977
2. T. Santonen, H. Stockmann-Juvala, A. Zitting, Finnish Institute of Occupational Health, Helsinki, Finland (2010).
3. Technical document guidelines on metals and alloys used as food contact materials.2002, Council of Europe retrieved on Mar. 13, 2002 from: http://www.coe.int/t/e/social_cohesion/soc-sp/public_health/food_contact_e.html.
4. a) F. S. Mohammad, E. A. H. Al Zubaidy, G. Bassioni, , *Int. J. Electrochem. Sci.*, 6 (2011) 222; b) G. Bassioni, F. S. Mohammad, E. A. H. Al Zubaidy, I. Kobrsi, *Int. J. Electrochem. Sci.*, 7 (2012)

4498; c) F. S. Mohammad, E. A. H. Al Zubaidy, G. Bassioni, *Int. J. Electrochem. Sci*. 9 (2014) 3118.
5. P. Agarwala, S. Srivastavaa, M.M. Srivastava, S. Prakasha, M. Ramanamurthyb, R. Shrivastav, S. Dassa, *The Science of the Total Environment* 199 (1997) 271
6. M. Accominotti, M. Bost, P. Haudrechy, B. Mantout, P. J. Cunat, F. Comet, C. Mouterde, F. Plantard, P. Chambon, J. J. Vallon, *Contact Dermatitis*,38(1998)305
7. G. N. Flint, S. Packirisamy *Contact Dermatitis* 32(1995) 218
8. Expert Group on Vitamins and Minerals. Safe upper levels for vitamins and minerals. Great Britain: Food Standards Agency; 2003.
9. G. Herting, I. Odnevall Wallinder, C. Leygraf, Journal of Food Engineering, 87(2008), 291
10. R. Cornelis, J. Duffus, P. Hoet, Elemental speciation in human health risk assessment, Environmental health criteria, 234(2006)
11. M.Cempel, G. Nikel, *J. Environmental Studies*, 15(2006) 375.
12. V. Herbert, *Journal of the American Dietetic Association*,92.12(1992) 1502.
13. D. Y. Liu, Z. G. Chen, H. Q. Lei, M. Q. Lu, R. Li, L. X. Li, *Biomedical and environmental sciences*, 3(1990) 276.
14. H.C Brittin, C. E. Nossaman, *Journal of the American Dietetic Association*, 86(1986) 897
15. Lorente, S. Vegara, N. Martí, A. Ibarz, L. Coll, J. Hernández, M. Valero, D Saura, *Food chemistry*, 162(2014) 186.
16. Physico-chemical and antioxidant properties of four mango (Mangifera indica L.) cultivars in China, Feng-Xia Liu, Shu-Fang Fu, Xiu-Fang Bi, Fang Chen, Xiao-Jun Liao, Xiao-Song Hu, Ji-Hong Wu, *Food Chemistry* 138 (2013) 396–405.
17. N. Sinha, J. Sidhu, J. Barta, J. Wu, M. P. Cano, Handbook of fruits and fruit processing. John Wiley & Sons (2012).
18. F. Giampieri, S. Tulipani, J. M. Alvarez-Suarez, J. L Quiles, B. Mezzetti, M. Battino, *Nutrition* 28 (2012) 9.
19. Steel products manual: stainless steel. Iron and steel society, H. M. Cobb (Editor), Warrendale, PA, USA 1999
20. E. A. Al Zubaidy, F.S. Mohammad, G. Bassioni, *Int. J. Electrochem. Sci*., 6 (2011) 6424.
21. F. S. Mohammad, E. A. Al Zubaidy, G. F. Yacoub, G. Bassioni, *Int. J. Electrochem. Sci*, 7(2012) 363.
22. G. O. Avwiri., *Journal of Corrosion Science and Technology*, 1(2004) 58.