Int. J. Electrochem. Sci., 7 **(2012)** 7283 - 7294

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Estimating Aluminum Leaching from Aluminum Cookware in Different Vegetable Extracts

Layla A. Al Juhaiman

Chemistry Department, Faculty of science, King Saud University, Saudi Arabia, P.O. Box 25628, Code11476, Riyadh, Saudi Arabia
[*]E-mail: ljuhiman@ksu.edu.sa

Received: 5 July 2012 / *Accepted:* 19 July 2012 / *Published:* 1 August 2012

Aluminum leaching from Al cookware in different vegetable extract solutions is studied. Four kinds of Al cookware from different countries were chosen from the local market: China(C), India(I), Saudi Arabia(S) and Syria(Y). The determination of alloying elements was carried out by ICP-MS (Inductively coupled plasma using Mass Spectrometer). Extracts of six vegetables were prepared (tomato, onion, potato, green been, carrots and zucchini) to make 10-50% (w/v) concentrations. Gravimetric method and Atomic absorption method were used. The surface study was done using SEM. It was found that Al leaching from Al cookware into vegetable extract solutions depends upon Al composition, kind of vegetable extracts, water quality, table salt (NaCl), temperature, and immersion time. The estimated Al intake in 30% vegetable extract ranged from 4.56-5.85 mg/hr for potato extract to the highest value of 7.44-16.44 mg/hr for tomato extract. Comparing the present results with the Provisional Tolerable Weekly Intake of Al approved by the FDA/WHO of 1mg/kg body weight per week showed that Al leaching from Al cook wares in some vegetable extracts may add large doses of Al into the diet. Thus monitoring of Al intake for the elderly, children, and those with renal problems is recommended.

Keywords: Al leaching; vegetable extract; Gravimetric method; Atomic absorption

1. INTRODUCTION

Aluminum (Al) is widely used in the industry; it is commonly used in transport, household utensils and packaging materials. Sources of Al entering human body are food, water, beverages, cosmetics, medicines, food additives and leaching from Al cook wares. Aluminum was associated with serious diseases, bone disorders (ostemalaicia) and neurological failures [1-4]. Al was considered inert until reports of its toxicity to humans were proven. It was regarded a neurotoxin agent since 1980 [5]. Thus public interest of the effects of Al on human health had increased in recent years. The Joint

Committee on Food Additives established in 2007 a Provisional Tolerable Weekly Intake (PTWI) for Al of 1 mg/kg body weight per week for an adult; this value applies to all aluminum compounds in food, including additives [6]. Moreover the daily intake of Al may increase by the inappropriate choices of food, method of preparation and medicines [7]. Al may leach into the diet through the use of Al cook wares and Al foils used in cooking or packing. Many studies have been conducted on Al leaching into food or drinks and the quantitative risk assessment of Al [8-14]. In these studies, the extent of Al leaching was strongly related to several factors such as pH of the food or drink, cooking medium, composition of food, duration of contact/cooking and presence of fluoride. However, there is not an agreement about the safety of Al leaching from Al cook wares.

It is well known that Al exhibits a passive behavior in aqueous solutions due to the protective compact Al_2O_3 film on its surface. However the solubility of this protective film increases in acidic and alkaline medium.

Al cook wares and Al foil are used in cooking in different countries including Saudi Arabia despite its association with serious health problems. The first part of this study was about Al leaching in aqueous solutions of meat extract and milk [15].

The aim of this work is to study Al leaching of four kinds of Al cook wares in aqueous solutions containing six different vegetable extracts (carrots, onion, green been, potato, tomato and zucchini). The amount of Al leaching into food due to the effect of vegetable constituents and the important factors which influence Al dissolution will be investigated in the present study.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

1. Four kinds of Al cook wares were chosen from the local market from four different countries: China (C), India (I), Saudi Arabia(S) and Syria(Y). The four different Al cook wares were cut into rectangular specimens of dimensions 2 x 2.5 cm and 2 mm thickness. The average exposed area was 11.80 $cm^2 \pm 0.20$.
2. The analytical determination of elements was carried out by ICP-MS (Inductively coupled plasma using Mass Spectrometer) from Perkin Elmer Sciex Instruments ,Canada, ELAN 9000. The operating conditions are: RF power=1250W; Neubulizer gas flow 0.92 L/min.; Pulse Stage Voltage=1050V; Dwell time=40 ms. The number of replicate was 3.
3. The percentage of the alloying elements of the Al alloys is shown in Table 1.
4. All experiments were made in a clean lab where the amount of dust was kept to a minimum.
5. Six kinds of vegetables (carrot, onion, green been, potato, tomato and zucchini) were washed and cut into small pieces. Potato and onion only were peeled. Five hundred grams of each kind were weighed in a sensitive balance (0.0001g, Metler Toledo). Then each kind was boiled separately in a beaker with 500 mL distilled water at 90ºC for 1 hour to get the vegetable extract (VE). Each VE

solution was filtered into a 1L volumetric flask to obtain the stock solution of 50% w/v which was used immediately but kept in the fridge before use.

Table 1. Percentage of Aluminum alloying elements

Alloy	China	India	Saudi	Syria
%Al / %Elements	**97.902**	98.335	**98.583**	**98.348**
Cr	**0.030**	**0.021**	**0.041**	**0.061**
Cu	**0.069**	**0.352**	**0.380**	**0.147**
Fe	**0.522**	**0.206**	**0.103**	**0.223**
Ga	**0.018**	**0.014**	**0.012**	**0.013**
Mn	**0.351**	**0.080**	**0.190**	0. 230
Mo	**0.272**	**0.109**	**0.123**	**0.112**
Mg	**0.162**	**0.322**	**0.171**	**0.320**
Sn	**0.401**	**0.213**	**0.122**	**0.260**
Pb	**0.030**	**0.051**	**0.070**	0.015
Si	**0.062**	**0.099**	**0.097**	0.182
Se	**---**	**0.018**	**0.070**	**---**
Ti	**0.050**	**0.040**	**---**	**0.012**
Zn	**0.131**	**0.140**	**0.038**	**0.077**

2.2 Gravimetric method (Weight Loss)

In the present work weight loss method (WL) at 90ºC was used to study Al leaching due to VE solutions. The mean of two to three replicate experiments was reported. The proposed method to determine Al leaching from Al cookware is described elsewhere [15]. An experiment using the pieces of carrot and the VE of carrot showed no difference in terms of Al leaching. Thus the VE was used instead of the whole vegetable. The Al leaching was calculated from Corrosion rate (CR) using the following equation:

$$CR = \frac{\Delta W}{A * t} \qquad (1)$$

Where Δw is the weight loss of Al alloy calculated from subtracting the sample original weight minus the sample weight after immersion (mg); A is the surface area of Al sample (cm^2) and t is the immersion time (hour).

2.3 Atomic Absorption Method (AA)

The concentration of Al in distilled water used to prepare the test solutions was below the detection limit of AA (1ppb). Thus the Al concentration detected was mainly from Al leaching from the Al alloys due to VE. The remaining VE solutions after WL experiments were analyzed to determine the amount of dissolved Al^{+3} using AA method (Shimadzu 6701F). One mL of the remaining VE solutions was diluted to 10 mL by standard KCl solution. The calibration curve was prepared using standard Al solution in the concentration range 5-25 ppm. All standard Al solutions were diluted with KCl solution. The mean of two to three experiments were reported.

2.4 Surface study

The surface morphology of Al samples was studied using Scanning Electron Microscope (SEM) from (Joel-JSM-6380).

3. RESULTS AND DISCUSSION

3.1. Gravimetric Measurements

Corrosion rate of Al in 10-50% VE solutions is listed in Table 2. It is shown from this table that the amount of Al leaching generally increased with increasing concentration of the VE solutions. For each VE there is a difference in CR among the four Al alloys with alloy I having the highest leaching and alloy S having the lowest leaching which clearly reflects the effect of alloying elements. Some alloying elements may impair leaching rather than induce it as seen for alloy S where it leached less than the other alloys. The chemical analysis using ICP-MS showed that the percentage of Al ranges from 98.583- 97.902% with different alloying elements as shown from Table 1.

It is clear from Table 2 that there is a difference in Al leaching depending upon the composition of VE solutions. For example the order of Al leaching in 30 % VE solutions is:

Tomato > zucchini > onion > green beans > carrot > potato

It was established that cooking of acidic foods in Al utensils causes high leaching of Al into food [9, 16, 17]. It is known that tomato contains a high percentage of citric acid which explains the low pH of tomato extract (pH 4.5). From a previous study it was found that for 0.10 M citric acid the amount of Al leaching increased twice when the pH was changed from 6.5 to 4.5 [18]. The pH of the present study was almost neutral for the rest of VE solutions (pH 5.4-6.5), thus it is expected that Al leaching in vegetable will be increased when the pH becomes low as in real cooking. The present finding is in agreement with Ščančar et al.[19] that cooking some vegetables as sauerkraut (low pH) in Al cookware leach more Al into the solution where the concentration of Al reached 313 mg /kg. However it was difficult to compare the Al leaching of each vegetable type of the present study with the excellent study done by Ščančar et al. [19] because of the difference in methodology. Some of the vegetables were peeled in the present study and only the extract was used which exclude all non soluble Al compounds in the organic matter whereas in Ščančar et al study the vegetable samples were subjected to microwave digestion with HNO_3 to dissolve all Al compounds [19].

From this study VE solutions leach more Al than lamb or chicken [15]. This proves that the composition of food determine the amount of Al leaching which is in agreement with Takeda et al. who found that Al migration from Al foils depend on type of solvent, pH and temperature [20].

Table 2. Mean CR of Al from WL after immersion for 1 hour at 90°C in different concentrations of VE solutions

VE	alloy	Mean CR*10^2 (mg/cm^2.hr)±Sd		
		10% w/v	30% w/v	50% w/v
Carrot	China	1.80±0.24	2.72±0.12	3.26±0.23
	India	2.33±0.22	3.47±0.29	7.65±0.28
	Saudi	1.06±0.19	1.53±0.13	2.07±0.15
	Syria	1.04±0.10	1.87±0.15	3.00±0.23
Onion	China	1.70±0.17	2.17±0.23	2.87±0.14
	India	3.87±0.18	4.65±0.27	5.83±0.23
	Saudi	1.17±0.21	1.83±0.17	2.35±0.17
	Syria	1.41±0.16	2.37±0.14	2.92±0.18
G. Beans	China	1.78±0.12	2.04±0.18	2.43±0.10
	India	4.29±0.14	4.56±0.29	5.29±0.25
	Saudi	1.27±0.25	2.42±0.18	3.68±0.22
	Syria	1.10±0.13	1.71±0.14	2.46±0.19
Tomato	China	3.89±0.37	4.08±0.21	5.18±0.26
	India	3.12±0.18	5.48±0.24	8.28±0.34
	Saudi	1.70±0.13	2.48±0.16	3.23±0.14
	Syria	2.55±0.24	3.10±0. 23	3.60±0.25
Potato	China	1.07±0.11	1.52±0.16	2.32±0.21
	India	1.29±0.15	1.82±0.14	4.15±0.28
	Saudi	1.50±0.13	1.65±0.13	2.92±0.20
	Syria	1.48±0.12	1.95±0.21	1.99±0.16
Zucchini	China	1.67±0.15	2.36±0.22	2.63±0.18
	India	2.93±0.16	5.26±0.29	6.08±0.27
	Saudi	1.23±0.12	1.95±0.11	1.43±0.12
	Syria	1.12±0.13	1.74±0.15	2.10±0.17

3.2. Atomic absorption

Analysis of dissolved Al^{3+} ions in the VE solutions from WL experiments by AA are calculated in ppm (mg/L). To compare the AA results with WL data, the results from AA were multiplied by the appropriate dilution factor then divided by the area of Al sample used. As an example 30% solutions of VE solutions were analyzed by AA for alloy S only. The results of WL and AA are shown in Fig.1. A good consistency was observed between the data from WL and AA with WL being lower in all solutions which is logical since the extent of detection of AA is in the ppm range. Taking AA results as the standard method, the difference between the two methods was found to range between 5.4-9.8%. Using AA for analysis after WL was shown in previous studies to give comparable results [15, 18, 21].

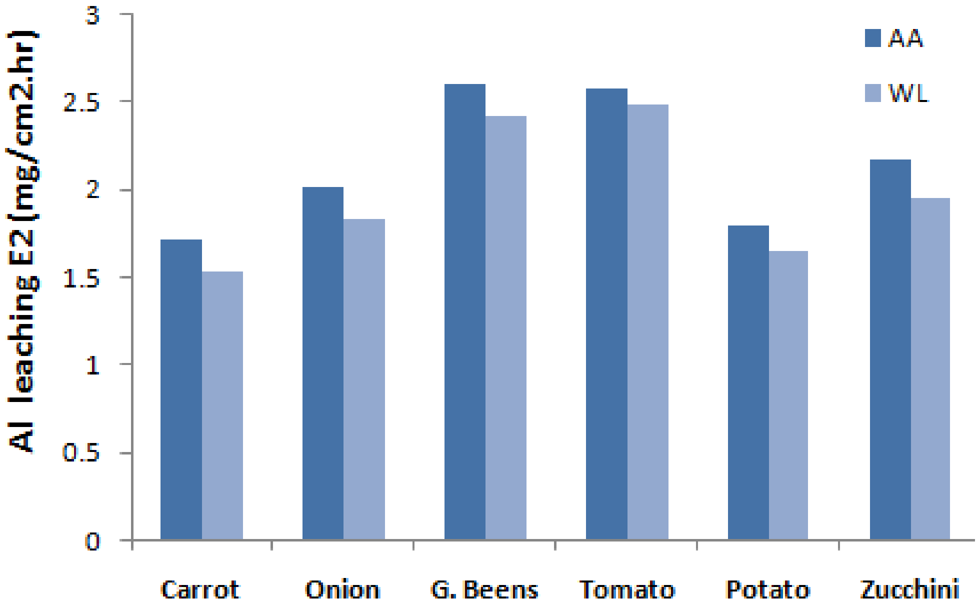

Figure 1. Comparison of Al leaching (E^2 mg/cm^2.hr) from AA and WL for 30% VE solutions and alloy S.

3.2.1. Effect of table Salt Addition

To study the effect of adding table salt on Al leaching, 0.5 g of table salt was added to 100 mL solutions of 30% VE solutions for alloy S only. The results are shown in Fig. 2 with the results of the original VE solutions for comparison. It was found that addition of table salt indiscriminately increased the amount of Al leaching in all solutions which reflects the role of chloride ions in stimulating dissolution of Al oxide layer. In real life during cooking people add table salt, lemon juice and other spices, which were proved by many researchers to leach more Al when using Al utensils [17, 22]. In a previous work of corrosion of Al in amino acids with sodium chloride, the current density values which is directly proportional to Al corrosion rate (or Al leaching) increased 3-4 times in presence of sodium chloride [21].

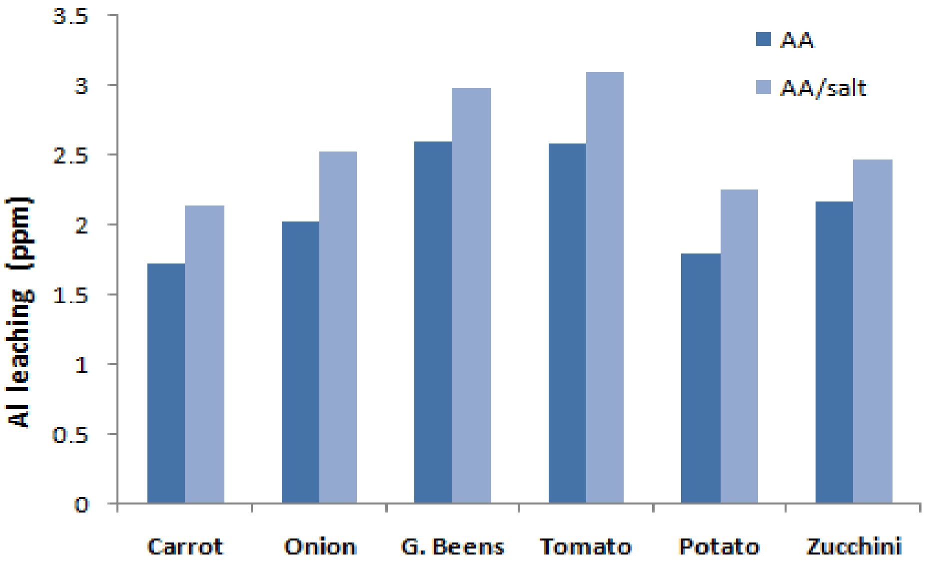

Figure 2. Comparison of Al leaching (ppm) from AA with/without table salt for 30% VE solutions and alloy S.

3.2.2. Effect of Tap water

To imitate real Al leaching, tap water was used instead of distilled water for 30% VE solutions and alloy S only. Comparison of Al leaching (ppm) from AA for 30% VE solutions are shown in Fig.3. It is found that Al leaching increased slightly in general in tap water. Al leaching from Al utensil using tap water leached more Al as found by our previous study when using Al alloy in 0.10M Citric acid with tap water and distilled water [21]. The accumulative effect of the anions including chloride in tap water may explain these findings.

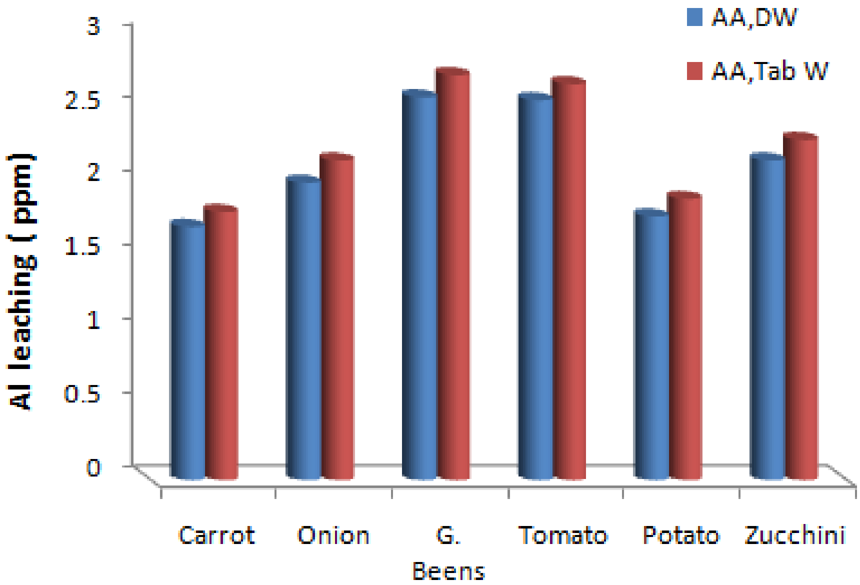

Figure 3. Comparison of Al leaching (ppm) from AA in distilled and tap water for 30% VE solutions and alloy S.

Boiling water only in Al utensils resulted in leaching Al into the medium which was explained by the presence of fluoride ions [16]. However another study conducted by Kharbouj and Nrtier found that boiling water in Al cookware before cooking actually decreased Al leaching by forming a protective layer of α-AlOOH [23]. These controversial conclusions need further elucidations.

3.2.3. Effect of temperature and time

To measure the amount of Al leaching at low temperatures like refrigerator, samples of alloy S were immersed in 30% tomato extract for different time intervals (6, 18, 24, 36 hr) in the refrigerator at 4 °C. The amount of Al leaching was calculated using AA method. The results are shown in Table 3. It was found that after 6 hours of immersion the Al concentration was below the detection limit. However it took 36 hours at 4 °C to produce Al leaching which is close to the amount of Al leaching in one hour at 90 °C. These results indicate that cooking temperature is more important in Al leaching than cooking time which is in agreement with another study about Al leaching at high temperature [10]. It was also reported that the Al concentrations in black currant juice and stewed rhubarb prepared in Al cookware increased with cooking time at the same temperature [8]. To my knowledge the extent of Al leaching at low temperatures was not reported before.

Table 3. Al leaching (ppm) from AA for 30% tomato extracts in the Saudi alloy at 4 °C and different time intervals.

Time(hr)	AA Mean Al leaching ±SD (ppm)
6	Below detection limit
18	0.930±08
24	1.21 ±0.11
36	2.26 ±0.15

3.2.4. Effect of Aluminum alloying elements:

It is pertinent to mention that there might be different Al cook wares from the same country. It was noticed that the total percentage of Aluminum in the cook ware had no influence on the amount that leach in the VE as the % of Al for the China alloy was the lowest (97.902%) whereas the values of Al leaching were in the middle in all VE. The percentage of Al in the Indian alloy (98.335%) is close to that of the Syrian alloy (98.348%); yet the amount that leaches from the Indian alloy was the highest in all VE except potato extract as shown from Tables 3 and 4. Moreover there was no obvious relation of the alloying elements to the amount of Al leaching. Trying to relate the percentage of alloying elements in each alloy to Al leaching was difficult. For example it is known that chromium, copper and titanium may lower the Al leaching. The percentage of Cr in the Indian alloy is 0.021% which is the lowest in all the Al alloys, yet the percentage of Cr in the Saudi alloy is 0.041% which is less than its amount in the Syrian alloy (0.061%). The percentage of Cu in the Indian alloy is 0.352% which is close to its percentage in the Saudi alloy (0.380%) and less than its amount in the Syrian alloy (0.061%). There is no detectable titanium in the Saudi alloy whereas its concentration in the Indian alloy is 0.040 % which is close to its percentage in the China alloy (0.050%). The collective effect of these alloying elements is manifested here as the addition of an element during casting may form the intermetallic XAl_y compound in the solid solution. In the previous studies about Al leaching from Al cook wares, the effect of the alloying elements was not discussed in detail because it is beyond the scope of these studies.

3.3 Surface study

To show the effect of Al leaching from Al utensil the Al sample was immersed in 30% tomato extract with /without table salt for 3 hours at 90 °C. Then the Al sample was dried and scanned with a SEM at 1000 magnification as shown in Fig. 4. The micrograph in presence of tomato extract only (Fig.4 A) shows that the smooth Al surface (not shown) was replaced by a surface with itching marks due to the leaching of Al. The presence of chloride ion (Fig.4 B) increased Al leaching which is shown as holes in the middle of the micrograph. This clearly shows that chloride ion induced pitting corrosion of Al and increased Al leaching into the tomato extract. This result is in agreement with the results obtained from AA analysis in Fig. 2.

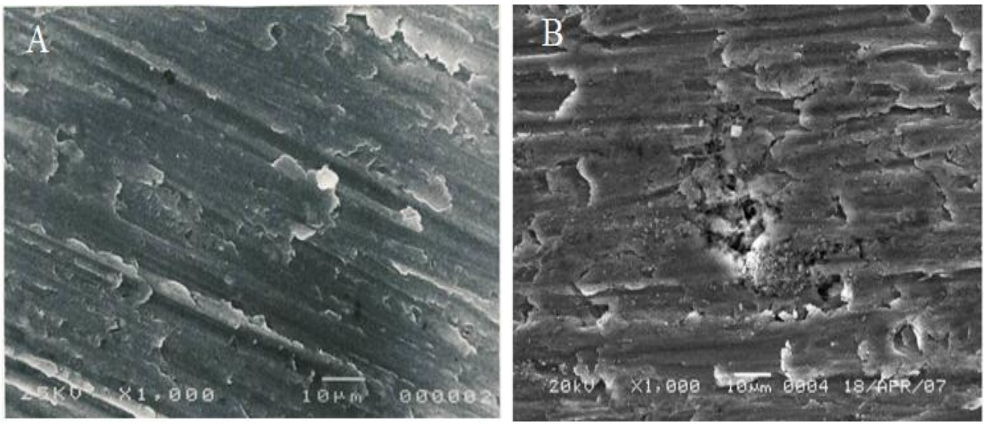

Figure 4. SEM of Al alloy S in 30% tomato extract (A) and 30% tomato extract plus table salt (B) both after 3 hours of immersion at 90 °C.

3.4 Comparison with PTWI

Most of the previous studies have reported Al leaching in ppm or in mg/kg but these units does not relate the Al leaching to the Provisional Weekly Tolerance Intake (PTWI) of 7mg of Al /Kg body weight of adult [6]. To make use of our data and to be able to compare them with PTWI, some assumption were made. It is assumed that a family of four persons is using an Al utensil of medium size with the following dimensions: diameter 20.0 cm, height 15.0 cm. The internal area of the Al utensil exposed to leaching will be about 1200.0 cm^2. As an example the concentration of 30% tomato VE and alloy S from Table 1 will be used. For a family of 4 persons it may be assumed that the average Al intake per hour will be:

2.48×10^{-2} mg cm^{-2} hr^{-1}x 1200.0 cm^2 = 29.76 mg hr^{-1} for the family = 29.76 mg hr^{-1}/4 persons = 7.4 mg hr^{-1} per person

The estimated values of Al intake per person from WL in 30% of vegetable extracts using the different Al alloys are listed in Table 4. These values refer to the estimated Al leaching for 30% VE in mg hr^{-1} per person which is almost equivalent to mg/day consumption. Using NaCl will definitely increase Al leaching as shown in Fig. 2.

Table 4. Estimated range of Al intake per person from WL in 30% VE solutions of all alloys

30% VE	pH	Al alloy	Mean $CR*10^2 \pm Sd$ ($mg/cm^2.hr$)	Estimated Al intake per person (mg/hr)	Estimated range of Al intake per person of all alloys for 30% w/v (mg/hr)
Carrot	5.9	China	2.72±0.12	8.16	4.59-10.41
		India	3.47±0.29	10.41	
		Saudi	1.53±0.13	4.59	
		Syria	1.87±0.15	5.61	
Onion	5.4	China	2.17±0.23	6.51	5.49-13.95
		India	4.65±0.27	13.95	
		Saudi	1.83±0.17	5.49	
		Syria	2.37±0.14	7.11	
Green Beans	6.5	China	2.04±0.18	6.12	5.13-13.68
		India	4.56±0.29	13.68	
		Saudi	2.42±0.18	7.26	
		Syria	1.71±0.14	5.13	
Tomato	4.5	China	4.08±0.21	12.24	7.44-16.44
		India	5.48±0.24	16.44	
		Saudi	2.48±0.16	7.44	
		Syria	3.10±0. 23	9.3	
Potato	6.1	China	1.52±0.16	4.56	4.56-5.85
		India	1.82±0.14	5.46	
		Saudi	1.65±0.13	4.95	
		Syria	1.95±0.21	5.85	
Zucchini	6.6	China	2.36±0.22	7.08	5.22-15.78
		India	5.26±0.29	15.78	
		Saudi	1.95±0.11	5.85	
		Syria	1.74±0.15	5.22	

From Table 4., the highest amount of leaching in 83% of the VE (5 out of 6) was from alloy I (India) and alloy Y(Syria) has the highest leaching in potato extract only. The lowest amount of leaching in 66.6 % of the VE (4 out of 6) was from alloy S(Saudi Arabia) and 33.7 % (2 out of 6) of the VE extract was from alloy Y(Syria). The Al leaching from alloy C (China) seemed to be in the middle range in all VE used.

There is no agreement about using Al utensils for cooking and the leaching of Al into the diet. Some studies regard using Al utensil and Al foil safe for cooking [17, 22, 24] other studies regard them hazardous and do not advice using them especially in acidic foods [8, 15, 19].

There are no reports of dietary Al toxicity to healthy individuals in the literature; even high doses of Al from antacids had not been associated with neurotoxicity [24].

Nevertheless, there is a continuing interest of Al content in food and its possible relation to Al toxicity especially to the elderly and to people with kidney failure [4, 10]. The Joint Committee on Food Additives established a Provisional Tolerable Weekly Intake (PTWI) for Al was recommended as 7mg/kg body weight per week for an adult in 1989 but was replaced with the PTWI of 1 mg/kg body weight per week for an adult; this value applies to all aluminum compounds in food, including food additives [6]. In the same report by FAO/WHO in 2007 the total estimated range of Al exposure to the adult population from different dietary sources (including additives) was 14-280 mg/week [6]. These represent the total Al exposure from different countries not taking into account using Al utensils or medicines. The safety of Al depends on whether it is absorbed or not but there is also conflicting reports about its bioavailability. According to Prescot 75-95% of Al we eat or drink is egested, the rest is absorbed and may accumulate in the different organs of the body [25]. Al accumulation in people with impaired renal functions was proved to cause encephalopathy, ostemalaicia and anemia [2, 3, 5].

From the present study and a previous study [15] we believe that using Al cookware will add extra amounts of Al into the diet and will increase the Al exposure to the population in general and to the elderly and children in particular. Therefore continuous monitoring of the Al level in the daily diet, water, medicines and food additives is highly recommended.

4. CONCLUSION

Al leaching depends on constituents and pH of VE solution, presence of sodium chloride, immersion time, water composition and alloying elements. Using Al cookware may leach significant amounts of Al into the diet, which raise the amounts of Al to high levels. This may reach the limits of PTWI and may lead to high exposure to the population in general and to the elderly and children in particular.

ACKNOWLEDGMENT
The author extend their appreciation to the Deanship of Scientific Research at King Saud University for funding this study. The work of research assistant Zainat Khayat and Raesah Al Shehrey is greatly valued.

References

1. M. Müller, M. Anke, I. Gunther , *Food Chem.,* 61(1989) 419.
2. K. Winship, *Adv. Drug React. Toxicol. Rev.*, 11(1993) 123.
3. R. Yokel, *J. Toxicol. Environ. Health*, 41(1994)131.
4. V. B. Gupta, A. Suram, M. L. Hegde, L. Zecca , R. M. Garruto, R. Ravid, *Cellular and Molecular Life Sciences*, 62(2005)1.
5. H. Gitelman ,*"Aluminum and Health"*, Marcel Dekker, Inc. (1989).
6. FAO/WHO Joint Expert Committee, *sixty-seventh report Series*, 58(2007) Geneva.
7. A. Lione , *Food chem. Toxicol.,* 21(1983) 103.
8. N. Fimreite, O. Ø. Hansen, H. C. Pettersen, *Bull. Environ. Contam. Toxicol.* 58(1997) 1.
9. S. P. Joshi, R. B. Toma , N. Medora, K. O'Connor , *Food Chem.,* 83(2003)383.
10. *S. Turhan, Meat Science*, 74(2006) 644.
11. *A. Fran˘kova , O. Drabek , J. Havlik , J. Szakova , A. Vane˘k, J. Inorganic Biochem.*, 103(2009) 1480.
12. B. Francisco , L.F. Caldas, D. M. Brum , R. J. Cassella, *J. Hazard. Mater.*,181(2010**)** 485.
13. M. A. Callahan, K. Sexton, *Environ. Health Perspect.*, 115(2007) 799.
14. S. Bi, *Environ. Pollut.*, 92(1996) 85.
15. L. Al Juhaiman, *J. Saudi Chem. Soc.*, 14(2010) 131.
16. B. M. Neelam, M. Kaladhar, *Food Chem.*, 70(2000) 57.
17. MIS. Verissimo, J.Oliveira, M. Gomes, *Sens. Actuators B,* 118(2006) 192.
18. A. Al-Mayouf, L. Al Juhaiman, A. Al-Suhybani, *Anti-Corros. Method M.*, 55(2008) 79.
19. J. Ščančar, V. Stibilj, R. Miačič, *Food Chem.*, 85(2004) 151.
20. Y. Takeda, Y. Kawamura, T.Yamada, *J. Food Hygienic soc. Japan*, 39(1998) 178.
21. L. Al Juhaiman, A. Al-Mayouf, A. Al-Suhybani, *J. Saudi Chem. Soc.*, 8(2004) 547.
22. *R. Ranau, J. Oehlensclager , H. Steinhart, Food Chem.*, 73(2001)1.
23. *R. Karbouj, P. Nrtier, Food Chem. Toxicol.*, 47(2009) 571.
24. *M. G. Soni, S. M. White, W. G. Flamm , G. A. Burdock , Regul. Toxicol. Farmacol.*, 33(2001) 66.
25. Prescot, *New Scientist*, 21(1989) 58.

© 2012 by ESG (www.electrochemsci.org)