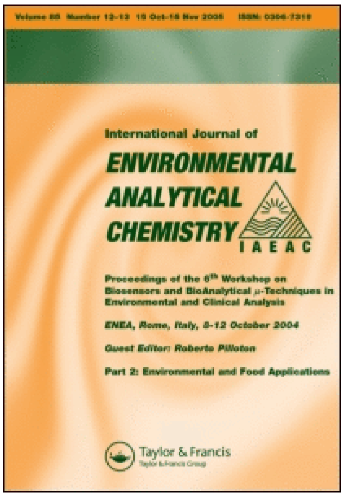

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Aluminum Contamination of Food from Using Aluminumware

L. Mei[a]; T. Yao[b]
[a] Dept. of Food Technology, Sichuan Institute of Technology, Chengdu, China [b] Dept. of Chemistry, Sichuan Normal University, Chengdu, China

To cite this Article Mei, L. and Yao, T.(1993) 'Aluminum Contamination of Food from Using Aluminumware', International Journal of Environmental Analytical Chemistry, 50: 1, 1 — 8
To link to this Article: DOI: 10.1080/03067319308027577
URL: http://dx.doi.org/10.1080/03067319308027577

Intern. J. Environ. Anal. Chem., Vol. 50, pp. 1-8
Reprints available directly from the publisher
Photocopying permitted by license only

ALUMINUM CONTAMINATION OF FOOD FROM USING ALUMINUMWARE

L. MEI

Dept. of Food Technology, Sichuan Institute of Technology, Chengdu 611744, China

T. YAO

Dept. of Chemistry, Sichuan Normal University, Chengdu 610066, China.

(Received, 10 June 1991; in final form, 19 May 1992)

Aluminum concentrations were determined in deionized water (adjusted to pH=2, 4, 6, 8, and 10), salt, soy, and vinegar solutions (diluted to three concentrations) after boiled in aluminum pots for 10, 30, 60 min or after contacting aluminum at room temperature for 5, 15, 25 days. The results showed that: (1) Pure water at pH=4—8 increased little its aluminum content in the test, at pH=10 increased slightly, and at pH=2 increased very significantly. (2) Soy solutions dissolved much more aluminum than salt solutions when in contact with aluminumware at room temperature for a long time. NaCl concentration was not the chief factor for aluminum dissolving in a soy solution. (3) Vinegar solutions dissolved more aluminum than soy solutions when boiled in aluminum pots for a short time, but the reverse occurred when contacted aluminum at room temperature for a long time. The main action responsible for increasing the aluminum concentration was chemical corrosion by acidic or alkaline materials when boiled in aluminum pots for a short time, and was electrochemical corrosion, which favored by the complexing reaction, when contacted aluminum at room temperature for a long time. (4) For most common foods, neither pH value nor NaCl concentration was the chief factor for increasing the aluminum content when using aluminumware.

KEY WORDS : Aluminum dissolution, cooking, storing, pH value, inductively coupled plasma atomic emission.

INTRODUCTION

The unfavorable effect of aluminum on human body is being given a good deal of attention by the public[1-3], especially in China[4-6] because of the very extensive use of aluminum cookware, eating utensils, and storing vessels. Usually, people think only of acidity (or alkalinity) and electrolyte concentration as the factors for the increase in aluminum content of foods when aluminumware are used. In this experiment, we designed tests to investigate systematically the action of water (with a given pH), salt, soy, and vinegar solutions in dissolving aluminum slowly from aluminumware under some simulated practical conditions. This was done to determine the factors and the rules on dissolving aluminum when cooking and storing food in aluminumware.

EXPERIMENTAL

Reagents and materials

Aluminum pots Three pieces (manufactured by Shanghai No. 1 Factory of Aluminum Products, Aluminum content > 99%, with diameter 16 cm and high 10 cm) were bought. After being washed carefully with running water, each pot was filled with distilled water that was heated to the boiling point and was kept boiling for about 30 min. Then it was washed with deionized water. If, after use, there was an obvious deposit that could not be washed off from the pot's surface, the pot was cleaned with an emery cloth and seasoned again in the manner described above for next use.

Aluminum flakes An aluminum board (thickness about 0.3 mm) was polished with an emery cloth to clean the surfaces, and then was washed with a rag under running water. Rectangles measuring 4cm×6cm were cut out from this board. Each rectangle was bent into an "S" shape (in order to be submerged when used) and was washed with running water and deionized water.

Water Deionized water (made from distilled water) was adjusted to the desired pH values using very dilute H_2SO_4 or NaOH solution. pH = 2—10 was taken into account because it covers the pH range of most common foods.

Salt solutions Three solutions with different NaCl concentrations were made of salt and deionized water: (1) Saturated solution at 9 °C marked as C; (2) Solution C diluted 2-fold was marked as C/2; (3) Solution C diluted 7-fold was marked as C/7.

Soy solutions Soy (made in Chengdu Soy-making Factory, grade 1, bottled) solutions of three concentrations were prepared: (1) The original solution undiluted was marked as C; (2) Solution C diluted 2- fold with deionized water was marked as C/2; (3) Solution C diluted 7- fold was marked as C/7.

Vinegar solutions Vinegar (Baoning Vinegar Chief Factory, Langzhong County, Sichuan Province, grade 2, bottled) was diluted to concentration C, C/2, and C/7 by the same method used in the preparation of soy solutions.

All concentrations of the above C/7 solutions were in the range of actual edible concentrations.

Inductively coupled plasma atomic emission spectrometer (ICP-AES) Model 8410, Labtam Limited, Australia. The operating conditions were: wavelength 396.152 nm, incident power 1.2 kw, carrier gas (Ar) at 0.98 l/min, outer Ar at 12.46 l/min, intermidiate Ar at 1.2 l/min, observation height 13 mm.

UV-visible spectrophotometer Model 721, Shanghai NO. 2 Analytical Instrument Factory, China. Optical measurements[7] were carried out with matched quartz cells of 1 cm path length.

pH meter Model pHS-2, Shanghai No. 3 Analytical Instrument Factory, China.

Table 1 Aluminum concentrations (in mg/l) of water, salt, soy and vinegar solutions boiling in aluminum pots and contacting aluminum at room temperature.

Sample	*pH*	*Co*	*Cx*	*Cx/Co*	*Cx*	*Cx/Co*	*Cx*	*Cx/Co*
Water			Boiling 10 min		Boiling 30 min		Boiling 60 min	
	2.0	0.120	48.8	507	114	950	141	1180
	4.0	0.030	0.052	1.73	0.072	2.40	0.097	2.63
	6.0	0.022	0.026	1.18	0.039	1.77	0.040	1.82
	8.0	0.058	0.873	15.0	1.26	21.7	1.14	19.6
	10.0	0.030	2.41	80.3	3.28	109	3.85	128
			Contacting 1 day		Contacting 7 days		Contacting 15 days	
	2.0	0.176	35.9	204	162	920	229	1300
	4.0	0.059	0.631	10.7	0.751	12.7	0.840	14.2
	6.0	0.059	0.111	1.88	0.193	3.27	0.234	3.97
	8.0	0.046	0.102	2.22	0.307	6.67	0.428	9.30
	10.0	0.013	1.68	129	1.27	97.7	1.69	130
Salt solution			Boiling 10 min		Boiling 30 min		Boiling 60 min	
C/7	6.5	0.208	0.798	3.84	1.11	5.34	0.927	4.46
C/2	6.7	0.682	2.65	3.88	4.83	7.08	3.75	5.50
C	7.8	1.61	4.52	2.81	4.52	2.81	5.20	3.23
			Contacting 7 days		Contacting 15 days		Contacting 30 days	
C/7	6.5	0.208	1.62	7.79	4.15	20.0	5.34	25.7
C/2	6.7	0.682	7.29	10.7	14.9	21.8	18.3	26.8
C	7.8	1.61	12.7	7.89	22.7	14.1	34.8	21.6
Soy solution			Boiling 10 min		Boiling 30 min		Boiling 60 min	
C/7	4.5	0.965	2.18	2.26	3.11	3.22	4.29	4.44
C/2	4.4	3.60	4.66	1.29	6.31	1.75	8.16	2.27
C	4.3	7.53	11.4	1.51	14.2	1.88	21.0	2.79
			Contacting 7 days		Contacting 15 days		Contacting 25 days	
C/7	4.5	0.719	5.87	8.16	31.3	43.5	46.2	64.3
C/2	4.4	2.73	43.3	15.9	122	44.7	185	67.8
C	4.3	5.36	53.7	10.0	150	28.0	197	36.8
Vinegar solution			Boiling 10 min		Boiling 30 min		Boiling 60 min	
C/7	3.8	7.89	8.24	1.04	8.03	1.02	8.38	1.06
C/2	3.8	24.6	40.5	1.65	50.1	2.04	65.3	2.65
C	3.7	47.7	76.9	1.61	113	2.37	165	3.46
			Contacting 7 days		Contacting 15 days		Contacting 25 days	
C/7	3.8	7.39	31.4	4.25	72.8	9.85	90.3	12.2
C/2	3.8	27.3	72.6	2.66	146	5.35	199	7.29
C	3.7	53.2	101	1.90	160	3.01	208	3.91

Co: initial concentration; Cx: concentration after the process. Values in Cx columns are means of 6 determinations of 3 parallel samples.

Methods

The effect of each solution indicated above towards dissolving aluminum when boiling in aluminum pots for 10, 30, and 60 min and contacting aluminum at room temperature for 5, 15, and 25 days has been examined.

In the process of the boiling test 700-ml of the tested solution was put into an aluminum pot, then the pot was covered with its lid and was heated on a hot-plate. When the liquid had boiled gently for 10 min, the pot was removed from the heat, and a 25 ml sample solution was removed. The remaining liquid was heated again and boiled gently for another 20 min. The liquid was poured into a graduated glass container and deionized water was added in order to make 675 ml. Then, the liquid was poured back into the pot and mixed. A 25 ml sample solution was drawn. The remaining liquid was heated again and boiled gently for another 30 min. The liquid was poured into the 1000-ml graduate and deionized water was added in order to make 650 ml. Then, the liquid was poured back into the pot and was mixed. A 25 ml sample solution was drawn. The whole process was performed independently with three aluminum pots during the same period, so three parallel samples were obtained.

In the process of the contacting test, four bottles of 125 ml were cleaned and each one was filled with 100 ml of the tested solution. To three of the bottles, a piece of aluminum flake was added. Then every bottle was covered with its lid. When a given time period had passed, 2 ml of the sample solution was drawn for determining aluminum concentration. The mean value of room temperatures during the testing was 10°C.

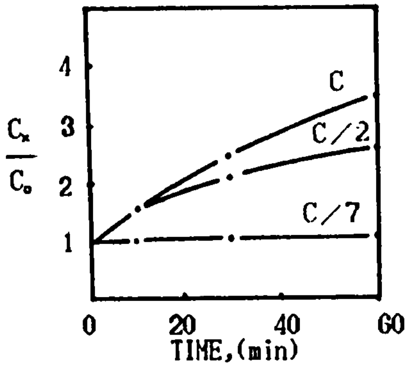

Figure 1 Variations in ratio Cx/Co of vinegar solutions boiling in aluminum pots.
Cx: Aluminum concentration after process.
Co: Aluminum concentration before process.

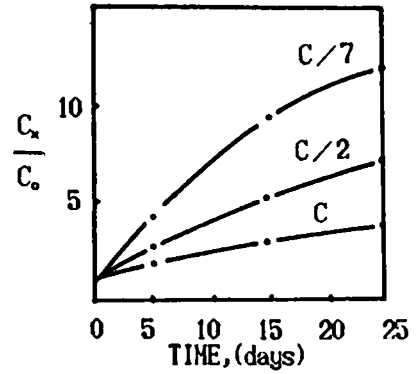

Figure 2 Variations in ratio Cx/Co of vinegar solutions contacting aluminum at room temperature.
Cx: Aluminum concentration after process.
Co: Aluminum concentration before process.

Analytical determination The water and salt solutions were examined by spectrophotometry[7] directly or after dilution. Suitable volumes of the soy and vinegar sample solutions were digested with concentrated HNO_3 by heating until the solutions were transparent. Afterwards, they were diluted to a proper volume with deionized water, and their aluminum concentrations were determined by ICP-AES. The results are shown in Table 1.

RESULTS AND DISCUSSION

Table 1 shows a notable relation between the pH of a solution and its capacity of dissolving aluminum. In both, the boiling and the contacting tests, the aluminum concentrations of solutions at pH2 increased up to three orders of magnitude. On the other hand, the aluminum concentrations of solutions at pH10 increased several times, whereas the aluminum concentrations of solutions at pH4, 6, and 8 changed less. This rule is consistent with the literature[8], in which the results of boiling tests with deionized water and 4% acetic acid solution were reported.

The salt, soy, and vinegar solutions dissolved aluminum notably, and the higher the material concentrations of the solutions were, the more the aluminum amounts increased.

Comparing Figures 1 and 2, we see that the major cause of aluminum dissolving in vinegar solution, when boiled in an aluminum pot for a short time, was not the same as that when contacted aluminum at room temperature for a long time. Figure 1 shows that the lower the vinegar concentration of the solution was, the earlier the aluminum dissolving process slowed down. The differences of Cx/Co among the three solutions increased with time, i.e. solution having higher vinegar concentration exhibit more intensive corrosivity for a longer time. This means that the main action might be chemical corrosion related to the acidoid concentration in the vinegar.

Figure 2 shows that electrochemical corrosion might play an important role in dissolving aluminum when the vinegar solutions were in contact with aluminum at room temperature for a long time. This action was not very strongly related to the concentration of vinegar, so the solution C was not in a much more favorable condition to dissolve aluminum than the solution C/2 and C/7. In addition, the initial aluminum concentration (Co) of solution C was very great. Therefore, the solution C had the minimum ratio Cx/Co.

Taking two groups of typical samples, those boiled for 10 min and those in contact with aluminum at room temperature for 15 days, to compare the aluminum dissolvability by these solutions (see Figure 3 and Figure 4), the results shows that:

i) Solutions of pH=2 dissolved aluminum very readily, whereas solutions of pH=10 dissolved aluminum slightly, and those of pH=4—8 were very weak in dissolving aluminum from aluminumware, on both the boiling and the contacting tests.

ii) The aluminum dissolvability of salt solutions and soy solutions were close when boiling for a short time; but when contacting aluminum at room temperature for a long time, the soy solutions' ability to dissolve aluminum was far greater than the salt solutions. The NaCl concentrations of soy solutions were not greater than those of the corresponding salt solutions, and although the pH of the soy solutions were lower than those of the salt solutions,

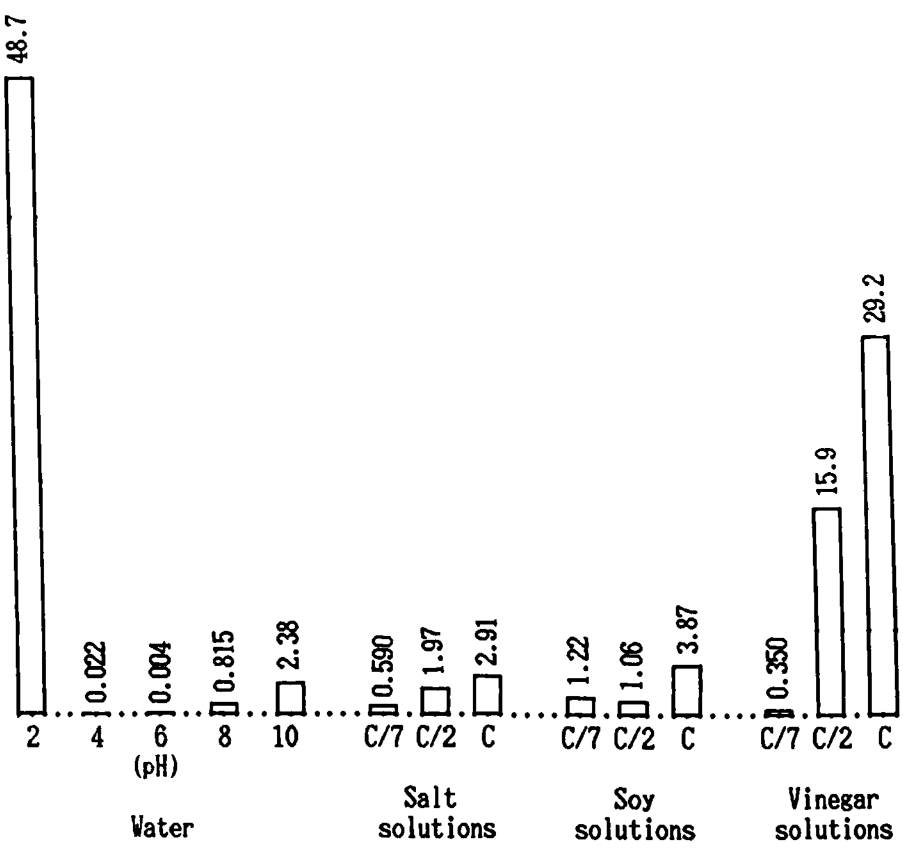

Figure 3 A comparison of ability to erode aluminum. Numbers indicate the quantities (μg) of aluminum that were dissolved per milliliter of solutions when boiled in aluminum pots for 10 minutes.

all of them were in the pH range which barely dissolved aluminum from aluminumware. These facts show that besides the factor that the electrolyte NaCl favored the electrochemical corrosion, there were more important factors when contacting aluminum at room temperature for a long time. One of these factors might be the complexing reaction. In soy, there are large quantity of substances, such as amino acid, which can complex aluminum ions in solution.

From the Nernst equation, the electrode potential of aluminum is $E=E^\circ+(RT/nF)\ln a_{AL}^{3+}$. The existence of complexing agents reduced greatly the activity of aluminum ion, a_{AL}^{3+}, so the E of aluminum was lowered and the reactivity increased. In the boiling tests, the high temperature did not favor the formation of complexes. Therefore, in the boiling tests, the major factors in the soy solutions were similar to those in the salt solutions, and so the quantities of aluminum that were dissolved by both solutions were similar. When contacting aluminum at room temperature for a long time, the complexing reaction in the soy solutions, which contained much more substances than the salt solutions, kept the aluminum ion

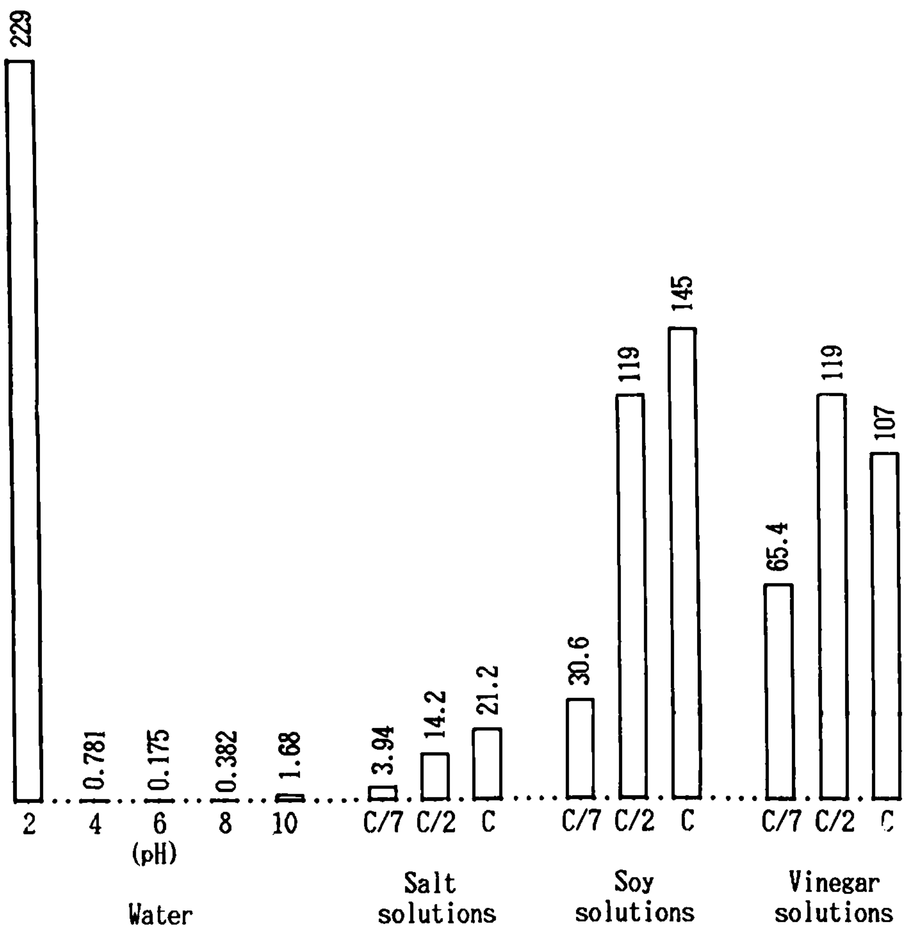

Figure 4 A comparison of ability to erode aluminum. Numbers indicate the quantities (μg) of aluminum that were dissolved per milliliter of solutions when contacted aluminum at room temperature for 15 days.

activity at very low levels, so the electrochemical corrosion could go on continuously under favorable conditions. Cui et al[9] reported that aluminum concentration of raw water, which had much more complicated composition than distilled and deioined water, could increase to about 3 mg/l after boiling in an aluminum pot for 30 min. Comparing this report with our tests, it could be seen that their result supports the opinion that in some cases there were more important factors than pH and NaCl concentration in aluminum dissolution.

iii) When boiled for a short time, the aluminum dissolving action of the vinegar solutions was far greater than that of the soy solutions; but when contacting aluminum at room temperature for a long time, the aluminum dissolving action of the soy solutions was as strong as that of the vinegar solutions. This could be explained as follows. The pH values of the vinegar solutions were out of the pH range which barely corrode aluminum, but the pH values of the soy solutions were within the pH range. When boiling for a short time, the major action was chemical corrosion by acid. This action is faster than electrochemical corrosion and can be speeded by higher temperature[10]. Therefore, the aluminum amounts in the vinegar solutions increased quickly. However, as pointed out above, this rapid corrosion action will weaken quickly with diminution in quantity of acidic substances. In addition, the electrochemical corrosion by the vinegar solutions was lower than that by the soy solutions (in soy solutions, the amounts of electrolyte (NaCl) and substances that can complex aluminum ions were higher). Therefore, the amounts of dissolved aluminum in the vinegar solutions did not increase much after some time. On the other hand, the electrochemical corrosion by the soy solutions was easier than that by the vinegar solutions. Furthermore, because this reaction does not consume the concerned substances of the solutions, the electrochemical corrosion can last a long time. Therefore, in the test that solutions contacted aluminum at room temperature for a long time, the amounts of dissolved aluminum in the soy solutions could be as great as and even more than those in the vinegar solutions.

CONCLUSIONS

The main action of a liquid to dissolve aluminum from aluminumware is chemical corrosion by acid or alkali when boiling for a short time, and is electrochemical corrosion favored by the presence of complexing agents and electrolytes (such as NaCl) when contacting the aluminumware at room temperature for a long time.

Solutions of $pH<4$ or >10 can dissolve aluminum readily, but most of foods are near neutral. The electrolyte NaCl favors electrochemical corrosion on aluminumware, but it is not the chief factor. So, for most of common foods, neither pH nor NaCl concentration is the chief factor for increase in aluminum content. There are more important factors, one of which might be the complexing reaction of aluminum ions.

References

1 G.L. Klein, *Nutr. Res. Rev.*, **3**, 117-141(1990).
2 J. Orme and E.V. Ohanian, *Envir. Geochem. and Health*, **12**, 55-58(1990).
3 T.B. Drueke, *et al.*, *Proceedings of the Conference on Aluminum-Related Disease* (Newport Beach, California, USA. 18-20 June 1984) *Kidney Int.*, **29**, (Suppl. 18), s45-s48(1986).
4 D. Yu *et al.*, *Weisheng Dulixue Zazhi*, **4**, 227-229, 249(1990)
5 Renmin Ribao, Sep. 7, 1986.
6 Z. Liu, Zhongguo Shipin Bao, Sep. 25, 1989.
7 L. Mei, M.Sc. Thesis, Sichuan Normal University, 1988.
8 J. Zhang *et al.*, *Shanxi Yiyao Zazhi*, **12**, 129-130 and 133(1983).
9 W. Cui, Y. Ma and H. Shi, *Henliang Fenxi*, **1**, 81-84(1986).
10 G. Mu, *Yunnan Daxue Xuebao*, **7**, 451-456(1985).