Bull. Environ. Contam. Toxicol. (1999) 63:271-276

Bulletin of Environmental Contamination and Toxicology

Aluminum Leaching from Surrogate Aluminum Food Containers Under Different pH and Fluoride Concentration

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Received: 10 February 1999/Accepted: 3 June 1999

Aluminium (Al) utensils are considered as potential source of dietary Al. Reports suggests that acidic food cooked or stored in Al vessels contain high concentrations of Al (Aikoh and Nishio 1996; Gramiccioni et al. 1996; Fimreite et al. 1997; Rajwanshi et al. 1997b). Wide use of Al skillets, pressure cookers, roasting pans, pots, sauce pans, frozen dinner trays, foils and wrappers etc. may increase substantially the amount of Al in food. Greger (1985) has estimated the average daily intake of Al from food additives in American diets as 20-25 mg, while in U. K. a total diet study showed its value as 3.9 mg (HMSO 1993). WHO/FAO expert committee on food additives has established a provisional tolerable weekly intake (PTWI) of 7 mg Al per kg of body weight (HMSO 1993). Much interest over Al in food, beverages and water stems from the suggestion that it may be a factor in the aetiology of various diseases such as dialysis, encephalopathy, dementia (Stewart 1989), osteomalacia, fractures and or high levels of bone Al (Boyce et al. 1982) and the most intriguing Alzhemier's disease (Edwardson et al. 1989). The extent of Al leaching from cooking utensils mainly depends on the impurities present in the metal, geometry and the previous use pattern of the utensils, pH of the cooking medium, duration of the cooking and the presence of salt, sugar and the other ions like fluoride, chloride and carbonate. A recent study (Tennakone and Wickramanayake 1987) indicated that the presence of fluoride (F) significantly increases the dissolution of Al into dilute solutions of organic acids. However, Savory et al. 1987, later found that at 1 mg/L F concentration, which is the normal concentration in water, no significant rise in Al leaching occurs. Studies on various aspects of Al leaching have been performed by different workers (Ondereicka et al. 1971; Koning 1981; Tennakone and Wikramanayake 1988; Moody et al. 1990; Liukkonen and Piepponen 1992; Seruga et al. 1994; Rajwanshi 1995) and often results are contradictory, mainly due to non- standard experimental conditions. This aspect has been covered in detail in a review article by the authors (Rajwanshi et al. 1997a).

Present article deals with a systematic study on F induced leaching of Al from standard size (area 6 inch^2, thickness 0.06 inch) rectangular coupons made up of 2S alloy (Al, 99%, conforming to IS 19000 equivalent to AA 1200, commercially used in making utensils) under the action of acetic (AA), citric (CA), oxalic (OA), tartaric acids (TA) and sodium bicarbonate (SBC) at different pHs. In order to explore the role of above mentioned species, which are often present in many foods, in Al leaching from cookwares in this study, standard size Al coupons obtained from the single lot from the manufacturer,

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were preferred over utensils having different geometries due to the constant surface topography of the former. Each coupon was subjected to four consequent leachings under similar conditions in order to observe the leaching pattern on prolonged use.

MATERIALS AND METHODS

Aluminium coupons of constant geometry and size (2" x 3") were cut, in the shearing machine, from Al sheets of similar make, which were provided gratis by Indian Aluminium Company, INDAL, Bombay.

Stock solutions of F and AA, CA, OA and TA were prepared by dissolving AR grade sodium fluoride and the corresponding organic acids, respectively, in deionized double distilled water. The F solutions were calibrated employing Fluoride Ion Selective Electrode (model Orion 9409BN) and Orion Ion Analyzer (EA 940). Test solutions (F concentrations: 0, 1, 2, 3, 5, 10 mg/L, pH: 2, 3 and 4) were prepared by mixing appropriate volumes of stock solutions of F and organic acids, and in 200mL test solution (taken in acid washed Borosil glass beaker). Organic acids of different molarity (AA: 2.67 M, 2.38×10^{-2}M, 5.95×10^{-4}M; CA: 0.10 M, 2.22×10^{-3}M, 1.64×10^{-4}M; OA 5×10^{-3} M, 6.66×10^{-4}M, 8.93×10^{-5} TA: 0.10M, 7.14×10^{-4}M, 7.14×10^{-5}M) were used for achieving the desired pH of 2, 3, and 4, respectively in the test solutions. Al coupons (one per beaker) were soaked overnight. The solution was then boiled for 10min. and the contents were cooled. After removing the Al coupons, the solutions were stored in polythene bottles and analysed for Al contents employing the direct current atomic emission spectrophotometer (Beckman Spectraspan V) under the following conditions: Argon flow rates: sleeves-50 psi, nebuliser-20 psi; slit: entrance- 50 x 300 µm, exit- 50 x 3000 µm, PMT voltage: 500-600V; signal integration time: 5s repeats; 3s wavelength: 369.1 nm.

On account of non-availability of standard reference material the samples were fortified with known amount of dissolved Al and the percentage recovery ranged between 93-99%. Reagent blanks were also included along with different samples and substracted from main data. These blanks ranged between 0.002-0.12 µg/mL (mean 0.04 µg/mL) with s.d.= ± 0.072. The instrument was calibrated employing the two standard solutions (0.1 and 20 µg/mL) prepared from the metal of 99.9% purity. Preliminary scan was carried out for a few typical samples using the dynamic background corrector (DBC-33). No background correction was found to be necessary. The calibration standard was run between every six samples to check and correct for any drift in the calibration. Experiments were performed in triplicate and each coupon was boiled four times under similar conditions to observe the extent of consequent leachings. Results were subjected to blank and volume corrections.

RESULTS AND DISCUSSION

Varying the experimental conditions, the Al leachings from coupons were observed and Figure 1 (a-e) depicts the averages of four sequential leachings performed with one coupon under similar conditions.

The results clearly indicate that the extent of metal leaching increases with the fall in pH and rise in F concentration in solution. In case of all the acids, containing 10ppm F (pH 2), maximum Al was found to be leached (29, 30, 138 and 25 ppm respectively, for AA, CA, OA and TA). Above values were closely followed by 24 and 27 ppm, values obtained at pH 3 in case of AA and CA, respectively. However, the values at pH 3 were significantly less in case of OA (12ppm) and TA (6ppm). In all the acid solutions minimum Al leached at pH 4 in the absence of F. Experiments with SBC solution also resulted in maximum Al leaching (31 ppm) at 10ppm F, while minimum (18ppm) Al leached in the absence of F.

The above pattern of Al leaching can be attributed to the combined actions of F, H^+ ions and the acid anions on Al coupons. The direct dependence of Al leaching on F concentrations may be due to the existence of Al at pH 5, as octahedral hexahydrate (often abbreviated as $A1^{3+}$), which forms relatively strong complexes with F ions. However, in case of distilled water, containing only the F and no complexing acids, the Al leaching was found to be very low. Apparently in this case, F ions present in solution are not able to break the protective Al_2O_3 film on the coupons and, hence lesser amount of Al is leached. The extent of Al leaching from coupons was found to be inversely proportional to pH. Further, it was also observed that even in absence of F considerable Al is leached by the action of acids.

The leaching of metals apparently involves two process viz. i) the dissolution of Al_2O_3 film by the action of acid, and ii) complexation of resultant Al^{3+} with F^- and carboxylic acid anions. The greater Al leaching at lower pH is perhaps attributable to the fact that at lower pH the oxide layer formed on the surface of the coupons is more easily attacked, thereby making more Al available in the aqueous medium, and simultaneously a fresh and active Al surface is exposed to further action. Results also indicate that the Al leaching is not only a function of pH, since at any pH the leaching, in general, follows the trend: OA > AA > TA > CA. Thus, it appears that the anions of the respective acids also perhaps play an active role on the process of metal leaching. Studies at pH 9, using SBC solutions (0.048M), demonstrate that the Al leachings are high, as compared to distilled water values, at all F concentrations. This can be attributed to the carbonate ion assisted attack of alkaline medium on the protective oxide layer, resulting in latter dissolution.

Finally, it is apparent from this study that, F alone is unable to cause significant Al leaching from utensils, but assists in leaching of this metal in presence of acids. Hence, Al dissolution from cooking utensils is perhaps significantly influenced by carboxylic acids present in variety of foods. Higher concentrations of F and lower pH enhance Al leaching to a great extent. Boiling water and cooking food in near neutral conditions (PH 7) do not

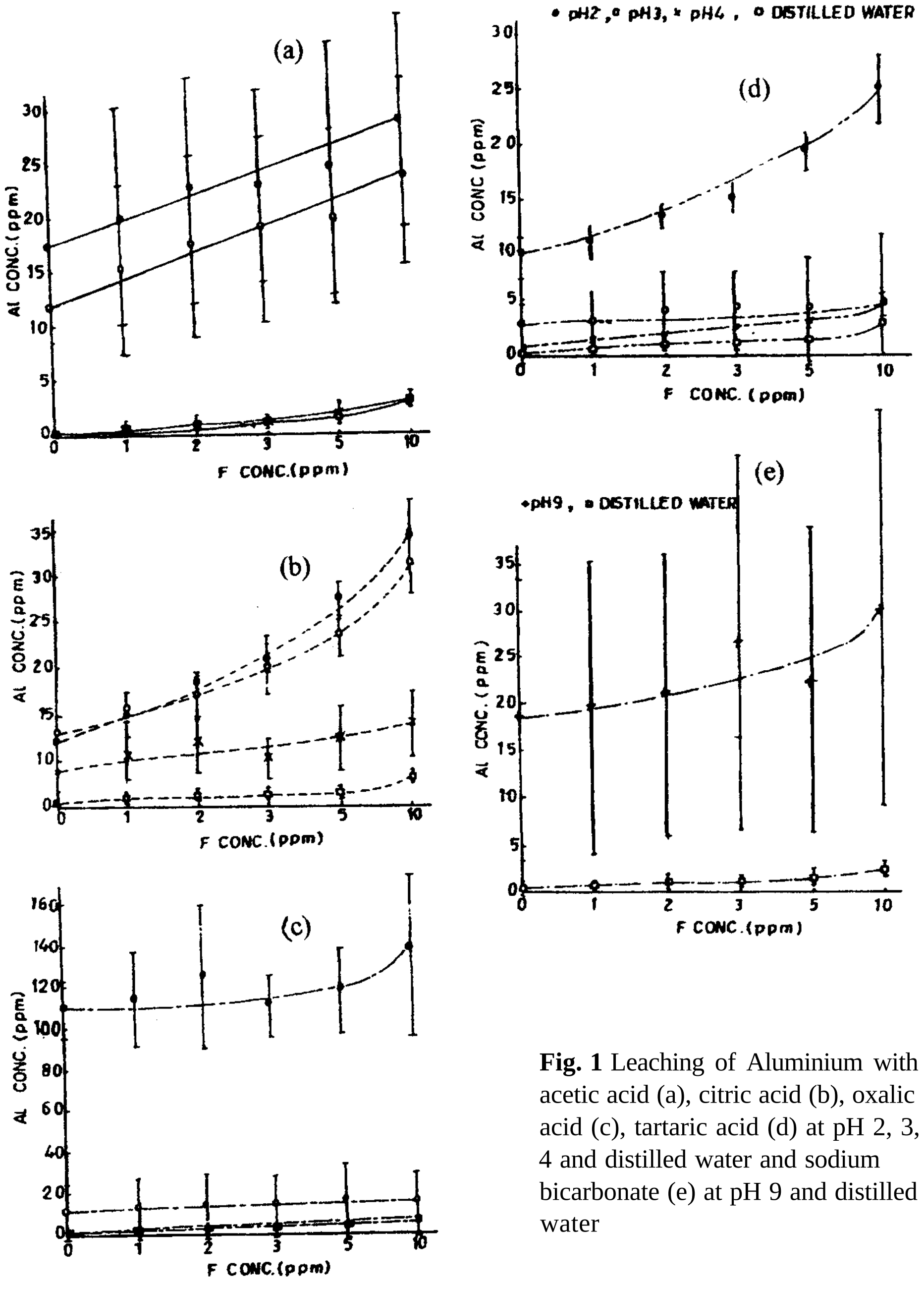

Fig. 1 Leaching of Aluminium with acetic acid (a), citric acid (b), oxalic acid (c), tartaric acid (d) at pH 2, 3, 4 and distilled water and sodium bicarbonate (e) at pH 9 and distilled water

result in much Al leachings even at high fluoride concentration (10 ppm). Further, the leaching Al was found to be comparatively quite low in the presence of tartaric acid (a common ingredient of tamarind). It can thus, be concluded that cooking acidic food, containing tamarind, in Al vessel leads to leaching of lesser Al than cooking in presence of lime or vinegar.

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