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To estimate the contribution of aluminium (Al) leaching from different materials used for food preparation and serving to the dietary Al intake, Al release from foodware typically used in everyday life was investigated using multilevel factorial design (MFD) of experiments. For Al characterisation, sample preparation and an analytical method using inductively coupled plasma atomic emission spectroscopy was developed and validated. Parameter influence (temperature: x_1, contact time: x_2, pH: x_3, salt concentration: x_4, viscosity: x_5), was evaluated with analysis of variance suggesting that the influence of viscosity is not significant compared to the other four studied parameters. Therefore, predictive, exponential quadratic regression models were established with x_1–x_4. Cross-validation and a set of independent experiments in real food products were used to test the prediction force of the different models. They both suggest that the quality of the models established for Al foil, Al plate and ceramic ware is satisfactory, but less good for glassware and stainless steel. Indeed, in the studied conditions, leaching from these latter food wares was often close to or even below the limit of quantification suggesting that the principal sources of Al intake from food contact materials during food processing are utensils made of Al and ceramic ware.

Keywords: chemometrics; metals analysis, ICP; method validation; aluminium; beverages

Introduction

Our ability to extract aluminium (Al) from its ores has resulted in an unimaginably large increase in the use of Al during the past 100 years. No other metal is better suited for the numerous applications of Al. Many of these applications bring us in direct contact with Al through our food and drink (Exley 2003). Hitherto, even though Al is the commonest metal in the earth's crust, it has not been shown to have any essential biological function (Yang et al. 1994; Williams 1996). In the past, Al has been regarded as relatively biologically inert (Muller et al. 1997; Krewski et al. 2007; Hellstrom et al. 2008). However, an increasing number of toxic effects have been established (Ganrot 1986; DeVoto and Yokel 1994; Darbre 2006; Exley et al. 2007; Krewski et al. 2007). Precisely, due to its potential to affect the reproductive and developing nervous system in experimental animals at doses lower than those used in establishing the previous Provisional Tolerable Weekly Intake (PTWI), in 2006, the Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives (JECFA) followed by the European Food Safety

Authority (EFSA) in 2008 have re-evaluated the safety of Al (WHO 2007; EFSA 2008). The PTWI was lowered by seven-fold to 1 mg/kg body weight (bw) including additives.

The concern for public health reinforced the need for an accurate knowledge of Al content in our food. Besides an increased exposure to Al resulted by man-made acidification of the environment and the use of Al-containing additives, other factors, such as kitchenware containing Al, influences the dietary Al intake, depending on the conditions used for food processing and the type of food.

Relevance of Al release into food was recognised at the beginning of the 1980s. This potential source of Al exposure is considered negligible by some (Trapp and Cannon 1981; Lione 1983; Greger 1985; Muller et al. 1993; Ranau et al. 2001; Soni et al. 2001; Verissimo et al. 2006) and important by others (Liukkonen-Lilja and Piepponen 1992; Fimreite et al. 1997; Scancar et al. 2004; Al Mayouf et al. 2008; Frankova et al. 2009; Al Juhaiman 2010). These articles generally agree that when cooking acid food in uncoated Al sauce-pans, release of potentially important amounts of Al

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may occur. An early study suggests that fluoride content of the food enhances importantly Al leaching (Tennakone et al. 1988), whereas other research demonstrated only minimal enhancement in the presence of fluoride (Fairweather-Tait et al. 1987; Savory et al. 1987; Baxter et al. 1988). Rajwanshi et al. (1999) suggested that pH rather than fluoride content is important. Besides pH, temperature is a typical parameter influencing Al leaching. It may also strongly depend on the presence of other species dissolved in the extractant, for example, complex forming ligands in liquids (Karbouj 2007). Al leaching also depends on the presence of a common ion in the solution. To a lesser extent, it depends on the ionic strength of solutions. The rate of dissolution on the other hand depends on the nature of the extractant and the solute, temperature (and to a small degree pressure), degree of saturation, interfacial surface area and presence of inhibitors.

Considering all these influencing parameters, in the present study, Al release was investigated by varying temperature, contact time, pH, salt concentration and viscosity in typical food contact materials (FCM) used during cooking and serving. As a result, prediction models were established using multilevel factorial design of experiments (MFD) explaining the release pattern of Al from the studied kitchenware. MFD was explored as an alternative to traditional single variable experiments. Designs of experiments have been already utilised throughout the pharmaceutical and biotechnology industries. This technique is a cost-effective approach for studying the effects of many variables simultaneously as well as their interactions (Lin et al. 2007; Prakasham et al. 2007; Ray et al. 2009).

Most of the studies investigating Al leaching found in the literature are single variable types and focus on Al leaching from utensils made of Al. However, it is recognised that all materials can release small amounts of their chemical constituents when they touch certain types of food. For example, glassware, ceramic ware and stainless steel ware may contain Al. Al release from ceramic ware is known and was, among other essential and non-essential trace elements, studied as a function of different food simulants and glazes (Demont et al. 2012). Therefore, the following FCMs were studied: Al plate, Al foil, ceramic-, glass- and stainless steel ware. The established prediction models explain the importance of each variable on Al release as well as their interactions for each FCM. For Al analysis, a method was developed and validated using the powerful technique of inductively coupled plasma atomic emission spectroscopy technique (ICP-AES).

Material and methods

Instrumentation

Al concentrations were measured by Optima 4300 DV inductively coupled plasma atomic emission spectrometry, ICP-AES, (Perkin Elmer, Shelton, CT, USA). ICP-AES was equipped with a cyclonic spray chamber (Glass Expansion, Inc., West Melbourne, Australia) and a pneumatic nebuliser (GemCone-type). The operating conditions are summarised in Table 1.

Experimental design

The present study, aimed at establishing prediction models for different FCMs and subsequently evaluating their importance as source of Al in the diet, consisted of two parts:

- method validation
- modelling

An overview of the present study is given in Figure 1.

Method validation

Sample preparation and Al determination was validated over the whole range of concentration and for each matrix. To "confirm the fitness for purpose of" this particular analytical method" (Fearn et al. 2002), performance characteristics of the method were determined.

Injection-to-injection and day-to-day repeatability were calculated, as well as the confidence interval, all of them for three concentration levels (in the low, middle and high concentration range). For the injection-to-injection measurements, the same solution was analysed on the same day three times, whereas for the day-to-day measurements solutions prepared on three different days were analysed on three different days. All solutions were prepared in triplicates.

As performance statistics characterising the trueness, z-score was calculated for a certified reference material (CRM). CRM was acid wet digested and analysed in triplicates on three different days. Recoveries of known amount of spiked analytes in the following matrixes: milk cream, tomato sauce, black tea, salted lemon juice, were investigated. These food products were used for prediction model testing (in Step 4, see Figure 1). Both the spiked and the non-

Table 1. ICP-AES instrumental operating conditions.

RF generator (W)	1300
Plasma argon flow (l min^{-1})	15
Nebulizer argon flow (l min^{-1})	0.5
Auxiliary argon flow (l min^{-1})	0.2
Liquid uptake (ml min^{-1})	1
Optical viewing	Axial
Replicates	3
Spectral lines (nm)	396.153

spiked samples were treated identically prior to analysis.

Moreover, limit of detection (LOD) and limit of quantification (LOQ) were calculated. As a quality control criterion, it was verified that LOD is within three times the instrumental detection limit (IDL). Finally, day-to-day linearity was assessed.

Modelling

STATGRAPHICS Plus 5.1 for Windows (Statistical Graphics, Washington, DC, USA) was used to create multilevel factorial designs aiming at establishing experimental conditions, optimising the number of experiments, investigating variable significance, and modelling Al release.

First, a 5-factor MFD was constructed to explore the significance of the selected parameters (Step 2 in Figure 1). The idea of using a design of experiments is to limit the number of experiments, compared to the one-variable-at-a-time approach, by carefully selecting those experiments that cover the complete experimental design space. Estimation of the interaction effects is an additional advantage over the one-variable-at-a-

time approach. The experiments were randomly performed in triple and the effects of the different factors were interpreted using regression. A quadratic response surface area was constructed, represented by the following general equation:

$$\ln y = b_0 + b_1 x_1 + b_2 x_2 + \cdots + b_i x_i + b_{11} x_1^2$$
$$+ b_{22} x_2^2 + \cdots + b_{ii} x_i^2$$
$$+ b_{12} x_1 x_2 + b_{13} x_1 x_3 + \cdots + b_{ij} x_i x_j$$

where b_0 represents the intercept, b_i and b_{ij} the regression coefficients and x_i the factors tested. In this case, x_1–x_5 corresponds to temperature, contact time, pH, salt concentration and viscosity, respectively. The significance of the regression coefficients is a value for the significance of the effects of the different factors on the response. The regression coefficients of the products of two factors represent the significance of their interaction effects. The significance of the regression coefficient was investigated using ANOVA.

Second, a 4-factor MFD was created aiming at modelling Al leaching from different FCMs (Step 3 in Figure 1). Only parameters that were found to be significant in the 5-factor MFD were used for modelling. The parameters that were taken into account to establish predictive leaching models for each type of material were x_1–x_4.

Predictive force of the different models was investigated both with cross-validation and an independent data set carried out in different food products (Step 4 in Figure 1).

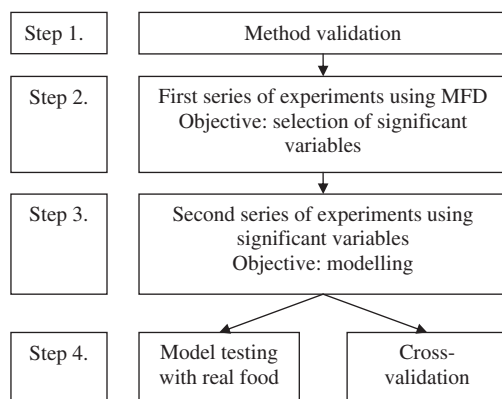Parameter intervals and levels of leaching experiments are given in Table 2.

Figure 1. Overview of the experimental design.

Materials and methods

All studied kitchenware, i.e. Al foil and plate, ceramic ware; glassware and stainless steel ware, and the food products used for model validation (milk cream,

Table 2. Variables and intervals for multilevel factorial designs of experiments.

	(Step 2) Parameter selection		(Step 3) Modelling	
	50[a]		50[a]	
Number of experiments	Interval	No. levels	Interval	No. levels
Temperature (°C)	20–200	4	20–180	3
Contact time (min)	30–120	4	30–120	3
pH	2–7	4	2–7	3
Salt concentration (g l^{-1})	0–10	3	0–10	3
Thickener concentration (g l^{-1})	0–40[b]	3	–	–

Notes: [a]Number of experiments optimised with STATGRAPHICS Plus. All experiments were carried out in triplicates in random order.
[b]0, 20, and 40 g l^{-1} corresponds to 1, 3.91 and 35.8 mPa.s.

tomato sauce, black tea, salted lemon juice, and light soup) were purchased in local retail stores.

To get accurate measurements at the $\mu g\,l^{-1}$ level, it is essential to perform detailed and reliable blank determination. It also allows the determination of Al contamination from the experimental conditions (Desboeufs et al. 2003). Ensuring clean conditions gives lower detection limits; thus the working environment was kept as clean as possible during the whole procedure. Therefore, the highest quality reagents were used when necessary to eliminate contamination and to ensure accuracy of results. Ultrapure, deionised Milli-Q® water (Millipore, Milford, MA, USA, specific resistivity $>18\,M\Omega\,cm^{-1}$) was used throughout the study. Ultrapur® nitric acid (HNO₃, 60%), used for digestion and for calibration standards, was purchased from Merck (Darmstadt, Germany). Prior to leaching tests, all kitchenware was washed in a detergent solution to remove small dust particles and abundantly rinsed with Milli-Q® water. Plastic labware and acid-cleaning procedures were used as necessary to eliminate contamination. As the importance of analytical environment and procedures is recognised as extremely important, digestion tubes were boiled with 10% of ultrapure® HNO₃ for at least an hour, and rinsed abundantly with Milli-Q® water before use. Disposable 15 and 50 ml Falcon tubes with caps were used to hold solutions. The rinsing solution used between the measurements is a high-purity Milli-Q® water acidified to 2% (v/v) with ultrapure® HNO₃. Atomic spectroscopy standard solution of Al was purchased from PerkinElmer (Shelton, CT, USA). Citric acid ($>99.5\%$ w/w) was purchased at Merck (Darmstadt, Germany). High purity sodium chloride was purchased from RPL (Leuven, Belgium). For viscosity measurements, modified starch, purchased in local retail store, was employed. All simulants were used immediately after preparation.

DORM-2 (Dogfish Muscle Certified Reference Material for Trace Metals), with a certified value for Al ($10.9 \pm 1.7\,mg\,kg^{-1}$) was purchased from National Research Council of Canada (Institute for National Measurement Standards, Montreal, Canada).

The experiments were carried out as follows: Al foil and Al plate were immersed in 20 ml extractant in decontaminated, loosely closed Teflon tubes. Al plate, ceramic ware, glassware, and metal ware (made of stainless steel) were filled with 20 ml of extractant and covered with decontaminated Teflon plates. For analysis, 5 ml of extractant was taken. At high temperatures (180 and 200°C) the evaporated simulant was replaced every 30 min with Milli-Q® water. Before analysis, extractant samples were digested with 5 ml of ultrapure® HNO₃. Digestion took place in three steps: first, the tubes were placed in an ultrasound bath for 1 h at 60°C. Afterwards, they were placed in an oven preheated at 190°C for 30 min in firmly closed Teflon

tubes and left to cool down to ambient temperature overnight. Finally, they were placed in the oven in loosely closed Teflon tubes at 190°C. Once the level of the sample reached $\sim 0.5\,ml$, digestion was stopped. The content of the tubes was poured into 15 ml Falcon tubes and diluted to a volume of 10 ml with MilliQ water (Elik 2005; Kazi et al. 2009). During experiments testing the prediction models with food products in different conditions, a volume of 0.45–5 ml of sample was digested in 5 ml of ultrapure® HNO₃ as described above. Each leaching experiment, as well as each digestion series was accompanied by two method blanks placed in decontaminated Teflon tubes. HNO₃ matrixes were chosen for digestion due to the oxidising ability of HNO₃, solubility of the nitrates, low blank values and its relative freedom from chemical and spectral interferences.

Increase in sample concentration may occur due to container transpiration defined as loss of vapour through the container walls or between the cap and threads. To avoid any changes in the concentration due to transpiration or contamination from the atmosphere, samples were kept closed and out of the hood area as much as possible (Gaines 2011). They were analysed in a short period of time (maximum 1 night).

The analyte concentration was obtained through external calibration. For mathematical simplicity, linear functions are preferred (Massart et al. 1997). Calibration of the instrument was performed by using low concentration standards.

Results and discussion

Method development and validation

All numerical results and their respective expressions relative to the method validation are summarised in Table 3.

Accuracy measurements were characterised with standard deviations (SD), relative standard deviations (RSD%), confidence intervals (CI) and z-score. All values were calculated at three concentration levels (5, 25 and 50 $\mu g\,l^{-1}$) as well as for DORM-2. The obtained values for RSD%, excerpted in Table 3, were compared to the Horwitz function and were all found to be within the suggested values (Massart et al. 1997). Results are considered satisfactory for z-scores when $|z\text{-score}| < 2$ (Yip and Tong 2009). However, the use of CRM does not necessarily guarantee trueness of the results owing to matrix differences between the CRM and the samples (Quevauviller 2004). Thus, recoveries from spiked food matrixes used for testing the prediction models were calculated. Matrices of interest were split into two portions: one portion was left unchanged, while the other was spiked with a known amount of standard. The concentration range of food matrixes was in the range 5.43–34.66 $\mu g\,l^{-1}$.

Table 3. Method validation parameters.

Parameter	Concentration / Figures of merit			
	$5\,\mu g\,l^{-1}$	$25\,\mu g\,l^{-1}$	$50\,\mu g\,l^{-1}$	$10.9 \pm 1.7\,\mu g\,l^{-1}$ (DORM-2)
Inj-to-inj SD[a]	0.08	0.09	0.26	0.26
Day-to-day SD[b]	0.19	0.51	0.85	1.06
Inj-to-inj RSD%[c]	1.76	0.36	0.52	0.96
Day-to-day RSD%[d]	3.74	1.99	1.65	11.11
Horwitz function[e]	12.56	9.86	8.88	11.17
Day-to-day CI[f] ($\mu g\,L^{-1}$)	5.07 ± 0.32	25.52 ± 0.86	50.40 ± 1.43	9.52 ± 1.19
z-score[g]				0.98
Recovery from spiking[h]		R (%) = 93 – 115%		
LOD[i]		$1.77\,\mu g\,l^{-1}$		
LOQ[j]		$5.89\,\mu g\,l^{-1}$		

Notes: [a,b]$SD = \sqrt{\frac{\sum(x-\bar{x})^2}{n-1}}$.
[c,d]$RSD\% = 100\frac{SD}{\bar{x}}$.
[e]$RSD\% = 2^{(1-0.5\log_{10}c)}$ with c: concentration expressed as decimal fraction in $kg\,kg^{-1}$.
[f]$CI = \bar{x} \pm \frac{SD \times t}{\sqrt{n}}$ with $t = 2.920$ for $n = 3$ at the confidence level 95%.
[g]$z = \frac{\bar{x}-x_{certified}}{SD}$.
[h]$R\% = 100\frac{c_{spiked}-c_{non-spiked}}{c_{spike}}$ with $c_{spike} = 20\,\mu g\,l^{-1}$.
[i]$x_{LOD} = \bar{x}_{bl} + 3SD$.
[j]$x_{LOQ} = \bar{x}_{bl} + 10SD$.

Recovery percentages were compared to the acceptable recovery percentages as function of the analyte concentration as outlined by the AOAC Peer Verified Methods program and were found to be within range (Taverniers et al. 2004).

Limit of detection (LOD), and limit of quantification were determined from 10 independent method blanks, prepared and measured each on different days (EURACHEM 1998). LOD was within three times the instrumental limit of detection IDL ($=0.91\,\mu g\,l^{-1}$). IDL characterises the internal variations of the instrument (van de Wiel 2003) and is calculated from 10 replicates of a blank as $3 \times SD$.

Day-to-day linearity was assessed by plotting the relative responses of the data points in function of the concentration on a log scale. The data points laid horizontally over the full range with a positive deviation at low concentrations, as expected from literature (Taverniers et al. 2004).

Leaching modelling

The extent of leaching depends:

- on the nature of the material and its composition (Al foil, Al plate, ceramic ware, glassware and stainless steel ware)
- physical conditions (temperature: x_1, contact time: x_2)
- capability of food to extract substances contained in the material (pH: x_3, salt concentration: x_4, viscosity: x_5)

In the present study, citric acid was used as food simulant. The choice of citric acid was motivated by different considerations. When compared to acetic acid and malic acid, it appears that citric acid is the strongest extractant of Al from ceramic ware with different glazes (Demont et al. 2012). These findings are in agreement with (Bi 1996). This latter article estimates also the extraction force of oxalic acid and suggests it to be stronger than that of citric acid. Karbouj (2007) suggest that the release of aluminium is higher with citrate than that with both oxalate and lactate. Moreover, citric acid is present in abundance in fruits and vegetables and used throughout the world as a food additive. Therefore, citric acid was chosen as food simulant in the present study.

The predictive forces of the models were tested with two different methods:

- 10-fold cross-validation
- Experimental, independent dataset investigating Al leaching of real food products

This latter test is especially important due to the high variety of the physical–chemical properties of foods and food products.

Five-factor multilevel factorial design of experiments: parameter significance

Multilevel factorial design of experiments (MFD) has been chosen as a mean to study the influence of five parameters. The experimental conditions were established, and the number of experiments optimised with
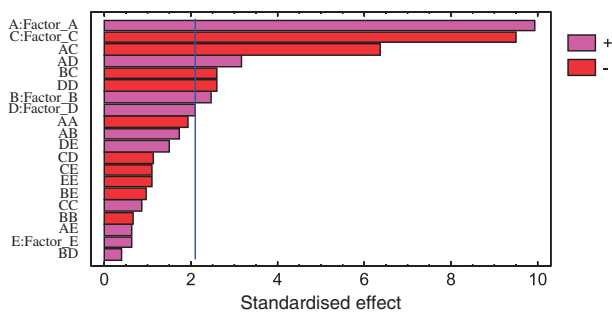
Figure 2. Standardised Pareto chart for Al plate as a result of the 5-factor MFD with Factor A: temperature; Factor B: contact time; Factor C: pH; Factor D: salt concentration; and Factor E: viscosity.
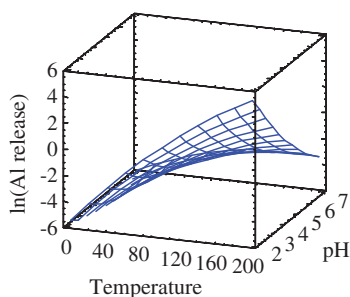

Figure 3. Response surface for temperature and pH with contact time $=75$ min, salt concentration $=5$ g l^{-1}.

STATGRAPHICS Plus. Experiments were conducted on Al plates in triplicates. For practical reasons, only two level interaction effects were studied here. In general, it can be considered that higher interaction levels are insignificant (Massart et al. 1997).

A first series of MFD experiment allowing the selection of the significant parameters among the studied parameters was carried out in Al plate (Step 2 in Figure 1). The standardised Pareto chart, established for Al plate with STATGRAPHICS Plus, is given in Figure 2. In this case, eight effects have *p*-values less than 0.05, indicating that they are significantly different from zero at the 95% confidence level. It can be observed that interaction effects are important, especially between temperature and pH. This means that these variables are significantly varying together as is shown by the response surface in Figure 3. It can be concluded that the highest leaching occur with the highest temperature and lowest pH. On the other hand, neither viscosity nor its interaction effects did appear to significantly influence Al release from Al plate.

The r^2 statistic of the 5-factor MFD indicates that the model as fitted explains 96.95% of the variability in Al release and 95.89% when excluding viscosity. Thus, it can be concluded that viscosity does not influence significantly the extent of Al release from Al plate in

the studied experimental conditions compared to the four other parameters.

Four-factor multilevel design of experiments: modelling

The prediction models were established with temperature, contact time, pH and salt concentration. The experimental conditions were established and the number of experiments optimised with STATGRAPHICS Plus. The experimental results obtained with this new MFD were used to establish a model for each type of contact material. Regression coefficients, according to Equation (1), are listed in Table 4. For each material, temperature, time, pH, salt concentration and temperature/pH interaction are significant factors (see Table 4 in bold).

In Figure 4, models established for Al plate with 5-factor MFD excluding viscosity and 4-factor MFD were compared to each other. Temperature, time, pH and salt concentrations are varied together from 20 to 180°C, from 30 to 142 min, from 7 to 2.2, and from 0 to 9.6 g l^{-1}, respectively, at regular intervals. The two models are closely following each other. It can be concluded, therefore, that the significance of viscosity compared to the other factors in the present experimental conditions is negligible. Concerning the high Al release values at extreme conditions, during experiments, complete dissolution of both Al foil and Al plate was observed at extreme conditions ($x_1 = 180$°C, $x_2 = 120$ min, $x_3 = 2$ and $x_4 = 10$ g l^{-1}). Moreover, small difference of path between the two models can be due to the fact that two different brand of Al plate was used for the respective sets of experiments.

Because the model has been built for prediction purposes, validation is of great importance. Both cross-validation and an independent experimental data set have been used to assess of how accurately the models will perform. The results of 10-fold cross-validation are suggesting that models have a good prediction force for Al foil, Al plate, and ceramic ware as illustrated in Figure 5. On the other hand, for glassware and stainless steel ware, the predictive forces of the models are estimated to be less good, $r^2 = 0.5825$ and 0.4605, respectively. The poor quality of both glassware and stainless steel ware models can be explained by the low Al content of the respective food wares, low leaching rates and interspecific variability of commercially available materials (Bolle et al. 2000). Indeed, in these two kitchenwares, the quantity of the extracted Al is generally close to, or below LOQ. As illustrated on Figure 6d and e, at pH 4.5 and salt concentration of 5 g l^{-1}, typical pH and salt concentration of tomato sauce, the leaching of Al from both glass and stainless steel ware is below the limit of quantification (experimental datapoints sit on the LOQ line owing to the upper bound limit

Table 4. Regression coefficients for 4-factor MFD in different kitchenware materials according to Equation (1).

	b_0	b_1	b_2	b_3	b_4	b_{11}	b_{12}	b_{13}	b_{14}	b_{22}	b_{23}	b_{24}	b_{33}	b_{34}	b_{44}
Al foil	-6.95	$\mathbf{4.67 \times 10^{-2}}$	$\mathbf{2.37 \times 10^{-2}}$	-2.35×10^{-1}	$\mathbf{3.30 \times 10^{-2}}$	-3.04×10^{-5}	$\mathbf{1.25 \times 10^{-4}}$	$\mathbf{-4.79 \times 10^{-3}}$	1.14×10^{-3}	-8.76×10^{-5}	-2.80×10^{-3}	$\mathbf{2.14 \times 10^{-3}}$	5.88×10^{-2}	-1.44×10^{-2}	-7.08×10^{-3}
Al plate	-7.97	$\mathbf{7.38 \times 10^{-2}}$	$\mathbf{4.88 \times 10^{-2}}$	-3.64×10^{-1}	$\mathbf{5.16 \times 10^{-1}}$	-1.56×10^{-4}	9.73×10^{-5}	$\mathbf{-4.41 \times 10^{-3}}$	1.87×10^{-5}	-1.41×10^{-4}	$\mathbf{-5.85 \times 10^{-3}}$	$\mathbf{1.30 \times 10^{-3}}$	8.69×10^{-2}	-5.17×10^{-2}	-2.03×10^{-2}
Al plate*	-7.97	$\mathbf{6.94 \times 10^{-2}}$	$\mathbf{5.40 \times 10^{-2}}$	-5.61×10^{-1}	$\mathbf{5.93 \times 10^{-1}}$	-1.01×10^{-4}	9.25×10^{-5}	$\mathbf{-8.21 \times 10^{-3}}$	$\mathbf{2.27 \times 10^{-3}}$	-2.44×10^{-4}	$\mathbf{-4.56 \times 10^{-3}}$	-8.34×10^{-4}	1.37×10^{-1}	-5.58×10^{-2}	-4.54×10^{-2}
Ceramic	-5.79	$\mathbf{1.33 \times 10^{-2}}$	$\mathbf{6.54 \times 10^{-3}}$	-4.00×10^{-1}	$\mathbf{6.77 \times 10^{-2}}$	-8.14×10^{-6}	$\mathbf{-3.71 \times 10^{-5}}$	$\mathbf{-1.11 \times 10^{-3}}$	-1.65×10^{-4}	1.24×10^{-5}	3.02×10^{-4}	-1.46×10^{-4}	$\mathbf{3.43 \times 10^{-2}}$	-2.26×10^{-4}	-2.10×10^{-3}
Glass	-2.52	$\mathbf{-3.20 \times 10^{-3}}$	$\mathbf{1.16 \times 10^{-2}}$	$\mathbf{-2.32}$	$\mathbf{-2.37 \times 10^{-1}}$	-1.12×10^{-6}	5.09×10^{-5}	$\mathbf{1.54 \times 10^{-3}}$	4.41×10^{-4}	-8.74×10^{-5}	3.06×10^{-4}	1.17×10^{-4}	$\mathbf{2.00 \times 10^{-1}}$	-2.05×10^{-2}	2.23×10^{-2}
Metal	-5.55	$\mathbf{-1.50 \times 10^{-3}}$	$\mathbf{-3.39 \times 10^{-2}}$	$\mathbf{-2.69 \times 10^{-1}}$	$\mathbf{-7.62 \times 10^{-2}}$	9.19×10^{-6}	$\mathbf{1.33 \times 10^{-4}}$	$\mathbf{-1.38 \times 10^{-3}}$	1.82×10^{-4}	$\mathbf{2.62 \times 10^{-4}}$	-2.21×10^{-3}	7.98×10^{-4}	2.53×10^{-2}	1.39×10^{-2}	1.52×10^{-3}

Notes: Figures in bold are significant parameters.
*Regression coefficients for 5-factor MFD excluding viscosity from model.
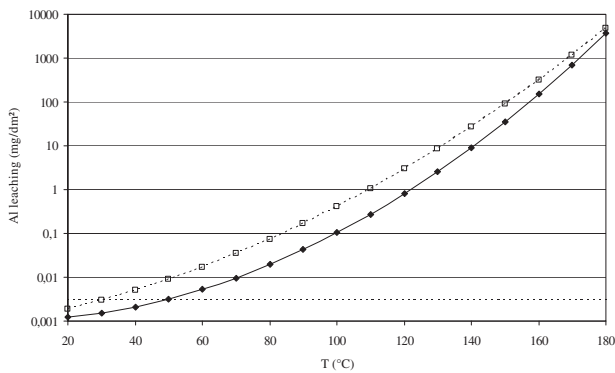
Figure 4. Five-factor MFD model excluding viscosity (◆) and 4-factor MFD model (□) varying together temperature from 20 to 180°C; contact time from 30 to 142 min; pH from 7 to 2.2; salt concentration from 0 to 9.6 g l^{-1}. Regression coefficients are excerpted in Table 4.

consideration). It is, however, worth noting that the established models predict quantities below LOQ when the measured Al release is indeed below LOQ. On the other hand, in Al foil, Al plate and ceramic ware (Figure 6a, b and c, respectively), the released Al is quantifiable in the considered experimental conditions and is above the LOQ. The quality of the model for ceramic ware is less good than for Al foil and Al plate which can be explained by the variability of the commercially available objects supposed to be alike. That may explain the order of quality of the models: Al foil > Al plate > ceramic ware > glassware > stainless steel ware.

Besides cross-validation, the models, established with a food simulant, were also evaluated in real food samples. Milk cream, tomato sauce, tea, salted lemon juice and light soup were used as extractants in Al foil, Al plate, ceramic ware, glassware and stainless steel
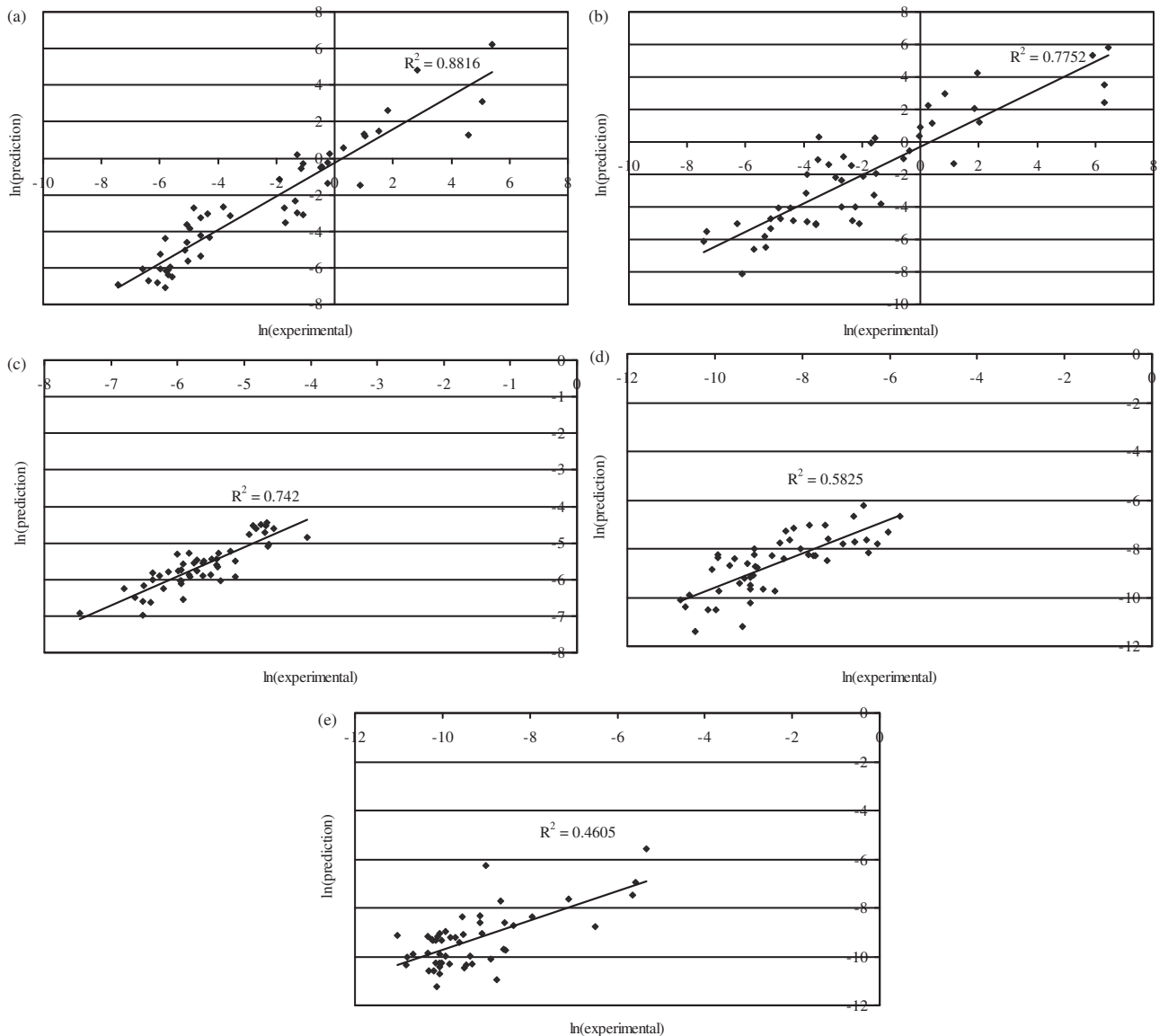

Figure 5. Cross-validation of models for (a) Al foil, (b) Al plate, (c) ceramic ware, (d) glassware, and (e) stainless steel ware.

ware, respectively. Experimental leaching values and prediction are given in Table 5. For Al foil, Al plate and ceramic ware, the results are in the same order of magnitude, giving acceptable errors (see Table 5). For glass and stainless steel ware, prediction is less good, but stays in the same order of magnitude. The high error values for these two latter kitchen wares can be explained by the fact that the measured Al concentrations in the respective food products were lower than the predicted ones. Thus, it can be concluded that glassware and stainless steel do not contribute significantly to Al intake, and Al leaching reaches a quantifiable level only at extreme conditions.

On the other hand, Al ingestion due to the use of Al plate, Al foil, and to a lesser extent ceramic ware may be important, as illustrated in the following example. With the help of the prediction models, Al release into commercially available lasagnes was calculated. The salt concentration of these lasagnes, sold in Al plate,

varies from 7.84 to $9 \, \mathrm{g \, l^{-1}}$ of salt (stated on the labels). Their pH lay between 5.13 and 6.06. Following instructions, the lasagne should be heated up to 180°C for 30 min. After the prediction model, it corresponds to $0.55–1.61 \, \mathrm{mg \, dm^{-2}}$ of Al. With the surface of the Al plate being equal to $\sim 3 \, \mathrm{dm^2}$, it means that by eating a portion of lasagne (m = 400 g), one may ingest an extra 1.04–2.63 mg of Al. It corresponds to $0.02–0.04 \, \mathrm{mg \, kg^{-1}}$ bw for an average person weighing 60 kg, which is 12–31% of the maximal daily ingestion after the PTWI. By replacing the Al plate with ceramic ware, this would drop to 0.10–0.12%, 0.03–0.05% in glassware, and 0.007–0.008% in stainless steel. This example demonstrates the importance of choice of the contact material used for food preparation. Moreover, it illustrates the usefulness of the prediction models to estimate the food enrichment in Al while using FCMs for food preparation and serving.
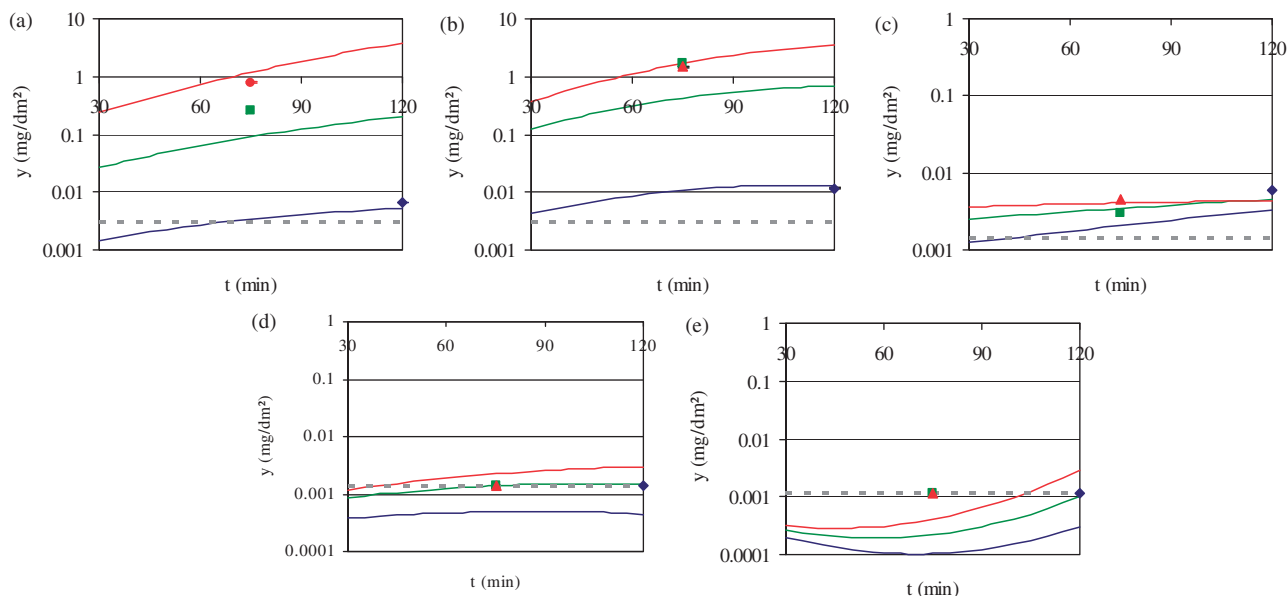

Figure 6. Predicted (blue/lowest line at 20°C, green/middle line at 100°C, red/upper line at 180°C) and experimental (♦ at 20°C, ■ at 100°C, ▲ at 180°C) leaching data at pH 4.5 and salt concentration = $5 \, \mathrm{g \, l^{-1}}$ in (a) Al foil; (b) Al plate; (c) ceramic ware; (d) glassware; and (e) stainless steel. LOQ is schematised with a discontinuous line.

Table 5. Evaluation of prediction models with real food.

Kitchenware	Extractant	Temperature (°C)	Contact time (min)	Prediction $(\mathrm{mg \, dm^{-2} \, h^{-1}})$	m/S $(\mathrm{mg \, dm^{-2} \, h^{-1}})$	Error* (%)
Al foil	Milk cream	180	60	5.97×10^{-2}	$7.20 \times 10^{-2} \pm 3.11 \times 10^{-2}$	17.1%
Al plate	Tomato soup	180	45	3.48×10^{-1}	$4.81 \times 10^{-1} \pm 1.56 \times 10^{-1}$	27.6%
Ceramicware	Tea	80	30	3.69×10^{-3}	$1.43 \times 10^{-3} \pm 2.40 \times 10^{-3}$	74.2%
Glassware	Lemon juice with salt	120	75	2.10×10^{-3}	$5.66 \times 10^{-4} \pm 3.23 \times 10^{-4}$	271%
Metalware	Light soup	100	20	9.65×10^{-4}	$3.65 \times 10^{-4} \pm 3.85 \times 10^{-5}$	164%

Note: *Error (%) = $\left| \dfrac{(m/S)_{\mathrm{prediction}} - (m/S)_{\mathrm{experimental}}}{(m/S)_{\mathrm{experimental}}} \right| \cdot 100$.

Together with the surface of kitchenware used by a given population, the models also allow one to calculate the Al intake from kitchenware. Thus, from the models, it appears that the materials used for food preparation and releasing the most important quantities of Al are Al foil and Al plate. Ceramic ware, however, should not be ignored due to its more frequent use in everyday life, especially because they generally serve as FCMs for preparations necessitating high temperatures, parameter that played the most important role after pH in Al release from ceramic ware. By replacing these three FCMs with alternative food ware, preferably glass or stainless steel ware, the intake of Al could be greatly reduced. Moreover, it is also suggested that in future directives, if any, aiming at control Al release from FCM, temperature, contact time, pH and salt concentration must be carefully chosen since these parameters significantly influence Al release. Temperature and pH need special attention because their interaction is significant in Al leaching from each FCM.

Conclusion

A reliable analytical method, preceded by wet digestion as sample preparation, using ICP-AES was developed and validated for Al analysis in both food simulants and five different food products. LOD and LOQ were found to be within the typical range reported in the literature (Desboeufs et al. 2003). Repeatability on three concentration levels over the full range of the analytical method prepared three times and measured on three different days are acceptable. The *z*-score is below 2% and recovery percentages as a function of the analyte concentration are satisfactory.

Prediction models of Al release from kitchenware under typical cooking and serving conditions were established for Al foil and plate, ceramic ware, glassware, and stainless steel ware, all of them potential source of Al. Multilevel factorial design of experiments was chosen as a tool to study the influence of the following variables: temperature, contact time, pH, salt concentration, and viscosity, and their interactions. The use of design of experiments allowed reducing the number of experiments and, at the same time, evaluating the influence of each studied variable as well as their interaction effects. It was concluded that viscosity did not significantly influenced Al release compared to the other four variables (temperature, contact time, pH and salt concentration). Therefore, predictive models were established with temperature, contact time, pH and salt concentration (4-factor MFD). A good correlation (0.9982) between the 5-factor MFD and the 4-factor MFD model for Al plate was found, reinforcing the conclusion that viscosity, compared to the four other studied parameters, was not significant.

The following parameters and interaction effect were in each FCM significant: temperature, contact time, pH and salt concentration, and the interaction effect between temperature and pH. Therefore, for future directives aiming at testing Al release from FCMs, experimental conditions including temperature, contact time, pH, and salt concentration should be carefully considered. The cross-validation indicated that the predictive force of the models of Al plate, Al foil, and ceramic ware is good, whereas for glassware and stainless steel ware it is less good. Three reasons were found that could explain the weak predictive force of these models: first, low Al content of the food ware (0.69% (wt) and 0.03% of Al of the total mass); second, the low Al release resulting in concentrations to be measured close to or even below the LOQ; third, the inter-specific differences between "identical" vessels. Besides cross-validation, the established prediction models were tested with real foods. It was concluded that, for all materials, the prediction and the experimental results are within the same range, but predictions are working less efficiently for glassware and stainless steel ware, as expected from the results obtained with cross-validation.

The present results suggest that the main contribution of Al coming from FCM is mainly due to the use of Al foil and Al plate, and, to a lesser extent, ceramic ware.

The established models can serve to predict the amount of Al released into food from the studied FCMs if the variables of temperature, contact time, pH and salt concentration are known or can be estimated. In combination with data on the surface of utensils used, they can serve as a tool to estimate the dietary intake of Al through Al leaching from FCMs.

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