Speciation study of aluminium in beverages by Competitive Ligand Exchange–Adsorptive Stripping Voltammetry

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ABSTRACT

Competitive Ligand Exchange–Adsorptive Stripping Voltammetry (CLE–AdSV) was used for determining the speciation of aluminium in commonly consumed beverages (water, tea, infusion, coffee, orange juice, tomato juice, beer and red wine). Aluminium determination involves the adsorption of Al-complexes with the ligand cupferron onto a hanging mercury drop electrode. All samples were studied at pH 6.5 with an accumulation step at −0.60 V (all potential values in the paper are given versus the Ag/AgCl, [KCl]=3 M reference electrode) during 60 s, and a final cupferron concentration of 4×10^{-4} M. These conditions were used to establish (i) the concentration of electro-labile aluminium, (ii) the range of ligand concentrations and (iii) the conditional stability constants of beverage samples using titration procedures. The results based on Ruzic plots were compared to computer simulation with Visual MINTEQ. This comparison suggests that labile monomeric Al-forms and soluble organic complexes of low molecular weight can be quantified by the CLE–AdSV procedure. Overall the relative uncertainties on the determination of the electro-active Al fraction and the complexing parameters, i.e., concentration and conditional stability constant of natural ligands in the samples, are less than 15%. Thanks to these results, information on Al bioavailability in beverages was collected and discussed. This study also illustrates the value of computer simulations when complex, time-consuming voltammetric techniques are applied.

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1. Introduction

Human exposure to aluminium has dramatically increased over the past decades [1]. Aluminium is, however, a detrimental metal, suspected of an active role in various diseases [1,2]. Many applications, such as food processing and packaging, bring humans in direct contact with Al through foods and drinks [3–6]. Moreover, acid rains release Al from soils and introduce it into the food chain [7–9]. This chronic exposure through diet, although much lower than exposure at therapeutic levels, is worrying. Numerous papers have been published on the toxicity of Al referring to its potential threat in terms of public health [10–22]. Al speciation is a key factor determining its bioavailability and toxicity. While most Al species are harmless, "labile" Al forms can be absorbed into the blood in the small intestine, and consequently are potentially toxic. Thanks to speciation analysis, information on bioavailability can be collected [23–24].

In the present study, Al speciation was studied in some of the most consumed beverages (water, tea, infusion, coffee, orange juice, tomato juice, beer and red wine). The ion Al^{3+} is mainly absorbed from the gastrointestinal tract in its hydrated form by solvent drag, i.e., para-cellular passive diffusion. This probably explains why drinking water appears as the first quantifiable source of Al contamination, while containing less Al than solid food [1,24].

Next to water, coffee and tea are the most widely consumed beverages in the world. Tea is one of the very few plants that accumulate Al [25]. Dietary acids occur in fruits and vegetables and are found in their respective juices (such as orange juice and tomato juice). These acids commonly serve as taste enhancers, acting as potential ligands for the Al^{3+} ion and enhance Al absorption [26]. Citric acid is one of the most predominant taste enhancers in foods and beverages, and its influence on Al speciation in tea and infusion was investigated. On the other hand, it has been suggested that silicon, in the form of silicic (Si) or orthosilicic acid may decrease the bioavailability of Al [27–29]. Bioavailable Si is abundantly present in beer [30–31]. Red wine may also contain elevated Al levels due to aluminium storage material, aluminium content in soil, use of vine pest treatment products, filtration of wine on diatomaceous earth, and addition of bentonite [32].

To determine Al speciation in beverages, a sensitive and accurate method is required. Among all speciation methods, electrochemistry has been used to measure trace metal speciation [33],

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and stripping voltammetry is probably the most widespread technique. It offers high sensitivity, selectivity, low detection limit and low risk of sample contamination during analysis. Only few studies have focused on Al speciation in foods and drinks by Competitive Ligand Exchange–Adsorptive Stripping Voltammetry (CLE–AdSV) [34–36]. The technique consists of adding a specific ligand to the sample, which will form an adsorptive complex with aluminium. The metal ion as its complex is adsorbed onto the working electrode at a fixed potential, the reduction of the electro-active functional groups of the metal–ligand complex enables the determination of the metal concentration. To complex Al in waters, a variety of ligands has been used, e.g. cupferron [37], DASA [38], oxine [39], pyrogallol red [40], arseno III [41], solochrome violet RS [42–43]. The lowest detection limits were obtained with cupferron and DASA [37–38].

The present paper aims at developing a sensitive adsorptive stripping method with cupferron as ligand and to apply it to determine aluminium speciation in beverages. In addition computer generated data with Visual MINTEQ were used in support of the experiments in order to check the relevance of the speciation outcomes.

2. Materials and methods

2.1. Reagents and instrumentation

All solutions were prepared with Milli-Q water (Millipore, 18.2 MΩ cm) and all reagents (HNO$_3$, KCl) used were of analytical grade (Merck). Standard solution of aluminium was prepared daily by dilutions of a stock solution of 1000 mg L^{-1} (Spectrosol grade, Merck) in 2% HNO$_3$. A stock solution of the cupferron ligand 0.02 M (AnalaR grade, Merck) was prepared weekly in water. A pH acetate buffer stock solution (0.1 M) of pH=6.5 was prepared weekly and used as supporting electrolyte.

Voltammetric measurements were performed using a 663 VA stand (Metrohm, Switzerland) equipped with electrodes, a μAutolab III potentiostat and GPES 4.9 software. A hanging mercury drop electrode (HMDE) with a surface of 0.52 mm^2 (size 3) was used as a working electrode. The potential was measured against Ag/AgCl, KCl=3 M reference electrode (E=+0.208 V versus NHE at 25 °C) and a glassy carbon rod was used as counter electrode. HR-ICP-MS measurements (Thermo Finnigan Element II) were carried out to determine the total dissolved metal concentrations in the

previously filtrated samples at 0.45 μm and acidified at pH~2 with 1 M suprapur nitric acid solution (Merck); 1 ppb of indium was used as internal standard. For a multi-element analysis, three standards were necessary to carry out an external calibration (XIII from Merck, ICM-224 and SM70 from Radion). The detection limit of the method was 24 nM for Al in the high resolution mode.

2.2. Analytical procedure for AdSV determinations

Different beverages such as mineral water, tea, coffee, fruit juices or alcohol (beer, wine) were bought in a local supermarket to have a panel of the drinks consumed by the Belgian population.

2.2.1. Sample preparation

All beverages were filtered on 0.45 μm before analysis by voltammetry. As fruit juices contain pulp, these samples were previously centrifuged before filtration. Additionally, for samples containing high concentration of total aluminium, dilution of 1:10 (fruit juices and red wine) or 1:100 (green and black tea) was carried out.

2.2.2. Sample analysis

Prior to the measurement, dissolved oxygen was removed by purging the solution with nitrogen for 10 min and for an additional 20 s before each scan. The procedure to determine the electro-labile aluminium concentration by CLE/AdSV was adapted from Wang et al. [37] and Qiong et al. [36]. In addition to the 20 μL of acetate buffer solution, 20 μL of 0.02 M cupferron solution were added to 20 mL of filtered sample. This solution was then allowed to equilibrate for 24 h to achieve a new thermodynamic equilibrium previously disturbed by the ligand addition. After this rest period, the solution was transferred into the voltammetric cell and purged with nitrogen. The voltammetric cell potential was set to – 0.6 V for 60 s while stirring at 1500 min^{-1}. After a rest period of 5 s, the stripping step occurred in negative direction. After the electro-active species accumulation at the mercury drop electrode, the differential pulse ramp employed for the redissolution process was used with the following parameters: pulse amplitude 20 mV, potential step increment 2 mV, time between pulses 0.1 s and pulse duration 0.04 s. With the CLE/AdSV method, the added cupferron ligand and the naturally occurring organic ligands enter in competition. The concentration of electro-labile aluminium
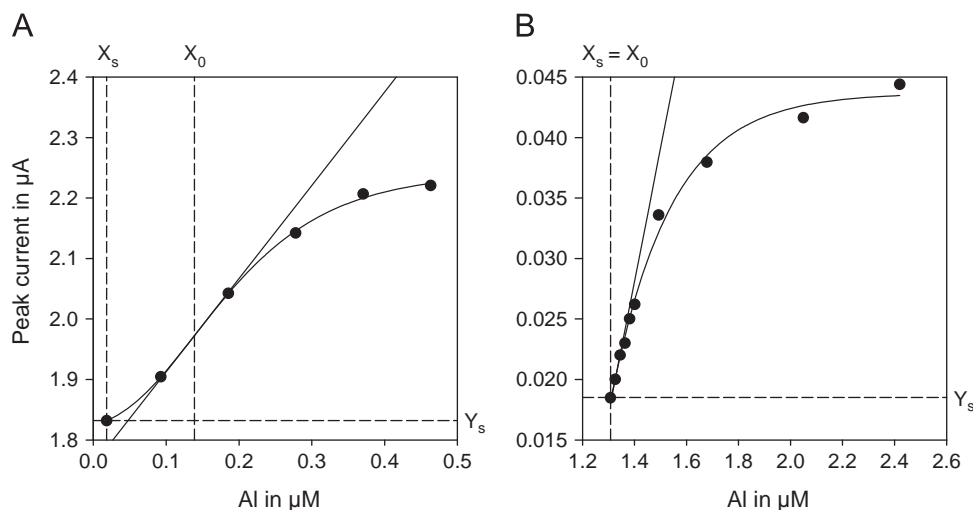

Fig. 1. Determination of aluminium by titration. X_s is the initial concentration of Al in the sample, X_0 is the concentration of Al at the inflection point and Y_s is the peak current at the measurement electrode corresponding to X_s. The titration curve has the appearance of a sigmoid (A) or a hyperbole (B) when the complexing capacity of the system is saturated.

[Al]$_{AdSV}$ corresponds approximately to:

$$[Al]_{AdSV} = [Al'] + [Al-cupferron] \tag{1}$$

where [Al'] is the remaining concentration of inorganic aluminium and [Al–cupferron] the concentration of aluminium complexed by cupferron. With this technique, the CLE/AdSV aluminium concentration is equal to the ratio of the aluminium reduction peak current (A) by the sensitivity S (A mol^{-1}) of the Al–cupferron titration curve.

2.3. Data analysis

Titration is an important technique in voltammetry because it allows the simultaneous determination of (i) the concentration of the labile fraction, (ii) the concentrations of organic ligands and (iii) the values of the equilibrium constants or stability constants associated with the reactions of complexion in the sample. It consists of measuring the electrochemical response by gradually increasing the concentration of aluminium in the sample by the method of standard additions. Usually the titration curve has the appearance of a sigmoid, sometimes hyperbole when the complexing ability of the system is saturated (Fig. 1). In the linear part, the aluminium is no longer complexed by organic ligands. The titration curve was fitted by means of a least square technique using a Gompertz function with 3 parameters:

$$y = a e^{(-e^{(x_0 - x/b)})} \tag{2}$$

where a, b and x_0 are the model parameters to be optimized. As indicated in Fig. 1, [Al]$_{AdSV}$ in the sample is determined by the y_s/p ratio where y_s is the reduction current in the measuring electrode and p the slope of the tangent to the curve

$$p = \left(\frac{\partial y}{\partial x}\right) = \frac{a}{b} e^{\left(\left(x_0 - x - b e^{(x_0 - x/b)}\right)/b\right)} \tag{3}$$

when the titration curve follows a sigmoidal function (Fig. 1A), the slope of the tangent is calculated at the inflection point ($x \rightarrow x_0$). Under this condition, Eq. (2)=0.37a/b. When the titration curve follows a hyperbolic function (Fig. 1B), the slope of the tangent is calculated at the origin ($x \rightarrow x_s$).

Linearization of the titration data was performed using the Ruzic transformation [44]. This allows determining the concentration of the ligands naturally present in the sample and the apparent equilibrium constant K_{Al-L} according to the following reaction:
$$Al + L Al \Leftrightarrow L$$

$$\text{with} \quad K_{Al-L} = \frac{[Al-L]}{[Al][L]} \tag{4}$$

At any point of the titration curve, the total concentrations of aluminium and ligands are given by the following relationships:

$$\begin{cases} [Al]_T = [Al](1 + K_{Al-L}[L]) \\ [L]_T = [L](1 + K_{Al-L}[Al]) \end{cases} \tag{5}$$

If [Al]$_{AdSV}$ is determined by the ratio y_s/p, the non-electro labile fraction at any point of the titration curve is given by [Al]$_T$ − [Al]$_{AdSV}$. Rearranging Eq. (5) gives the following relationship:

$$[Al]_{AdSV}/[Al]_{non-labile} = [Al]_{AdSV}/[L]_T + 1/([L]_T K_{Al-L}) \tag{6}$$

Accordingly, a plot of [Al]$_{AdSV}$/[Al]$_{non-labile}$ versus [Al]$_{AdSV}$ provides a straight line with slope=1/[L]$_T$ and intercept=1/([L]$_T K_{Al-L}$) from which the complexing ability of the system is inferred (Fig. 2). The application of this method requires, however, the knowledge of [Al]$_T$ in the sample before titration, which was determined using a HR-ICP-MS as described in Section 2.1.

Visual MINTEQ, an equilibrium computer modelling program, was then used as a complement to CLE/AdSV in speciation
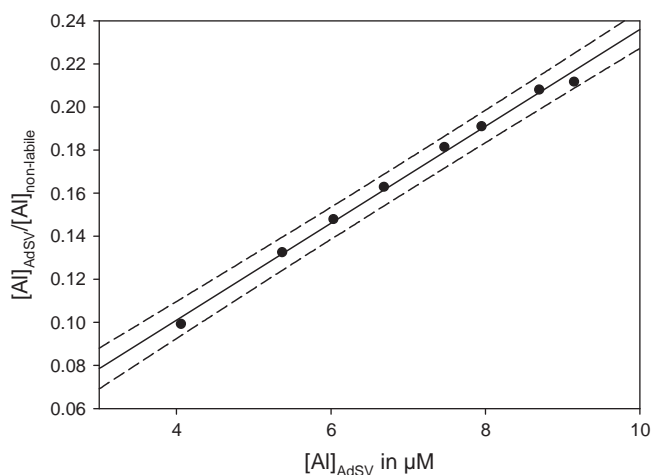

Fig. 2. Transformation of Ruzic [44] for a black tea sample. Experimental conditions are described in Section 2.2. Dotted lines represent the 95% prediction interval.

assessment because it allows predicting the species, concentration and percentage for all of the species in the Al organic and inorganic fraction. Visual MINTEQ was compiled in Visual Basic Net 2005 and released by Gustafsson in 2011 [45]. In parallel a code for computing Al speciation in Matlab was implemented. This code used conditional stability constants for Al-complexes provided by Visual MINTEQ and performed Monte-Carlo analyses. In these computations, a random sampling from distributions assigned to each model variable was carried out, the speciation model was then solved and the process repeated until a probability distribution function (pdf) of the results was generated. The pdfs of the modelling outputs were then directly compared with the available CLE/AdSV measurements and their uncertainty.

3. Results and discussions

Preliminary measurements have been carried out by cyclic voltammetry to check the possibility of determining Al concentrations in drinking water samples in the presence of cupferron. At pH 6.5, an aluminium/cupferron peak is detected at −1.40 V in agreement with the study of Wang et al. [37] and Kefala et al. [46]. All experiments were carried out at pH 6.5 because it represents the median value found in the small intestine where much of the absorption of nutrients and mineral takes place [47].

3.1. Performance parameters of the CLE/AdSV procedure

The voltammetric parameters were optimized to improve the sensitivity and the precision of the method. These parameters are summarized in Table 1. Overall, a deposition time of 60 s at a potential of −0.6 V was chosen to obtain a satisfactory compromise between the detection limit and the duration of the experiment. Additionally, to ensure an efficient complexation of the electro-active aluminium fraction in the samples, the cupferron concentration was fixed at 4×10^{-4} M. Under these experimental conditions, a linear concentration range was obtained for each metal titration curve at pH 6.5. Using CLE–AdSV, the linear range corresponds to the situation where all of the stronger natural ligands present in the samples have been saturated with aluminium (see Fig. 1). We noticed that the extent of this response was variable depending on the studied matrix ranging from ∼0.4 μM (e.g. Tea) to 2 μM (e.g. Tomato juice). The limit of detection (LoD) was defined by a current peak for which the signal/noise ratio was equal to 3/1 at a deposition time of 60 s. This LoD is also variable

according to the matrix with values ranging from 0.05 to 0.1 μM. The repeatability of the method was estimated on a tea sample ($n=21$) dosing ∼4 μM of electro active aluminium. The relative standard deviations obtained in this experiment were 3%. These results are quite comparable to those provided by Kefala et al. [46] but with a limit of detection 2–3 times higher, which could be explained by the selected deposition time, i.e., 4 times lower than that of [46] (Table 1) and by the complexity of some sample matrices (e.g. orange and tomato juices).

The accuracy of the method was established with a reference material made of riverine water (SRLS-5) and with a sample of green tea acidified to pH 2. The CLE–AdSV results were cross-checked with those measured with HR-ICP-MS. Table 2 indicates satisfactory agreement both regarding the measurement techniques (CLE–AdSV versus ICP-MS) and the certified value, confirming thereby that all the Al species in the CRM and in the acidified tea sample were present under electro-active metal forms.

Table 1
Optimized parameters for Al determination by CLE–AdSV in beverages.

CLE–AdSV	Parameters
Purge	600 or 20 s
Accumulation step	
Deposition potential	−0.6 V
Deposition time	60 s
Equilibration time	5 s
Measuring step	
Potential window	−0.4 to −1.7 V
Step potential	2 mV
Amplitude	20 mV
Modulation time	0.04 s
Interval time	0.1 s

Table 2
Analytical results of Al concentrations in CRM SLRS-5 and in a green tea sample acidified at pH 2. The certified value of SLRS-5 is 1.8 ± 0.2 μM.

Sample	Method	[Al] (μM)	St. dev. (μM)
SLRS-5 ($n=5$)	HR-ICP-MS	1.7	0.2
	CLE–AdSV	1.6	0.1
Green tea ($n=5$)	HR-ICP-MS	40	4
	CLE–AdSV	37	4

3.2. Speciation of aluminium in beverage samples

The CLE–AdSV method described above was used to determine the "labile (=electro active Al species or $[Al]_{AdSV}$) and non-labile" Al fractions (=$[Al]_T - [Al]_{AdSV}$) in popular beverages, and to assess the complexing capacity of the samples (concentration and condition stability constant of natural ligands). The Al concentrations, which were determined from the titration curves (see Fig. 1), are summarized in Table 3. The levels of $[Al]_T$ measured by HR-ICP-MS in mineral waters and tap water in Brussels were generally very low < 0.1 μM (< 2.7 μg L^{-1}). Although below the LoD for the CLE–AdSV procedure, it is likely that the dissolved aluminium was mainly present under labile monomeric forms, i.e. aqueous inorganic complexes easily exchangeable depending on the pH. The speciation of Al calculated using Visual MINTEQ and the concentrations of ions listed on the bottled labelling is illustrated in Fig. 3. In mineral waters containing very low concentrations of dissolved organic matter, the solubility of aluminium increases at lower pH due to the formation of complexes $Al(OH)_2^+$ and $Al(H_2O)_6^{3+}$, often abbreviated Al^{3+} and called free aluminium. $Al(OH)_3$ is an important solid species at pH between 6 and 8, whereas at pH 8, the predominant species is $Al(OH)_4^-$, which is soluble again [48]. The form in which aluminium is present in water also depends on

Fig. 3. Distribution of aluminium species in mineral water as a function of pH. The profiles are calculated using the software Visual MINTEQ and the concentrations of ions listed on the bottled labelling.

Table 3
Al concentrations and complexing parameters in usual consumption beverages. Concentrations $\pm$ standard deviations are expressed in μM. LoD reflects a peak current whose signal/noise ratio is $\leq 3/1$. $[Al]_T$=total aluminium concentration; $[Al]_{AdSV}$=electro-active aluminium concentration; NA=not available.

Sample	$[Al]_T$ (μM)	$[Al]_{AdSV}$ (μM)	$[Al]_T/[Al]_{AdSV}$ (%)	$[L]_T$ (μM)	Log K (M^{-1})
Evian	0.04 ± 0.004	$\leq$ LoD	–	–	–
Vittel	0.09 ± 0.01	$\leq$ LoD	–	–	–
Spa	0.06 ± 0.006	$\leq$ LoD	–	–	–
Contrex	0.05 ± 0.005	$\leq$ LoD	–	–	–
Tap water	0.06 ± 0.005	$\leq$ LoD	–	–	–
Coffee	0.9 ± 0.1	0.2 ± 0.03	23	0.3 ± 0.02	7.9 ± 0.4
Infusion	1.3 ± 0.1	0.02 ± 0.01	2	1.3 ± 0.02	8.7 ± 0.4
Infusion with lemon juice	1.3 ± 0.1	0.2 ± 0.02	16	1.2 ± 0.01	8.1 ± 0.1
Green tea	40 ± 2	3.5 ± 0.5	9	38 ± 0.4	6.8 ± 0.3
Green tea with lemon juice	40 ± 4	4.6 ± 0.2	12	41 ± 0.3	7.2 ± 0.4
Black tea	45 ± 3	4.1 ± 0.3	8	44 ± 1	6.3 ± 0.2
Black tea with lemon juice	45 ± 3	7.9 ± 1	18	47 ± 6	6.6 ± 0.3
Orange juice	2.8 ± 0.3	0.5 ± 0.1	17	3 ± 0.1	6.8 ± 0.1
Tomato juice	20 ± 1	0.3 ± 0.2	1	22 ± 0.3	8.2 ± 0.05
Beer	1.9 ± 0.2	NA	NA	NA	NA
Red wine	10 ± 1	0.07 ± 0.01	1	10 ± 0.1	8.7 ± 0.3

the water fluoridation because fluoride has a high affinity with aluminium, especially under acidic conditions (Fig. 3):

i. In non-fluoridated water, at a pH greater than 6.5 and $[Al]_T = 0.05 \mu M$ (Table 3), the predominant species is $Al(OH)_4^-$ (46%). The other two important species are $Al(OH)_2^+$ (24%) and $Al(OH)_3$ (27%).

ii. In water containing fluorine (average concentration of 0.4 mg/L for mineral water according to labelling), complexes AlF_3 (7%) and AlF_2^+ (36%) are among the predominant species found at pH 6.5 with complexes $Al(OH)_2^+$ (12%), $Al(OH)_3$ (14%) and $Al(OH)_4^-$ (24%).

It should be noted that while most of the aluminium species in mineral or tap waters are in the dissolved phase, we cannot exclude the presence of particulate aluminium under colloidal forms. A principle component analysis (PCA) was conducted to study the correlations between the Al fractions and the complexing parameters ($[L]_T$ and log K) of beverage samples other than mineral waters. All the data were log transformed to stabilize the variance and make nearly symmetrical distributions ($-0.6 \leq$ skew ≤ 0.05). In the biplot used to recap the results (Fig. 4), the coordinates of the vectors represent the spearman correlations of the variables with the new components, while the bubble chart provides a map of how the samples relate to each other. Fig. 4 indicates strong relationships ($\rho > 0.9$, $p < 0.05$) between log $[Al]_T$ and log $[L]_T$ and weak relationships ($\rho < 0.6$; $p \sim 0.05$) between log $[Al]_T$, log $[L]_T$ and log K. The spearman correlation between log $[Al]_{AdSV}$ and log K is negative ($\rho = -0.9$, $p < 0.05$) with a non-linear relationship between both variables. With such characteristics, the fraction of electro active aluminium $[Al]_{AdSV}$ rarely exceeded 10% of the total aluminium concentration in the different beverages samples (Table 3). The cut-point of a perpendicular from a specific bubble to the vector line approximates the value of the sample regarding the variable that the vector represents. If the cut-point falls near the origin, the value of the observation is approximately the average of the respective variable. Cut-points far off in the direction of the vector line indicate high values, while cut-points far off on the vector line, which has been extended through the origin, represent low values. It appears that samples exhibiting the highest ligand concentrations are spread into the right panels, while samples with log K values below average are clustered into the upper right panels (Fig. 4).

Although the concentrations of aluminium in tea were significantly higher than those found in the other beverages (Table 3), Al was almost exclusively ($> 90\%$) present as organic complexes of high molecular weight, which are not easily absorbed [49–50]. Our data showed that the addition of lemon juice in tea and infusion significantly modified the $[Al]_{AdSV}$ fraction (Table 3). This result was not surprising because the conditional stability constant of Al–citrate complex is very high (log $K \sim 10$), and well above the parameter values determined in the tea and infusion samples ($6.3 \leq$ log $K \leq 8.7$). The addition of lemon juice may, therefore, change the thermodynamic equilibrium towards the formation of Al–citrate complexes, which are soluble at pH 6.5. This might also explain the percentage of $[Al]_{AdSV}$ found in the orange juice, which contains on average 10 mg of citric acid per gram juice. In a recent publication, Laglera et al. [51] showed that poor estimates of $[L]_T$ and log K might result from a lack of fit in the linear regression when using Ruzic transformations (see Fig. 2). This is why, the $[Al]_{AdSV}$ concentrations obtained in tea and infusion samples after addition of lemon juice were compared with those generated by Monte-Carlo simulations and speciation modelling. This comparison was performed to determine which electro-active Al species are likely to be determined by the CLE–AdSV method. In the Monte
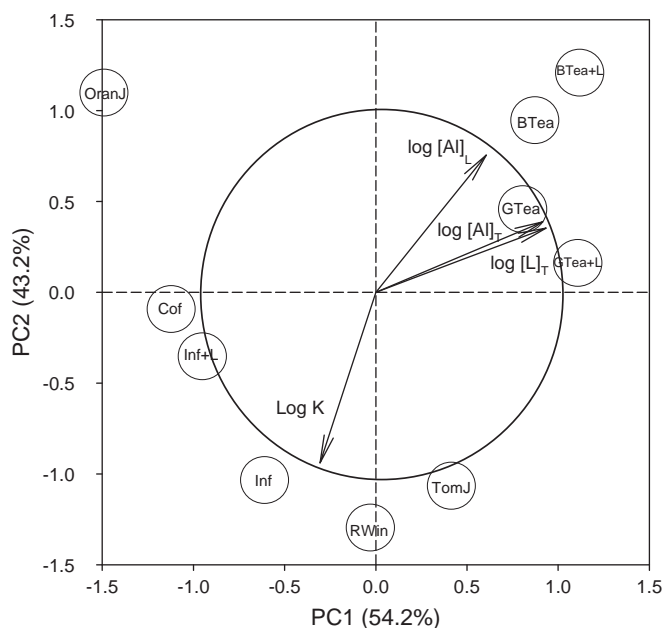

Fig. 4. Principal component analysis obtained after Varimax rotation for the whole dataset (Table 3). The first component explains 54.2% of the variation and the second component 43.2%. The vectors represent the Spearman correlations between the original variables and the principal components. The unit circle corresponds to 100% explained variance. The bubble chart represents the factor scores of the data.
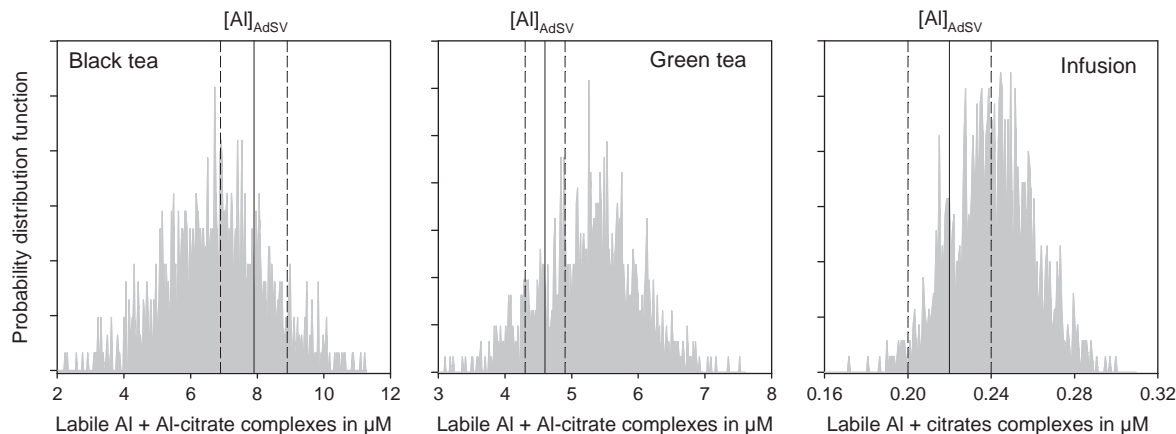

Fig. 5. Comparisons between CLE–AdSV results and those generated by Monte-Carlo simulations and speciation modelling. Approximately 10^3 simulations were carried out. The probability density axis has arbitrary units, so they are omitted. The solid line represents the measured values and the dashed lines delimit the uncertainty interval (1 sigma).

Carlo analysis, the values of the input variables ($[Al]_T$, $[L]_T$ and log K) were randomly sampled from normal distributions, for which mean and variance values were taken from Table 3. Fig. 5 indicates that the probability distribution functions of the computer outcomes representing "Al-inorganic and citrate-complexes" agreed reasonably with the available measurements; the latter being included in the 95% confidence interval of the generated distributions. These results suggest that labile monomeric Al-forms and soluble organic complexes of low molecular weight are probably quantified by the CLE–AdSV procedure.

4. Conclusions

The degree of aluminium absorption from the gastrointestinal tract depends on a number of parameters, including pH, the speciation of aluminium and dietary factors. In the gut, at near neutral pH, a large portion of the aluminium changes into insoluble Al complex $Al(OH)_3$, and is therefore not available for uptake. The portion that remains available for transport and absorption is formed by labile complexes $Al(OH)_2{}^+$ and $Al(OH)_4{}^-$, and by Al reacting with dietary ligands (e.g. citrate, lactate, and other carboxylic acids or complexing agents such as fluoride) in the intestines [52]. Our results support this statement showing that the addition of fluoride or citric acid may change Al speciation patterns in water, tea and infusions. Thanks to speciation analysis by cyclic voltammetry in the presence of cupferron, information on Al bioavailability was collected in beverages. The CLE–AdSV procedure, which relies on titration curves, is time-consuming but allows simultaneous determination of the electro active aluminium fraction and the complexing capacity of the samples. Overall the median uncertainties on $[Al]_{AdSV}$, $[L]_T$ and log K are $< 15\%$, $< 3\%$ and $< 5\%$, respectively. Results obtained with titration data agree reasonably with those predicted by speciation modelling. This cross-validation is recommended for testing the relevance of the results obtained when applying Ruzic transformations [51].

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