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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 M Ω cm) and all reagents (HNO₃, 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% HNO₃. 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 μ Autolab III potentiostat and GPES 4.9 software. A hanging mercury drop electrode (HMDE) with a surface of 0.52 mm² (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 μ m 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 μ m 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 μ L of acetate buffer solution, 20 μ L 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

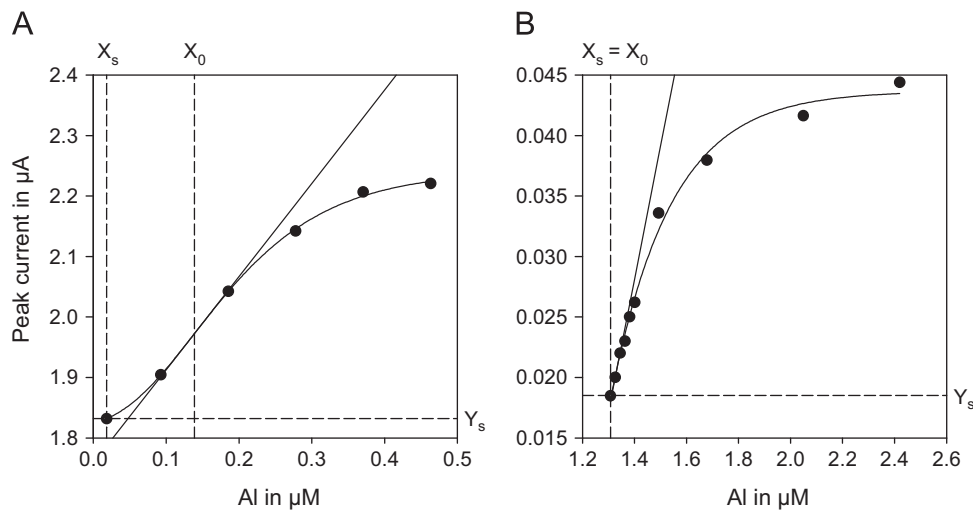


Fig. 1. Determination of aluminium by titration. X_s is the initial concentration of Al in the sample, X_0 is the concentration of Al at the inflection point and Y_s is the peak current at the measurement electrode corresponding to X_s . The titration curve has the appearance of a sigmoid (A) or a hyperbole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

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