Journal of Chromatography A, 1492 (2017) 144–150

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Analysis and characterization of aluminum chlorohydrate oligocations by capillary electrophoresis

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ARTICLE INFO

Article history:
Received 15 November 2016
Received in revised form 2 February 2017
Accepted 5 February 2017
Available online 6 February 2017

Keywords:
Aluminium chlorohydrates
Oligocations
Antiperspirant ingredients
Indirect UV detection
Counterions
Capillary coatings

ABSTRACT

Aluminum chlorohydrates (ACH) are the active ingredients used in most antiperspirant products. ACH is a water soluble aluminum complex which contains several oligomeric polycations of aluminum with degrees of polymerization up to Al_{13} or Al_{30}. The characterization and quantification of ACH oligo-cations remain a challenging issue of primary interest for developing structure/antiperspirant activity correlations, and for controlling the ACH ingredients. In this work, highly repeatable capillary electrophoresis (CE) separation of $A_{l3}{}^{+}$, Al_{13} and Al_{30} oligomers contained in ACH samples was obtained at pH 4.8, owing to a careful choice of the background electrolyte counter-ion and chromophore, capillary I.D. and capillary coating. This is the first reported separation of Al_{13} and Al_{30} oligomers in conditions that are compatible with the aluminum speciation in ACH solution or in conditions of antiperspirant application/formulation. Al_{13} and Al_{30} effective charge numbers were also determined from the sensitivity of detection in indirect UV detection mode. The relative mass proportion of Al_{13} compared to $Al_{13} + Al_{30}$ could be determined in different aluminum chlorohydrate samples. Due to its simplicity, repeatability/reproducibility, minimal sample preparation and mild analytical conditions, CE appears to be a promising analytical separation technique for the characterization of ACH materials and for the study of structure/antiperspirant activity correlations.

1. Introduction

Antiperspirant activity is of primary interest in the cosmetic industry as antiperspirants and deodorants are of common use worldwide. Deodorants attempt to control body odor by acting on the bacterial flora of the underarm area, whereas antiperspirants act on reducing the sweat flow by obstructing sweat ducts. Aluminum chlorohydrates (ACH) are the active ingredients in most antiperspirant formulations. Their synthesis is based on the neutralization of aluminum chloride by metallic aluminum, leading to highly concentrated aluminum polycation solutions. Some antiperspirants are formulated from similar aluminum salts which may also contain zirconium [1,2].

ACH is a water soluble aluminum complex which contains several oligomeric polycations of aluminum [3–6]. In acidic or neutral conditions, aluminum monomer Al^{3+} do form complexes with H_2O molecules and OH^- ions leading to the aluminum monomer of general formula $[Al(OH)_h(H_2O)_{n-h}]^{(3-h)+}$. Polycondensation of aluminum monomers leads to polycationic oligomers with degrees of polymerization up to Al_{13} or $Al_{30,}$ that were described as a layout of octahedral structures within the "cage-like" Keggin model [7,8]. The interactions of those aluminum polycationic oligomers with bovine serum albumin among other proteins were investigated by Deschaumes et al. [9,10]. The coexistence in solution of those oligomeric species result of a very fragile equilibrium that notably depends on the aluminum concentration and on the pH of the solution. For each monomer/oligomer, or for an oligomeric mixture, the hydrolysis ratio h is defined as the ratio of the total number of OH^- ligands to the total number of Al elements in solution. It can be also expressed in terms of concentrations as: $h = [OH^-]/[Al]_{tot}$ [10], and can be determined by potentiometric titration [11]. Thus, the hydrolysis ratio gives an idea of the average composition of an ACH solution ($h = 2.46$ for $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and $h = 2.40$ for $[Al_{30}O_8(OH)_{56}(H_2O)_{24}]^{18+}$). In basic conditions, maximum hydrolysis ratio of 3 is reached leading to the formation of aluminum hydroxide ($Al(OH)_3$). The characterization and quantification of

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http://dx.doi.org/10.1016/j.chroma.2017.02.008
0021-9673/

Table 1
Description of the analyzed chlorohydrate aluminum samples and quantification of Al_{13} and Al_{30} oligomers in the samples by CE using im-MES BGE. Experimental conditions as in Fig. 3.

Sample	Concentration of sample (g/L)	pH	Formula	h^a	Measured concentration (mg/L)^b		$\% \frac{Al_{13}}{Al_{13}+Al_{30}}$ ^{c}
					Al_{13}	Al_{30}	
Al_{13}	0.80	4.7	$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$	2.46	–	60 ± 4	–
Al_{30}	1.01	4.5	$[Al_{30}O_8(OH)_{56}(H_2O)_{24}]^{18+}$	2.40	57 ± 6	–	–
ACH	0.49	4.8	Mixture	2.49	51 ± 6	471 ± 7	9.8
AACH	1.19^d /0.40^e	4.6	Mixture	2.51	^{d}160 ± 10	e225 ± 5	19.0
AASH	1.24	4.3	Mixture	2.41	230 ± 20	922 ± 14	20.0

^{a}h is the hydrolysis ratio defined as the ratio of the total (OH^-) ligand to the total number of Al in solution.
^{b}Quantification using Al_{13} and Al_{30} samples as external standards for calibration and Tris as an internal standard.
^{c}Mass proportion of Al_{13} relative to $Al_{13} + Al_{30}$.
^{d,e}Injected AACH concentrations were adjusted for better accuracy in the Al_{13} proportion in the sample.

ACH oligocations remain a challenging issue of primary interest for developing structure/antiperspirant activity correlations, and for controlling the ACH ingredients.

Among the different techniques used for the characterization of ACH oligomers, ^{27}Al NMR is a powerful technique for the structural elucidation of the Keggin forms of Al_{13} and Al_{30} [8,12,13]. Size exclusion chromatography (SEC) with refractive index detection has been used for the separation of ACH oligo-cations [13–15] in acidic conditions (diluted HNO_3 eluent). Five different peaks were detected and attributed to five different aluminum oligomers that were not clearly identified. Antiperspirant activity was correlated to peak 4 to peak 3 ratio [13,16,17]. However, the conditions of the SEC analysis, and especially the pH of the eluent (pH ~ 1–2), are far from the conditions of application, or from the pH of the ACH solutions (pH ~ 4–5). Therefore, the oligomeric distribution obtained in SEC may be very different from the distribution/speciation of ACH oligomers in the injected sample (typically 1% m/v ACH in water). To our knowledge, no other separation technique has been developed so far for the characterization of ACH oligomers.

The separation of inorganic and organic ions (anions and cations) is one of the first application of capillary electrophoresis (CE) due to short analysis time, minimal sample preparation, low sample consumption and low running cost [18,19]. Both indirect UV detection mode [20–23] and capacitively coupled contactless conductimetry (C^4D) [24–28] can be used online for the detection of non-UV absorbing ions. The application of CE for metal ions has been also widely developed since early 90′s [29–35], including the hyphenation with the sensitive and selective ICP-MS detection [36,37]. As pointed out by Liu et al. [35], it is surprising that in the large number of publications dealing with the separation of metal ions by CE, Al is ignored. This is likely due to the special nature of Al ions with high charge and slow kinetics to reach equilibrium. These specificities make very difficult to develop suitable separation methods, not only in CE [38] but also in LC [39].

One of the pioneering work on CE of aluminum was performed by Wu et al. [40]. Fluoro and oxalato aluminum complexes were separated at pH 3.5 in an imidazole/sulfuric acid BGE and detected by indirect UV detection. Quantification of free aluminum (Al^{3+}) and complexed forms allowed plotting the speciation diagram of Al^{3+}, AlF^{2+} and $AlF_2{}^+$ species according to the F/Al mole ratio introduced in the sample. These results demonstrated the slow kinetics of dissociation of these aluminum complexes during the electrophoretic process. Later, Bachmann et al. showed that the use of a strong complexing agent (desferrioxamine) added in the aluminum sample allowed the quantification of total aluminum content in any sample having a pH between 2 and 10 [41]. Barger et al. quantified Al^{3+} ions at sub-ppm levels using a BGE based on ephedrine and α-hydroxyisobutyric acid at pH 2.8 [42]. Gottlein used CE to quantify free Al^{3+} ions (separated from complexed aluminum forms) in soil extract samples [43]. Sarazin et al. developed a method for the simultaneous analysis of nitrate, chloride and aluminum ions in acid-aluminum burst residues [44]. Finally, Schmid et al. [45] demonstrated that capillary isotachophoresis was well suited for the selective quantification of $[Al(H_2O)_6]^{3+}$ in inorganic samples from soil (LOD of 50 ppb). So far, there is no report about the CE separation/quantification of ACH oligomers.

The main objectives of this work was to characterize the oligocation distribution of ACH ingredients by CE, and notably to separate and quantify the Al_{13} and Al_{30} oligomers in aluminum chlorohydrate samples. Separation and quantification of Al_{13} and Al_{30} oligomers in mild condition, close to the condition of application, or close to the condition of the ACH solution, was of primary importance for the future development of structure-antiperspirant activity studies.

2. Experimental section

2.1. Chemicals

4-Morpholinoethanesulphonic acid (MES), imidazole and hydrochloric acid (HCl) were purchased from Acros Organics (New Jersey, USA). Didodecyldimethylammonium bromide (DDAB) was purchased from Aldrich (Milwaukee, WI). Aluminum nitrate was from Sigma Aldrich (St-Louis, Missouri, USA). UltraTrol^{TM} LN was acquired from Target Discovery, Palo Alto, CA, USA. Acetic acid was from VWR Prolabo chemicals (Fontenay-sous-Bois, France). Ultrapure water was prepared with a Milli-Q system from Millipore (Molsheim, France). Several aluminum standards and ingredients were kindly provided by L'Oréal (Aulnay-sous-bois, France): Al_{13} or Al_{30} were synthetized using the protocol of Chen et al. [46]; ACH was provided in a 50% m/v water solution; AACH and AASH were under solid form. The hydrolysis ratio of each aluminum chlorohydrate sample is provided in Table 1. It was theoretically estimated for Al_{13} and Al_{30} oligomers considering the chemical formula of the polycation. For ACH, AACH and AASH, the hydrolysis ratio was determined by potentiometric titration.

2.2. Capillary electrophoresis

CE experiments were carried out on a G7100A CE Agilent Technologies system (Waldbronn, Germany) equipped with a diode array detector and coupled with a capacitively coupled contactless conductivity detector (C^4D) from TraceDec® (Innovative sensor technologies GmbH, Vienna, Austria). Bare fused silica capillary was purchased from Polymicro Technologies (Phoenix, Ar. USA). Capillary dimensions were 38.5 cm (30 cm to the UV detector; 25 cm to the C^4D cell) × 50 or 25 μm I.D., except for the study of the influence of the effective capillary length for which longer capillaries were used (see Figure caption for exact dimensions). The temperature of the capillary cassette was set at 25 °C. Background