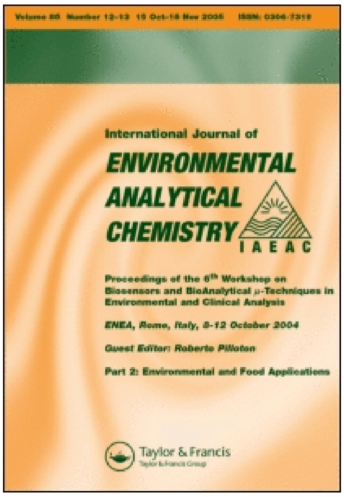

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Comparison of hydrolysis products of $AlCl_3 \cdot 6H_2O$ in different concentrations by electrospray ionization time of flight mass spectrometer (ESI TOF MS)

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Hydrolysis of 0.100, 0.010, and 0.001 mol L^{-1} aqueous solutions of $AlCl_3 \cdot 6H_2O$, each at two pH values ranging from 3.27 to 7.00, was compared by electrospray ionization time-of-flight mass spectrometry. The differences between 4 h and 14 day aged solutions were also studied. Various charges and compositions for species of the same size were observed. At lower pH values, dimeric and trimeric aluminium oxo-hydroxo-complexes were the major molecular species. With higher pH levels, precipitation and formation of $Al(OH)_4^-$ took place. Multiple charged signals assigned to polynuclear complexes (Al_{10}–Al_{15}) were found at a narrow pH area range before precipitation occurred. The diversity of different species increased strongly as a function of concentration. The pH of the solution dominated the profile even more than the concentration. All the main species were formed in 4 h.

Keywords: Aluminium; Hydrolysis; Polymeric complexes; Distribution; Speciation; ESI TOF MS

1. Introduction

In the last few decades, considerable attention has been paid to aluminium and its distribution in the environment. Aluminium is one of the most abundant elements in the earth's crust, and by far the most abundant metal [1]. Thus, it is not surprising that aluminium is one of the major components of atmospheric aerosol particles from natural sources, i.e. volcanic activity and Aeolian dust [2]. The default concentration of solvated species of aluminium in most natural waters is well below the ppm level. This is because minerals containing aluminium have a relatively low solubility. However, near solid/aqueous boundaries, the concentrations can be much higher. Moreover, due to an

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increased input of acids into the environment and, more recently, increased land use, a considerable release of this element has occurred [3, 4].

The increased total aluminium concentrations in natural waters and soils have been reported to be toxic to fish and bacteria living in seawater [5] as well as to plants [6]. The monomeric, positive charged hydroxyl-complex ions ($AlOH^{2+}$, $Al(OH)_2^+$) are considered to play a main role in the toxicity of aluminium in water environments [7], although polymeric species existing in the same pH range may considerably enhance the toxicity by decreasing the fluidity of membrane as well as cross-linking biomolecules [8]. The Al_{13} complex has been observed to be the major species in acidified soils [9], and polynuclear aluminium species have been reported to be involved in plant toxicity [10, 11]. Thus, there is strong evidence that the distribution of aluminium among various species is more relevant than the total aluminium concentration when evaluating the toxicity of the natural waters. The release and interactions of aluminium are widely studied by modern methods [12–14].

In water purification, attempts have been made to use aluminium ions with high charges due to their extensive coagulating power [15]. In addition, oxido-hydroxido-polymers form large, three-dimensional nets used in the purification process to precipitate microbes, dissolved organic matter (DOM), ions, and mineral particles [16]. When the coagulating salts are partially hydrolysed in the manufacturing process, they are much more efficient purification agents. Examples of these partially hydrolysed chemicals are polyferric- and polyaluminium chlorides and sulphates [17–19]. The high basic forms of these coagulants enable coagulation/focculation at a higher pH. The structure of these oligomers is still unknown, and the material published to date is inconsistent.

The electrospray ionization mass spectrometry (ESI MS) used in this study is a well-established method of transferring almost intact pre-existing ions from solution to the gas phase, where they may be examined by conventional mass-spectrometric detection techniques [20]. It has been shown, that in almost every case where the identity of the ions in a solution has been established by some other technique, such as NMR spectroscopy or electrochemistry, the ions observed by ESI MS agreed with prior identification experiments [21]. Even though the method is not quantitative, the presence or absence of a certain species can be deduced.

ESI MS has proven to be useful method of characterizing the hydrolysis products of aluminium in aqueous solutions [22–24]. This article describes experiments in which distributions of Al in different concentrations are investigated with these methods. The aim is to clarify how the aqueous speciation of aluminium changes as a function of concentration, pH, and reaction time. The results can be utilized by following the progress of dissolution, mobilization, and toxicity in natural waters as well as in coagulation/flocculation phases of water purification.

2. Experimental

The concentrations of the prepared aluminium chloride hexahydrate (Merck, purum) solutions were 0.100, 0.010, and 0.001 $mol\,L^{-1}$ of aluminium in deionized water (18.2 $M\Omega\,cm$). The following procedure was performed for all three concentrations. The solutions were divided into parts so that the first parts were left at their initial

Table 1. Concentrations and pHs of solutions investigated.

Concentration ($mol\,L^{-1}$)	Initial pH	Adjusted pH								
0.100	3.27[a]	3.92		4.20[a,b]		4.50[c]				
0.010	3.72[a]	3.92	4.10	4.20	4.35[b]	4.50[a]	4.75	5.00	7.05[c]	10.00
0.001	3.92[a]			4.20		4.50	4.72[a,b]	5.00	7.00	

[a] Spectra used in comparing the concentrations.
[b] First signals assigned for multi-charged complexes.
[c] Precipitation, visual observation.

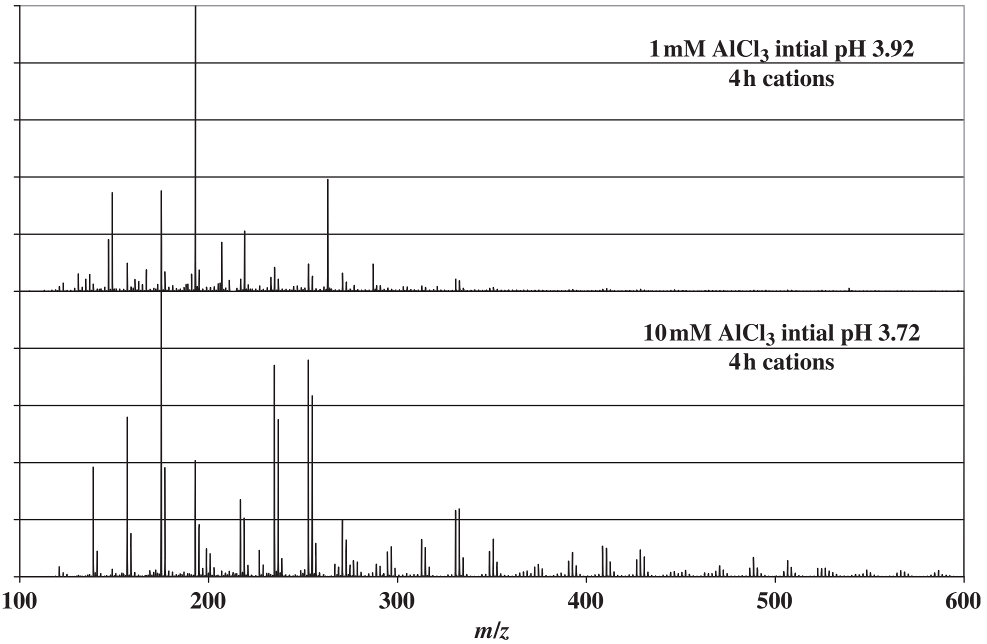

Figure 1. Cationic spectra of $0.001\,mol\,L^{-1}$ (1 mM) fresh (4 h) solution at initial pH 3.92 and $0.010\,mol\,L^{-1}$ (10 mM) fresh (4 h) solution at initial pH 3.72. This figure illustrates the strong effect of concentration on the spectra.

pH (3.27 for $0.100\,mol\,L^{-1}$, 3.72 for $0.010\,mol\,L^{-1}$, and 3.92 for $0.001\,mol\,L^{-1}$). The other parts were adjusted to higher pH values, given in table 1, by dropwise (>1 mL) addition of concentrated tetramethyl ammonium hydroxide pentahydrate (TMA, Fluka, reinst) [23]. Comparisons were made between the initial pH values and the pH values in which the multiple charged signals assigned to oligomeric polynuclear aluminium complexes (Al_{10}–Al_{15}) were clearly seen [23] (4.20 for $0.100\,mol\,L^{-1}$, 4.50 for $0.010\,mol\,L^{-1}$ and 4.72 for $0.001\,mol\,L^{-1}$) (figure 1). Samples were allowed to equilibrate prior to recording for 4 h (fresh solution). After the recording of the ESI TOF mass spectra, the solutions were aged for 14 days (aged solution), after which the spectra were re-recorded [25, 26].

The number of different species was counted and presented as histograms (bar charts) as a function of time, concentration, and pH (figures 2–4). The same species was always counted as a separate observation whenever it was found in different circumstances (concentration, pH, and time). Only the number of aqua ligands was ignored in

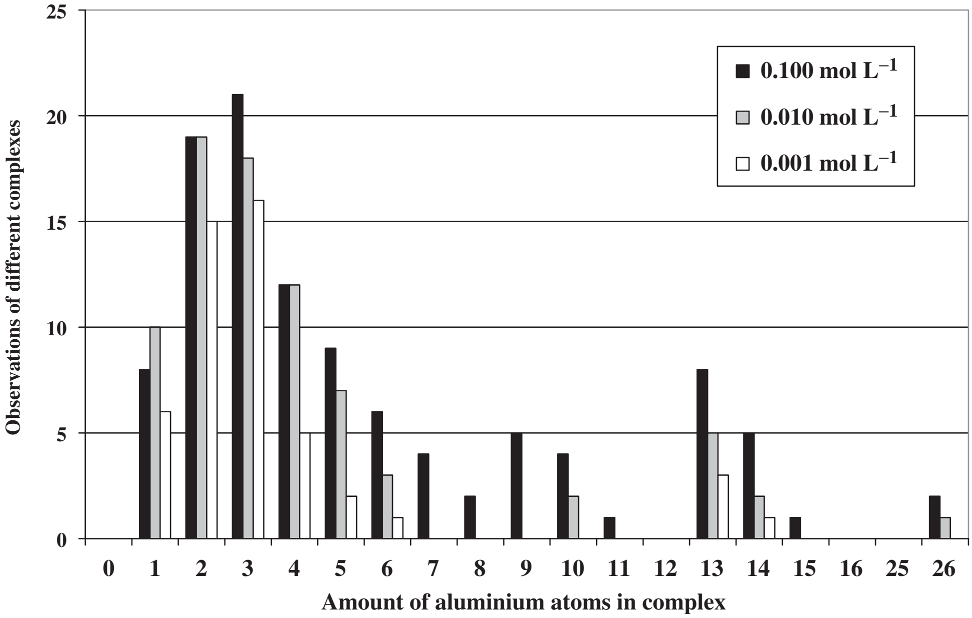

Figure 2. Histogram illustrating how the presence and variation of the complexes were strongly dependent on concentration.

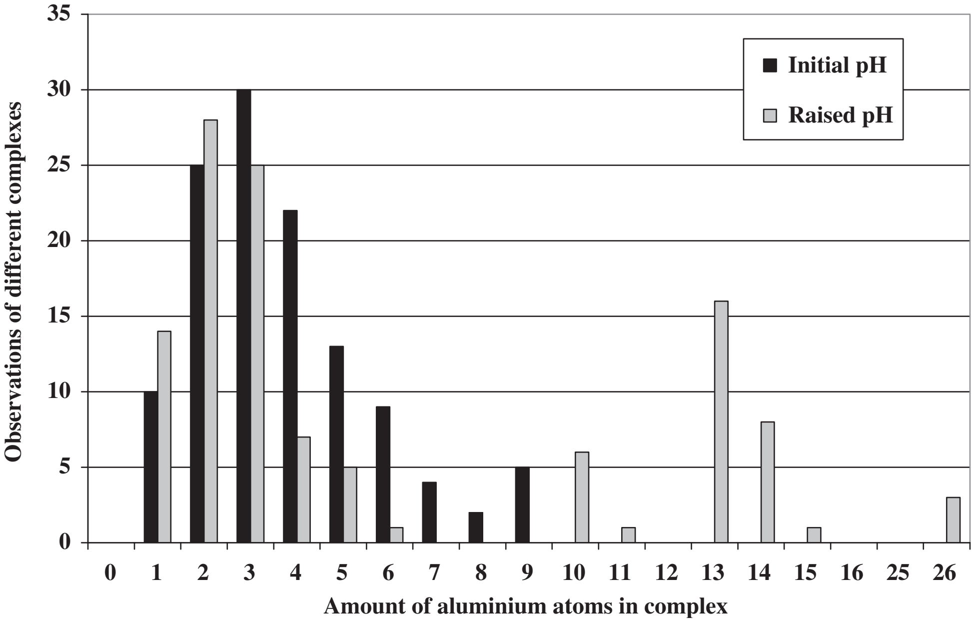

Figure 3. Histogram illustrating how the presence and variation of the complexes were strongly dependent on pH.

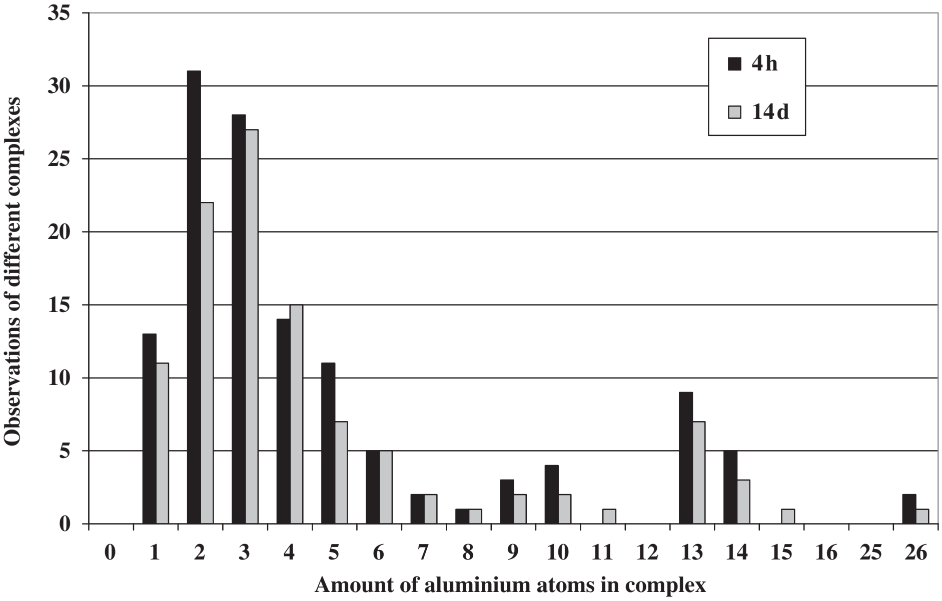

Figure 4. Histogram illustrating illustrates how the presence and variation of the complexes were not strongly dependent on time. Only Al_{11} and Al_{15} were formed during the ageing process. In the fresh solution dimeric complexes dominated but after 14 days, dominating species became trimeric and the shape of distribution approached a Gaussian form.

this approach. The data were collected from eight spectra for $0.100\,mol\,L^{-1}$ (tables 2 and 3) and $0.010\,mol\,L^{-1}$ (tables 4 and 5). Since the anionic spectra of the aged $0.001\,mol\,L^{-1}$ solutions were too complicated for extensive identification, only six spectra were chosen for the comparison (tables 6 and 7). For example, the amount of dimeric aluminium in the concentration of $0.100\,mol\,L^{-1}$ consisted of 19 observations according to tables 2 and 3, in elevated pH 28 observations according to tables 3, 5, and 7, and in fresh solution 31 observations according to all tables 2–7. The $[Al_2O(OH)_3]^+$ cation could be found in several circumstances: $0.100\,mol\,L^{-1}$ fresh raised pH, $0.010\,mol\,L^{-1}$ fresh initial pH, $0.010\,mol\,L^{-1}$ fresh raised pH, $0.001\,mol\,L^{-1}$ fresh initial pH, $0.001\,mol\,L^{-1}$ aged initial pH, $0.001\,mol\,L^{-1}$ fresh raised pH, and $0.001\,mol\,L^{-1}$ aged raised pH. Therefore, this was counted as seven observations.

The pHs of the solutions were determined with a Mettler Toledo MP 220 pH meter using a Mettler Toledo InLab 410 Ag/AgCl electrode calibrated with FF-Chemical buffer solutions pH 4.00 and 7.00. The ESI TOF mass spectra were recorded by a Micromass LCT mass spectrometer equipped with a Z-spray electrospray interface. The solutions were introduced into the spectrometer by a Harvard Apparatus Model 11 syringe pump. The operation and interpretation procedures are reported in detail in our previous paper [23].

3. Results and discussion

The initial pH of the solution with a concentration of $0.100\,mol\,L^{-1}$ was 3.27, and the adjusted pHs were 3.92, 4.20, and 4.50 (table 1). The spectra of the solutions with

Table 2. Observed species in 0.100 mol L^{-1} at initial pH 3.27.

4 h		14 days	
Cations	Anions	Cations	Anions
$[Al_2O(OH)_2Cl(H_2O)_{0-3}]^+$	$[AlCl_4]^-$	$[Al_2(OH)_5(H_2O)]^+$	$[Al(OH)Cl_3]^-$
$[Al_3O(OH)_6(H_2O)_{0-1}]^+$	$[Al_2O_2Cl_3(H_2O)_{0-1}]^-$	$[Al_2(OH)_4Cl(H_2O)_{1-2}]^+$	$[AlCl_4]^-$
$[Al_3O(OH)_4Cl_2(H_2O)_{0-3}]^+$	$[Al_2OCl_5]^-$	$[Al_3O(OH)_6(H_2O)_{0-1}]^+$	$[Al_2O_2Cl_3(H_2O)_{0-1}]^-$
$[Al_4O_3(OH)_3Cl_2(H_2O)_{0-1}]^+$	$[Al_3O_3Cl_4(H_2O)_{0-2}]^-$	$[Al_3(OH)_7Cl(H_2O)_{0-1}]^+$	$[Al_2O(OH)Cl_4]^-$
$[Al_4O_2(OH)_4Cl_3(H_2O)_{0-2}]^+$	$[Al_3O(OH)_3Cl_5]^-$	$[Al_3(OH)_6Cl_2(H_2O)]^+$	$[Al_2OCl_5]^-$
$[Al_5O_3(OH)_6Cl_2]^+$	$[Al_4O_3(OH)_4Cl_3]^-$	$[Al_3(OH)_4Cl_4]^+$	$[Al_3O_3(OH)Cl_3]^-$
$[Al_5O_4(OH)_2Cl_4(H_2O)_{0-4}]^+$	$[Al_4O_4Cl_5]^-$	$[Al_4O_3(OH)_3Cl_2(H_2O)_{0-2}]^+$	$[Al_3O_3Cl_4(H_2O)_{0-2}]^-$
$[Al_6O_7Cl_3(H_2O)_{0-3}]^+$	$[Al_5O_4(OH)_4Cl_4(H_2O)_{0-1}]^-$	$[Al_4O_2(OH)_4Cl_3(H_2O)_{0-2}]^+$	$[Al_3O(OH)_3Cl_5]^-$
$[Al_6O_5(OH)_2Cl_5(H_2O)_{0-5}]^+$	$[Al_5O_4Cl_8]^-$	$[Al_5O_3(OH)_4Cl_4(H_2O)_{0-3}]^+$	$[Al_4O_3(OH)_4Cl_3]^-$
$[Al_7O_6(OH)_3Cl_5(H_2O)_{0-3}]^+$	$[Al_6O_4(OH)_6Cl_5]^-$	$[Al_6O_2(OH)_9Cl_4]^+$	$[Al_4O_4Cl_5(H_2O)_{0-3}]^-$
$[Al_7O_2(OH)_{11}Cl_5(H_2O)_{0-1}]^+$		$[Al_6O_2(OH)_8Cl_5(H_2O)_{0-1}]^+$	$[Al_5O_6Cl_4(H_2O)_{0-4}]^-$
$[Al_8O_7(OH)_2Cl_7(H_2O)_{0-5}]^+$		$[Al_7O_3(OH)_{11}Cl_3]^+$	$[Al_6O_7Cl_5(H_2O)_{0-3}]^-$
$[Al_9O_9(OH)Cl_7(H_2O)_{0-3}]^+$		$[Al_7O_4(OH)_7Cl_5(H_2O)_{0-2}]^+$	
$[Al_9O_6(OH)_6Cl_8]^+$		$[Al_8O_7(OH)_2Cl_7(H_2O)_{0-3}]^+$	
$[Al_9O_6(OH)_5Cl_9]^+$		$[Al_9O_7(OH)_5Cl_7(H_2O)_{0-1}]^+$	
		$[Al_9O_6(OH)_6Cl_8]^+$	
15	10	16	12

pHs 3.27 and 3.92 were very similar. In the spectra of pH 4.20, the signal series assigned to multiple charged polyaluminium complexes were clearly observable. At pH 4.50, part of the aluminium precipitated and therefore could not be investigated by mass spectrometric methods.

The initial pH of concentration 0.010 mol L^{-1} was 3.72. The solution was divided into 10 parts, and the pHs were adjusted to 3.92, 4.10, 4.20, 4.35, 4.50, 4.75, 5.00, 7.05, and 10.00 (table 1). The spectra of pHs 3.92, 4.10, and 4.20 did not differ remarkably from the spectra of the initial pH, 3.72. In the spectra of pH 4.35, signals assigned to the multiple charged polyaluminium complexes were first observed. In the spectra of pHs 4.50 and 4.75, these signals could be seen clearly. In the fresh spectra of pH 5.00, the multiple charged water series were predominant. The spectra at pH 7.05 showed several multiple charged series and a signal assigned to aluminate anion $[Al(OH)_4]^-$, but there was also precipitation, and the major signals that were assigned to TMA_xCl_y adducts. From the spectra of pH 10.00, no aluminium-containing complexes were found, and all the signals identified were assigned to TMA complexes.

The initial pH of concentration 0.001 mol L^{-1} was 3.92. The solution was divided into five parts, and the pHs were adjusted to 4.20, 4.50, 4.72, and 5.00. The spectra of pHs 4.20 and 4.50 did not differ remarkably from that of the initial pH, 3.92. In the cationic spectra of pHs 4.75 and 5.00, signals of the multiple charged complexes were observed. In the fresh anionic spectra, all the identified signals were assigned to mono-charged complexes.

The observed diversity profiles were strongly dependent on the concentration, as shown in figures 1 and 2. The total number of identified pure aluminium core species from the 0.100 mol L^{-1} solution was 107, including both cationic and anionic species. As for the concentrations of 0.010 and 0.001 mol L^{-1}, 79 and 49 different species were identified, respectively. The degree of polymerization of growing aluminium complexes

Table 3. Observed species in $0.100\,\mathrm{mol\,L^{-1}}$ at raised pH 4.20.

4 h		14 days	
Cations	Anions	Cations	Anions
$[Al_2O(OH)_3]^+$	$[Al(OH)Cl_3]^-$	$[Al_2(OH)_5(H_2O)_{0-1}]^+$	$[AlOHCl_2]^-$
$[Al_2O(OH)_2Cl]^+$	$[AlCl_4]^-$	$[Al_2(OH)_4Cl(H_2O)_{1-2}]^+$	$[Al(OH)Cl_3]^-$
$[Al_3O(OH)_6(H_2O)_{0-1}]^+$	$[Al_2O_2Cl_3(H_2O)_{0-1}]^-$	$[Al_2(OH)_3Cl_2(H_2O)_2]^+$	$[AlCl_4]^-$
$[Al_3O(OH)_4Cl_2(H_2O)_{0-1}]^+$	$[Al_2O(OH)Cl_4]^-$	$[Al_3O(OH)_6]^+$	$[Al_2O_2Cl_3(H_2O)_{0-1}]^-$
$[Al_{10}O_7(OH)_{13}Cl(H_2O)_{0-7}]^{2+}$	$[Al_2OCl_5]^-$	$[Al_3O(OH)_5Cl(H_2O)_{0-1}]^+$	$[Al_2O(OH)Cl_4]^-$
$[Al_{13}O_{11}(OH)_{15}(H_2O)_{0-6}]^{2+}$	$[Al_3O_3Cl_4(H_2O)_{0-2}]^-$	$[Al_3(OH)_6Cl_2(H_2O)_{0-1}]^+$	$[Al_2OCl_5]^-$
$[Al_{13}O_{10}(OH)_{16}(H_2O)_{0-7}]^{3+}$	$[Al_3O(OH)_3Cl_5]^-$	$[Al_3(OH)_4Cl_4]^+$	$[Al_3O_3Cl_4(H_2O)_{0-2}]^-$
$[Al_{14}O_{10}(OH)_{19}Cl(H_2O)_{0-3}]^{2+}$	$[Al_4O_5Cl_3(H_2O)_2]^-$	$[Al_4O_3(OH)_2Cl_3(H_2O)_{0-3}]^+$	$[Al_3O(OH)_3Cl_5]^-$
$[Al_{14}O_7(OH)_{25}(H_2O)_{0-2}]^{3+}$	$[Al_5O_4(OH)_4Cl_4(H_2O)_{0-1}]^-$	$[Al_5O_2(OH)_{10}]^+$	$[Al_4O_3(OH)_4Cl_3]^-$
	$[Al_5O_4Cl_8]^-$	$[Al_{11}O_8(OH)_{16}(H_2O)_{0-3}]^+$	$[Al_4O_4Cl_5]^-$
	$[Al_{10}O_{12}(OH)_4Cl_4(H_2O)_{0-2}]^{2-}$	$[Al_{13}O_{14}(OH)_9(H_2O)_{0-4}]^{2+}$	$[Al_{10}O_6(OH)_{15}Cl_5(H_2O)_{0-1}]^{2-}$
	$[Al_{10}O_6(OH)_{15}Cl_5(H_2O)_{0-1}]^{2-}$	$[Al_{13}O_{10}(OH)_{16}Cl(H_2O)_{0-6}]^{2+}$	$[Al_{13}O_{16}(OH)_4Cl_5(H_2O)_{0-2}]^{2-}$
	$[Al_{13}O_{16}(OH)_4Cl_5(H_2O)_{0-2}]^{2-}$	$[Al_{14}O_{10}(OH)_{19}Cl(H_2O)_{0-6}]^{2+}$	$[Al_{13}O_{16}(OH)Cl_8(H_2O)_{0-1}]^{2-}$
	$[Al_{13}O_{16}(OH)Cl_8(H_2O)_{0-1}]^{2-}$	$[Al_{15}O_{12}(OH)_{17}Cl_2(H_2O)_{0-5}]^{2+}$	$[Al_{14}O_{18}Cl_8(H_2O)_{0-1}]^{2-}$
	$[Al_{14}O_{18}Cl_8(H_2O)_{0-1}]^{2-}$		$[Al_{26}O_{15}(OH)_{48}Cl_4]^{4-}$
	$[Al_{26}O_{15}(OH)_{48}Cl_4]^{4-}$		
9	16	14	15

Table 4. Observed species in 0.010 mol L^{-1} solution at initial pH 3.72.

4 h		14 days	
Cations	Anions	Cations	Anions
$[Al_2O(OH)_3(H_2O)_{0-4}]^+$	$[AlCl_4]^-$	$[Al_2O(OH)_2Cl(H_2O)_{0-3}]^+$	$[AlOCl_2(H_2O)]^-$
$[Al_2O_2Cl(H_2O)_3]^+$	$[Al_2O_2Cl_3]^-$	$[Al_3(OH)_8]^+$	$[Al(OH)Cl_3]^-$
$[Al_3(OH)_8]^+$	$[Al_2(OH)_5Cl_2]^-$	$[Al_3O(OH)_4Cl_2]^+$	$[AlCl_4]^-$
$[Al_3(OH)_7Cl]^+$	$[Al_2OCl_5]^-$	$[Al_3O_2(OH)Cl_3(H_2O)_{0-2}]^+$	$[Al_2O_2Cl_3]^-$
$[Al_3O(OH)_3Cl_3(H_2O)_{0-1}]^+$	$[Al_3O_3Cl_4(H_2O)_{0-1}]^-$	$[Al_4O_3(OH)_2Cl_3]^+$	$[Al_2O(OH)Cl_4]^-$
$[Al_4(OH)_{11}(H_2O)_{0-1}]^+$	$[Al_3O(OH)_3Cl_5]^-$	$[Al_4O_3(OH)Cl_4]^+$	$[Al_2OCl_5]^-$
$[Al_4O(OH)_6Cl_3(H_2O)_{0-2}]^+$	$[Al_4O_4(OH)Cl_4]^-$	$[Al_4O(OH)_6Cl_3(H_2O)_{0-1}]^+$	$[Al_3(OH)_6Cl_4]^-$
$[Al_5O_2(OH)_6Cl_4(H_2O)_{0-3}]^+$	$[Al_4O_4Cl_5]^-$	$[Al_5O_3(OH)_4Cl_4(H_2O)_{0-3}]^+$	$[Al_3O_3Cl_4]^-$
$[Al_6O_4(OH)_5Cl_4(H_2O)_{0-4}]^+$	$[Al_5O_4(OH)_4Cl_4]^-$	$[Al_5O(OH)_7Cl_5(H_2O)_{0-1}]^+$	$[Al_3O(OH)_3Cl_5(H_2O)_{0-1}]^-$
		$[Al_6O_4(OH)_4Cl_5(H_2O)_{0-3}]^+$	$[Al_4(OH)_9Cl_4]^-$
			$[Al_4O_3(OH)_3Cl_4(H_2O)_{0-1}]^-$
			$[Al_4O_2(OH)_4Cl_5]^-$
			$[Al_4O_4Cl_5]^-$
			$[Al_5O_4(OH)_4Cl_4]^-$
			$[Al_5O_4(OH)_3Cl_5]^-$
9	9	10	15

Table 5. Observed species in 0.010 mol L^{-1} solution at raised pH 4.50.

4 h		14 days	
Cations	Anions	Cations	Anions
$[Al_2O(OH)_3(H_2O)_{0-1}]^+$	$[AlOCl_2(H_2O)_{0-1}]^-$	$[Al_2O(OH)_2Cl(H_2O)_{0-2}]^+$	$[AlOCl_2(H_2O)]^-$
$[Al_2(OH)_5(H_2O)_3]^+$	$[Al(OH)Cl_3]^-$	$[Al_3O_2(OH)Cl_3(H_2O)_{0-2}]^+$	$[Al(OH)Cl_3]^-$
$[Al_2(OH)_4Cl(H_2O)_{0,2}]^+$	$[AlCl_4]^-$	$[Al_{10}O_4(OH)_{20}(H_2O)_{0-6}]^+$	$[AlCl_4]^-$
$[Al_3(OH)_8]^+$	$[Al_2(OH)_5Cl_2]^-$	$[Al_{13}O_{10}(OH)_{17}(H_2O)_{0-3}]^{2+}$	$[Al_2O(OH)Cl_4]^-$
$[Al_3(OH)_7Cl]^+$	$[Al_2O_2Cl_3]^-$	$[Al_{13}O_{10}(OH)_{16}(H_2O)_{0-6}]^{3+}$	$[Al_2OCl_5]^-$
$[Al_3O(OH)_3Cl_3]^+$	$[Al_2O(OH)Cl_4]^-$	$[Al_{14}O_7(OH)_{25}(H_2O)_{0-2}]^{3+}$	$[Al_3O_2(OH)_3Cl_3]^-$
$[Al_5O_2(OH)_{10}(H_2O)_{0-2}]^+$	$[Al_2OCl_5]^-$		$[Al_3O_2(OH)Cl_5]^-$
$[Al_{13}O_{10}(OH)_{17}(H_2O)_{0-4}]^{2+}$	$[Al_3O_3Cl_4(H_2O)_{0-2}]^-$		$[Al_4O_4Cl_3(H_2O)]^-$
$[Al_{13}O_7(OH)_{22}(H_2O)_{0-6}]^{3+}$	$[Al_{10}O_3(OH)_{21}Cl_5(H_2O)_{0-2}]^{2-}$		$[Al_6O_5Cl_5(H_2O)_3]^-$
	$[Al_{13}O_{16}(OH)Cl_8(H_2O)_{0-1}]^{2-}$		
	$[Al_{14}O_{17}(OH)_2Cl_8(H_2O)_{0-2}]^{2-}$		
	$[Al_{26}O_{15}(OH)_{48}Cl_4]^{4-}$		
9	12	6	9

was not a continuum. Small complexes, containing one to six oxo hydroxo bridged aluminium, were found in all concentrations. Signals of these complexes were always only mono-charged. Seven, eight, and nine aluminium-containing complexes existed only at the highest concentration investigated, 0.100 mol L^{-1}, and all these signals were also mono-charged. Ten aluminium-containing oxo-hydroxo-complexes were seen in the spectra of the 0.100 and 0.010 mol L^{-1} solutions. Al_{11} were found only in the aged 0.100 mol L^{-1} solution. Signals assigned to 12 aluminium-containing oxo-hydroxo-complexes were not observed in these studies. Al_{13} and Al_{14} complexes were found in all concentrations, but with Al_{15} only in the highest concentration. In addition, Al_{26}

Table 6. Observed species in 0.001 mol L^{-1} solution at initial pH 3.92.

4 h		14 days	
Cations	Anions	Cations	Anions
$[Al_2O(OH)_3(H_2O)_{0-4}]^+$	$[Al(OH)_2Cl_2(H_2O)_{0\&3}]^-$	$[Al_2O(OH)_3(H_2O)_{0-1}]^+$	
$[Al_2O_2Cl(H_2O)_3]^+$	$[Al(OH)Cl_3]^-$	$[Al_2O(OH)_2Cl(H_2O)_{0-2}]^+$	
$[Al_3(OH)_8]^+$	$[AlCl_4]^-$	$[Al_3(OH)_8]^+$	
$[Al_3(OH)_7Cl]^+$	$[Al_2O(OH)Cl_4(H_2O)_{0\&2}]^-$	$[Al_3O(OH)_4Cl_2]^+$	
$[Al_3(OH)_6Cl_2(H_2O)_{0-1}]^+$	$[Al_2(OH)Cl_4(H_2O)_6]^-$		
$[Al_4O(OH)_6Cl_3(H_2O)_{0-1}]^+$	$[Al_2OCl_5]^-$		
$[Al_4O_3(OH)_2Cl_3]^+$	$[Al_2(OH)_2Cl_5(H_2O)]^-$		
$[Al_5O_3(OH)_4Cl_4(H_2O)_{0-4}]^+$	$[Al_3(OH)_{10}(H_2O)_3]^-$		
$[Al_6O_4(OH)_5Cl_4(H_2O)_{0-4}]^+$	$[Al_3O_3Cl_4(H_2O)_{0-1}]^-$		
	$[Al_3O_2(OH)Cl_5(H_2O)_{0-2}]^-$		
	$[Al_4O_2(OH)_2Cl_7]^-$		
9	11	4	0

Table 7. Observed species in 0.001 mol L^{-1} solution at raised pH 4.72.

4 h		14 days	
Cations	Anions	Cations	Anions
$[Al_2O(OH)_3(H_2O)_{0-1\&4}]^+$	$[Al(OH)_2Cl_2(H_2O)_3]^-$	$[Al_2O(OH)_3]^+$	
$[Al_2(OH)_4Cl(H_2O)_{0-1}]^+$	$[Al(OH)Cl_3]^-$	$[Al_2O(OH)_2Cl(H_2O)_{0-3}]^+$	
$[Al_3(OH)_8]^+$	$[AlCl_4]^-$	$[Al_3(OH)_8]^+$	
$[Al_3O(OH)_4Cl_2(H_2O)_{0-1}]^+$	$[Al_2O_2Cl_3(H_2O)_{0-1}]^-$	$[Al_3O(OH)_4Cl_2(H_2O)_{0-1}]^+$	
$[Al_3O_2(OH)Cl_3(H_2O)_2]^+$	$[Al_2O(OH)Cl_4]^-$	$[Al_3O_2(OH)Cl_3(H_2O)_2]^+$	
$[Al_4O(OH)_6Cl_3]^+$	$[Al_2OCl_5]^-$	$[Al_{13}O_{10}(OH)_{17}(H_2O)_{0-5}]^{2+}$	
$[Al_5O_2(OH)_{10}(H_2O)_{0-3}]^+$	$[Al_3O_3Cl_4]^-$		
$[Al_{13}O_7(OH)_{22}(H_2O)_{0-4}]^{3+}$	$[Al_3O_2(OH)_2Cl_4(H_2O)_{0-1}]^-$		
$[Al_{13}O_{10}(OH)_{17}(H_2O)_{0-5}]^{2+}$	$[Al_4O_3(OH)_3Cl_4]^-$		
$[Al_{14}O_7(OH)_{25}(H_2O)_{0-2}]^{3+}$			
10	9	6	0

complexes were seen in the spectra of the 0.100 mol L^{-1} [23] and 0.010 mol L^{-1} solutions. These were identified as $[Al_{26}O_{15}(OH)_{48}Cl_4]^{4-}$, which could consist of two Al_{13} units.

The diversity of species as a function of pH is presented in figure 3. The solutions at initial pH had the highest frequency (30 observations) for trimeric aluminium complexes, with almost a Gaussian distribution of small complexes from Al_1 to Al_6. The solutions with raised pHs had the highest frequency at dimeric species, of which 28 different observations were made. The numbers of tetrameric, pentameric, and hexameric complexes were clearly diminished in comparison with the solutions of the initial pH values. Also, complexes containing seven, eight, and nine aluminium atoms were entirely missing from the higher-pH solutions. Instead, when considering species containing 10 or more aluminium atoms, it can be seen that they exclusively existed in the solutions with elevated pH values. These complexes were usually found as multiple charged states. This could indicate a change in structure of the polymers from simple cyclic structures to more complex tetrahedral and stable structures as the intensity of hydrolysis increased with pH.

Figure 4 indicates that the ageing process from 4 h to 14 days did not change the shape of the diversity histogram remarkably: the same Gaussian distributions with two of the highest frequency values existed in both cases. In the course of 14 days, the first frequency top value shifted from dimers to trimers, and only Al_{11} and Al_{15} were formed as new species. This indicates that the aluminium dimer is perhaps the first polynuclear species formed in solution [27].

In this investigation, the only evidence of unhydrolysed aluminium was the very intensive signal of $[AlCl_4]^-$. This indicates that the major mono-aluminium species is unhydrolysed octahedral m/z 45 $[Al(OH_2)_6]^{3+}$ surrounded by the outer sphere chloride counter anions. Due to the low m/z value, the cation itself could not be found. During the nebulation, the aqua ligands likely evaporated and the counter anions attached to aluminium cation [23, 24].

In this study, 10 different Al_5 species were observed, indicating a great diversity of pentameric species in the bulk solutions. All the Al_5 species had at least one dehydrated oxo-ligand, which could correlate with the structure of the species. All the smaller species, Al_2, Al_3, and Al_4, were found at least once with only hydroxide ligands. Similar results for the different structures of Al_5 complexes have been found by Gianotto *et al.* using quite a different approach [28].

One of the chloride-containing Al_5 species was $[Al_5O_3(OH)_4Cl_4(H_2O)_{0\text{–}3}]^+$ (tables 2 and 8). If the counter-anions were attached to the core during the nebulation, this

Table 8. Different Al_5 species collected, their aluminium oxo-hydroxo cores, and how they would be introduced to distribution calculations.

Observed species		
0.100 mol L^{-1}	0.010 mol L^{-1}	0.001 mol L^{-1}
$[Al_5O_2(OH)_{10}]^+$	$[Al_5O_2(OH)_{10}(H_2O)_{0\text{–}2}]^+$	$[Al_5O_2(OH)_{10}(H_2O)_{0\text{–}3}]^+$
$[Al_5O_3(OH)_6Cl_2]^+$	$[Al_5O_2(OH)_6Cl_4(H_2O)_{0\text{–}3}]^+$	$[Al_5O_3(OH)_4Cl_4(H_2O)_{0\text{–}4}]^+$
$[Al_5O_3(OH)_4Cl_4(H_2O)_{0\text{–}3}]^+$	$[Al_5O_3(OH)_4Cl_4(H_2O)_{0\text{–}3}]^+$	
$[Al_5O_4(OH)_2Cl_4(H_2O)_{0\text{–}4}]^+$	$[Al_5O(OH)_7Cl_5(H_2O)_{0\text{–}1}]^+$	
$[Al_5O_6Cl_4(H_2O)_{0\text{–}4}]^-$	$[Al_5O_4(OH)_4Cl_4]^-$	
$[Al_5O_4(OH)_4Cl_4(H_2O)_{0\text{–}1}]^-$	$[Al_5O_4(OH)_3Cl_5]^-$	
$[Al_5O_4Cl_8]^-$		
Oxo-hydroxo cores		
$[Al_5O_2(OH)_{10}]^+$	$[Al_5O_2(OH)_{10}]^+$	$[Al_5O_2(OH)_{10}]^+$
$[Al_5O_3(OH)_6]^{3+}$	$[Al_5O_2(OH)_6]^{5+}$	$[Al_5O_3(OH)_4]^{5+}$
$[Al_5O_3(OH)_4]^{5+}$	$[Al_5O_3(OH)_4]^{5+}$	
$[Al_5O_4(OH)_2]^{5+}$	$[Al_5O(OH)_7]^{6+}$	
$[Al_5O_6]^{3+}$	$[Al_5O_4(OH)_4]^{3+}$	
$[Al_5O_4(OH)_4]^{3+}$	$[Al_5O_4(OH)_3]^{4+}$	
$[Al_5O_4]^{7+}$		
Hydroxide ligand species		
$[Al_5(OH)_{14}]^+$	$[Al_5(OH)_{14}]^+$	$[Al_5(OH)_{14}]^+$
$[Al_5(OH)_{12}]^{3+}$	$[Al_5(OH)_{10}]^{5+}$	$[Al_5(OH)_{10}]^{5+}$
$[Al_5(OH)_{10}]^{5+}$	$[Al_5(OH)_{10}]^{5+}$	
$[Al_5(OH)_{10}]^{5+}$	$[Al_5(OH)_9]^{6+}$	
$[Al_5(OH)_{12}]^{3+}$	$[Al_5(OH)_{12}]^{3+}$	
$[Al_5(OH)_{12}]^{3+}$	$[Al_5(OH)_{11}]^{4+}$	
$[Al_5(OH)_8]^{7+}$		

Table 9. Different Al_{13} species collected.

$0.100\,mol\,L^{-1}$	$0.010\,mol\,L^{-1}$	$0.001\,mol\,L^{-1}$
$[Al_{13}O_{14}(OH)_9(H_2O)_{0\text{–}4}]^{2+}$	$[Al_{13}O_{10}(OH)_{17}(H_2O)_{0\text{–}3}]^{2+}$	$[Al_{13}O_{10}(OH)_{17}(H_2O)_{0\text{–}5}]^{2+}$
$[Al_{13}O_{11}(OH)_{15}(H_2O)_{0\text{–}6}]^{2+}$	$[Al_{13}O_7(OH)_{22}(H_2O)_{0\text{–}6}]^{3+}$	$[Al_{13}O_7(OH)_{22}(H_2O)_{0\text{–}4}]^{3+}$
$[Al_{13}O_{10}(OH)_{16}(H_2O)_{0\text{–}7}]^{3+}$	$[Al_{13}O_{10}(OH)_{16}(H_2O)_{0\text{–}6}]^{3+}$	
$[Al_{13}O_{10}(OH)_{16}Cl(H_2O)_{0\text{–}6}]^{2+}$	$[Al_{13}O_{16}(OH)Cl_8(H_2O)_{0\text{–}1}]^{2-}$	
$[Al_{13}O_{16}(OH)_4Cl_5(H_2O)_{0\text{–}2}]^{2-}$		
$[Al_{13}O_{16}(OH)Cl_8(H_2O)_{0\text{–}1}]^{2-}$		

species could exist in the solution as highly coagulating $[Al_5O_3(OH)_4]^{5+}$ with aqua ligands in free coordination places. When the conventional distribution diagrams are made, the oxo ligands are usually considered as two hydroxo-ligands due to the rareness of aqueous oxide anions O^{2-}. Thus, this species would be $[Al_5(OH)_{10}]^{5+}$. If all the pentameric species (table 8) were present with hydroxo-ligands, there would still be six different species from $[Al_5(OH)_{14}]^+$ to $[Al_5(OH)_8]^{7+}$, missing only $[Al_5(OH)_{13}]^{2+}$. This result suggests that there were various charges and compositions of aqueous pentameric species. The same phenomenon can be seen with all smaller complexes from Al_1 to Al_9. Perhaps the larger complexes have a less flexible coordination, and their diversity is not so wide. In conventional solution chemistry, only one kind of species of a certain size was chosen for equilibrium calculations.

The Keggin cation, $[Al_{13}O_4(OH)_{24}]^{7+}$ [29], has been considered the main unit in larger precipitated and soluble complexes [30]. The complex $[Al_{26}O_{15}(OH)_{48}Cl_4]^{4-}$ found in this study could consist of two Al_{13}-Keggin units. $[Al_{30}O_8(OH)_{56}(H_2O)_{24}]^{18+}$ has been found previously by X-ray diffraction (XRD) to consist of two Al_{13}-Keggin units bonded by four AlO_6 octahedras [31].

At all concentrations, Al_{13} was found with charges +2 and +3. In the solution $0.100\,mol\,L^{-1}$, pH 4.20, 14 d, one chlorido ligand had attached to the triple-charged aluminium oxido-hydroxido-complex $[Al_{13}O_{10}(OH)_{16}(H_2O)_{0\text{–}7}]^{3+}$, lowering the charge to +2 ($[Al_{13}O_{10}(OH)_{16}Cl(H_2O)_{0\text{–}6}]^{2+}$). Also, from the same solution, Al_{13}^{3+} was found as $[Al_{13}O_{16}(OH)_4Cl_5(H_2O)_{0\text{–}2}]^{2-}$ by using the anionic ESI mode, and some signals were assigned to the Al_{13}^{6+} cation as $[Al_{13}O_{16}(OH)Cl_8(H_2O)_{0\text{–}1}]^{2-}$. Thus, Al_{13} is a very stabile oligomer in solutions with different charges (table 9).

Because Al_{14} was found at all concentrations and Al_{15} complexes also in $0.100\,mol\,L^{-1}$ solutions (figure 2), it could be assumed that in an aqueous chloride-containing environment, the tetrahedral AlO_4^- central unit of the Al_{13} complex could be surrounded by open chains, which vary in lengths or cyclic substructures [23].

As a main conclusion of this investigation, the diversity profile of hydrolysed aluminium complexes varied strongly as a function of concentration and pH. The effect of ageing time was smaller. Species of certain sizes had different charges and structures. Multiple-charged signals assigned to polynuclear multiple-charged aluminium complexes (Al_{10}–Al_{15}) were found in a narrow pH range preceding precipitation. But there still remains the question as to whether the stabile Al_{13} in solutions is the best coagulating agent, or whether there are still more charged species or colloids which cannot be found with MS spectroscopy. Investigations of aluminium solutions using other methods like zeta- and streaming potentials, as well as molecular modelling studies, are currently in progress by the authors.

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