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Application of a new HPLC-ICP-MS method for simultaneous determination of Al^{3+} and aluminium fluoride complexes

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Abstract

The paper presents the new HPLC-ICP-MS method used for conducting speciation analysis of aluminum as free Al^{3+} and aluminum fluoride complexes during one analysis. In the study, 5% HNO$_3$ was used as a derivative reagent in order to minimize the possibility of clogging the torch in ICP-MS. Using the new HPLC-ICP-MS method, speciation analysis of aluminum and aluminum fluoride complexes was conducted on the basis of model solutions and real samples (soil-water extracts and groundwater samples). The analysis in the presented analytical system lasts only 4 min.

Keywords: Earth sciences, Chemistry, Analytical chemistry applications, Analytical chemistry, HPLC

1. Introduction

Aluminum fluoride complexes are most stable and the occurrence of $AlF_x^{(3-x)}$ complexes in natural acid solutions is limited by the general concentration of fluoride ions in complex formation reactions (Karthikeyan and Elango, 2009; Suwalsky et al., 2004). The form in which aluminum occurs in the environment affects its mobility, bio-availability and toxic influence on living organisms and vegetation (Bi et al., 2001; Platt et al., 2007; Frankowski 2015). The labile form of inorganic aluminium is responsible for toxic impact of aluminium on particular components of the natural environment consists of a free Al^{3+} ion, bonds of aluminium with fluorides, sulfates and hydroxy groups. Among these, Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ are considered to be the most toxic aluminium forms. Aluminium and fluoride form as soluble complexes, mainly AlF^{2+}, AlF_2^+, AlF_3^0, AlF_4^-, both in water and soil are less toxic than hydroxy forms and the Al^{3+} form (e.g. Bi et al., 2001; Mitrović and Milačič, 2000; Ruszczyńska et al., 2004). Nevertheless, simultaneous activity of fluorides and aluminium both in water and in the food chain, as well as their broad use in industry, medicine and agriculture, contributes to causing various diseases resulting in changes in metabolism, growing processes and homeostasis of living organisms. The negative influence of aluminium and fluorides, considering their ability to form AlF_x complexes, initiated research on the toxicity of these compounds (Frankowski et al., 2010a). Considering the complexity of aluminum forms in the environment, quantitative and qualitative analysis of the most available form of a given individual is an important aspect. The determination of the aluminium fluoride complexes was conducted by spectrophotometric and fluorometric techniques, HPLC technique with UV detection along with various type of post-column reagents and HPLC with atomic absorption spectrometry with electrothermal atomization (ET-AAS) as the detector off-line system. However, none of these methods did not enable the full separation between the aluminium fluoride forms and Al^{3+} during one analysis (Frankowski et al., 2010a). Only the developed new analytical system like HPLC-FAAS and HPLC-UVVIS enabled the full separation of all aluminium fluoride complexes (AlF^{2+}, AlF_2^+, AlF_3^0, AlF_4^-) and Al^{3+} form during single analysis (Zioła-Frankowska et al., 2009; Frankowski et al., 2010b; Frankowski and Zioła-Frankowska, 2010c). However, another analytical system used in speciation analysis of aluminum fluoride complexes is chromatography with ICP-MS detection. It is well know, that chromatographic separations coupled with ICP-MS for detection can give a lot combination for elemental speciation studies and offers the advantages of high sensitivity and selectivity (Ponce de León et al., 2002; Seubert, 2001). Nevertheless, the use of this type of analytical systems is associated with some problems. This problem is mainly related to mobile phases with organic solvents or high salt

content, which is cause the quenching of plasma and clogging of the torch, nebulizer or sampling cone (Hils et al., 1999). Bayón et al. (1999) used the ICP-MS detection in the HPLC system and obtained chromatographic separation of two forms: AlF^{2+} and Al^{3+}. The solution of 0.45 mol/L HNO_3 was used as the eluent because, contrary to the K_2SO_4 solution also used as an eluent, it did not clog the main duct of the burner. Similarly, Fairman et al. (1998) used HPLC-ICP-MS in his study in order to conduct the speciation analysis in water. The author obtained chromatographic separation of forms AlF^{2+} and Al^{3+}. However, the high content of salt in the eluent (0.08 mol/L K_2SO_4), which caused clogging the main duct of the burner in a short time, was really problematic.

The aim of this research was to: (1) develop the application for separation and determination of aluminium and aluminium fluoride complexes by HPLC-ICP-MS in one simple online analysis without the effect of clogging the torch (2) apply the analytical system for environmental samples of soil water extracts and groundwater.

2. Materials and methods

2.1. Analytical system

An ICP-MS instrument Agilent 7500ce (Agilent Technologies, Japan) coupled with Agilent 1100 Series HPLC system was used for our experiments. ICP operates at 1500 W with 15 L min^{-1} plasma gas flow. The concentric (MicroMist) nebuliser with 1.1 L min^{-1} (carrier + make-up) argon gas flow was used for nebulising HPLC eluent. 27Al isotope was used for data acquisition with 0.5 s integration time. The HPLC is equipped with a quaternary pump, a vacuum degasser, an autosampler and a heated column compartment (Agilent Technologies, Japan). Ion-exchange column - Dionex IonPac CS5A (analytical column, 250 mm, 4.0 mm i.d., particle size 9.0 μm, containing mixed anion and cation beds with sulfonic acid and alkanol queternary ammonium functional groups) (Dionex, USA) and IonPac CG5A (guard column, 50 mm, 4 mm i.d., particle size 9.0 μm) (Dionex, USA) were used. The Table 1 summarizes the basic HPLC parameters. The information about choosing NH_4Cl as a mobile phase has been deeply presented by Zioła-Frankowska et al. (2009).

2.2. Sample preparation

The environmental samples (groundwater and soil) were taken in the area of Chemical Plants situated in Luboń (Poland). The detailed description of the study area has been presented in Frankowski et al. (2010a, 2013). Groundwater for the analysis was collected after exchanging the water in the hole at least

Table 1. Basic HPLC parameters used in HPLC-ICP-MS analytical system.

Parameters of HPLC analytical system (linear gradient elution program)	
eluent A	1.5 M NH_4Cl pH $\approx$ 3.0
eluent B	water acidified to pH $\approx$ 3.0
column	Dionex IonPac CS5A with IonPac CG5A
eluents flow	2.0 ml·min^{-1}
injection volume	100 µL
column temperature	25 °C
detection limit for 100 µL loop	1 ng L^{-1}
linearity to:	1000 mg·L^{-1} for ICP-MS and 100 mg·L^{-1} for HPLC-ICP-MS (capacity of analytical column)
accuracy	Relative Standard Deviation <5%

three times and after stabilizing the basic physical parameters in the pumped water. Water samples were collected in 100 ml polyethylene bottles. In order to avoid the disturbance of speciation balance, the samples were not fixed. The water extraction was conducted at the temperature of 25 °C for 1 h using a magnetic mixer. The extracts were prepared in proportion 1:10 (v/v) for the predominant fraction in a 100 g soil sample with 0.1–0.25 mm grain size. The samples were then centrifuged (6000 rpm) for 15 min. The solution was taken for the analysis. The pH (H_2O) determinations were performed in groundwater and soil water extracts prepared for the analysis, using the Orion 5-star Plus meter (Thermo, USA) with a Single Pore pH electrode (Hamilton, USA). Furthermore, the determinations of fluorides using an ion selective fluoride electrode (FISE) with TISAB buffer solution used for adjustment of pH and total ionic strength (Thermo-Orion, USA) were conducted in the same samples. The concentration of aluminium in soil water extracts and groundwater was determined using a Shimadzu AA7000 spectrometer (Shimadzu, Japan) with a nitrous oxide-acetylene flame atomization. Measurement of Al was performed in three replications and the Relative Standard Deviation did not exceed 7%. The speciation analysis was performed in groundwater and soil water extracts by HPLC-ICP-MS method.

2.3. Model solution

The samples of model solutions were prepared in the way that allowed for observing the variability of occurrence of aluminum and aluminum fluoride complexes depending on the F/Al stoichiometry. The types of model solutions prepared for the studies in the HPLC-ICP-MS analytical system were:
2.5 mg L^{-1} of Al and variable concentration of fluorides: 0.5; 1.0; 2.0; 4.0; 6.0; 8.0 and 10.0 mg L^{-1}.

3. Results and discussion

Based on the conducted analysis of model solutions characterized by variable fluoride concentration in relation to the concentration of aluminum, the separation of aluminum complexes with fluorides (AlF_2^+, AlF_3^0, AlF_4^-, AlF^{2+}) and form Al^{3+} was obtained in a single analytical cycle. During the process of chromatographic separation, the precipitation of eluent salt and clogging of the torch were observed, which was also previously found by Bayón et al. (1999). The problem related to the torch clogging was solved by using 5% HNO_3 as the post-column eluent in this work. The application of derivation allowed for minimizing the effect of torch clogging and for conducting the research in the analytical cycle without the necessity to clean the torch. The variable concentration of HNO_3 (from 1% to 5%) was checked. No effects resulting from the use of 5% HNO_3, which would affect determination results, were observed. It should be underlined that 5% HNO_3 dissolved the NH_4Cl salt after separation, so the crystallization of salts in torch does not exist. The quantitative analysis confirmed previous studies concerning the process of chromatographic separation: first signal (AlF_2^+, AlF_3^0, AlF_4^-), second signal (AlF^{2+}) and third signal (Al^{3+}). The detection in the HPLC-ICP-MS system confirmed the previous studies connected with the formation of fluoride aluminum complexes depending on aluminum concentration in relation to the concentration of fluorides (Frankowski and Zioła-Frankowska, 2010c). Table 2 presents the comparison of results obtained in the HPLC-ICP-MS and HPLC-UVVIS systems.

Based on the obtained study results, it was found that the concentration values are similar for particular aluminum forms, which suggests the selectivity and proper functioning of the HPLC-ICP-MS analytical system. In order to apply the new method, a series of determinations of soil water extracts samples (n = 9)

Table 2. Comparison of the results obtained for mix standard solution F/Al for the HPLC-ICP-MS and HPLC-UVVIS systems.

| F/Al [mg L^{-1}] | HPLC-ICP-MS [mg L^{-1}] this work | | | HPLC-UVVIS [mg L^{-1}] (Frankowski and Zioła-Frankowska, 2010c) | | |
	AlF_2^+, AlF_3^0, AlF_4^-	AlF^{2+}	Al^{3+}	AlF_2^+, AlF_3^0, AlF_4^-	AlF^{2+}	Al^{3+}
0.5/2.5	0.015	0.631	1.854	n.a.	n.a.	n.a.
1.0/2.5	0.045	1.233	1.222	n.a.	n.a.	n.a.
2.0/2.5	0.674	1.215	0.611	0.742	1.075	0.683
4.0/2.5	1.719	0.739	0.042	1.873	0.543	0.083
6.0/2.5	2.203	0.272	0.025	2.271	0.193	0.036
8.0/2.5	2.355	0.117	0.028	2.387	0.1	0.013
10.0/2.5	2.383	0.095	0.022	2.348	0.061	0.091

n.a. not analysed by Frankowski and Zioła-Frankowska, (2010c).

and groundwater samples (n = 19) were conducted. The samples were collected in the area of the former post-crystallization leachate disposal site and from the areas located around the disposal site. In the case of analysing the environmental samples, the concentration of aluminum, the concentration of fluorides and pH reaction of the analysed samples were taken into consideration. The example results of speciation analysis in the HPLC-ICP-MS system for samples of soil water extracts (Fig. 1) and groundwater (Fig. 2) have been presented in the chromatograms, alongside the determined concentration of aluminum, the concentration of fluorides, the pH of the sample and the corresponding concentrations of particular aluminum forms depending on the F/Al proportion and pH (Table 3, Table 4).

Speciation analysis of groundwater and soil water extracts samples by HPLC-ICP-MS method allowed to separate three forms of aluminium, similarity like for model solutions. The obtained results comply with theoretical calculations obtained using the Mineql program for chemical modeling. However, both for model solutions and real samples the degradation of Al forms to Al^{3+} was observed. It was also founded by Frankowski (2012, 2014). The results of the studies of total concentration of aluminum are similar to the results obtained as the sum of forms of aluminum fluoride complexes and form Al^{3+}. Only for the determined groundwater sample, where the result of 0.141 mg L^{-1} was obtained
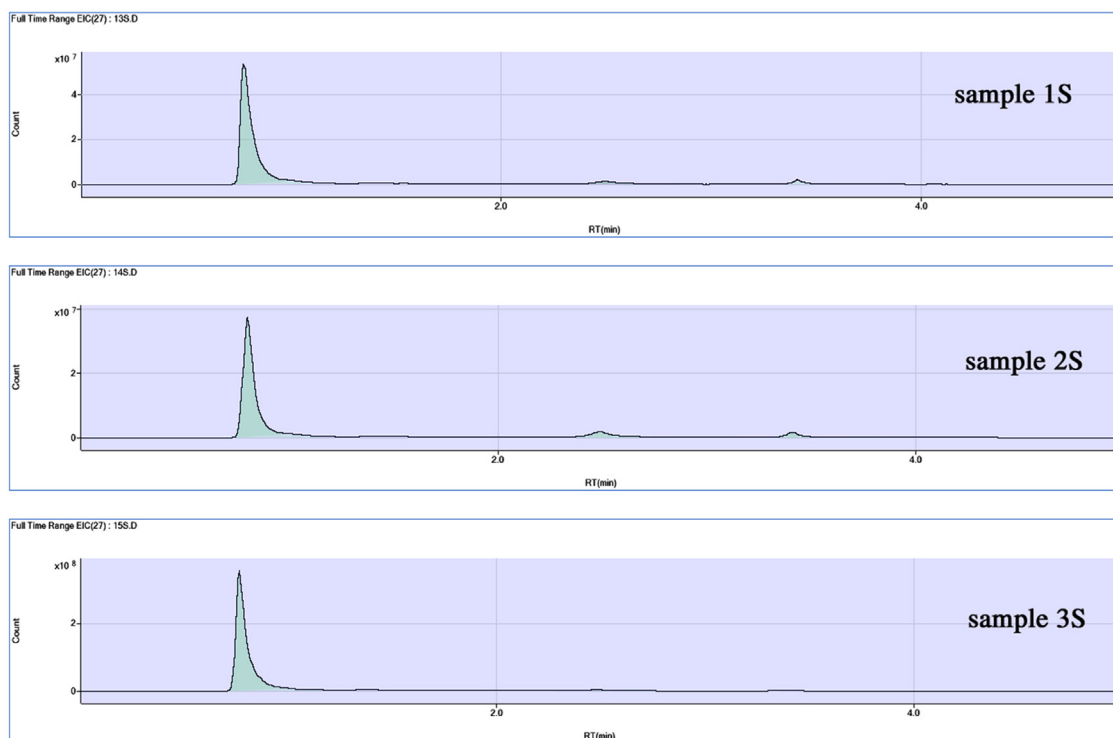
Fig. 1. Chromatograms obtained for soil water extracts by HPLC-ICP-MS analytical system.
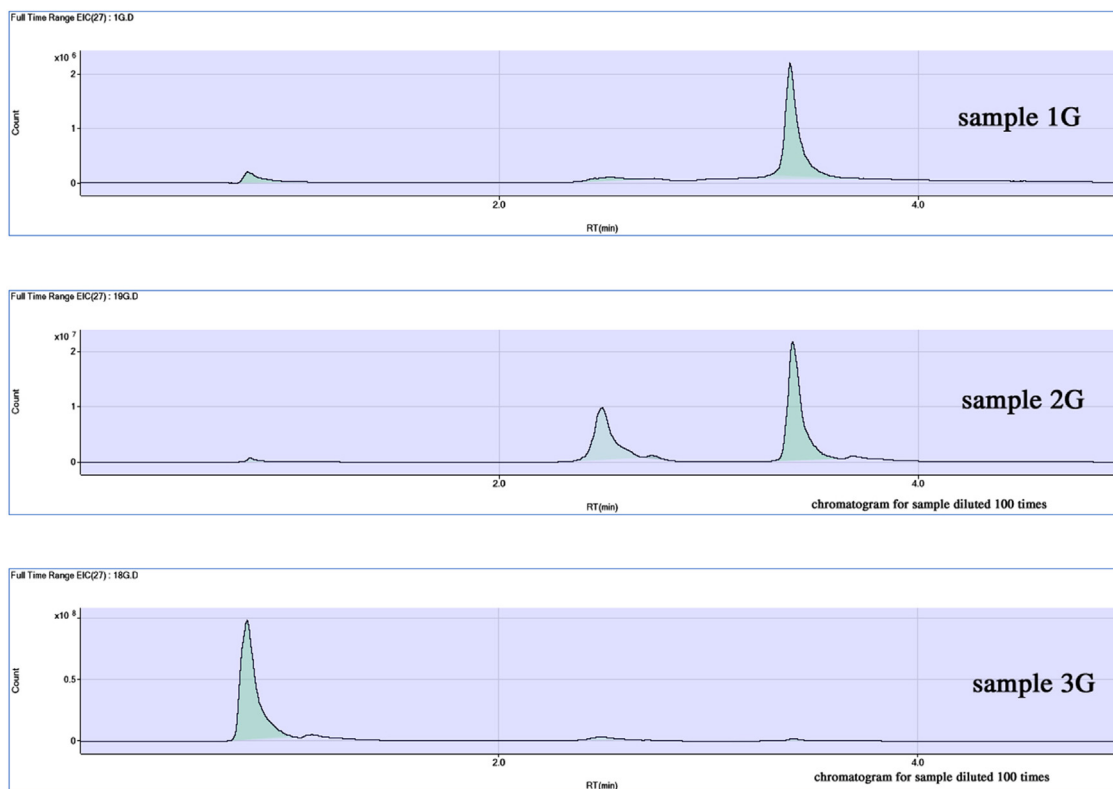
Fig. 2. Chromatograms obtained for groundwater samples by HPLC-ICP-MS analytical system.

for form Al^{3+}, it may be observed that the signal does not come from this form, which is related to the sample pH. Most probably, the transformation (degradation) of aluminum in hydroxy form into form Al^{3+} occurs, caused by the influence of the mobile phase. In the case of the variability evaluation of the occurrence of aluminum, fluorides and aluminum fluoride complexes depending on pH, the occurrence of aluminum fluoride complexes can be observed. Especially at the low pH reaction and predominance of fluorides (this particularly concerns both soil water extracts and groundwater samples) the occurrence of aluminum in the form

Table 3. Results obtained for soil water extracts samples in [mg kg^{-1}] by HPLC-ICP-MS and by Frankowski et al. (2013).

Sample	Source	Al	F$^-$	pH	AlF$_2^+$, AlF$_3^0$, AlF$_4^-$	AlF^{2+}	Al^{3+}	Σ of Al forms
1S	This work	-	209		76.21	2.325	0.578	79.11
	Frankowski et al. (2013)	77.93	-	5.04	-			
2S	This work	-	74.5		30.76	2.719	0.659	38.36
	Frankowski et al. (2013)	34.83	-	3.81	-			
3S	This work	-	990		237.2	5.566	0.365	243.1
	Frankowski et al. (2013)	234.8	-	3.83	-			

Table 4. Results obtained for groundwater samples in [mg L^{-1}] by HPLC-ICP-MS and by Frankowski (2012).

Sample	Source	Al	F$^-$	pH	AlF$_2^+$, AlF$_3^0$, AlF$_4^-$	AlF^{2+}	Al^{3+}	Σ of Al forms
1G	This work				0.017	0.012	0.141	0.17
	Frankowski (2012)	0.21	4.52	7.09	0.065	0.028	0.099	0.19
2G	This work				1.43	27.56	217.6	246.6
	Frankowski (2012)	251.1	27.1	3.21	1.17	26.14	202.9	230.2
3G	This work				669.7	26.80	16.25	712.7
	Frankowski (2012)	721.2	1830	4.16	621.4	71.23	11.33	703.9

of first signal was observed, in which aluminum occurs in the form of aluminum fluoride complex AlF$_3^0$ and AlF$_4^-$, which can also be observed for model solutions.

4. Conclusions

The HPLC-ICP-MS method with post-column derivation using 5% HNO$_3$ is a good tool in speciation analysis of free aluminum (Al^{3+}) and aluminum fluoride complexes. This method does not cause the clogging of the torch in the ICP-MS spectrometer and it allows for the quick determination of interesting aluminum forms in aluminum fluoride complexes in the time of only 4 min during one analysis. The method has been tested both based on the model studies, previous studies and studies of soil water extracts and groundwater samples. The HPLC-ICP-MS method can be successfully applied in speciation analysis of samples of different nature and matrix, not only in the environmental studies.

Declarations

Author contribution statement

Anetta Zioła-Frankowska: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Jan Kuta: Performed the experiments.

Marcin Frankowski: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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