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Speciation analysis of aluminium and aluminium fluoride complexes by HPIC-UVVIS

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ABSTRACT

The study presents a new analytical method for speciation analysis in fractionation of aluminium fluoride complexes and free Al^{3+} in soil samples. Aluminium speciation was studied in model solutions and soil extract samples by means of high performance ion chromatography (HPIC) with UV–VIS detection using post-column reaction with tiron for the separation and detection of aluminium fluoride complex and Al^{3+} forms during one analysis. The paper presents particular stages of the chromatographic process optimization involving selecting the appropriate eluent strength, type of elution or concentration and quantity of derivatization reagent. HPIC was performed on a bifunctional analytical column Dionex IonPac CS5A. The use of gradient elution and the eluents A: 1 M NH_4Cl and B: water acidified to pH of eluent phase, enabled full separation of fluoride aluminium forms as AlF_2^+, AlF_3^0, AlF_4^- (first signal), AlF^{2+} (second signal) and form Al^{3+} in a single analytical procedure. The proposed new method HPIC-UVVIS was applied successfully in the quantitative and qualitative analysis of soil samples.

1. Introduction

Aluminium complexes with fluorides (AlF_2^+, AlF^{2+}, AlF_3, AlF_4^-, AlF_5^{2-}, AlF_6^{3-}) significantly influence the increase in solubility of aluminium compounds. According to Martin [1], the occurrence of fluorides will reduce the toxicity of Al^{3+} in relation to plants, fish and people. Stevens et al. [2] observed that the presence of the $AlF_x^{(3-x)}$ aluminium fluoride complexes increases phytotoxicity of aluminium. Stevens's research showed that such forms as AlF^{2+} and AlF_2^+ are also toxic but to a lesser extent than Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ forms [2]. According to Strunecká et al. [3], simultaneous activity of fluorides and aluminium both in water and the food chain as well as their broad use in industry, medicine and agriculture cause various diseases which result in changes in metabolism, growing processes and homeostasis of living organisms. The negative interaction of both aluminium and fluorides, considering their ability to form AlF_x complexes, initiated research on the toxicity of these compounds, mainly at the intracellular level [4–7]. High aluminium concentration and low pH values are favourable conditions for forming soluble forms of aluminium complexes, including aluminium fluoride complexes. The chemical reaction describing formation process of aluminium fluoride complexes are presented in [8,9] and also in the library of Mineql programme. The most common chromatographic techniques include the HPLC (with cation or anion analytical column) combinations with different detectors. The following systems may be used to conduct speciation analysis: SEC/HPLC with ICP-MS, UV, ICP-OES, ETAAS, ES-MS–MS detectors [10–12], FPLC systems with the following detectors: ICP-MS, ICP-OES, ICP-AES and ETAAS, ES-MS–MS [13–17] and RP-HPLC with a UV-PDA detector [18]. HPLC–ICP-MS analytical system was used to determine aluminium in the general order: $AlL_x^{<+2}$, AlL_x^{2+}, Al^{3+} [19,20]. HPLC with a FAAS detector enabled the separation and qualitative determination of Al^{3+}, AlF^{2+}, AlF_2^+ [21]. HPLC with a FAAS detector enabled the full speciation analysis of cation and anion aluminium complexes with fluorides: AlF^{2+}, AlF_2^+, AlF_3^0, AlF_4^- and Al^{3+} form within one analytical procedure [22]. Among the numerous analytical procedures, the most frequently represented one comprises HPLC systems with UV detectors with different types of reagents used in post-column derivatization, e.g.

Abbreviations: oxine, 8-quinolinol,8-hydroxyquinoline; PCV, pyrocatechol violet; ferron, 7-iodo 8-hydroxy quinoline 5-sulfonic acid; aluminon, triammonium salt of 5-[(3-carboxy-4-hydrox~henyl)(3-carboxy-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]-2-hydroxybenzoic acid; ECR, Eriochrome Cyanine RC; morin, 2′,3,4′,5,7-pentahydroxyflavone; lumogallion, 2,2′,4′-Trihydroxy-5-chloroazobenzene-3-sulfonic Acid tiron (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt); HPLC, high-pressure liquid chromatography; ICP-MS, inductively coupled plasma mass spectrometry; ICP-AES, inductively coupled plasma atomic emission spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry; SEC/HPLC, size-exclusion HPLC; FPLC, fast protein liquid chromatography; ETAAS, electro thermal atomic absorption spectrometry; UV-PDA, UV-photodiode array detector; ES-MS–MS, electrospray tandem mass spectrometry; FAAS, flame atomic absorption spectrometry.

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oxine [23–32], PCV [8,33–37], ferron [38], aluminon [38], ECR [39], morin [40,41], lumogallion [8,42], tiron [8,43–45]. In order to determine stable AlF_x complexes, Bertsch and Anderson used the HPLC technique with CS3 column (Dionex, USA) with UV detection along with the post-column derivatization with tiron. The determination conditions were used in the model solution analysis to isolate Al^{3+} from fluoride, citrate and oxalate complexes. The Authors separate only AlF^{2+} and Al^{3+} forms [46]. Willet used the CG2 guard column in his research along with the post-column derivatization with PCV and 1.10-phenanthroline and hydroxylamine. Despite the quick chromatographic process, full separation between the AlF^{2+} and $AlF^{+}{}_2$ forms was not achieved, the forms were eluted close to the solvent front [47]. Motellier and Pitsch used the CS2 cation column with CG2 and the detection with post-column derivatization with 3×10^{-4} M tiron in 3 M ammonium oxalate. They did not obtain the full separation of the AlF^{2+} and $AlF^{+}{}_2$ forms [48]. Sutheimer and Cabbaniss [8] presented their studies of aluminium speciation (III) in aquatic environment for model aluminium solutions with: fluorides, silicates, citrates and acetates. The chromatographic process was conducted using the Synchropack Cation CAT15 cation column with the CATPC guard column. The determination was performed using the post-column derivatization with lumogallion as the chelating reagent and fluorescent detection. The separation of three aluminium forms was obtained in bonds with the analysed ligands (for all complexes in particular analyses). It was stated that the signals obtained for aluminium fluoride complexes elute according to the increasing charge: $AlF_2{}^+$ $AlF_3{}^0$, AlF^{2+} and Al_f (as Al^{3+} and hydroxy-aluminium forms). In order to verify the analytical method, the authors analysed a lake water sample and obtained the separation of 3 forms of aluminium, which according to the authors derived from complexes +1, +2 and +3. These, however, appeared not to be the AlF_x complexes, but organic complexes because the particular signals in all the analysed complexes were obtained in close retention times [8]. Borman and Seubert [49], in order to conduct speciation analysis of aluminium in its complexes with fluorides, oxalates and citrates, used the post-column derivatization reagent tiron with UV and ICP-AES detection. Depending on the proportion of ligands in model solutions, in the case of AlF_x complexes in the amount of 1:1 (Al:F), the obtained signals were related to the following forms: $AlF^{+}{}_2$, AlF^{2+} and Al^{3+}. Hara et al. [43] used the methodology of Sutheimer and Cabbaniss [8] to determine aluminium fluoride complexes in atmospheric sediments samples. Drabek et al. also conducted speciation analysis in the HPLC-UV system using the cation column. The authors, referring to the studies [50,51], obtained partial separation of aluminium and aluminium complexes with other ligands. In their study [52], the authors present the research on aluminium speciation in forest soils and in non-afforested soils. However, their study concerns only the cation aluminium forms. It should be underlined that the previous research into aluminium speciation [51] and the conducted qualitative analysis indicated significant participation of the $Al(X)^+$ form. In the studies by Drabek et al. [51,52], the authors probably did not take into consideration the $AlF_3{}^0$ and $AlF_4{}^-$ forms. Using the cation column and obtaining one signal, similarly to the case of $Al(X)^+$ aluminium in study [52], which constitutes about 80% of the whole aluminium in a sample, shows that the forms elute in the dead time, or the first signal indicates forms with neutral and negative charge, while the second signal comes from aluminium fluoride complexes (+1 and +2), and the third signal is the Al^{3+} form (also as polymerised forms) [51,52].

The aim of the study was to develop new, fast and simple method for speciation analysis of aluminium and aluminium fluoride complexes by HPIC-UVVIS in model solutions. To confirm data from analytical system the computer modelling programme was used. To conduct speciation analysis of aluminium and aluminium complexes with fluorides in soil water extracts the proposed new method was applied. The new aspects of speciation analysis of aluminium and aluminium fluoride complexes by HPIC-UVVIS in fractionation was presented.

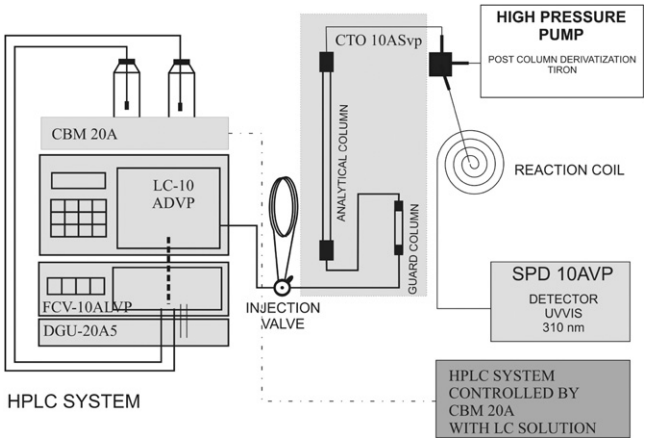

Fig. 1. Analytical system: HPIC with post-column derivatization by tiron reagent and UV–VIS detector (310 nm).

2. Materials and methods

2.1. Instrumentation and optimization

The chromatographic separation was performed by liquid chromatography system consisting of: Shimadzu solvent delivery module LC-10 ADVP liquid chromatograph and low pressure gradient flow control valve Shimadzu FCV-10 ALVP, degasser DGU-20A5, column oven CTO-10ASvp with Rheodyne Model 7725i Injection Valve (Rheodyne LLC, USA) and with ion-exchange column – Dionex IonPac CS5A (analytical column, 250 mm, 4.0 mm i.d., particle size 9.0 μm) and IonPac CG5A (guard column, 50 mm, 4 mm i.d., particle size 9.0 μm). HPIC system was controlled by CBM-20A (Shimadzu Corporation, Japan) communication bus module with LC Solution software. The post-column derivatization unit was based on the high-pressure pump (Dionex, USA). The tiron 6×10^{-4} M (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt) reagent solution was buffered at pH ≈ 6.5 with 1 M CH_3COONH_4. Rapid kinetics of $AlF_n{}^{3-n}$ dissociation and complex of aluminium with tiron occur as these species successively react with tiron before reaching the detector cell. The line of the reagent for post-column derivatization of tiron was connected with chromatographic system by T-shape interface and a reaction coil 0.82 mm i.d. PEEK transfer tubing was used in chromatographic and post-column derivatization system. A mixing coil was placed in line between the Dionex high-pressure pump and the Shimadzu UVVIS detector which was set at 310 nm. Data acquisition and peak integration were performed using LC Solution software system. Fig. 1 presents the diagram of the HPIC-UVVIS analytical system.

The optimization work involved selecting the appropriate eluent strength, establishing the conditions in the isocratic-gradient system, selecting the size of injection valve, checking the influence of temperature on the process of chromatographic separating and selecting a proper length of the reaction loop. The conditions of chromatographic separation presented in Table 1. These conditions were complemented by the value of phase flow of the derivatization reagent and the experimental reaction loop lengths of 3 and 6 m were selected.

Table 1
Conditions of chromatographic process for the HPIC-UVVIS system (optimization).

Parameters	Initial parameters (gradient elution)	Isocratic elution	
Eluent	1.5 NH_4Cl pH ≈ 3.0	1.0 M NH_4Cl pH ≈ 3.0	0.1 M NH_4Cl pH ≈ 3.0
Post-column reagent	Tiron 6×10^{-4} M in 1 M CH_3COONH_4 pH ≈ 6.5		
Eluent flow	1 mL min^{-1}	1 mL min^{-1}	2 mL min^{-1}
Post-column reagent flow	1 mL min^{-1}	0.5 mL min^{-1}	1.0 mL min^{-1}
Injection volume	20 μL	100 μL	100 μL
Reaction loop	3.0 m	1.0 m	1.0 m
Wavelength		310 nm	
Column temperature		20 °C	

2.2. Sample information and preparation

The soil samples were collected from two soil profiles (P1 and P2) (P1: N 521932.3 E 165344.6; P2: N 521932.7 E 165347.0) located in the area of Chemical Plant in Luboń (Poland). The Chemical Plant has been producing aluminium fluoride since 1971. The post-crystallization leachate generated in the production process has been collected at the post-crystallization leachate disposal site in the form of semi-fluid pulp. In the 1980s of the last century such chemicals as superphosphate, hydrofluoric acid, aluminium fluoride, potassium fluorborate and vanadium catalyst were also produced here.

The samples were collected in PE containers every 1 m or at each lithology change. The samples from soil profiles were marked by high participation of fine or medium grained sands fractions. Only sample No. 6 from profile 1 was marked by high participation of fine fractions <0.063 mm and was classified as silt. The samples were dried at room temperature. The hygroscopic water and the substances dissolved in it were treated as an integral component of the sample. After drying a sample was passed through sieves with mesh sizes of 2.0, 1.0, 0.5, 0.25, 0.1, and 0.063 mm, according to the Polish Norms PN-ISO 565:2000 and PN-ISO 3310-1:2000, using a sieve shaker LAB-11-200/UP (EKO-LAB, Brzesko, Poland). Grain size fraction 0.125–0.25 mm was dominating and this fraction was used to prepare soil water extracts (only for sample No. 6, silt: grain size fraction <0.063 mm). In order to produce extracts, 1.00 g of sample was weighed and extracted in 10 ml (1) of deionised water – water soluble fraction and (2) 1 M NH_4Cl – exchangeable aluminium fraction for 1 h using a magnetic stirrer.

3. Results and discussion

Based on the conditions presented in Table 1, the analyses of standard (10 mg L^{-1}), a model (10 mg L^{-1}) of aluminium and a fluoride (5 mg L^{-1}) solutions were prepared. Fig. 2 presents the chromatograms. The separation of AlF_x and Al^{3+} was not achieved in this case.

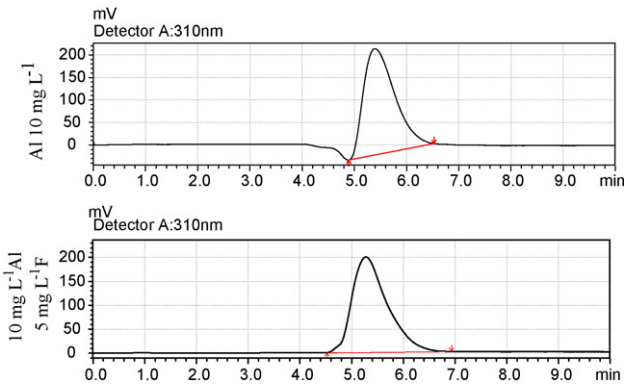

Fig. 2. Chromatograms obtained for HPIC-UVVIS system according to the elution program analogous to HPLC-FAAS system.

The use of 1.5 M NH_4Cl eluent along with gradient elution did not achieve the separation of aluminium forms in the suggested analytical procedure. The eluting forms co-elute, which resulted in one signal. Moreover, an intense signal deriving from the eluent was also obtained. The relationship between the eluent flow and the derivatization reagent flow was then optimized. Also in this case the separation of aluminium fluoride forms and the Al^{3+} form was not obtained. Based on the offline study, it was stated that the complex formation reaction occurs quickly, which may be linked to the mixing of aluminium forms separated in the column. The length of reaction loop was shortened to 10 cm. The use of a shorter reaction loop caused signal 'pulsation'. The optimal reaction loop size was experimentally determined to be 100 cm and further analytical work focused particularly on the flow of the mobile phase and the derivatization reagent. It was assumed that, due to their charge, the forms will elute along with the increasing charge depending on the growing elution strength of the eluent. In further studies, due to the high signal deriving from the eluent, isocratic elution with NH_4Cl eluent with the concentration of 1 M was used. The use of 1 M NH_4Cl eluent enabled the separation of 2 signals (for the solution with the aluminium concentration of 10 mg L^{-1} and fluoride concentration of 5 mg L^{-1}). Fig. 3 presents chromatograms obtained for the conditions in Table 1.

The use of 1 M ammonium chloride and enabled the separation of aluminium forms in the form of two signals. The first signal most probably represents aluminium complexes with fluorides with the charge of (+1, 0, −1, +2), while the other signals from Al^{3+}. Fig. 4 presents the chromatograms for the model solution Al:F (10:5 mg L^{-1}) in relation to temperature.

Based on the results, it may be stated that better separation of peaks deriving from different forms was obtained in higher temperature. The separation of forms deriving aluminium complexes

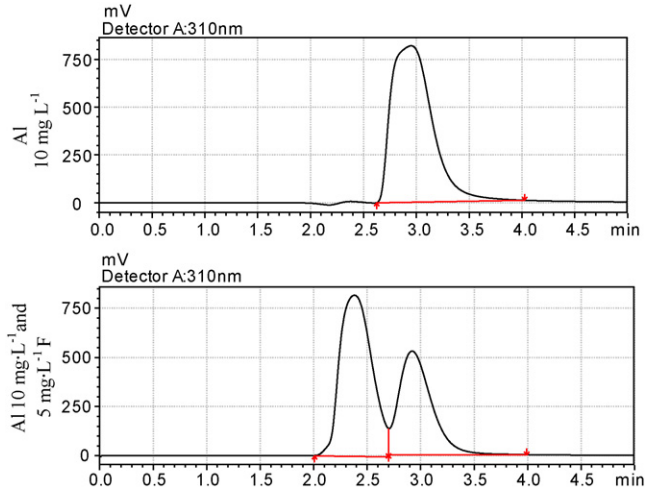

Fig. 3. Results obtained for conditions presented in Table 2 for the aluminium solution with the concentration of 10 mg L^{-1} and for the solution with the concentration of 10 mg L^{-1} aluminium and 5 mg L^{-1} fluorides.

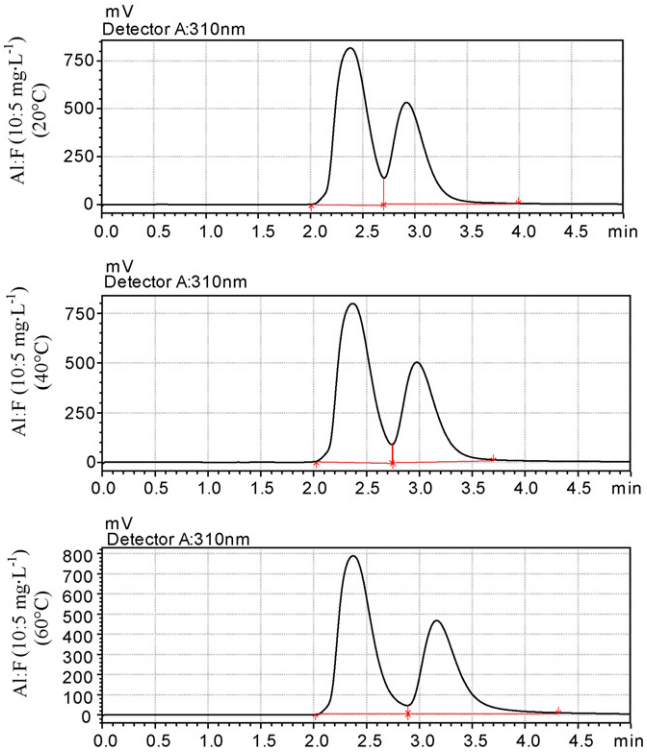

Fig. 4. Influence of temperature on chromatographic process of Al^{3+} and aluminium fluoride complexes.

with fluorides was not obtained. Considering the fact that two signals was obtained for the eluent with the concentration of 1 M NH_4Cl, the charge was taken into consideration and the separation of the first signal coming from aluminium fluoride complex forms (+1, 0, −1, +2) was attempted. In order to improve the resolution during separation, the solution of ammonium chloride with 0.1 M concentration was prepared. The separation of aluminium fluoride forms without the Al^{3+} signal was obtained. The conditions have been presented in Table 1. In the conditions of isocratic elution using 0.1 M NH_4Cl, two signals most probably derived from the aluminium fluoride forms without the signal from Al^{3+} form. It was assumed that the gradient elution will result in obtaining proper conditions of chromatographic process and the signal from the Al^{3+} form. For this purpose the linear gradient elution with 1 M NH_4Cl was used as well as deionised water acidified to the pH reaction of about 3.0. Moreover during the chromatographic process the high signal from the eluent was also observed. Table 2 presents basic, appropriately selected parameters of the HPIC-UVVIS system used in the determination of aluminium and aluminium complexes with fluorides.

Table 2
Appropriately selected parameters of chromatographic process for the HPIC-UVVIS system.

Eluent A	1 M NH_4Cl pH ≈ 3.0
Eluent B	Water acidified to pH ≈ 3.0
Post-column reagent	Tiron 6×10^{-4} M in 1 M CH_3COONH_4 pH ≈ 6.5
Eluents flow	2.0 mL min^{-1}
Post-column reagent flow	1.0 mL min^{-1}
Injection volume	100 μL
Reaction loop	1.0 m
Wavelenght	310 nm
Column temperature	20 °C

Table 3
Concentration of model solution Al:F for which the speciation analysis was performed.

Chromatogram	1	2	3	4	5	6	7
Al [mg L^{-1}]	0	2.5	2.5	2.5	2.5	2.5	2.5
F [mg L^{-1}]	0	0	2.0	4.0	6.0	8.0	10.0

Based on the appropriately selected parameters of the HPIC-UVVIS system, a series of analyses of model solutions (Table 3) was conducted. The results of speciation analysis in the form of chromatograms for standard solutions for different Al:F proportions in the form of overlapping chromatograms have been presented in Fig. 5.

The optimal conditions indicate the successful process of chromatographic separation of forms AlF_2^+, AlF_3^0, AlF_4^- (first signal), AlF^{2+} (second signal) and the Al^{3+} form. The obtained chromatograms indicate the variability resulting from the relation between aluminium and fluorides in aluminium fluoride complexes. Moreover, Table 4 presents the values of peak area and peak height, as well as the retention time and concentration for particular analytical signals. It should be underlined that the analysis of aluminium in the form of complexes is definitely more difficult due to the lack of possibilities to determine the precise concentration of a given form.

Based on the calculations it may be stated that, at much higher concentration of fluorides in relation to the concentra-

Table 4
Basic chromatographic parameters and calculated concentration of aluminium forms for particular signals of model solutions.

Sample signal	Al[a]	F[a]	RT	PA	PH	Σ PA[b]	c[a]
0	0	0	4.347	155,182.2	26,300.2	–	–
1		0	4.333	3,065,371	517,208.4	2,910,188	2.500
2.1		2.0	1.053	940,817.2	178,894.9		0.742
2.2			3.281	1,362,810	254,840.1	3,169,676	1.075
2.3			4.34	1,021,231	185,229.1		0.683
3.1		4.0	1.068	2,254,538	412,017.2		1.873
3.2			3.314	653,571.5	127,900.2	3,008,561	0.543
3.3			4.35	255,633.5	46,320.1		0.083
4.1	2.5	6.0	1.059	2,665,858	438,911.7		2.271
4.2			3.368	227,109.2	45,499.8	2,935,273	0.193
4.3			4.354	197,487.5	36,650.1		0.036
5.1		8.0	1.044	2,901,101	468,465.1		2.387
5.2			3.367	121,442.6	24,670.4	3,038,612	0.100
5.3			4.357	171,250.5	32,272.5		0.013
6.1		10.0	1.027	2,919,395	4,71,910.5		2.348
6.2			3.361	75,326.3	15,649.5	3,107,982	0.061
6.3			4.352	268,443.4	46,134.6		0.091

[a] mg L^{-1}.
[b] Minus the sum of the signal form the eluent.

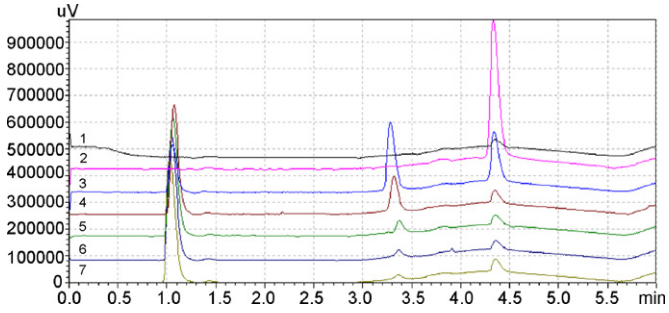

Fig. 5. Overlapping chromatograms for model solutions (values 1–7 see Table 3).

tion of aluminium, AlF_3^0 and AlF_4^- forms dominate. The method using a UV–VIS detector confirms the relations in forming aluminium complexes with fluorides [15,16]. Fig. 6 presents the graph of occurrence variability of aluminium forms depending on the aluminium–fluorides proportion. It was assumed that, at such order of elutions and at the concentrations obtained from particular forms of aluminium, the forms will elute according to their charge: the first signal (forms AlF_2^+, AlF_3^0, AlF_4^-), the second signal (form AlF^{2+}) and the third signal form Al^{3+}. The signals have been described as 1PA, 2PA, 3PA, respectively.

Already at the molar proportion of Al:F = 0.88, over 50% of forms are aluminium complexes with fluorides, with the dominating concentration of AlF^{2+} form. At the molar proportion of Al:F = 0.44, the concentration of Al^{3+} form remains at the level of 3%. However, despite high concentration of fluorides, this form still occurs. Further increase of the fluorides concentrations in relation to the molar relation coefficient value of Al:F = 0.18 causes almost total domination of aluminium complexes with fluorides with the charge of 0 and +1. In order to confirm the results obtained in the HPIC-UVVIS system, the Mineql 4.5 computer modelling was performed. The graph in Fig. 7 shows the relation between the constant aluminium concentration (9.26×10^{-5} M) and variable fluoride concentration ($(0–5.26) \times 10^{-4}$ M).

After the comparison of the results obtained using the Mineql program, it may be stated that these results overlap and comply with the occurrence of particular forms. The application of the HPIC-UVVIS system in model solutions and the application of modelling programs in determining the order of elution based on the real samples in relation to modelling are good tools for conducting speciation analysis of aluminium in different systems. The

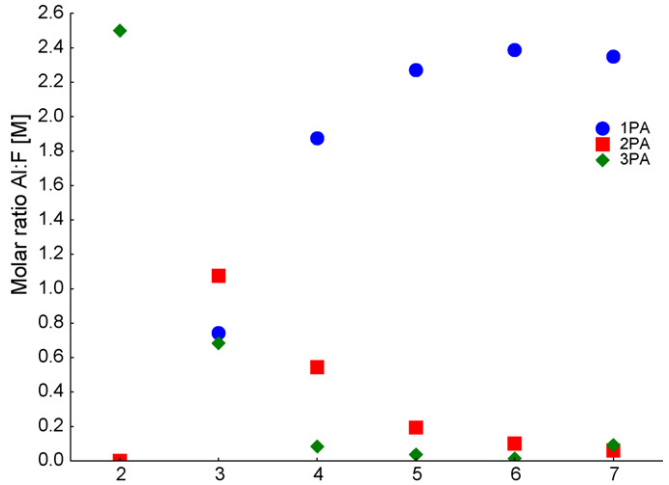

Fig. 6. Variability of the occurrence of aluminium forms depending on the aluminium–fluorides proportion (*1PA: AlF_2^+, AlF_3^0, AlF_4^-; 2PA: AlF^{2+}; 3PA: Al^{3+}). Values 2–7 indicate variable relation of aluminium to fluorides.

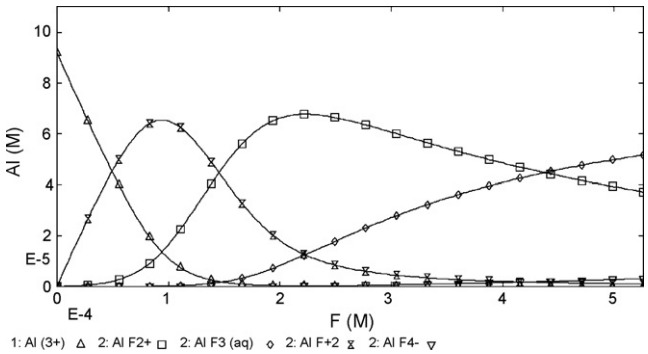

Fig. 7. The graph showing the relation of stable aluminium concentration (9.26E−05 M) and variable fluorides concentration (0–5.26E−04 M) obtained in Mineql 4.5+ program.

method has been fully optimized and used in speciation analysis of aluminium and aluminium complexes with fluorides in model solutions.

4. Speciation analysis of aluminium in soil samples by HPIC-UVVIS system

The soil samples collected in the chemical plant area were marked by pH reaction of 4.55–5.78 for water soluble fraction and 5.09–6.99 for exchangeable fraction. Fluoride concentration was determined using Ion Selective Electrode

Table 5
Concentration values of aluminium forms for particular signals in water soluble fraction.

Sample/profile	Aluminium form	[mg kg^{-1}]	Σ of forms
1/1	AlF_2^+, AlF_3^0, AlF_4^-	287.9	
1/1	AlF^{2+}	4.05	351.1
1/1	Al^{3+}	59.1	
2/1	AlF_2^+, AlF_3^0, AlF_4^-	453.1	
2/1	AlF^{2+}	10.2	544.3
2/1	Al^{3+}	80.9	
3/1	AlF_2^+, AlF_3^0, AlF_4^-	324.6	
3/1	AlF^{2+}	4.09	412.8
3/1	Al^{3+}	84.1	
4/1	AlF_2^+, AlF_3^0, AlF_4^-	477.4	
4/1	AlF^{2+}	8.83	553.6
4/1	Al^{3+}	67.4	
5/1	AlF_2^+, AlF_3^0, AlF_4^-	112.7	
5/1	AlF^{2+}	0.299	166.3
5/1	Al^{3+}	53.3	
6/1	AlF_2^+, AlF_3^0, AlF_4^-	7.16	
6/1	AlF^{2+}	nd	70.9
6/1	Al^{3+}	63.8	
7/2	AlF_2^+, AlF_3^0, AlF_4^-	488.2	
7/2	AlF^{2+}	12.9	548.9
7/2	Al^{3+}	47.8	
8/2	AlF_2^+, AlF_3^0, AlF_4^-	377.3	
8/2	AlF^{2+}	9.25	434.5
8/2	Al^{3+}	47.9	
9/2	AlF_2^+, AlF_3^0, AlF_4^-	410.6	
9/2	AlF^{2+}	10.9	466.7
9/2	Al^{3+}	45.2	
10/2	AlF_2^+, AlF_3^0, AlF_4^-	488.9	
10/2	AlF^{2+}	14.3	543.8
10/2	Al^{3+}	40.6	
11/2	AlF_2^+, AlF_3^0, AlF_4^-	291.6	
11/2	AlF^{2+}	7.32	339.8
11/2	Al^{3+}	40.9	

Table 6
Concentration values of aluminium forms for particular signals in exchangeable fraction extracted with NH_4Cl.

Sample/profile	Aluminium form	[mg kg^{-1}]	Σ of forms
1/1	AlF_2^+, AlF_3^0, AlF_4^-	345.8	
1/1	AlF^{2+}	0.794	672.1
1/1	Al^{3+}	325.5	
2/1	AlF_2^+, AlF_3^0, AlF_4^-	502.1	
2/1	AlF^{2+}	1.91	748.7
2/1	Al^{3+}	244.6	
3/1	AlF_2^+, AlF_3^0, AlF_4^-	399.4	
3/1	AlF^{2+}	28.5	496.7
3/1	Al^{3+}	68.8	
4/1	AlF_2^+, AlF_3^0, AlF_4^-	521.5	
4/1	AlF^{2+}	27.8	626.0
4/1	Al^{3+}	76.7	
5/1	AlF_2^+, AlF_3^0, AlF_4^-	nd	
5/1	AlF^{2+}	18.2	75.2
5/1	Al^{3+}	57.1	
6/1	AlF_2^+, AlF_3^0, AlF_4^-	3.38	
6/1	AlF^{2+}	11.2	160.7
6/1	Al^{3+}	146.1	
7/2	AlF_2^+, AlF_3^0, AlF_4^-	561.0	
7/2	AlF^{2+}	4.11	606.9
7/2	Al^{3+}	41.8	
8/2	AlF_2^+, AlF_3^0, AlF_4^-	449.6	
8/2	AlF^{2+}	3.74	494.4
8/2	Al^{3+}	41.1	
9/2	AlF_2^+, AlF_3^0, AlF_4^-	518.4	
9/2	AlF^{2+}	4.27	576.0
9/2	Al^{3+}	53.3	
10/2	AlF_2^+, AlF_3^0, AlF_4^-	579.3	
10/2	AlF^{2+}	9.18	637.1
10/2	Al^{3+}	48.6	
11/2	AlF_2^+, AlF_3^0, AlF_4^-	347.3	
11/2	AlF^{2+}	18.8	407.1
11/2	Al^{3+}	40.9	

for fluorides. In the analysed extracts, the fluoride concentration reached for P1: 70–2020 mg F^- L^{-1} and for P2: 1260–3000 mg F^- L^{-1}.

4.1. Water soluble fraction of aluminium

Speciation analysis of aluminium was conducted in extracts for water soluble fraction treated as the most available environment. The obtained investigation results for the HPIC-UVVIS system have been presented in Table 5.

Based on the speciation analysis of aluminium in soil samples in the separated water soluble fraction, it may be stated that the application of speciation analysis in the HPIC-UVVIS system was successful. The chromatograms for particular samples from the profile indicate the formation of aluminium complexes with fluorides in the forms mainly connected by large amounts of fluoride ligands. The aluminium forms combined with AlF_2^+, AlF_3^0 and AlF_4^- dominate. Nevertheless, the concentration of Al^{3+} form is also high in the whole spectrum of the analysed samples. Form AlF^{2+} occurred especially in the samples with lower concentration of fluorides, which results from the order of aluminium fluoride complexes formation. Based on previous study occurrence of aluminium fluoride complexes (AlF^{2+}, AlF_2^+), the hydroxo complexes may coexist [14,53].

5. Speciation analysis in fractionation

5.1. Exchangeable aluminium extracted with NH_4Cl

The concentration of aluminium using NH_4Cl as the extractant was in the whole spectrum of the analysed samples higher than for the water soluble fraction of aluminium. Speciation analysis for exchangeable aluminium fraction may be helpful in understanding what forms constitute the source of aluminium which may be activated in changeable conditions of the natural environment. As indicated by the study in soil profile (1,2), the migration of aluminium compounds may be relatively easy due to the reaction of these soils.

Table 6 presents the results of speciation analysis obtained for exchangeable aluminium fraction extracted with NH_4Cl.

The obtained results indicate, similarly to the water soluble fraction, significant participation of aluminium in combination with fluorides, especially forms AlF_3^0 and AlF_4^-. Nevertheless, the values obtained for the Al^{3+} form are much higher for samples 1, 2, 6 in the exchangeable fraction extracted with NH_4Cl, and they may indicate the fact that in the pH conditions, aluminium fluoride complexes are not formed despite the predominance of fluorides over aluminium.

6. Conclusions

The presented new method of speciation analysis of aluminium and aluminium fluoride complexes in the HPIC-UVVIS system is allowed to separate both anionic and cationic aluminium fluoride and Al^{3+} forms, which has not be achieved by other researchers before. Also used bifunctional analytical column, which is containing mixed anion and cation beds with sulfonic acid and alkanol quaternary ammonium functional groups allowed to separate forms with different charge. Besides the method is fast (at least 5 min) and selective. The analysis of model solutions enabled the separation of three signals deriving from aluminium in the form of aluminium fluoride complexes with the charge +1, 0, −1 as the first signal, +2 as the second signal and the aluminium form Al^{3+} as the third signal in an analytical system. The obtained results comply with theoretical calculations obtained using the Mineql program for chemical modelling. The analysis of real samples from polluted area (Chemical Plant in Luboń, Poland) enabled the application of the HPIC-UVVIS system and determination of variability of aluminium forms in soil profiles samples. Despite requiring post-column derivatization reaction, the new method is cheap and it creates new possibilities in the analysis of aluminium, both in environmental and biological samples. Also the optimized conditions of chromatographic process and detection is ready to use like a standard procedure to routine analysis of particulate aluminium fluoride forms and the most toxic Al^{3+} species. Based on the presented study of speciation analysis of aluminium and aluminium fluoride complexes, it may be stated that such systems (HPIC-UVVIS) are indispensable to the analysis of this element in various components of the environment. It should be stress that speciation analysis in fractionation creates new cognitive possibilities in the field of aluminium migration mechanisms in the environment.

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References

[1] R.B. Martin, Coord. Chem. Rev. 141 (1996) 23–32.

[2] D.P. Stevens, M.J. McLaughlin, A.M. Alston, Plant Soil 192 (1997) 81–93.
[3] A. Strunecká, O. Struneckỳ, Potočka, J. Physiol. Res. 51 (2002) 557–564.
[4] A. Oguro, J. Cervenka, K. Horii, Pharmacol. Toxicol. 67 (1990) 411–414.
[5] J.R. Dodam, N.C. Olson, J. Appl. Physiol. 78 (1995) 569–577.
[6] M. Suwalsky, B. Norris, F. Villena, F. Cuevas, P. Sotomayor, P. Zatta, Food Chem. Toxicol. 42 (2004) 925–933.
[7] P.J. Morgan, M.H. Hastings, M. Thompson, P. Barrett, W. Lawson, G. Davidson, J. Mol. Endocrinol. 72 (1991) 134–144.
[8] S.H. Sutheimer, S.E. Cabaniss, Anal. Chim. 303 (1995) 211–221.
[9] N. Radić, M. Bralić, Sci. Tot. Environ. 172 (1995) 237–243.
[10] A. Hills, M. Grote, E. Janßen, J. Eichhorn, Fres. J. Anal. Chem. 364 (1999) 457–461.
[11] B. Mitrović, R. Milačič, Sci. Tot. Environ. 258 (2000) 183–194.
[12] B. Krajl, Križaj, P. Bukovec, S. Slejko, R. Milačič, Anal. Bioanal. Chem. 383 (2005) 467–475.
[13] B. Mitrović, R. Milačič, B. Pihlar, Analyst 121 (1996) 627–634.
[14] B. Mitrović, R. Milačič, B. Pihlar, Analysis 26 (1998) 381–388.
[15] T. Bantan, R. Milačič, B. Pihlar, Talanta 47 (1998) 929–941.
[16] B.A. Soldado-Cabezuelo, M.M. Bayón, E.B. González, J.I.G. Alonso, A. Sanz-Medel, Analyst 123 (1998) 865–869.
[17] T. Bantan-Polak, B. Mitrović, R. Milačič, Anal. Chim. 540 (2005) 83–89.
[18] H. Lian, Y. Kang, S. Bi, Y. Arkin, D. Shao, D. Li, Y. Chen, L. Dai, N. Gan, L. Tian, Talanta 62 (2004) 43–50.
[19] K.I. Tsunoda, T. Yagasaki, H. Aizawa, K. Satake, Anal. Sci. 13 (1997) 757–764.
[20] K.I. Tsunoda, T. Umemura, K. Ohshima, S. Aizawa, E. Yoshimura, K. Satake, Water Air Soil Pollut. 130 (2001) 1589–1594.
[21] A. Zioła-Frankowska, M. Frankowski, J. Siepak, Talanta 78 (2009) 623–630.
[22] M. Frankowski, A. Zioła-Frankowska, J. Siepak, Talanta 80 (2010) 2120–2126.
[23] C.T. Driscoll, Int. J. Environ. Anal. Chem. 16 (1984) 267–283.
[24] P. Matúš, J. Kubová, Anal Chim. 573 (2006) 474–481.
[25] E. Dixon, M. Gardner, Chem. Spec. Bioavail. 10 (1998) 11–17.
[26] L. Xia, B. Hu, Z. Jiang, Y. Wu, L. Li, R. Chen, J. Anal. At. Spectrom. 20 (2005) 441–446.
[27] A.B. Tabrizi, Food Chem. 100 (2007) 1698–1703.
[28] B. Fairman, A. Sanz-Medel, P. Jones, J. Anal. At. Spectrom. 10 (1995) 281–285.
[29] N. Clarke, L.G. Danielsson, A. Sparén, Water Air Soil Pollut. 84 (1995) 103–116.
[30] L.G. Danielsson, A. Sparén, Anal. Chim. 306 (1995) 173–181.
[31] B. Fairman, A. Sanz-Medel, Fres. J. Anal. Chem. 355 (1996) 757–762.
[32] D. Berggren, A. Sparén, Int. J. Environ. Anal. Chem. 62 (1996) 115–128.
[33] G. Wauer, H.J. Heckemann, R. Koschel, Micochim. Acta 146 (2004) 149–154.
[34] J. Liu, S. Bi, L. Yang, X. Gu, P. Ma, P. Gan, X. Wang, X. Long, F. Zhang, Analyst 127 (2002) 1657–1665.
[35] S. Bi, W. Tang, N. Gan, L. Ye, J. Liu, G. Chen, L. Dai, M. Cao, Y. Chen, Anal. Lett. 33 (2000) 677–689.
[36] D.C. McAvoy, R.C. Santore, J.D. Shosa, C.T. Driscoll, Soil Sci. Soc. Am. J. 56 (1992) 449–455.
[37] F. Oulehle, J. Hruška, J. Inorg. Biochem. 99 (2005) 1822–1829.
[38] N. Clarke, L. Danielsson, A. Sparén, Pure Appl. Chem. 68 (1996) 1597–1638.
[39] M.A. Zanjanchi, H. Noei, M. Moghimi, Talanta 70 (2006) 933–939.
[40] H. Lian, Y. Kang, Y. Arkin, S. Bi, A. Yasin, D. Shao, Y. Chen, L. Dai, L. Tian, Anal. Bioanal. Chem. 376 (2003) 542–548.
[41] H. Lian, Y. Kang, A. Yasin, S. Bi, D. Shao, Y. Chen, L. Dai, L. Tian, J. Chromatogr. A 993 (2003) 179–185.
[42] E. Yamada, T. Hiwada, T. Inaba, M. Tokukura, Y. Fuse, Anal. Sci. 18 (2002) 785–791.
[43] H. Hara, H. Kobayashi, M. Maeda, A. Ueno, Y. Kobayashi, Anal. Chem. 73 (2001) 5590–5595.
[44] J. Tria, P.R. Haddad, P.N. Nesterenko, J. Sep. Sci. 31 (2008) 2231–2238.
[45] O. Happel, A. Seubert, Anal. Bioanal. Chem. 392 (2008) 1373–1381.
[46] P.M. Bertsch, M.A. Anderson, Anal. Chem. 61 (1989) 535–539.
[47] I.R. Willet, Soil Sci. Am. J. 53 (1989) 1385–1391.
[48] S. Motellier, H. Pitsch, J. Chromatogr. A 660 (1994) 211–217.
[49] G. Borrmann, A. Seubert, Anal. Chim. 332 (1996) 233–239.
[50] O. Drabek, L. Mladkova, L. Boruvka, J. Syakowa, A. Nikodem, K. Nemecek, J. Inorg. Biochem. 99 (2005) 1807–1816.
[51] O. Drabek, L. Boruvka, L. Mladkowa, M. Kocarek, J. Inorg. Biochem. 97 (2003) 8–15.
[52] O. Drabek, B. Lubos, L. Pavlu, A. Nikodem, I. Pirkova, O. Vacek, J. Inorg. Biochem. 101 (2007) 1224–1233.
[53] M. Frankowski, A. Zioła-Frankowska, J. Siepak, Microchem. J. 95 (2010) 366–372.