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## DIFFERENTIATION OF $\text{Al}^{3+}$ AND $\text{Al}$ SPECIES IN ENVIRONMENTAL SAMPLES BY ISOTACHOPHORESIS

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(First received December 22nd, 1988; revised manuscript received January 24th, 1989)

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### SUMMARY

An isotachophoretic method for the determination of free  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ions in different aluminium salt solutions was developed. The electrolyte system consists of 0.01 *M* sodium acetate (leading system) and 0.01 *M* tris(hydroxymethyl)amino-methane (terminating system). Separation was effected with a precapillary tube (diameter 0.05 cm) followed by a main capillary tube of length 20 cm and of smaller cross-section. The detection limit for  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ions was 0.05 mg/l. The method was applied to the determination of free  $\text{Al}^{3+}$  ions  $\{[\text{Al}(\text{H}_2\text{O})_6]^{3+}\}$  in soil leachates and aqueous soil extracts.

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### INTRODUCTION

The increasing acidification of soils by deposition of acid rain in the forest ecosystem results in leaching and washing out of nutrient elements in the soil and also causes the release and mobilization of phytotoxic metals in soil<sup>1</sup>. In this process the release of bioavailable aluminium is of special importance. Especially the free  $\text{Al}^{3+}$  species  $\{[\text{Al}(\text{H}_2\text{O})_6]^{3+}\}$  is responsible for the high phytotoxic effect of aluminium in acidic soils<sup>2–4</sup>. The release of aluminium depends on the buffer system of the soil, the exchange buffer range (pH 4.2–5.0) and the aluminium buffer range (pH 3.8–4.2)<sup>5</sup>.

In soil solutions or pore solutions, elements such as Pb, Cd, Cu, Ca, Mn and Al exist in both free and complex forms. The kind of linkage has a decisive influence on the bioavailability of these ions and therefore also on their phytotoxicity. The different species of aluminium are of great importance for its phytotoxic potential, as shown by studies on hydroponics.

The microbial decomposition of the organic materials in soils results in soluble organic acids such as fulvic acids and humic acids or further hydrophilic degradation products (salicylic acid, phenols, carbon acids). As  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ions can be bound by these organic acids, the activity and mobility of  $\text{Al}^{3+}$  ions depends strongly on the content and composition of the organic substances in the soil solution. The amount of organically bound aluminium decreases with increasing soil depth, whereas that of inorganically bound aluminium increases.

Previous studies on the characteristics of organically bound aluminium did not

describe the actual kind of linkage of aluminium to organic molecules in soil solutions. In addition, there has been a need to develop an appropriate method for the determination of free  $\text{Al}^{3+}$  ions  $\{[\text{Al}(\text{H}_2\text{O})_6]^{3+}\}$  in soil solutions. The conventional methods differentiate between kinetically unstable aluminium and total aluminium<sup>6</sup> or inorganic mononuclear and organically bound aluminium<sup>7</sup> as well as mononuclear and polynuclear aluminium species<sup>8</sup>. A disadvantage of these methods is that the real distribution of aluminium species in soil solutions cannot be established, as the addition of buffer or other reagents modifies the original character on analysis.

This paper reports a feasible method for determining environmentally relevant concentrations of free  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ions in soil solutions.

## EXPERIMENTAL

### *Lysimeters*

The release of aluminium into soil leachate was investigated using lysimeters with a surface area of  $1 \text{ m}^2$ . Six lysimeters with different depths were installed on the ground in the Institute to observe the vertical gradients of aluminium: two lysimeters L (LI/F, LII/F), depth 25 cm, surface humus; two lysimeters L (LIII/F, LIV/F), depth 40 cm, surface humus with A/B horizons; and two lysimeters L (LV/F, LVI/F), depth 70 cm, surface humus with 50 cm A/B horizons. The lysimeters contained undisturbed soil monoliths from Hunau, a hill in the Rothaargebirge. In spring 1987, one of each group of lysimeters was treated with the equivalent to 3 t/ha of calcium carbonate/magnesium carbonate–lime to study the effect of liming. In December 1987 the second lysimeter, which was protected against natural rainfall, was watered with 5-fold concentrated artificial precipitation to simulate stress in soils under strong acidic conditions. The amount of artificial precipitation was identical with the original precipitation at this site.

### *Apparatus*

The total content of aluminium in the leachates was determined with a Perkin-Elmer 3030 graphite furnace atomic absorption spectrometer with Zeeman-effect background correction in pyrolytic graphite-coated graphite tubes and an argon/argon–methane atmosphere. Each sample was acidified and measured three times for statistical assessments.

The content of free  $\text{Al}^{3+}$  ions  $\{[\text{Al}(\text{H}_2\text{O})_6]^{3+}\}$  was determined by isotachopheresis (ITP) using an LKB 2127 Tachophor equipped with a high-voltage power supply (0.1–30 kV, 10–500  $\mu\text{A}$ ), an integrated conductivity detector and a UV detector. For the detection of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ions only the linear and differential conductivities were registered (GILA 2000 Laumann recorder). Additionally, a precapillary tube (6 cm  $\times$  2 mm I.D.) from ITABA (Sweden) was installed to separate irrelevant ions and to increase the sensitivity. The main capillary tube (20 cm  $\times$  0.3 mm I.D.) served to separate free  $\text{Al}^{3+}$  ions from other mononuclear and polynuclear aluminium species. The samples were injected with various microsyringes.

### *Reagents*

All solutions were prepared using analytical-reagent grade chemicals.

*Aluminium standard solutions.* 1 g/l  $\text{AlCl}_3$ –tritolol (Merck)  $\equiv$  1 g/l  $\text{Al}^{3+}$ ; 13.89 g/l

$\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O} \equiv 1 \text{ g/l } \text{Al}^{3+}$ ;  $12.35 \text{ g/l } \text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O} \equiv 1 \text{ g/l } \text{Al}^{3+}$ ;  $17.57 \text{ g/l } \text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O} \equiv 1 \text{ g/l } \text{Al}^{3+}$ .

*Solution of sodium citrate.*  $1.56 \text{ g/l sodium citrate} \cdot 2 \text{H}_2\text{O} \equiv 1 \text{ g/l citrate}$ .

*Buffer solutions for the ITP method.*  $1.36 \text{ g/l sodiumacetate} \cdot 3 \text{H}_2\text{O}$ ;  $1.21 \text{ g/l tris(hydroxymethyl)aminomethane (Tris)}$ .

### Procedure

The aluminium standard solutions were diluted so as to contain  $1 \text{ mg/Al}^{3+}$ . The compositions of the two buffer systems are shown in Table I.

Mixtures of aluminium chloride and sodium citrate were prepared by adding various amounts of a solution of sodium citrate (10 or 100 mg/l citrate) to a standard solution of  $0.37 \cdot 10^{-3} \text{ mol/l (1 mg/l) } \text{Al}^{3+}$  to obtain  $\text{Al}^{3+}$ : citrate molar ratios between 0 and 1.5. The pH of these solutions was  $4.67 \pm 0.2$ .

The soil solutions were analysed as soon as possible after collection. The samples were filtered through a  $0.45\text{-}\mu\text{m}$  membrane filter (Millipore). The injection volumes,  $V$ , of the soil solutions depended on the concentration of  $\text{Al}^{3+}$  ( $V \leq 50 \mu\text{l}$ ).

### RESULTS AND DISCUSSION

Isotachopheresis is based on carrier-free electrophoretic methods inducing migration of ionic species in an electric field. With two different electrolyte systems (leading and terminating electrolyte), ITP represents a discontinuous electrophoretic system. All ions that have the same velocity in the electric field but are mobile between the leading and the terminating electrolyte are separated and determined.

Various electrolyte systems were tested to find an appropriate system for separating the free  $\text{Al}^{3+}$  ions in solutions from other cations. An electrolyte system consisting of  $0.01 \text{ M}$  sodium acetate (leading electrolyte) and  $0.01 \text{ M}$  Tris (terminating electrolyte) proved to be most suitable, as the mobility of free  $\text{Al}^{3+}$  ions lay between those of the leading cation  $\text{Na}^+$  and the terminating cation Tris.

An aluminium solution of  $1 \text{ mg/l}$  was acidified to pH 2.0. The equilibrium



TABLE I

COMPOSITION OF AQUEOUS ELECTROLYTE SYSTEM FOR SEPARATING  $\text{Al}^{3+}$  IONS IN SOIL SOLUTIONS

Parameter	Leading electrolyte	Terminating electrolyte
Cation	$\text{Na}^+$	Tris
Concentration	$0.01 \text{ M}$	$0.01 \text{ M}$
pH	3.6	3.3
Additions	1% HPMC	1% HPMC
Counterion	Acetate	Acetate
Temperature	Room temperature	Room temperature
Current	$30 \mu\text{A}$	$30 \mu\text{A}$

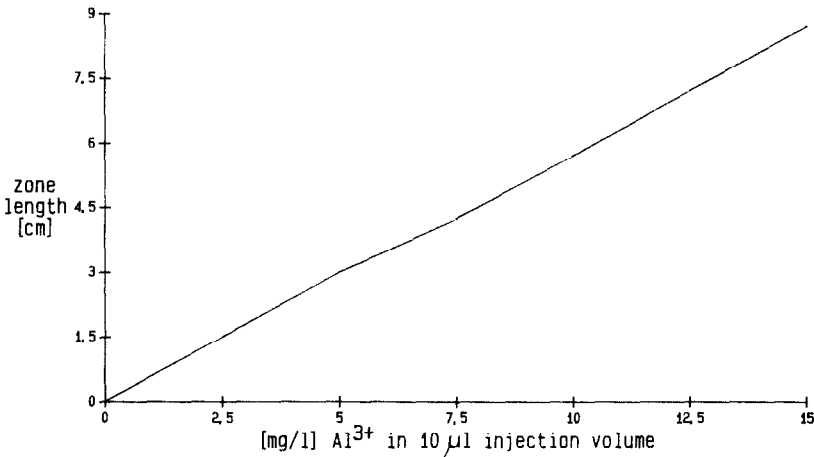


Fig. 1. Calibration graph for  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ .

was shifted in favour of the initial products. Under these conditions, aluminium occurs predominantly as free  $\text{Al}^{3+}$  ion. In the range 0.1–2.0 mg/l  $\text{Al}^{3+}$  we obtained a linear calibration graph (Fig. 1). The detection limit for  $\text{Al}^{3+}$  ions was 0.05 mg/l. The kinetics of the aluminium hydrolysis reaction depends on the ratio of Al to OH and it may take from 1 h to several months to reach equilibrium<sup>9–11</sup>. After the preparation of an aluminium solution and adjusting the pH with sodium hydroxide immediate measurement of the solutions resulted in higher concentrations of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  than in measurements performed 1 day later. To obtain equilibrium, the solution was given a reaction time of 1 week before measurement.

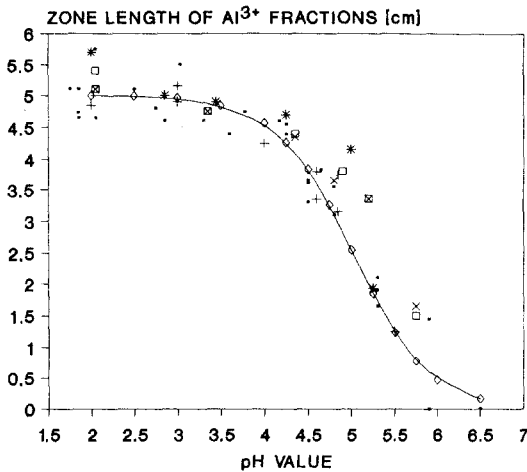
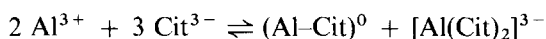


Fig. 2. Determination of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  in different Al salt solutions as a function of the pH of the samples. Volume injected: 10–50  $\mu\text{l}$ .  $\bullet$  =  $\text{AlCl}_3$ ;  $+$  =  $\text{Al}_2(\text{SO}_4)_3$ ;  $*$  =  $\text{KAl}(\text{SO}_4)_2$ ;  $\square$  =  $\text{Al}(\text{NO}_3)_3$ ;  $\times$  =  $\text{Al}(\text{NO}_3)_3$ ;  $\diamond$ — $\diamond$  = theoretical Al.

To establish the effect of various anionic and cationic complexes, different aluminium salt solutions [ $\text{AlCl}_3$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{KAl}(\text{SO}_4)_2$ ] were acidified to pH 1.7. Identical calibration graphs were obtained for all solutions, indicating that no measurable interferences of non-complexed cations and anions are to be expected in the determination of free  $\text{Al}^{3+}$  ions.

If only free  $\text{Al}^{3+}$  ions are detected by the described method, it should be possible to determine the  $\text{p}K_s$  value of the first hydrolysis equilibrium (see eqn. 1). For each of the aluminium salt solutions with various pH values, identical pH dependence curves were obtained. A comparison with the calculated pH curve (see Fig. 2) showed no differences between the curves. From the pH curves a  $\text{p}K_s$  value of  $5.05 \pm 0.15$  was calculated, which is comparable to literature values, ranging from 4.60 to 5.69<sup>9,11,12</sup>.

Another verification of the method is the determination of the formation constant of a weak Al complex. As a tridentate ligand citrate was selected, which forms different metal–ligand complexes:



For this experiment a mixture of aluminium chloride and sodium citrate was prepared and 10  $\mu\text{l}$  of the different solutions were injected. The results of these measurements are shown in Fig. 3. From the inflection point on the curve the formation constant,  $\text{p}K$ , was calculated as  $\text{p}K(\text{Al-Cit})^0 = -7.87 \pm 0.32$  (literature values  $-7.37$ <sup>12</sup> and  $-7.87 \pm 0.32$ <sup>13</sup>).

As the aim of this study was to develop a method for the determination of free  $\text{Al}^{3+}$  ions in environmental solutions, various soil solutions were tested using the above method. In soil solutions with a high content of dissolved organic carbon, the zone length of free  $\text{Al}^{3+}$  ions between pH 6 and 7.5 does not decrease as far as zero.

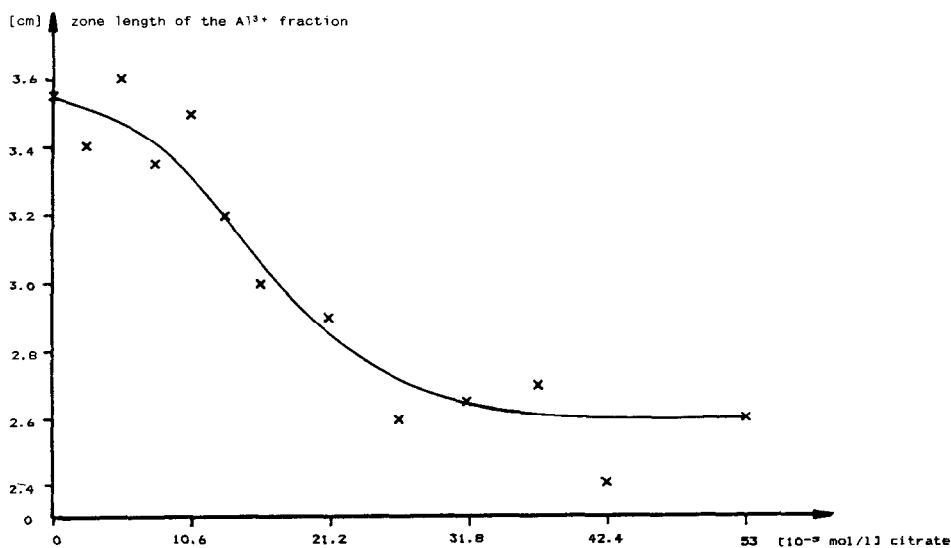


Fig. 3. Determination of "free  $\text{Al}^{3+}$  ions",  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ , in an aluminium–citrate mixture. pH of the mixture:  $4.67 \pm 0.2$ . Al concentration:  $0.37 \cdot 10^{-3}$  mol/l. Volume injected: 10  $\mu\text{l}$  of the mixture.

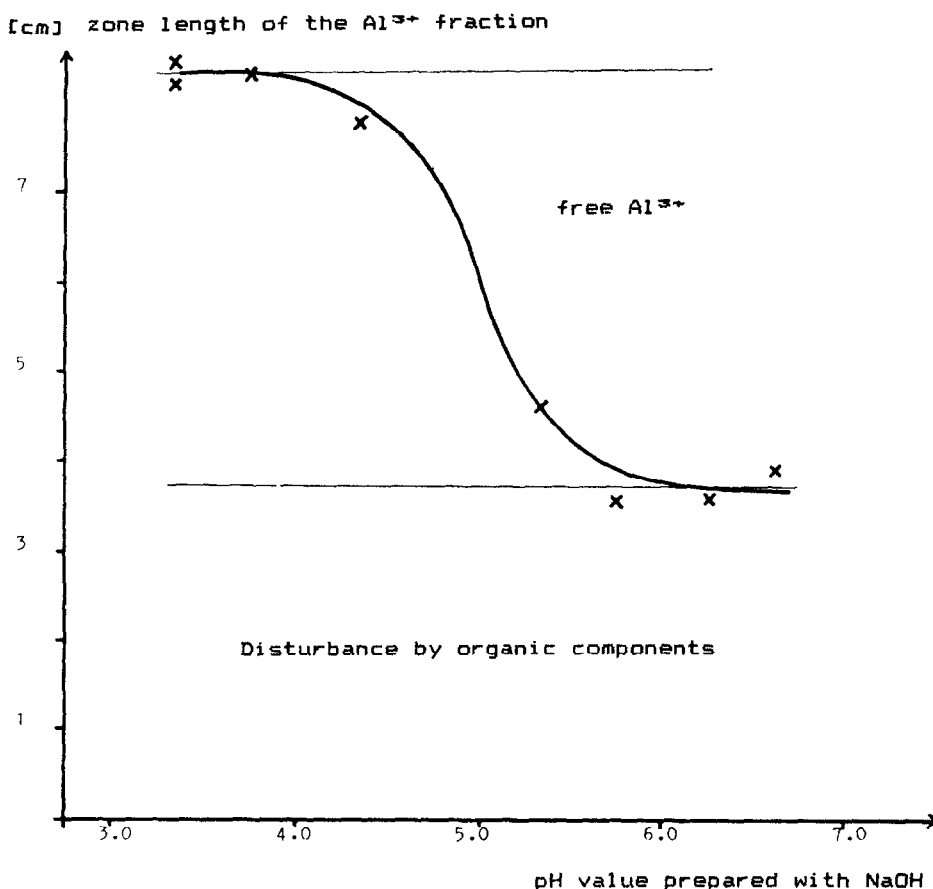


Fig. 4. Analysis of a soil extract of a surface soil and the pH dependence of the  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  signal. Volume injected: 10  $\mu\text{l}$ . The pH values on the abscissa relate to the sample solutions.

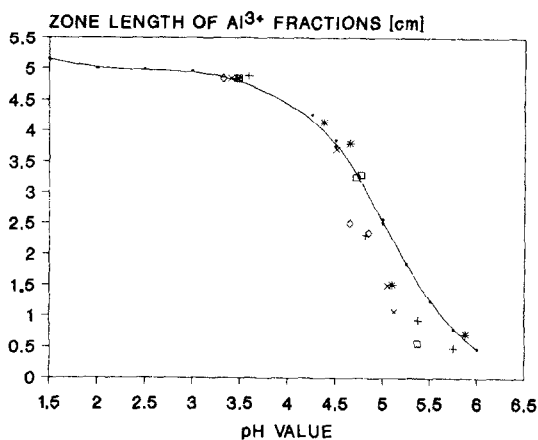


Fig. 5. Determination of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  in soil solutions of lysimeters [LI/F (25 cm), LIII/F (40 cm), LV/F (70 cm), LI/A (100 cm)] by variation of the pH of the samples and comparison with a pure  $\text{AlCl}_3$  solution. Volume injected dependent on the pH: 10–50  $\mu\text{l}$ . ●—● =  $\text{AlCl}_3$ ; + = LI/F, 10.8.87; \* = LIII/F, 10.8.87; □ = LV/F, 10.8.87; × = LI/A, 11.8.87; ◇ = LIII/F, 2.3.87. Extrapolation to pH 3.5.

Several organic substances seem to have mobilities in the electric field which are comparable to that of free  $\text{Al}^{3+}$  ions and therefore a complete separation is impossible. As the concentration of free  $\text{Al}^{3+}$  ions between pH 6 and 7.5 is zero according to the first equilibrium of hydrolysis (eqn. 1), the value can easily be corrected, however, by subtracting the zone length of the signal at neutral pH from the zone length of the signal at the original pH value. This is demonstrated by the shape of the pH dependence curve for a soil extract (Fig. 4) representing the results obtained on checking this method in the presence of low-molecular-weight organic complexes occurring in original soil solutions.

The theoretical curve for  $\text{Al}^{3+}/\text{Al}(\text{OH})^{2+}$  is compared with the pH dependence curves of some soil solutions with lysimeters by standardization and extrapolation to pH 3.5 (Fig. 5). This correction was not carried out in Fig. 4, representing the original state. All measurements in Fig. 5 show the same shape as inferred from eqn. 1. In

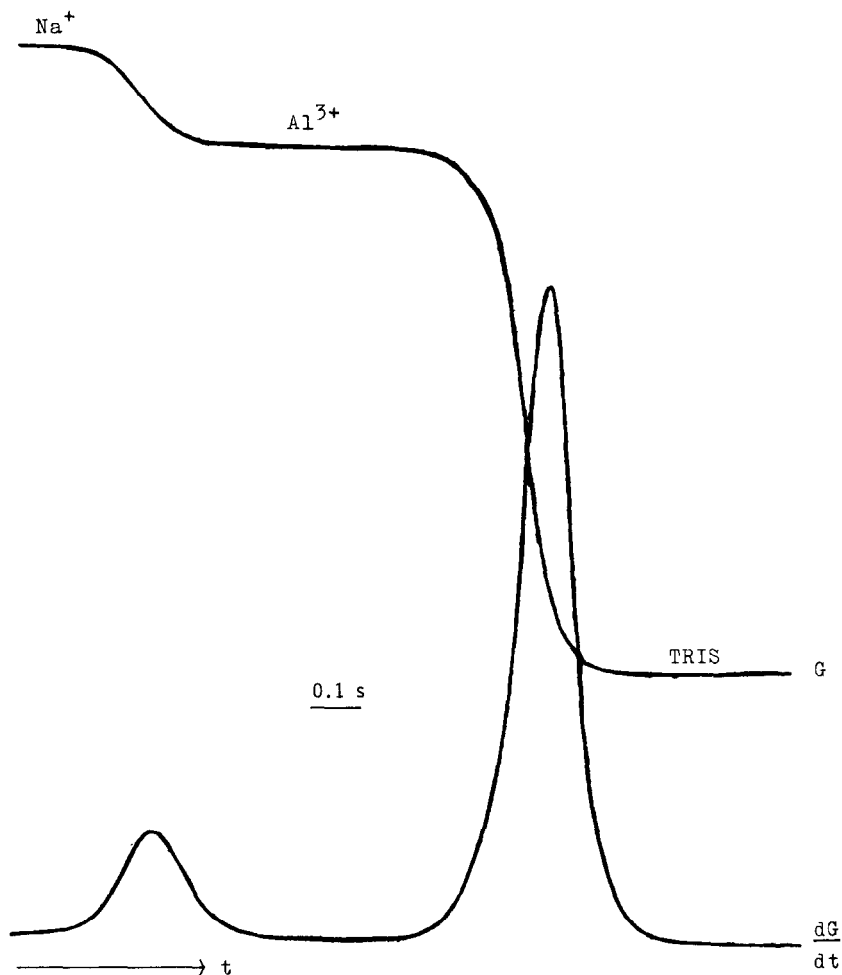


Fig. 6. Isotachopherogram of a soil extract (pH 4.23). Volume injected:  $10 \mu\text{l}$ ,  $t$  = Time;  $G$  = response of the conductivity detector;  $dG/dt$  = time derivative of the conductivity detector response.

TABLE II

COMPARISON OF THE RESULTS OF THE DETERMINATION OF  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  AND TOTAL Al UNDER DIFFERENT CONDITIONS

Sampling date, November 20–23, 1987; AAS = atomic absorption spectrometry; concentration of Al in mg/l. Various types of treatment of the lysimeters: (a) untreated variant; (b) liming in spring 87; (c) 5-fold concentrated rain.

Lysimeters	AAS (total Al)			ITP (free $\text{Al}^{3+}$ )		
	Not treated	Liming	Acid rain	Not treated	Liming	Acid rain
LI, 25 cm		1.22			0.50	
LII, 25 cm	0.86		3.29	0.56		2.94
LIII, 40 cm		4.89			2.73	
LIV, 40 cm	1.01		2.54	0.67		1.40
LV, 70 cm		1.15			0.89	
LVI, 70 cm	0.91		1.53	0.72		1.36

addition, this comparison shows that no other substances interfere with the signal of free  $\text{Al}^{3+}$  ions (Fig. 6).

The reproducibility depends on the composition of the samples and varies between 1% and 10%, depending on the impurities and aluminium concentration.

In Table II the total content of aluminium (determined by atomic absorption

TABLE III

## COMPARISON OF THE RESULTS OF THE DETERMINATION OF Al IN SOIL SOLUTIONS OF LYSIMETERS OBTAINED BY AAS, ITP AND CLASSICAL METHODS

Various types of treatment of the lysimeters: (a) liming in spring 87 (sampling date, 25.1.88–2.2.88); (b) untreated variant (sampling date, 25.9.87–13.10.87); (c) 5-fold concentrated rain (sampling date, 25.1.88–2.2.88). Photometric methods: OXIN = 8-hydroxyquinoline method; CV = catechol violet S method. DOC = dissolved organic carbon.

Lysimeters	Free $\text{Al}^{3+}$ (mg/l)	Al(OXIN) (mg/l)	Al(CV) (mg/l)	Total Al (mg/l)	DOC (mg/l)	pH
LI, 25 cm, (a)	0.08	0.47	0.83	0.96	25.40	4.45
LII, 25 cm, (b)	0.04	0.61	0.83	0.82	12.90	4.49
LII, 25 cm, (c)	4.07	4.74	4.90	5.80	5.90	4.18
LIII, 40 cm, (a)	3.36	3.72	3.76	4.15	3.70	4.49
LIV, 40 cm, (b)	0.48	0.46		0.64	2.00	4.64
LIV, 40 cm, (c)	2.83	3.44	4.63	4.88	0.80	4.45
LV, 70 cm, (a)	0.72	1.54	1.23	1.72	2.00	4.67
LVI, 70 cm, (b)	0.18	0.36	0.28	0.63	2.60	4.75
LVI, 70 cm, (c)	1.57	1.73	2.15	2.15	1.50	4.62
LII/A, 70 cm (control)	0.36	0.72	0.81	0.89	0.20	4.82



spectrometry) and the concentration of "free  $\text{Al}^{3+}$  ions" (determined by isotachopheresis) are compared for the fertilization and acidification experiments. Over the investigation period of 1 year, fertilization with lime did not reduce the concentration of total aluminium. The high content of dissolved organic carbon in the soil solutions of the 25-cm deep lysimeters immobilized all "free  $\text{Al}^{3+}$  ions" that had been released from soil (Table III). After watering with "acid rain", however, the content of aluminium in the soil solutions immediately increased considerably. The content of "free  $\text{Al}^{3+}$  ions" increased between 2- and 5-fold, which is illustrated by the values obtained for LII/F (25 cm), LIV/F (40 cm) and LVI/F (70 cm).

## CONCLUSION

The results show that ITP is suitable for detecting the species " $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ " in soil solutions at environmentally relevant concentrations  $\{ > 0.05 \text{ mg/l } [\text{Al}(\text{H}_2\text{O})_6]^{3+} \}$ . The aluminium complexes and further cations and anions did not influence the determination of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  in soil solutions. In contrast to the photometric methods of complexing aluminium mentioned in the Introduction, which change the original soil solutions by displacing the systems with buffer solutions of different pH values (see Table III), the advantage of the ITP method is that the original condition of the solution is maintained and the actual situation in soil solutions is registered.

## ACKNOWLEDGEMENTS

The investigations were supported by the Ministerium für Umwelt, Raumordnung und Landwirtschaft des Landes Nordrhein-Westfalen (grant No. FP 04). The authors thank Mr. U. Henrichs and Mrs. M. Decker for technical assistance.

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