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FLUORIMETRIC DETERMINATION TRACES OF ALUMINIUM IN SOIL EXTRACTS

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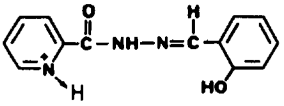
Summary—Salicylaldehyde picolinoylhydrazone (SAPH) form a fluorescent complex with aluminium ($\lambda_{ex} = 384$ nm, $\lambda_{em} = 468$ nm) in acidic medium (stoichiometry 1:3, Al:SAPH). Two procedures based on the direct or standard additions methods has been proposed for the determination of concentrations down to 1–2 $\mu g/dm^3$ of Al(III). The effects of 72 ions in the method has been evaluated and different masking agent reactions have been tested. The method has been used satisfactorily for the determination of aluminium at a level of $\mu g/dm^3$ in acetate extracts of several agricultural soils. The method has been compared favourably with ICP spectroscopy emission.

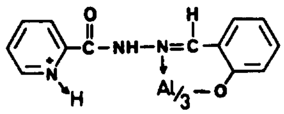
Aluminium is one of the most common elements of the earth's crust (over 8%), and the total Al content of soils is inherited from parent rocks. However, only that fraction of Al which is easily mobile and exchangeable plays an important role in soil fertility;[1] as well as on some invertebrates.[2] As aluminium is insoluble as aluminium hydroxide and other forms around pH6, but easily dissolved at pH 4–5, a variety of Al ions (inorganic, organic, particulate, dissolved) dominate in acid soils and natural waters. The solutions of neutral soils contain Al in the order of about 400 $\mu g/dm^3$, while in the soil solution at pH 4.4, Al concentration was reported to be 5700 $\mu g/dm^3$.[3] Thus, the exchangeable Al determination in acetate extracts of agricultural soils is of great interest.

Several methods have been described for the fluorimetric determination of aluminium, based on the formation of metal complex.[4,5] The methods based on the fluorescence of aluminium with eriochrome red B, morin, or salicylidene *o*-amino-phenol, show high sensitivity and low selectivity.[5] A common characteristic of the structure of the aluminium fluorescent systems is the presence in the chelating molecule of an OH group in the ortho position with respect to an atom or atom group with donor character.[5] In this way hydrazone derivatives having this characteristic have also been studied, such as benzoylhydrazones[6,7] and acylhydrazones,[6,8–10] which have an OH group in the *ortho* position with respect to an amine one.

Salicylaldehyde picolinoylhydrazone (SAPH) (I) having the above common characteristic of fluorescent aroylhydrazone systems gives a fluorescent chelate with aluminium of stoichmetric ratio 1:3 aluminium: reagent, Al(-SAPH)$_3^{3+}$ (II). Optimum conditions for the spectrofluorimetric determination of trace amounts of aluminium were reported. The SAPH reagent has been used in this work for the first time to determine aluminium, using a fluorimetric method. The method is very sensitive, scarcely affected by foreign ions and has been applied satisfactorily for the determination of exchangeable aluminium in agricultural soils.



(I) SAPH^{+}



(II) Al(SAPH)$_3^{3+}$

EXPERIMENTAL

Reagents

The salicylaldehyde picolinoylhydrazone (SAPH) was prepared by condensation of equimolar amounts of the salicylaldehyde (SA) and picolinoylhydrazide (PH) as other related aroylhydrazones.[7] The compound PH was prepared according to Grammatikakis,[11] through an addition reaction between picolinic acid ethyl ester and hydrazine compounds. Ethanol absolute (Merck GR) must be used as solvent. The product was filtered off and recrystallized from ethanol, it had mp 174°C. Elemental analysis gave the empirical formulae $C_{13}H_{11}N_3O_2$. SAPH is soluble ($s > 30$ g/l.) in dimethylformamide (DMF); soluble (2 g/l $< s <$ 10 g/l.) in ethanol, acetone, methyl isobutyl ketone and chloroform; and has a low solubility ($s < 1$ g/l.) in water and isobutyl alcohol. A reagent solution in water or chloroform shows a main absorption maximum at 294 nm ($\epsilon = 6300$ $dm^3 . mol^{-1} . cm^{-1}$) or at 339 nm (16,400 $dm^3 . mol^{-1} . cm^{-1}$), respectively.[12]

The main IR bands of SAPH (KBr disk) were: 3060–3010 cm^{-1} mw ($\nu_{=CH}$); 1680 cm^{-1} vs (amide I); 1520 cm^{-1} (amide II).[13-15] The position of the OH stretching vibration was observed at 3275 cm^{-1} and the OH deformation mode occured at 1370 cm^{-1}.[13] Selected mass fragmentation fragments of SAPH were: $C_{13}H_{12}N_3O_2$ [M + 1], m/z 242 (4.03%); $C_{13}H_{11}N_3O_2$ [M], m/z 241 (19.89%); HOPhCH = NNH, m/z 135 (1.7%); $PyCONH_2$ m/z 122 (19.2%); OHPhCHN m/z 120 (3.4%); OHPhCN m/z 119 (6.1%) and PyCO, m/z 106 (15.4%).[13].

All other reagents used were of analytical grade. A standard solution of 1008 g Al(III) per litre was prepared by dissolving aluminium nitrate. Further dilutions were made daily as required. Ethanolic and dimethylformamide solutions of SAPH of several concentrations were used. Several acetate buffers ($4.4 \leqslant pH \leqslant 6.30$) 1$M$ were prepared. As Al is very rapidly released from glassware all reagent and sample bottles and reaction flasks must be of polyethylene or PVC material.

Apparatus

A Perkin–Elmer LS-5 spectrofluorimeter was used with 1-cm quartz cells and a Xenon-arc source, as well a ICP spectrometer (Applied Research Laboratories, ARL-3520 model), Perkin–Elmer 1600 IR-spectrophotometer and a VG 12250 (70 eV) mass spectrometer were also used.

Spectrofluorimetric method for determination of aluminium

Direct. To 25-cm^3 volumetric flasks, containing appropriate volumes of Al(III) solutions (to give a final concentration of aluminium up to 50 $\mu g/dm^3$), 5 cm^3 of the acetate buffer (pH 5.5) and 10 cm^3 of 0.0125% w/v SAPH ethanol solution or 5 cm^3 of 0.04% w/v DMF solution were added, and the mixture diluted to the mark with deionized-distilled water. The fluorescence intensity ($\lambda_{ex} = 384$ nm, $\lambda_{em} = 468$ nm) was measured after 25 min against a reagent blank prepared in a similar way without aluminium, using appropriate slit width for both excitation and emission.

Standard additions method (SAM). Two sets (I and II) of increasing, known amounts of Al(III) [I: 0, 2.25, 0.5, 0.75 and 1.0 μg, and II: 0, 0.05, 0.10, 0.15 and 0.20 μg of Al(III)] were added to aliquots of sample solution containing 0.10–0.25 or 0.025–0.05 μg of Al(III), respectively, and then the procedure described above followed.

Determination of aluminium in extracts of soils

The extract of soil was prepared by stirring an exactly weighed *ca.* 10 g of a wet sample and 33 ml of 1 eq dm^3 ammonium acetate (pH 7) for 5 min. After repeating the extraction twice, the extracts were quantitatively transferred to a 100 cm^3 volumetric flask, followed by dilution with ammonium acetate solution to the mark.[16] Following the standard addition method [first set of Al(III) standard concentrations] in ethanolic medium described above, a 0.5 cm^3 aliquot of soil extract solution and ferrocyanide (20 mg dm^3) was used as masking agent. The relative fluorescences were plotted against the concentration of the five aluminium-containing solutions of each sample. The straight line was extrapolated back to the concentration axis and the negative intercept gives the concentration of the sample solution. In order to overcome problems and to carry out the analysis in a faster way, a statistical method was applied and all parameters in the regression equation were calculated by the least squares method.

RESULTS AND DISCUSSION

Study of the aluminium(III)—SAPH complex

SAPH form coloured systems with Fe(II, III), Ti(IV), Co(II), Ni(II) and V(V) at pH 4.5 and Ti(IV) at pH 8.5. Only the reactions with aluminium(III) or titanium(IV), at pH 4.5–8.5 or 4.5, respectively, give rise to a fluorescent system. Aluminium ions form a colourless complex with SAPH, which shows a maximum blue-green fluorescence ($\lambda_{ex} = 384$ nm, $\lambda_{em} = 468$ nm) at pH 5.0–5.9 (Fig. 1). Acetate ions (0.1–0.5M final concentration) is the more adequate

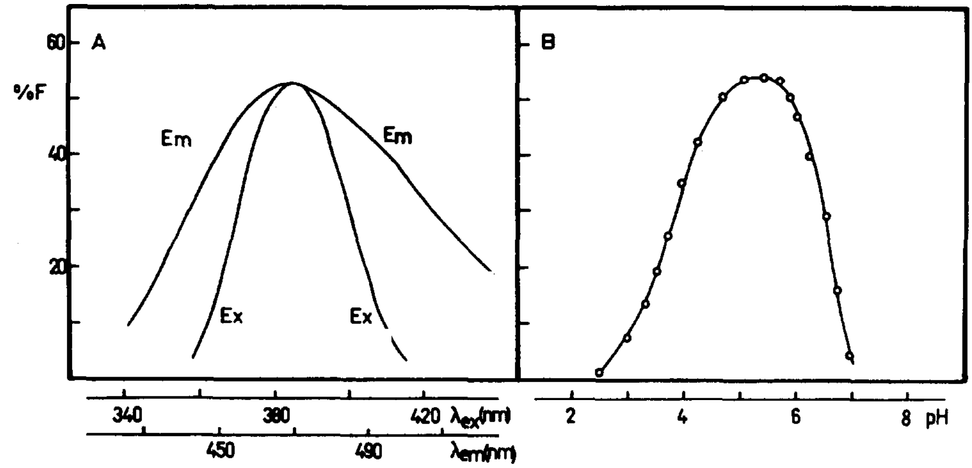


Fig. 1. (A) Excitation and emission spectra at pH 5.3 of aluminium–SAPH complex. (B) Relative fluorescence intensity *vs*. pH graph for the aluminium–SAPH complex. In both cases the reaction conditions were: water–ethanol medium, 3:2 v/v; aluminium (III) concentration, 50 μg/dm^3; SAPH concentration, 0.02% w/v; and instrumental slits, 5 nm.

medium for the reaction development, since in the absence of these ions a time higher elapsed (1 hr, at least) was required to reach the maximum fluorescence. The Al(III)–SAPH system in acetate medium (pH 5.5) and aqueous–ethanolic solution (3:2, v/v) remained stable for at least 12 hr, after a reaction time of 25 min.

The maximum constant relative fluorescence was obtained within 10–30°C temperature range. An increase in temperature above 30°C decreased the intensity by 0.40/°C. The fluorescence of the system increased when SAPH was added to Al(III), but when the SAPH molar ratios were between 50 and 300, no fluorescence change was observed. Molar ratios of more than 300 caused low fluorescence, probably by inner filter effects. Variation of ionic strength from 0 to 0.5 (KCl, KNO_3 or $NaClO_4$) and the order of addition of reagents did not affect the fluorescence.

The effect of solvent nature (EtOH, and DMF) on the Al(III)–SAPH complex was also studied. The fluorescence does not really vary in EtOH when the percentage of it is from 20 to 60. If there is more than 20 per cent DMF a sudden decrease of the fluorescence is produced when the percentage of DMF increases. A medium containing 40% v/v of ethanol or 20% v/v of DMF was chosen for further experimental work.

In ethanol medium, buffered with acetate ions, the stoichiometry of the aluminium(III)–picolinoylhydrazone was evaluated by the continuous variation method, the corresponding value being 1:3 (Fig. 2A). A spectrofluorimetric method[7] was used to determine the apparent stability constant of the metal chelate. The K_f average value obtained was $(2.95 \pm 0.24) \times 10^{15}$, therefore, the complex in acetate medium is relatively dissociated.

Potentiometric titration was also used to verify that the aluminium ion reacts with three molecules of SAPH, to give three hydrogen ions per Al(III) ion. Two samples were prepared by dissolving 0.3938 g of SAPH in 25 cm^3 EtOH and 0.2082 g of $Al(NO_3)_3 \cdot 9H_2O$ in 50 cm^3 of water. The precipitate had to be filtered (after 1 or 2 hr) and the filtrate and the washing water titrated with solutions of 1 and 0.5*N* KOH (Fig. 2B). The reaction was probably:

$$\underset{\text{(I)}}{Al^{3+} + 3SAPH^+} \overset{\text{pH 5.3}}{\rightleftharpoons} \underset{\text{(II)}}{Al(SAPH)_3^{3+}} + 3H^+.$$

The successive production of H$^+$ ions, was also checked by conductometry. Several titrations of aqueous–ethanolic solution of Al^{3+} with ethanolic solution of SAPH 0.05*M* were made. The results are given in Fig. 2C. It was observed that turbidity appears in the medium of the reaction due to the formation of the insoluble metal-chelate. In order to avoid such turbidity it was necessary to add enough to the medium (this is shown in Fig. 2C, lines 1 and 2). The corresponding reactions may be written as:

$$Al^{3+} + SAPH^+ \rightleftharpoons Al(SAPH)^{3+} + H^+$$

$$Al(SAPH)^{3+} + SAPH^+ \rightleftharpoons Al(SAPH)_2^{3+} + H^+$$

$$Al(SAPH)_2^{3+} + SAPH^+ \rightleftharpoons Al(SAPH)_3^{3+} + H^+.$$

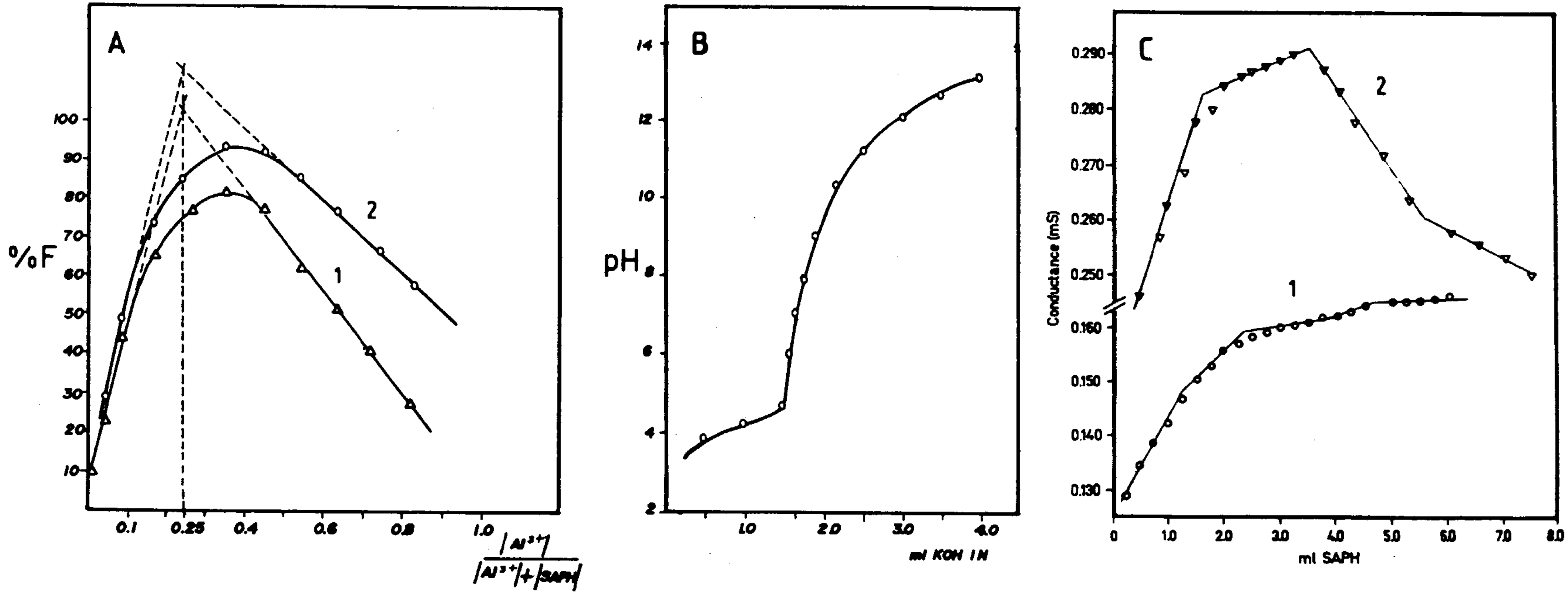


Fig. 2. Determination of the stoichiometry Al(III)–SAPH complex. (A) Continuous variations method: curve 1, used concentrations of aluminium $0.37 \times 10^{-4}M$ and SAPH $1.85 \times 10^{-4}M$; curve 2, used concentrations of aluminium and SAPH $1.85 \times 10^{-4}M$. (B) Potentiometric titration of released protons for reaction of 1.63×10^{-3} and 5.44×10^{-4} moles of SAPH and $Al(NO_3)_3 \cdot 9H_2O$ respectively, in aqueous–ethanolic medium, 2:1 v/v. (C) Conductimetric titration of 100 ml Al(III) (aqueous–ethanolic solution), with SAPH 0.05M (ethanolic solution). Curve 1, Al(III) $6 \times 10^{-4}M$; water–ethanol, 3:2 v/v. Curve 2, Al(III) $8 \times 10^{-4}M$; water–ethanol, 4:1 v/v.

Table 1. Methods for fluorimetric determination of Al(III)

Medium*	Regression ($a_1x + a_0$)	Correlation coefficient	RSD†	Al(added) ($\mu g/dm^3$)	Al(found) ($\mu g/dm^3$)
		Direct method			
EtOH	$1.1439x - 0.06$	0.9962	2.98‡	≤50	—
DMF	$1.3944x + 0.15$	0.9977	3.27‡	≤50	—
EtOH	$5.7712x - 0.15$	0.9999	1.66§	≤10	—
DMF	$5.7700x + 0.45$	0.9992	3.53§	≤10	—
		Standard addition method			
EtOH	$1.171x + 10.58$	0.9931	1.78‖	10	9.04
DMF	$1.434x + 12.02$	0.9836	2.74‖	10	8.38
EtOH	$5.770x + 11.40$	0.9999	0.11‖	2	1.98
DMF	$6.895x + 12.76$	0.9985	1.26‖	2	1.85

*Water–EtOH (3 + 2 v/v), water–DMF (4 + 1 v/v).

†Relative standard deviation for 11 samples with $\alpha = 0.05$.

‡Sample concentration = 20 μg/dm^3 Al(III).

§Sample concentration = 6 μg/dm^3 Al(III).

‖Given by the square root of the variance:

$$S_c^2 = (-1/a_1)^2 . S^2(a_0) + (a_0/a_1^2)^2 . S^2(a_1) - 2(1/a_1)\,(a_0/a_1^2).\ S^2(a_0a_1).$$

The metal complex charge and reagent were determined by ion exchange resins (Lewatit S 100, sodium form and Lewatit M 500, chloride form). The overall charge of the aluminium complex and the free ligand at pH 5.3 is positive. Therefore, it is probable that the reagent acts as a bidentate ligand in the aluminium chelate and that the charge might be supported by the pyridine N-atom. In this way, Garcia–Villanova's method was used for the determination of reagent ionisation constants.[17] The average pK values found were 1.0, 2.4, 5.6, 9.12 and >12. The first and second pK values may be due to biprotonation of the $C{=}\overset{+}{N}H{-}NH{-}$ and $C{=}N{-}\overset{+}{N}H_2{-}$ groups, respectively.[17] The third pK value is produced by protonation of the N-pyridine atom, in agreement with analogous results obtained with benzoylhydrazone of 2-acetylpyridine.[14,15,18] The fourth pK value may be caused by deprotonation of the hydroxyl group.[9,19] The last pK value may be attributed to deprotonation of the CONH group giving rise to an azine group.[14,15,17,20]

Spectrofluorimetric determination of Al(III)

Two calibration methods (direct and SAM) were performed. By using the direct method, two calibration lines [≤50 and ≤10 μg/dm^3 of Al(III)] for two aqueous–organic media (ethanol, 3:2 v/v and dimethylformamide, 4:1 v/v) were done (Table 1). Appropriate selection

Table 2. Tolerance limits in the determination of 50 μg/dm^3 of Al(III)

Conc. tolerated ($\mu g/dm^3$)	Species tested*
50000	CH_3COO^-, AsO_3^{3-}, AsO_4^{3-}, ClO_4^-, Cl^-, $Fe(CN)_6^{3-}$, NO_3^-, SeO_4^{2-}, SO_3^{2-}, IO_3^-, IO_4^-, I^-, K(I), La(III) Li(I), Na(I), Rb(I), U(VI), TGA, TEA
25000	BrO_3^-, $Fe(CN)_6^{4-}$, PO_4^{3-}, WO_4^{2-}, Ce(IV), S^{2-}
20000	CN^-,$BO_3H_2^-$, Pb(II), Ca(II)
15000	Benzoate
10000	NO_3^-, TGA, Hg(II)^b
7500	SCN^-
5000	$S_2O_8^{2-}$, CO_3^{2-}, Tl(I), AA
2500	SO_4^{2-}, Be(II), Ba(II), Bi(III), YB(III), F^{-c}
1000	MoO_4^{2-}, Ho(III), Ti(IV), TEA, Cu(II),^{d} Fe(II,^{e} III^f), $C_2O_4^{2-g}$
750	Mn(II), Mg(II), Sn(II)
500	CrO_4^{2-}, $S_2O_3^{2-}$, Br^-, F^-, phen, Au(III),^{h} Cd(II),^{b} Co(II),^{h} Sb(III),^{b} Zn(II),^{d} Ti(IV),^{i}, MnO_4^{-k}
250	$Cr_2O_7^{2-}$, VO_3^-, Sb(III)
150	$C_2O_4^{2-}$, Fe(II), Er(III), Zr(IV)
100	Ag(I), Au(III)
75	Citrate, Cd(II), Hg(II)

*TGA, thioglycolic acid; AA, ascorbic acid; TEA, triethanolamine; phen, *o*-phenanthroline. Exponents refer to tolerance limits in presence of masking agents. b, S^{2-} (5 mg/dm^3); c, Be^{2+} (2 mg/dm^3); d, TGA (10 μg/dm^3); e, $Fe(CN)_6^{3-}$ (5 mg/dm^3); f, $Fe(CN)_6^{4-}$ (20 mg/dm^3); g, $MnO_4^- + Q$ (before Al complex formation); h, CN^- (5 mg/dm^3); i, AA (5 mg/dm^3); k, $H_2O_2 + Q$ (before Al complex formation).

Table 3. Characteristics of fluorimetric methods for aluminium

Compound	Optimum acidity	$\lambda_{Exc}/\lambda_{Em}$ (*nm*)	Colour	Sensitivity (*ppb*)	Major interferences	Ref.
Pontachrome Blue Blak Red	4.8	350/650	Red	<10	Fe,Cu,Cr,Ni, Co,Ti,V,Zr	21
2′,3′,4′,5,7-Pentahydroxyflavone	3	440/525	Blue	0.25	F^-,PO_4^{3-},Cu,Cr	22
2-Hydroxy-3-naphthoic acid	5.8	370/460	Blue	<2	Fe,Ti,Cu,Zr, Sc,Be,$B_4O_7^{2-}$	23
[1-(2-pyridylazo)-2-Naphthol]	—	436/530	Orange	800	Not studied	24
Salicylidene-*o*-aminophenol	5–6	410/520	Yellow	0.27	Cr,Th,Zr	25
N-Salicylidene 2-amino-3-hydroxyfluorene	5.2	445/525	Yellow-brown	0.001 μmol	F^-,PO_4^{3-},Fe Lantanides	26
Salicyloylhydrazone of pyridine-2-aldehyde	5.4	382/440	Blue	4	Be,Bi,In,As,F^-	7
This method	5.3	384/468	Green-blue	0.42	Co,Ni,Fe,Pd,Zn	

of both slit widths (5/5 and 5/10 for excitation/emission) and integration time (4.2 and 8.4 sec) for construct work lines, were performed. From the precision of both methods (ethanol and dimethylformamide media), it can be concluded that the water–ethanol mixture is more suitable than the DMF one (Table 1).

In order to increase the accuracy and precision of the SAPH fluorimetric model, SAM was also applied in both aqueous–ethanolic (3:2, v/v) and aqueous–dimethylformamide (4:1, v/v) media. To study the accuracy of this method in both media, two aluminium-containing solutions were made, with 50 and 10 μg of Al(III) in 1000 cm^3 of free-aluminium deionized-distilled water. The SAM was applied to 1-cm^3 sample aliquots as described in the Procedure section using both first and second set of additions, respectively (Table 1). The data show that the method in aqueous–ethanolic medium is more accurate and precise than in aqueous–dimethylformamide medium. Final concentrations down to 2 μg/dm^3 Al(III) can be determinated with a relatively good accuracy and precision.

The effect of 72 ions on the proposed method has been also evaluated (Table 2). The tolerance limit was the concentration of a species which gives a relative error lower than 4% for the 50 μg/dm^3 Al(III) concentration. Cations were added as chloride, nitrates or acetates and anions were added as sodium or potassium salts;

Table 4. Comparison between ICP and molecular spectrofluorimetric methods for the Al(III) determination on soil extracts

			SAPH-Al method		ICP Method*	
Sample	Weight wet(*g*)	Weight dry(*g*)	Extract (*μg/dm*^{3})	Dry sample (*μg/g*)	Extract (*μg/dm*^{3})	Dry sample (*μg/g*)
1	10.1713	9.1440	253.2	2.77	267	2.92
2	10.4073	9.9301	213.2	2.15	218	2.20
3	10.3189	8.7914	384.0	4.37	405	4.61
4	10.1049	8.6480	189.6	2.19	204	2.36
5	10.4361	9.6892	175.6	1.81	184	1.90
6	10.2939	9.1567	364.0	3.78	386	4.22
7	10.5084	9.6232	238.4	2.48	243	2.53
8	10.3981	9.0144	232.0	2.57	237	2.63
9	10.0350	8.4322	278.4	3.30	252	2.99
10	10.1484	9.1488	190.2	2.08	207	2.26
11	10.2498	8.3875	398.2	4.75	415	4.95
12	10.2621	9.4060	398.6	4.24	421	4.47
13	10.2661	9.3153	477.4	5.12	499	5.36
14	10.1468	9.0826	294.6	3.24	322	3.55
15	10.1740	8.5029	249.2	2.93	236	2.78

*Detection limit for aluminium determination was 50 μg/dm^3.

the maximum concentration of foreign ion investigated was 50,000 $\mu g/dm^3$.

As can be seen from Table 2, almost all the anionic species are tolerated at relatively high concentrations, since 73% of the anions had tolerance limits higher than 2500 $\mu g/dm^3$. Citrate, oxalate, dichromate, chromate, vanadate and thiosulphate cause the highest interferences. The cations were mostly tolerated at concentrations higher than aluminium. However, the cationic species copper, iron, nickel, zinc, cobalt and palladium, interfered at the same concentration as that of aluminium. In order to reduce the interference levels, different masking reactions were tested. In this way, Cu(II), Fe(II and III), Zn(II), Co(II), Cd(II), and Hg(II) notably increased their tolerance limits (Table 2).

The proposed method has been compared to other existing alternatives for the spectrofluorimetric determination of aluminium in terms of sensitivity and selectivity (Table 3).

Application of the method in soil extracts

The proposed method has been applied satisfactorily to the determination of Al(III) in acetate extracts of agricultural soils, using the techniques described in the Procedures section. For the sake of comparison, aluminium was also determined by the ICP method (first order, 396.15 nm) in all samples (soil extracts). As shown in Table 4, both methods give results in good agreement with each other. At a significance level ($\alpha = 0.05$), the comparison of the null hypothesis (H_0: $\mu_1 = \mu_2$) that both means are equal against the alternative hypothesis ($H_A : \mu_1 \neq \mu_2$) shows that the experimental value of $|t|$ denoted as T, is smaller than corresponding $|t|$ value for normal distribution, so, $T = 0.3279 < t_{22,0.025} = 2.048$. Therefore, the alternative hypothesis is rejected. The fluorimetric method may be recommended for the analysis of exchangeable aluminium from soils when concentrations of Al(III) extract are below 50 $\mu g/dm^3$ and down to 1–2 $\mu g/dm^3$.

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