

EXCHANGEABLE ALUMINUM EVALUATION IN ACID SOILS

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ABSTRACT: One of the main factors limiting agricultural production in tropical climate regions is mainly related to the presence of exchangeable aluminum (Al^{3+}) in highly weathered acid soils. Four methods of Al^{3+} determination extracted with neutral 1 mol L^{-1} KCl solution were evaluated: three colorimetric methods (aluminon plus ascorbic acid, and eriochrome cyanine R by FIA) and the usual titrimetric method with back-titration. Surface samples from 20 soils of different Brazilian regions, with active acidity (0.01 mol L^{-1} CaCl_2 , pH) ranging from very high to medium (3.82 to 5.52), were used. The variance analysis revealed significant interaction among Al^{3+} determination methods and soil. Mean methods comparisons within each soil (Tukey, $P < 0.05$) indicated that, for most of the soils, the methods differed among each other, although there were high correlations between the obtained values. Al^{3+} values determined for soil samples by titration varied between 0.15 and $14.71 \text{ mmol}_c \text{ dm}^{-3}$. The colorimetric methods showed higher values than the titration method, mainly for those with aluminon (up to $18.75 \text{ mmol}_c \text{ dm}^{-3}$). The Al^{3+} contents of colorimetric methods correlated quadratically with the titration values, for the soil samples with $\text{Al}^{3+} > 10 \text{ mmol}_c \text{ dm}^{-3}$. Among colorimetric methods, in operational terms, the eriochrome with FIA method presented analytical performance up to 50 samples per hour, easiness and sensibility for routine Al analysis in soil samples. However, due to the specificity, the titration/back-titration method should be used, despite the moroseness, when the Al^{3+} ions are the objective. Key words: FIA, aluminon, colorimetry, eriochrome cyanine R, titrimetry

AVALIAÇÃO DE ALUMÍNIO TROCÁVEL EM SOLOS ÁCIDOS

RESUMO: Um dos principais fatores que afetam a produção agrícola em regiões de clima tropical, é a presença de alumínio trocável (Al^{3+}) em solos ácidos altamente intemperizados. Foram avaliados quatro métodos de determinação de alumínio trocável em solução neutra de KCl 1 mol L^{-1} : três métodos colorimétricos (aluminon, aluminon + ácido ascórbico e eriocromo cianina R por FIA) e o método titulométrico usual com retrotitulação ácida. Para obtenção dos extratos de KCl, foram usadas amostras superficiais de 20 solos de diferentes regiões brasileiras, com acidez ativa (pH em CaCl_2 $0,01 \text{ mol L}^{-1}$) variando de muito alta a média (3,82 a 5,52). A análise de variância revelou interação significativa entre os métodos de determinação e amostras de solos. O teste de médias (Tukey, $P < 0,05$) de métodos dentro de amostras evidenciou, para a maioria das amostras de solos, que os métodos analíticos diferenciaram entre si, embora tenha havido forte correlação entre os valores obtidos. Os valores de Al^{3+} determinados por titulação variaram de $0,15$ a $14,71 \text{ mmol}_c \text{ dm}^{-3}$. Os métodos colorimétricos apresentaram valores superiores aos da titulação, notadamente aqueles com aluminon (até $18,75 \text{ mmol}_c \text{ dm}^{-3}$). Os teores de Al^{3+} dos métodos colorimétricos se relacionaram quadraticamente com os teores obtidos por titulação, em amostras de solos com $\text{Al}^{3+} > 10 \text{ mmol}_c \text{ dm}^{-3}$. Dentre os métodos colorimétricos, o reagente eriocromo cianina R, em sistema FIA, mostrou-se operacionalmente confiável e eficiente para a análise de Al, de amostras de solos, em rotina, com frequência analítica de 50 determinações por hora. Todavia, devido à especificidade, o método titulométrico com retrotitulação deve ser usado, não obstante a morosidade, quando o objetivo é a determinação do íon Al^{3+} . Palavras-chave: FIA, aluminon, colorimetria, eriocromo cianina R, titulometria

INTRODUCTION

In acid mineral soils of tropical climate regions, the high aluminum (Al) content, associated to high acidity and low fertility, is one of the main constraints for agricultural production (McLean, 1965; Pavan, 1983; Coscione et al., 1998), since toxic concentrations of Al are often concerned as having detrimental effects on plants.

At soil pH 4 or below, the predominant aluminum form is Al^{3+} . As soil pH increases mononuclear hydrolysis species such as $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$ are formed. If pH increases high enough, these species are precipitated as $\text{Al}(\text{OH})_3^0$, and with further increases in pH, the amphoteric $\text{Al}(\text{OH})_4^-$ species appears (Barnhisel & Bertsch, 1982; Thomas & Hargrove, 1984). There are contradicting results on the relative phytotoxicity of

mononuclear Al species, except for the nonphytotoxicity of $\text{Al}(\text{OH})_4^-$ (Marschner, 1997).

The extraction of Al^{3+} (usually called as exchangeable Al) from soil samples using neutral solutions of non-buffered salts has been employed since the 1960's (Brauner, 1966). The 1 mol L⁻¹ KCl solution has been considered the most appropriate extractant (McLean, 1965; Raij et al., 1987; Hiradate et al., 1998), besides the fact of this solution being less susceptible to ion interferences (Coscione et al., 1998). The Al^{3+} determined in these extracts is subject to overestimation due to the dissolution of non-exchangeable aluminum species (hydroxi-Al). The dissolution of hydroxi-Al species is affected by pH, concentration, and chemical feature of the extractant, as well as the extraction time (Kissel et al., 1971; Oates & Kamprath, 1983). Although the extraction with KCl removes both exchangeable and some non-exchangeable Al (Oates & Kamprath, 1983), the contribution of non-exchangeable Al may be considered insignificant in Brazilian acid soils (Pavan, 1983).

The Al^{3+} is always displaced from exchange sites by non-buffered salt solutions. Since the soil pH raises and monomers are formed, there gradually occur increments on the OH/Al relation and of the polymerization of these monomers. The formed polymers, of variable size and charges, neutralize negative charges but are not displaced (Thomas & Hargrove, 1984). Despite of this, expressive amounts of low stability hydroxi-Al forms are supposed to occur in KCl extracts. The hydrogen ions (H^+), obtained by titration in KCl extracts of an acid mineral soil containing 1:1 clay minerals and Al, Fe oxides, are indeed a result of low stability hydroxi-Al hydrolysis. According to Kissel et al. (1971), the lower the hydroxi-Al form contents, the higher is the proportion of their hydrolysable forms, due to lower polymerization (stability) of these Al forms, which produce H^+ in KCl extract. Consequently, as the back-titration step is essential when Al^{3+} determination in KCl extract is the main target, the titrimetric method should be used.

Although the Al^{3+} in soil samples is generally determined by titrimetry (McLean, 1965; Raij et al., 1987; Coscione et al., 1998), colorimetric methods can also be used (Raij et al., 2001). Among the colorimetric methods, the aluminon (Frink & Peech, 1962; Brauner, 1966; Reis, 1978) and the eriochrome cyanine R (Reis, 1978; Zagatto et al., 1981; Pavan, 1983) are the most commonly used reagents.

Bertsch et al. (1981) and Barnhisel & Bertsch (1982), employing the aluminon colorimetric method for Al determination in soil extracts, reported low detection limits (2 $\mu\text{mol L}^{-1}$) and analytical interference of the ferric ion, which is also complexed by the reagent. According to Hawke & Powell (1994), ferric ions do not constitute impediment for using aluminon, since the interference caused by the ion can be eliminated with ascorbic acid treatment.

The titrimetric method may present inferior sensitivity in relation to the colorimetric methods for the determination of Al (Reis, 1978; Logan et al., 1985), but it is less subject to interferences from ions present in the extract (McLean, 1965; Coscione et al., 1998). Both titrimetric and colorimetric methods present low determination rates in face of the intrinsic slowness of these methods. Therefore, the determination of Al by colorimetry through flow injection analysis (FIA) using eriochrome cyanine R has been suggested (Zagatto et al., 1981; Kronka, 1996).

The objective of this work is to compare titrimetric (standard) and colorimetric methods, with aluminon, aluminon plus ascorbic acid (conventional) and eriochrome cyanine R using FIA system, for the determination of Al^{3+} in different extracts by 1 mol L⁻¹ KCl of Brazilian soil samples, to improve routine analysis.

MATERIAL AND METHODS

The experiment was carried out using samples of the surface layer (0 – 0.2 m depth) of 20 soils from different Brazilian regions (Table 1).

Air dried samples were homogenized, divided into three subsamples, ground in a porcelain crucible, passed through a 0.5 mm mesh sieve, and conditioned in plastic bags. For the chemical characterization of soil samples (Table 2), the methods described in Raij et al. (1987; 2001) were used, except for the exchangeable sodium which was extracted with 0.05 mol L⁻¹ HCl + 0.0125 mol L⁻¹ H₂SO₄ solution in 1:5 (v/v) soil/extractant ratio and determined by flame photometry.

For the evaluation of the Al^{3+} in the extracts of 1 mol L⁻¹ KCl solution, 1:10 (v/v) soil/solution ratio (McLean, 1965), the following procedures were used: a) **Titrimetric method** (standard method), according to the routine methodology adapted from McLean, (1965). Primarily, the exchangeable acidity ($\text{Al}^{3+} + \text{H}^+_{\text{tit}}$) is determined by titration of 25 mL KCl extract with 0.025 mol L⁻¹ NaOH, using 1 g L⁻¹ phenolphthalein as an indicator (titration from colorless to pink). Then, the concentration of Al^{3+} is obtained by back-titration of the same KCl extract, previously used, after the acidification with a drop of HCl and addition of 40 g L⁻¹ NaF, with 0.025 mol L⁻¹ HCl (titration from pink to colorless); b) **Colorimetric methods with aluminon** (ammoniacal salt of aurintricarboxylic acid) according to Wolf (1982), adapted for the KCl solution (e.g., 1 mL of KCl extract, 0.4 mL of sodium phosphate, 1 mL hydroxylamine hydrochloride, and 3 mL of aluminon solution). The intensity of developed color is read in a spectrophotometer at 555 nm, zeroing the equipment with the blank (1 mol L⁻¹ KCl); c) **Modified aluminon colorimetric methods by addition of ascorbic acid** to verify the effect of adding 1 mL of 20 g L⁻¹ ascorbic acid (prepared immediately before the

Table 1 - Legend, classification, and origin of the soil samples used in the experiment.

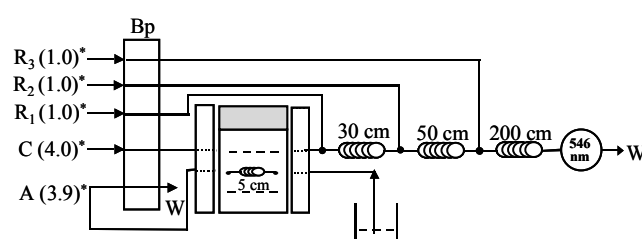
Soil sample legend	Soil classification (Estados Unidos, 1999; FAO, 1994; Embrapa, 1999; respectively)	Municipality	Geographic coordinate	State
GX	Typic Umbraquult/Dystric Gleisol/Gleissolo Háplico Tb Distrófico	Irاندوبا	3°14'05"S 60°11'10"W	AM
LA-1	Typic Acrudox/Geric Ferralsol/ Latossolo Amarelo Acriférrico	Viçosa	9°22'14"S 36°14'27"W	MG
LV-1	Typic Hapludox/Rhodic Ferralsol/ Latossolo Vermelho Distrófico	Três Lagoas	20°45'04"S 51°40'42"W	MS
LV-2	Typic Acrudox/Geric Ferralsol/ Latossolo Vermelho Acriférrico	Cuiabá	15°35'46"S 56°05'48"W	MT
LA-2	Typic Hapludox/Xantic Ferralsol/ Latossolo Amarelo Distrófico	Capitão Poço	1°44'47"S 47°03'34"W	PA
PVA-1	Typic Hapludult/Haplic Acrisol/ Argissolo Vermelho-Amarelo Distrófico	Capitão Poço	1°44'47"S 47°03'34"W	PA
LA-3	Typic Hapludox/Xantic Ferralsol/ Latossolo Amarelo Distrófico	Ipixuna	2°33'28"S 47°29'42"W	PA
LA-4	Typic Hapludox/Xantic Ferralsol/ Latossolo Amarelo Distrófico	Ipixuna	2°33'28"S 47°29'42"W	PA
NV-1	Typic Kandiodult/Rhodic Ferralsol/ Nitossolo Vermelho Distrófico	Maringá	23°25'31"S 51°56'19"W	PR
LA-5	Xantic Hapludox/Haplic Acrisol/ Latossolo Amarelo Distrófico Argissólico	Ariquemes	9°54'48"S 63°02'24"W	RO
PVA-2	Typic Hapludult/Haplic Acrisol/ Argissolo Vermelho-Amarelo Distrófico	Ariquemes	9°54'48"S 63°02'24"W	RO
LA-6	Xantic Eutrudox/Xantic Ferralsol/ Latossolo Amarelo Eutrófico Argissólico	Not identified	-	SC
PVA-3	Typic Hapludult/Haplic Acrisol/Argissolo Vermelho-Amarelo Distrófico	Capão Bonito	24°00'21"S 48°20'58"W	SP
LV-3	Typic Acrudox/Geric Ferralsol/ Latossolo Vermelho Acriférrico	Guataparά	21°29'48"S 48°02'16"W	SP
LV-4	Typic Hapludox/Rhodic Ferralsol/ Latossolo Vermelho Distrófico	Piracicaba	22°43'31"S 47°38'57"W	SP
PV	Typic Hapludult/Haplic Acrisol/Argissolo Vermelho Distrófico	Piracicaba	22°43'31"S 47°38'57"W	SP
PVA-4	Typic Hapludult/Haplic Acrisol/ Argissolo Vermelho-Amarelo Distrófico	Piracicaba	22°43'31"S 47°38'57"W	SP
NV-2	Typic Kandiodult//Rhodic Ferralsol/ Nitossolo Vermelho Distrófico	Piracicaba	22°43'31"S 47°38'57"W	SP
RQ	Typic Quartzipsamment/Haplic Arenosol/ Neossolo Quartzarênico Distrófico	São Pedro	4°39'30"S 40°35'56"W	SP
LVA	Typic Hapludox/Xantic Ferralsol/ Latossolo Vermelho-Amarelo Distrófico	São Pedro	4°39'30"S 40°35'56"W	SP

analysis) on Al^{3+} determination in the extract of KCl; and d) **Colorimetric methods with eriochrome cyanine R by flow injection analysis (FIA)** according to Zagatto et al. (1981), adapted for the KCl solution with modifications in the entrances of the FIA system and in eluent volume, following the Al determination by spectrophotometry of the formed colored complex at pH 6.4, and 546 nm (Figure 1).

Data were submitted to the analyses of descriptive statistics, of correlation and of regression. For the comparison of methods of Al^{3+} determination the variance analyses and of test of means (Tukey, $P < 0.05$), were used after the data transformation ($X+0.5$).

RESULTS AND DISCUSSION

There were differences among quantities of Al^{3+} evaluated by the different methods in the extracts of soil samples in neutral KCl solution (Table 3). The values of



*flow rate (mL min⁻¹)

Figure 1 - Flow diagram of the system for determining exchangeable aluminum (Al^{3+}) in soil samples, extracted with neutral 1 mol L⁻¹ KCl solution. **A** is the flow, in mL/min, of 1 mol L⁻¹ KCl extractant containing Al^{3+} extracted from the soil sample; **C** is the flow of carrier KCl solution; **R₁** is the flow of 20 g L⁻¹ ascorbic acid solution (prepared just before the analysis); **R₂** is the flow of 0.2 g L⁻¹ eriochrome cyanine R solution (prepared just before the analysis by dilution of 2 g L⁻¹ stock solution, pH 2.8, with deionized water); **R₃** is the flow of 4 mol L⁻¹ ammonium acetate buffer solution, pH 6.4; **Bp**, peristaltic pump; **W**, waste.

Table 2 - Chemical properties of soil samples of the 0 – 0.2 m layer.

Soil Sample	pH CaCl ₂	Organic mater g dm ⁻³	Resin P mg dm ⁻³	K ⁺	Ca ²⁺	Mg ²⁺	⁽¹⁾ Na ⁺	H ⁺ + Al ³⁺	Sum of bases	CEC	Base saturation %
				mmol _c dm ⁻³							
GX	4.56	12.7	11.0	1.45	27.2	6.8	1.1	36.2	36.4	72.6	50.1
LA-1	3.82	25.2	5.0	0.89	2.1	1.3	0.2	95.2	4.5	99.7	4.5
LV-1	5.52	22.2	4.9	2.84	26.4	14.6	0.3	21.3	44.1	65.4	67.4
LV-2	4.10	27.4	3.5	0.78	1.2	1.1	0.2	67.3	3.3	70.6	4.7
LA-2	3.78	22.9	5.0	0.71	4.8	2.2	0.5	50.8	8.4	59.2	14.2
PVA-1	3.98	25.0	3.3	0.74	8.1	2.5	0.8	40.5	12.1	52.7	23.1
LA-3	3.91	37.9	5.8	1.06	9.2	8.3	1.2	81.9	19.8	101.7	19.5
LA-4	4.72	32.6	3.9	1.92	21.2	6.0	0.5	28.6	29.7	58.3	50.9
NV-1	4.64	14.9	1.4	0.99	17.1	7.0	0.3	45.2	25.4	70.6	35.9
LA-5	4.52	19.9	6.9	2.62	15.5	3.6	0.4	30.3	22.1	52.4	42.2
PVA-2	4.54	22.4	4.9	1.32	7.9	3.6	0.2	24.6	13.1	37.7	34.8
LA-6	4.58	24.1	13.6	2.13	36.3	10.6	0.8	46.7	49.8	96.5	51.6
PVA-3	4.25	40.8	1.3	2.33	4.3	2.4	0.2	108.6	9.2	117.8	7.8
LV-3	4.63	30.1	4.3	1.07	13.4	8.7	0.2	41.4	23.3	64.7	36.0
LV-4	4.57	27.9	45.4	3.84	16.8	10.8	0.3	51.8	31.8	83.6	37.9
PV	4.72	27.9	2.8	0.70	22.3	8.1	0.2	40.4	31.4	71.8	43.7
PVA-4	4.28	25.1	3.6	0.74	10.3	3.5	0.3	38.3	14.8	53.1	27.8
NV-2	5.28	45.0	10.2	2.16	50.0	14.1	0.2	34.3	66.6	100.9	66.0
RQ	3.96	17.9	2.8	0.71	1.8	0.7	1.0	43.9	4.6	48.5	9.5
LVA	4.43	36.1	4.9	1.95	7.9	3.3	0.6	48.1	14.0	62.1	22.5

⁽¹⁾Sodium extracted by 0.05 mol L⁻¹ HCl + 0.0125 mol L⁻¹ H₂SO₄, 1:5 (v/v) soil/solution ratio. Other chemical analyses as described in Raji et al. (1987; 2001).

Al³⁺, in mmol_c dm⁻³, in the acid soil samples with pH ranging from 3.82 to 5.52 (Table 2), varied from 0.15 to 14.71 (median of 4.22) when determined by titration; from 0 to 18.75 (median of 3.94) by aluminon colorimetric method; from 0 to 18.27 (median of 4.00) by aluminon colorimetry with addition of ascorbic acid; and from 0 to 15.24 (mean of 4.17 and median of 2.66) by eriochrome cyanine R colorimetry in FIA system.

Quadratic relationships were verified between the Al³⁺ concentrations obtained by titration and those of the colorimetric methods (Figure 2), because in the soil samples with Al³⁺ > 10 mmol_c dm⁻³ the colorimetric methods gave higher values than by the titration method, mainly in those with aluminon (up to 18.75 mmol_c dm⁻³, e.g., soil samples LA-1 and PVA-3), owing to the strong acidity of these samples.

For the soil samples with Al³⁺ concentration between 1 to 10 mmol_c dm⁻³, generally, the modified aluminon colorimetric method with the addition of ascorbic acid and the titrimetric method did not differ from each other. However, the aluminon colorimetric method provided the highest Al³⁺ values, and the eriochrome cyanine R colorimetric methods by FIA gave the lowest values. The addition of ascorbic acid minimized the interference of Fe³⁺, in the KCl extracts, on the Al³⁺ analysis by the aluminon color reagent. The Al³⁺ analysis by the eriochrome cyanine R with FIA showed

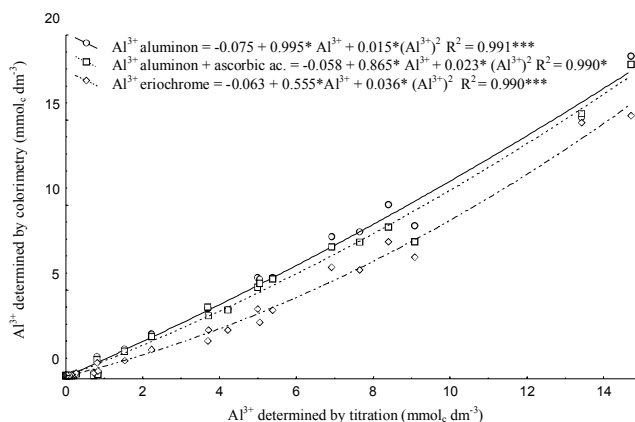


Figure 2 - Relationships between the exchangeable aluminum (Al³⁺) determined by titrimetric method (alkaline titration followed by acid back-titration), and by colorimetric methods of Al³⁺determination, aluminon, aluminon plus ascorbic acid (by conventional colorimetry), and eriochrome cyanine R (by flow injection analysis – FIA), respectively, in soil samples from different Brazilian regions, extracted with neutral 1 mol L⁻¹ KCl solution.

low efficiency due to the low concentration of the colorimetric reagent, as this method was adapted from that for analysis of total aluminum in vegetable material (Zagatto et al., 1981), for which the relative Al concentration in the extract is much higher than in KCl soil extract.

Table 3 - Concentration of exchangeable aluminum (Al^{3+}), extracted with neutral 1 mol L^{-1} KCl solution, determined by the titrimetric method (alkaline titration followed by acid back-titration), and by aluminon colorimetric method, modified aluminon colorimetric method with ascorbic acid addition through conventional colorimetry, and eriochrome cyanine R colorimetric method through flow injection analysis (FIA).

Soil sample	Titration	Aluminon		Eriochrome (FIA)
		without ascorbic acid	with ascorbic acid	
----- $\text{mmol}_c \text{ dm}^{-3}$ -----				
GX	3.71 ab [#]	3.92 a	3.50 b	2.65 c
LA-1	13.42 b	15.14 a	15.38 a	14.85 a
LV-1	0.20 a	0.00 b	0.00 b	0.00 b
LV-2	6.92 c	8.14 a	7.56 b	6.35 d
LA-2	7.65 b	8.43 a	7.83 b	6.19 c
PVA-1	4.99 b	5.71 a	5.16 b	3.90 c
LA-3	9.08 a	8.78 a	7.85 b	6.94 c
LA-4	0.73 a	0.15 b	0.0 b	0.13 b
NV-1	3.69 a	3.94 a	3.99 a	2.03 b
LA-5	1.53 a	1.54 a	1.40 a	0.85 b
PVA-2	0.83 a	0.19 b	0.05 b	0.25 b
LA-6	4.22 a	3.86 ab	3.83 b	2.65 c
PVA-3	14.71 c	18.75 a	18.27 a	15.24 b
LV-3	0.26 a	0.29 a	0.07 a	0.11 a
LV-4	2.23 a	2.42 a	2.28 a	1.50 b
PV	0.81 a	1.09 a	0.92 a	0.72 a
PVA-4	5.38 a	5.73 a	5.66 a	3.84 b
NV-2	0.15 a	0.00 b	0.00 b	0.00 b
RQ	8.39 b	10.04 a	8.72 b	7.84 c
LVA	5.04 a	5.64 a	5.41 a	3.10 b

[#]Means followed by same letters within a soil sample are not significantly different according to the mean separation Tukey test ($P < 0.05$) (Variance analysis with $X+0.5$ data transformation).

Brauner (1966) observed, unlike the results of the present work, that in samples with low Al^{3+} concentration the difference between the values obtained by titrimetric and aluminon colorimetric was higher than for samples with high concentration and this difference was attributed to the interference of Ca and Fe in the aluminon method. This Ca derives from the calcium chloride solution used as extractant and the Fe from the tioglycolic acid employed in the reagent solution. To remove the interference of these two elements during the Al^{3+} determination by the aluminon colorimetric method, Frink & Peech (1962) had proposed the exclusion of the calcium chloride as extractant and the substitution of tioglycolic acid, in the reagent solution, with hydroxylamine hydrochloride. Despite of this, the difference between results observed in the present study and those of Brauner (1966) is also due to the fact that the values of Al^{3+} obtained by titration by the last author, are actually equal to the titratable acidity, since the concentration was obtained without back-titration, after addition of NaF. The aluminon colorimetric method described by Wolf (1982) and used in the present work was similar to that proposed by Frink & Peech (1962).

The Al^{3+} determination by the titrimetric method presented standard deviations (SD, mean of three replicates for each soil sample) between 0.06 to $0.28 \text{ mmol}_c \text{ dm}^{-3}$ (except for soil sample LA-2, with a SD of $0.55 \text{ mmol}_c \text{ dm}^{-3}$), and coefficients of variation (CV%, mean of three replicates for each soil sample) between 1.3 to 20.8% (except for sample LV-3, $\text{CV}\% = 43.3$). For the colorimetric methods using the aluminon and aluminon + ascorbic acid reagent, the SD varied between 0.04 to $0.68 \text{ mmol}_c \text{ dm}^{-3}$, 0.07 to $0.23 \text{ mmol}_c \text{ dm}^{-3}$, and the CV% between 0.7 to 33.2 , 0.8 to 7.4 (excluding samples LA-4 and LV-3, $\text{CV} > 80\%$ due to the inverse relation between Al concentration and CV%), respectively. The lower and narrow range values of SD and CV% for the method with aluminon + ascorbic acid is also associated to the fact that ion interferences, mainly the Fe^{3+} ion, which is quite suppressed with ascorbic acid. Using the FIA system with the eriochrome cyanine R reagent, the values of SD and CV% varied between 0.03 and $0.46 \text{ mmol}_c \text{ dm}^{-3}$ and 0.7 and 19.7 , respectively. Positive correlations ($P < 0.05$) were observed between SD and Al^{3+} concentration in KCl extracts for all colorimetric methods as there was intrinsic relationship between intensity of developed color and Al content in the extract,

and conversely, the titrimetric method presented negative correlations between CV% and Al^{3+} concentration, due to the difficulty in the observation of the end-point.

Despite of this, for most of the acid soil samples of pH ranging from 3.8 to 4.7, the relative low values of SD and CV% indicate that all these tested methods presented good reproductibility for the analytical determination of the Al^{3+} . The titrimetric method, phenolphthalein being used as indicator, presented a limitation due to the difficulty in observing the end-point and the analytic moroseness, due to the need of two step analysis (back-titration), which limits the number of samples to be analyzed by each batch. The Al^{3+} values given by titration may be imprecise and untruthful in relation to solutions of known Al concentration (Logan et al., 1985). Raij et al. (2001) have proposed the Al^{3+} determination, when necessary, by some specific methods, such as the spectrophotometry with orange of xylenol in extracts of NH_4Cl or even by plasma spectrometry (ICP-AES) in KCl or NH_4Cl extracts.

Both aluminon colorimetric methods presented difficulties for cleaning the glassware and tubes in contact with the aluminon reagent. All glassware was stained with a rose-red coloration, mainly in the quartz vessel of the spectrophotometry, producing accumulative effect and provoking systematic errors for the Al^{3+} determination in the soil extracts. The FIA system, employed for Al determination by eriochrome cyanine R method, should also be carefully washed after the analysis to avoid the discoloration, although slow, of the polyethylene tubes by the colorimetric reagent (Zagatto et al., 1981).

Among colorimetric methods, in relation to operationality, the eriochrome cyanine R colorimetric method, with FIA system presented the best analytical quickness (allowing analysis up to 50 samples per hour), easiness and sensibility. In addition, the chemical analysis using FIA system can also turn simultaneous or sequential analysis of several elements easier (Kronka, 1996; Kachurina et al., 2000). The eriochrome-FIA procedure, with some modifications (improvements are needed for soil samples), should be preferred over the titration method when operational gains are the main aim in routine analysis of soil samples; nevertheless when the target is the research, titration should be used, because, despite this moroseness, with back-titration the procedure is specific for Al^{3+} ions.

REFERENCES

BARNHISEL, R.; BERTSCH, P.M. Aluminum. In: PAGE, A.L.; MILLER, R.H.; KEENEY, D.B. (Ed.) **Methods of soil analysis**: Part 2. Chemical and microbiological properties. Madison: ASA, 1982. p.275-300.

BERTSCH, P.M.; ALLEY, M.M.; ELLMORE, T.L. Automated aluminum analysis with the aluminon methods. **Soil Science Society of America Journal**, v.45, p.666-667, 1981.

BRAUNER, J.L. Extração e determinação do alumínio "trocável" do solo; variação no seu teor influenciado pela aplicação de carbonato de cálcio. Piracicaba: USP/ESALQ, 1966. 34p. (Dissertação - Mestrado)

COSCIONE, A.R.; ANDRADE, J.C.; RAIJ, B. van. Revisiting titration procedures for the determination of exchangeable acidity and exchangeable aluminum in soils. **Communications in Soil Science and Plant Analysis**, v.29, p.1973-1982, 1998.

EMBRAPA. Centro Nacional de Pesquisa de Solos. **Sistema brasileiro de classificação de solos**. Brasília: Embrapa Produção de Informação; Rio de Janeiro: Embrapa Solos, 1999. 412p.

ESTADOS UNIDOS. Department of Agriculture. **Soil taxonomy**: a basic system of soil classification form making and interpreting soil surveys. Washington: USDA, 1999. 869p. (Handbook, 436)

FAO. **Soil map of the world**. Revised legend with corrections. Rome: FAO; UNESCO; Wageningen: ISRIC, 1994. 140p. (World Resources Report, 60)

FRINK, C.R.; PEECH, M. Determination of aluminum in soil extracts. **Soil Science**, v.93, p.317-324, 1962.

HAWKE, D.J.; POWELL, H.K.J. Flow-injection analysis applied to the kinetic determination of reactive (toxic) aluminum: comparison of chromophores. **Analytica Chimica Acta**, v.299, p.257-268, 1994.

HIRADATE, S.; TANIGUCHI, S.; SAKURAI, K. Aluminum speciation in aluminum-silica solutions and potassium chloride extracts of acidic soils. **Soil Science Society of America Journal**, v.62, p.630-636, 1998.

KACHURINA, O.M.; ZHANG, H.; RAUN, W.R.; KRENZER, E.G. Simultaneous determination of soil aluminum, ammonium- and nitrate-nitrogen using 1 M potassium chloride extraction. **Communications in Soil Science and Plant Analysis**, v.31, p.893-903, 2000.

KISSEL, D.E.; GENTZSCH, E.P.; THOMAS, G.W. Hydrolysis of non-exchangeable acidity in soils during salt extractions of exchangeable acidity. **Soil Science**, v.111, p.293-297, 1971.

KRONKA, E.A.M. Determinação multielementar em sistemas de fluxo: amônio e ortofosfato, alumínio e ferro em digeridos vegetais. Piracicaba: USP/CENA, 1996. 107p. (Tese - Doutorado)

LOGAN, K.A.B.; FLOATE, M.J.S.; IRONSIDE, A.D. Determination of exchangeable acidity and exchangeable aluminum in hill soils: Part II. Exchangeable aluminum. **Communications in Soil Science and Plant Analysis**, v.16, p.309-314, 1985.

MARSCHNER, H. **Mineral nutrition of higher plants**. 2.ed. London: Academic Press, 1997. 889p.

McLEAN, E.O. Aluminum. In: BLACK, C.A. (Ed.) **Methods of soil analysis**: Part 2. Chemical methods. Madison: ASA, 1965. p.978-998.

OATES, K.M.; KAMPRATH, E.J. Soil acidity and liming: I. Effect of the extracting solution cation and pH on the removal of aluminum from acid soils. **Soil Science Society of America Journal**, v.47, p.686-689, 1983.

PAVAN, M.A. Alumínio em solos ácidos do Paraná: relação entre o alumínio não-trocável, trocável e solúvel, com o pH, CTC, porcentagem de saturação de Al e matéria orgânica. **Revista Brasileira de Ciência do Solo**, v.7, p.39-46, 1983.

RAIJ, B. van; ANDRADE, J.C.; CANTARELLA, H.; QUAGGIO, J.A. **Análise química para avaliação da fertilidade de solos tropicais**. Campinas: Instituto Agrônômico, 2001. 285p.

RAIJ, B. van; QUAGGIO, J.A.; CANTARELLA, H.; FERREIRA, M.E.; LOPES, A.S.; BATAGLIA, O.C. **Análise química do solo para fins de fertilidade**. Campinas: Fundação Cargill, 1987. 170p.

REIS, B.F. Determinação colorimétrica de alumínio em águas naturais, plantas e solos por injeção em fluxo contínuo. Piracicaba: USP/ESALQ, 1978. 64p. (Dissertação - Mestrado)

THOMAS, G.W.; HARGROVE, W.L. The chemistry of soil acidity. In: ADAMS, F. (Ed.) **Soil acidity and liming**. Madison: ASA, CSSA, SSSA, 1984. cap.1, p.3-56.

WOLF, B. An improved universal extracting solution and its use for diagnosing soil fertility. **Communications in Soil Science and Plant Analysis**, v.13, p.1005-1033, 1982.

ZAGATTO, E.A.G.; JACINTHO, A.O.; REIS, B.F.; KRUG, F.J.; BERGAMIN FILHO, H.; PESSEDA, L.C.R.; MORTATTI, J.; GINÉ, M.F. **Manual de análises de plantas e águas empregando sistemas de injeção em fluxo**. Piracicaba: CENA, Seção de Radioquímica e Química Analítica, 1981. p.19-21.

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