

# ALUMINIUM, EXTRACTABLE FROM SOIL SAMPLES BY THE ACID AMMONIUM ACETATE SOIL-TESTING METHOD

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A salt solution of strong acid is commonly used for the extraction of the exchangeable forms of soil aluminium, while the determination of soluble aluminium in soils is based on the extraction treatment by a salt solution of a weak acid (PRATT & BAIR 1961). Molar ammonium acetate solution adjusted to pH 4.8 with acetic acid is often used for this purpose (BLACK et al., 1965).

Our method of soil-testing uses an 0.5 molar ammonium acetate solution at pH 4.65 as extractant which is thus a half-neutralized, molar acetic acid solution. This extraction solution is nowadays in extensive use as a »universal» extractant for the estimation of the quantities of available plant nutrients in soil samples in Finland (VUORINEN & MÄKITIE 1955).

Aluminium is the most important soil acidity component in acid soils where the content of soluble aluminium is also considerably high. The toxic effect of extraneous aluminium in soluble form cannot be underestimated in acid soils. The extractability of soil aluminium, particularly by the soil-testing extractant, and the relations to the exchange characteristics in our soils, have been studied in the present work.

## *Experimental*

*Sample material.* The sample material consisted of 30 pre-treated soil samples which had been air-dried, homogenized and sieved through a 2 mm round-holed sieve. The soil types and some general characteristics are listed in Table 1.

*Extractions.* A modification of the original soil-testing procedure was used. The extractant used was the solution of 0.5 M ammonium acetate — 0.5 M acetic acid, at pH 4.65. The extraction was carried out not by volume but by weight basis of the soil sample and by repeated shaking and centrifugation of a 10 g lot of the sample with a total volume of 150 ml of the extractant. The procedure was similar to the common method for extraction of the total-exchangeable bases from soil samples (SCHOLLENBERGER & SIMON, 1945). The samples were also pre-treated by washing with 60 % ethanol/water solution.

The total-exchangeable cations were leached with molar ammonium acetate solution and centrifuged according to the common procedure (MÄKITIE & VIRRI, 1965).

The extractions with molar potassium chloride solution were similarly carried out. The acidity of the leachate was also titrated with sodium hydroxide solution against phenolphthalein (Table 1, column f).

The exchange acidity was determined with the molar ammonium acetate solution in accordance with the modification of BROWN's method (BROWN 1943, MÄKITIE 1965).

The extractions with molar acetic acid, and with the various ammonium acetate solutions were similarly carried out as with the molar ammonium acetate solution (MÄKITIE 1956).

*Determinations.* Aluminium was determined spectrophotometrically as aluminon (aurintricarboxylic acid) complex (BLACK et al. 1965, p. 988, ROLFE et al. 1951, FRINK & PEECH 1962, Hsu 1963). Iron was complexed with thioglycolic acid (CHENERY 1948, 1955). A Beckman Quartz spectrophotometer with 10-mm cells was used for the measurements of absorption at 525 m $\mu$ .

The determinations of the individual metallic cations were carried out by complexometric titration procedure and by flame photometric methods (Table 1, column k). BROWN's method was used for estimation of the »S»-value of the permanent exchange complex of soil (Table 1, column g).

The pH-measurements were taken by means of a Radiometer PHM 4c potentiometer with a glass electrode and an open bridge reference electrode filled with saturated potassium chloride solution.

### Results and discussion

Four different extraction solutions were at first used; M KCl solution, M acetic acid solution, the soil-testing extractant 0.5 acetic acid — 0.5 M ammonium acetate solution (pH 4.65), and M ammonium acetate solution. Table 1 shows the data of the different determinations.

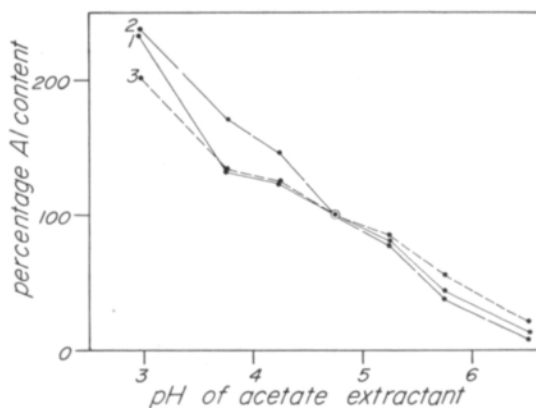


Fig. 1. Average percentages of aluminium in ammonium acetate extracts (molarity of acetate = 1.0) 1 = Coarse soils, 2 = Silts and clay soils, 3 = Organogenic soils. Soil-testing extractant = 100 %.

Table 1. Data of the samples. Al, H + and »S» concentrations in milliequivalents per 100 g of soil.

No	Soil type	O.M. %		Clay % (2 μ)		pH susp. (1:2.5)		M KCl extraction		M CH <sub>3</sub> COOH extraction		Soil-testing method		Exchangeable cations (M CH <sub>3</sub> COONH <sub>4</sub> )			
		a	b	c	d	e	f	g	h	i	j	»S» value	Al	»S» value	Al	H <sup>+</sup>	pH equil.
10	HHk (Sand)	4.8	14	5.5	4.8	0.04	0.65	13.5	1.51	12.1	0.56	11.0	0	5.9	6.72		
6	KHt (Finesand)	3.1	4	5.3	4.3	0.53	1.15	2.5	4.93	2.5	2.34	2.2	0.32	5.5	6.75		
16	KHt ( » )	4.0	8	5.2	4.2	0.87	3.75	3.8	4.45	3.8	1.98	3.4	0.04	7.8	6.67		
21	HHt (Fine finesand)	8.3	4	5.3	4.6	0.34	0.95	8.5	7.48	7.2	2.30	7.1	0.25	4.7	6.81		
22	HHt ( » )	6.7	4	5.9	5.0	0.11	0.60	10.5	7.41	9.0	2.57	7.9	0.20	3.6	6.86		
11	hsHHt (Silty » )	3.8	30	5.1	3.9	0.51	1.00	11.2	1.51	12.4	1.05	11.3	0	9.6	6.60		
4	sHHt (Clayey » )	8.5	28	6.0	5.0	0.05	0.48	15.8	1.73	16.1	1.04	15.7	0.56	7.7	6.67		
18	Hs (Silt )	4.4	30	6.5	5.6	0.01	0.65	17.2	2.03	15.8	0.58	14.2	0.06	4.9	6.80		
17	Hs ( » )	5.3	28	6.0	5.1	0.06	1.25	14.2	2.01	13.9	0.78	12.2	0.06	7.3	6.71		
2	sHs (Clayey silt )	2.8	42	6.1	5.0	0.06	0.50	10.1	1.96	8.5	1.04	9.1	0.38	4.3	6.80		
23	HtS (Sandy clay )	6.7	36	5.1	4.3	0.35	3.40	13.6	2.09	11.8	1.06	11.9	0.06	5.9	6.77		
24	HtS ( » )	6.0	36	5.7	4.5	0.18	0.53	13.4	1.82	13.9	1.10	13.1	0.10	9.8	6.63		
19	HsS (Silty clay )	5.9	42	6.3	5.3	0.06	1.60	16.7	3.22	19.4	1.07	17.3	0.07	7.8	6.69		
20	HsS ( » )	5.5	42	6.0	4.9	0.05	0.48	16.4	3.18	17.6	1.09	16.3	0.03	8.6	6.67		
1	AS (Heavy clay )	7.5	84	5.4	4.2	0.77	1.75	14.1	2.69	16.5	2.78	15.4	0.34	14.6	6.46		
13	AS ( » )	7.3	78	7.3	6.5	0.02	0.45	59.7	1.47	67.9	0.40	48.9	0	0.3	7.02		
12	AS ( » )	4.0	48	6.3	5.3	0.03	1.30	18.1	0.85	20.0	0.29	20.0	0	4.1	6.81		
9	AS ( » )	6.9	42	5.5	4.5	0.10	0.85	18.1	1.20	22.3	0.71	21.1	0	10.3	6.58		
5	LjS (Gytja clay )	20.7	58	5.4	4.3	0.64	1.65	14.3	5.56	15.5	3.50	14.9	0.58	16.8	6.41		
3	Lj (Gytja )	11.6		5.0	4.0	1.71	3.05	10.4	4.34	11.4	2.22	12.4	0.19	17.3	6.40		
14	Mm (Mould )	11.7		5.4	4.1	0.35	1.00	29.9	1.78	30.8	1.13	29.1	0	15.6	6.46		
25	Mm ( » )	20.8		5.3	4.5	0.35	0.75	16.0	4.56	15.4	2.22	14.3	0.32	17.9	6.42		
26	Mm ( » )	19.4		5.7	4.7	0.19	0.62	20.1	3.87	20.6	1.76	18.9	0.21	15.0	6.48		
8	Ct (Carex peat )			4.4	3.7	1.78	3.85	11.0	9.48	9.4	4.00	8.5	1.60	39.9	6.43		
15	Ct ( » )			5.6	4.9	0.07	1.22	41.8	1.20	48.9	0.67	49.7	0.07	18.2	6.41		
27	Ct ( » )			5.1	4.5	0.29	1.05	23.0	3.01	25.0	1.48	24.4	0.22	40.2	6.46		
28	Ct ( » )			5.4	4.6	0.21	0.74	28.0	2.54	31.4	1.36	29.6	0.31	21.2	6.35		
29	Ct ( » )			4.3	3.8	1.52	4.20	10.9	11.83	12.1	4.08	11.8	0.68	43.0	6.43		
30	Ct ( » )			5.0	4.2	0.58	1.10	24.8	5.50	27.1	3.21	24.4	0.49	39.3	6.47		
7	LSt (Ligno Sobagnum peat )			5.1	3.7	0.34	8.15	13.5	3.20	15.3	2.22	14.8	1.33	88.0	6.27		

Additional aluminium determinations were carried out from extracts where the acetic acid and ammonium acetate concentrations varied from 0.1 to 0.9 and where the total molarity was 1.0. The extractions were thus carried out at different pH ranges of the acetic acid — ammonium acetate system (MÄKITTIE 1956). All these extractions (at seven different pH, totally) are summarized in Fig. 1, where the extractability of aluminium is correlated with the extraction-pH.

The aluminium values show that relatively high amounts of soluble aluminium are extracted from acid soils when the hydrogen ion concentration in the extractant is high. When the extraction pH is over 5, only very little aluminium is extracted, particularly with the M ammonium acetate solution where the equilibrium pH of the extractant — soil suspension is mainly between 6.0 and 6.5.

The potassium chloride extraction represents the leaching of exchangeable aluminium of soils. When the aluminium values of this M KCl extraction are compared with the  $\text{pH}_{\text{KCl}}$  of soil suspension, a proper correlation is obtained (Fig. 2). In the figure, the upper limit of possible aluminium content in solution, decreasing with increasing pH, is shown.

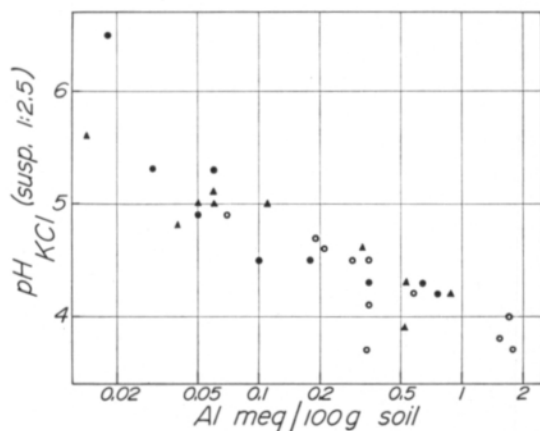


Table 2. Percentage extractability of aluminium by different extractants.

Method	Coarse soils (9)	Clay- soils (10)	Organogenic soils (11)	All soils (30)
M CH <sub>3</sub> COOH — extraction	242	227	199	222
0.5 M CH <sub>3</sub> COOH, 0.5 M CH <sub>3</sub> COONH <sub>4</sub> , pH = 4.65	100	100	100	100
M CH <sub>3</sub> COONH <sub>4</sub> — extraction	4	6	19	13
M KCl — extraction	18	18	30	24

### Summary

The extractant, 0.5 M acetic acid — 0.5 M ammonium acetate at pH 4.65, which is used in soil-testing, extracts relatively high amounts of aluminium from acid soils. The mean values of acetate-extractable aluminium at pH 4.65, 1.75 meq Al/100 g of soil, and of exchangeable aluminium (M KCl extraction), 0.41 meq Al were obtained from a material of 30 samples of acid soils (Table 2). Several other acetic acid — ammonium acetate extractants, from M acetic acid to M ammonium acetate solution were also used for studying the extractability of soil aluminium.

The soil-testing extractant can be used for the estimation of the soluble amounts of aluminium in acid soils, however, further studies are needed for a better interpretation of the ammonium acetate extractable (at pH 4.65) aluminium in our soils.

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## SELOSTUS

### MAAN ALUMIININ LIUKENEMISESTA VILJAVUUSANALYYSIN HAPPAMAAN AMMONIUMASETAATTILIUOKSEEN

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Happamista maista saadaan suhteellisen runsaasti helpoliukoista alumiinia uutetuksi 0.5 M etikkahappo — 0.5 M ammoniumasetatiliuokseen jota käytetään maanäytteiden viljavuusanalyysissa. pH 4.65:ssa asetaattiliuokseen uuttuneiden alumiinin määrien keskiarvo, 1.75 mekv. Al/100 g maata, edustaa liukoisen alumiinin määrää ja se on verrattavissa 1 M kaliumkloridiliuoksella saatun vaihtuvan alumiinin keskiarvolukuun 0.41 mekv. Al/100 g maata.

Näyteaineistona on ollut 30 maanäytteen aineisto, koottuna happamista maanäytteistä (Taulukko 1). Alumiinin uuttumista on myöskin tutkittu erilaisiin etikkahappo — ammoniumasetatti — liuoksiin ja todettu että pH:n osuus on ratkaiseva maan alumiinin liukenemisessä.

Viljavuustutkimuksen uuttoliuosta voidaan käyttää alumiinin uuttamiseen, joskin lisätutkimukset ovat tarpeen helpoliukoisen alumiinin määrien tulkitsemiseksi ja vertaamiseksi maanäytteen muihin kemiallisiin ominaisuuksiin.