

## Extractable aluminium, iron and manganese in mineral soils II Extractability by oxalate and pyrophosphate

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**Abstract.** The extractability of aluminium, iron and manganese by 0.05 M oxalate and pyrophosphate was studied in samples of 23 mineral soils. Dilute extractants were studied because conventional reagents may cause problems in analytical work. The mean values for Al, Fe and Mn extracted by conventional Tamm's oxalate were 67, 81 and 1.5 mmol/kg soil, respectively. On the average, 0.05 M oxalate solutions at pH 2.9 and 4.2 extracted Al, Fe and Mn amounts that were 103, 113 and 87 % and 72, 82 and 83 % of the amounts extractable by Tamm's oxalate, respectively. Each metal released by 0.05 M oxalates correlated closely with that dissolved by Tamm's oxalate; the *r* values ranged from 0.967\*\*\* to 0.997\*\*\*. The mean values for Al, Fe and Mn extracted by 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  and 0.05 M  $\text{K}_4\text{P}_2\text{O}_7$  were 38, 28 and 0.6 and 33, 29 and 0.6 mmol/kg soil, respectively. The amount of each metal extracted by  $\text{Na}_4\text{P}_2\text{O}_7$  correlated closely with that released by  $\text{K}_4\text{P}_2\text{O}_7$ ; the *r* values ranged from 0.87\*\*\* to 0.97\*\*\*.

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### Introduction

Acid ammonium oxalate (TAMM 1922, SCHWERTMANN 1964, McKEAGUE and DAY 1966) and 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  (ALEKSANDROVA 1960, McKEAGUE 1967) are conventionally used for the extraction of aluminium, iron and manganese from soil. Amorphous oxides and metals bound to organic matter in soil are dissolved by these solutions. The use of these reagents, however, may cause some problems in analytical work.

Traditional colorimetric, titrimetric and gravimetric techniques have commonly been superseded by atomic absorption spectrophotometry. Application of this technique may sometimes be hampered by the tendency of the nebulizer and burner slot to clog when solutions of high salt concentration are aspirated. Acid ammonium oxalate has often proved to be especially troublesome in this respect (e.g. WEBBER et al. 1974, SEARLY and

DALY 1977, SIMMONS and PLUES-FOSTER 1977). Difficulties may partially be overcome by dilution of the solutions to be analyzed. Pyrophosphate is difficult to use as an extractant because of soil dispersion. Especially with clay soils, normal filtration through paper is not enough for clarifying extracts (SHELDRIK and McKEAGUE 1975, SCHUPPLI et al. 1983).

These difficulties in analytical work should be alleviated by the use of more dilute extractants. A previous paper (NISKANEN 1989) showed that the ability of oxalate and pyrophosphate to extract soil aluminium, iron and manganese depends on the pH value, and that the extractability by 0.05 M reagents can reach the same order of magnitude as that by conventional methods. The aim of this paper was to study the possibility of employing 0.05 M oxalate and pyrophosphate solutions instead of the traditional reagents for the extraction of aluminium, iron and manganese from soil.

## Material and methods

The material was collected at 14 sampling sites on the Viikki Experimental Farm, University of Helsinki (Nos. 1—9) and in South Karelia (Imatra) (Nos. 10—14) (Table 1). At sampling sites Nos. 1—9 both surface (0—20 cm) and deeper layer (20—40 cm) samples were taken; at sampling sites Nos. 10—14 only surface samples were taken.

The soils were air-dried and ground to pass through a 2-mm sieve. The particle-size distribution of the inorganic material in the soil was determined by the pipette method (ELONEN 1971), the organic carbon content by the ALTEN wet combustion method (GRAHAM 1948). The soil pH was measured in a soil-0.01 M CaCl<sub>2</sub> suspension (1:2.5 v/v) (RYTI 1965).

The soils were extracted by the methods given in Table 2. Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> extracts were clarified by the addition of 1 M HCl and then filtration through hard paper, K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> ex-

Table 1. Soil samples (a = 0—20 cm, b = 20—40 cm, V = virgin soil).

Soil No.	pH(CaCl <sub>2</sub> )	Organic C, %	Particle-size distribution (µm), %				
			< 2	2—20	20—60	60—200	> 200
1a	4.6	3.3	37	13	15	30	4
1b	5.2	0.8	39	6	14	38	3
2a	4.3	4.7	36	8	21	34	3
2b	5.0	1.0	26	2	23	42	6
3a	5.9	5.3	58	14	12	13	3
3b	5.6	1.7	45	19	16	17	3
4a V	3.5	9.2	3	7	11	29	50
4b V	4.1	2.7	2	5	10	28	55
5a V	4.6	1.5	4	16	30	25	26
5b V	4.3	2.0	11	29	41	12	7
6a	4.8	2.4	29	30	20	15	6
6b	5.2	1.4	49	20	11	16	4
7a	4.5	3.4	43	33	18	3	2
7b	4.8	2.6	47	30	18	5	0
8a	5.3	4.4	10	7	15	61	7
8b	5.3	3.0	11	7	17	59	6
9a V	4.4	3.0	2	2	3	15	77
9b V	4.6	0.8	2	1	7	35	56
10a V	4.3	6.0	5	6	5	22	62
11a	5.7	3.8	22	31	27	16	5
12a	5.1	3.6	13	20	27	31	9
13a	4.7	4.7	51	27	11	5	7
14a	5.2	3.2	31	43	13	7	5
$\bar{x}$	4.8	3.2	25	16	17	24	18
s	0.6	1.9	19	12	9	16	24
range	3.5—5.9	0.8—9.2	2—58	1—43	3—41	3—61	0—77

Table 2. Extraction methods.

Extractant	pH	Extraction ratio, w/v	Shaking time, h	Reference
1. 0.18 M ammonium oxalate, 0.10 M oxalic acid	3.3	1:20	2	TAMM 1922
2. 0.026 M ammonium oxalate, 0.024 M oxalic acid	2.9	1:20	2	
3. 0.041 M ammonium oxalate, 0.009 M oxalic acid	4.2	1:200	3	
4. 0.029 M ammonium oxalate, 0.021 M oxalic acid	3.3	1:20	2	
5. 0.1 M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	10	1:20	4	McKEAGUE 1967
6. 0.05 M K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	10	1:100	3	

tracts by filtration through 0.2- $\mu$ m membrane filters. Aluminium, iron and manganese in filtrates were determined by atomic absorption spectrophotometry, iron and manganese with air-acetylene and aluminium with N<sub>2</sub>O-acetylene flame. The experiment was carried out in duplicate.

## Results and discussion

### *Extractability by oxalate*

Aluminium and iron extracted by Tamm's oxalate, respectively, were nearly of the same order of magnitude as those extracted by 0.05

Table 3. Extractable aluminium, mmol/kg soil.\*

Soil No.	Al extracted by				
	pH 3.3 Tamm's oxalate	0.05 M oxalate pH 2.9	0.05 M oxalate pH 4.2	0.1 M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	0.05 M K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>
1a	31 <sup>d</sup>	34 <sup>d</sup>	17 <sup>c</sup>	14 <sup>b</sup>	10 <sup>a</sup>
1b	17 <sup>b</sup>	29 <sup>c</sup>	8 <sup>a</sup>	2 <sup>a</sup>	4 <sup>a</sup>
2a	49 <sup>d</sup>	51 <sup>d</sup>	38 <sup>c</sup>	28 <sup>b</sup>	23 <sup>a</sup>
2b	11 <sup>b</sup>	12 <sup>b</sup>	5 <sup>a</sup>	4 <sup>a</sup>	4 <sup>a</sup>
3a	104 <sup>e</sup>	92 <sup>d</sup>	70 <sup>c</sup>	52 <sup>b</sup>	44 <sup>a</sup>
3b	63 <sup>c</sup>	68 <sup>d</sup>	27 <sup>a</sup>	30 <sup>b</sup>	26 <sup>a</sup>
4a	55 <sup>c</sup>	51 <sup>bc</sup>	41 <sup>a</sup>	47 <sup>ab</sup>	41 <sup>a</sup>
4b	81 <sup>b</sup>	82 <sup>b</sup>	58 <sup>a</sup>	81 <sup>b</sup>	79 <sup>b</sup>
5a	34 <sup>b</sup>	35 <sup>b</sup>	23 <sup>a</sup>	23 <sup>a</sup>	22 <sup>a</sup>
5b	58 <sup>c</sup>	61 <sup>c</sup>	40 <sup>a</sup>	46 <sup>b</sup>	44 <sup>ab</sup>
6a	53 <sup>d</sup>	54 <sup>d</sup>	37 <sup>c</sup>	28 <sup>b</sup>	21 <sup>a</sup>
6b	52 <sup>c</sup>	54 <sup>c</sup>	34 <sup>b</sup>	15 <sup>a</sup>	11 <sup>a</sup>
7a	79 <sup>d</sup>	74 <sup>d</sup>	66 <sup>c</sup>	37 <sup>b</sup>	31 <sup>a</sup>
7b	76 <sup>d</sup>	68 <sup>c</sup>	64 <sup>c</sup>	23 <sup>b</sup>	16 <sup>a</sup>
8a	23 <sup>c</sup>	24 <sup>d</sup>	19 <sup>b</sup>	15 <sup>a</sup>	15 <sup>a</sup>
8b	21 <sup>c</sup>	23 <sup>c</sup>	15 <sup>b</sup>	10 <sup>a</sup>	10 <sup>a</sup>
9a	59 <sup>b</sup>	69 <sup>c</sup>	54 <sup>b</sup>	46 <sup>a</sup>	46 <sup>a</sup>
9b	104 <sup>b</sup>	92 <sup>b</sup>	110 <sup>b</sup>	54 <sup>a</sup>	56 <sup>a</sup>
10a	67 <sup>d</sup>	65 <sup>d</sup>	57 <sup>c</sup>	46 <sup>b</sup>	35 <sup>a</sup>
11a	80 <sup>d</sup>	76 <sup>d</sup>	64 <sup>c</sup>	42 <sup>b</sup>	29 <sup>a</sup>
12a	186 <sup>c</sup>	161 <sup>b</sup>	158 <sup>b</sup>	92 <sup>a</sup>	82 <sup>a</sup>
13a	159 <sup>d</sup>	134 <sup>c</sup>	115 <sup>bc</sup>	108 <sup>b</sup>	74 <sup>a</sup>
14a	78 <sup>c</sup>	73 <sup>d</sup>	53 <sup>c</sup>	40 <sup>b</sup>	30 <sup>a</sup>
$\bar{x}$	67	64	51	38	33
s	42	34	37	27	23
range	11—186	12—161	5—158	2—108	4—82

\* Each soil tested separately. Values marked with the same letter do not deviate, with 5 % risk.

Table 4. Extractable iron, mmol/kg soil.\*

Soil No.	Fe extracted by				
	Tamm's oxalate	0.05 M oxalate pH 2.9	0.05 M oxalate pH 4.2	0.1 M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	0.05 M K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>
1a	34 <sup>c</sup>	43 <sup>d</sup>	29 <sup>b</sup>	13 <sup>a</sup>	12 <sup>a</sup>
1b	28 <sup>c</sup>	37 <sup>d</sup>	20 <sup>b</sup>	5 <sup>a</sup>	5 <sup>a</sup>
2a	47 <sup>b</sup>	59 <sup>d</sup>	55 <sup>c</sup>	26 <sup>a</sup>	28 <sup>a</sup>
2b	11 <sup>bc</sup>	14 <sup>c</sup>	9 <sup>b</sup>	3 <sup>a</sup>	5 <sup>a</sup>
3a	107 <sup>c</sup>	120 <sup>d</sup>	97 <sup>b</sup>	42 <sup>a</sup>	41 <sup>a</sup>
3b	157 <sup>c</sup>	162 <sup>c</sup>	112 <sup>b</sup>	40 <sup>a</sup>	41 <sup>a</sup>
4a	49 <sup>cd</sup>	56 <sup>d</sup>	41 <sup>b</sup>	31 <sup>a</sup>	47 <sup>bc</sup>
4b	44 <sup>c</sup>	55 <sup>d</sup>	35 <sup>b</sup>	27 <sup>a</sup>	36 <sup>b</sup>
5a	23 <sup>c</sup>	31 <sup>d</sup>	19 <sup>b</sup>	11 <sup>a</sup>	12 <sup>a</sup>
5b	60 <sup>d</sup>	71 <sup>c</sup>	55 <sup>c</sup>	34 <sup>a</sup>	40 <sup>b</sup>
6a	79 <sup>c</sup>	95 <sup>d</sup>	68 <sup>b</sup>	27 <sup>a</sup>	30 <sup>a</sup>
6b	93 <sup>d</sup>	105 <sup>c</sup>	70 <sup>c</sup>	20 <sup>b</sup>	17 <sup>a</sup>
7a	211 <sup>d</sup>	192 <sup>c</sup>	174 <sup>b</sup>	42 <sup>a</sup>	50 <sup>a</sup>
7b	223 <sup>c</sup>	202 <sup>b</sup>	213 <sup>c</sup>	38 <sup>a</sup>	40 <sup>a</sup>
8a	140 <sup>c</sup>	144 <sup>c</sup>	121 <sup>b</sup>	69 <sup>a</sup>	78 <sup>a</sup>
8b	115 <sup>b</sup>	135 <sup>c</sup>	101 <sup>b</sup>	47 <sup>a</sup>	53 <sup>a</sup>
9a	30 <sup>c</sup>	42 <sup>d</sup>	25 <sup>b</sup>	13 <sup>a</sup>	15 <sup>a</sup>
9b	32 <sup>b</sup>	39 <sup>c</sup>	31 <sup>b</sup>	10 <sup>a</sup>	9 <sup>a</sup>
10a	34 <sup>c</sup>	37 <sup>c</sup>	23 <sup>b</sup>	18 <sup>a</sup>	17 <sup>a</sup>
11a	60 <sup>d</sup>	61 <sup>d</sup>	37 <sup>c</sup>	16 <sup>b</sup>	12 <sup>a</sup>
12a	53 <sup>d</sup>	52 <sup>d</sup>	36 <sup>c</sup>	24 <sup>b</sup>	20 <sup>a</sup>
13a	159 <sup>c</sup>	124 <sup>d</sup>	113 <sup>c</sup>	55 <sup>b</sup>	40 <sup>a</sup>
14a	84 <sup>d</sup>	86 <sup>d</sup>	59 <sup>c</sup>	23 <sup>b</sup>	18 <sup>a</sup>
$\bar{x}$	81	85	67	28	29
s	60	53	52	17	19
range	11—223	14—202	9—213	3—69	5—78

\* Each soil tested separately. Values marked with the same letter do not deviate, with 5 % risk.

M oxalate at pH 2.9, but higher than those extracted by 0.05 M oxalate at pH 4.2 (Tables 3 and 4). In most samples Tamm's oxalate extracted more manganese than that extracted by dilute oxalates (Table 5). The metals extracted by dilute oxalates correlated closely to those extracted by Tamm's oxalate. Regression equations describing the relationship between extractabilities and corresponding linear correlation coefficients were as follows:

$$\begin{aligned} \text{Al(Tamm)} \text{ (mmol/kg)} &= -11.41 + 1.22\text{Al(oxal. pH 2.9)} \text{ (mmol/kg)} & r &= 0.992*** \\ \text{Al(Tamm)} \text{ (mmol/kg)} &= 10.32 + 1.11\text{Al(oxal. pH 4.2)} \text{ (mmol/kg)} & r &= 0.967*** \\ \text{Fe(Tamm)} \text{ (mmol/kg)} &= -13.14 + 1.11\text{Fe(oxal. pH 2.9)} \text{ (mmol/kg)} & r &= 0.982*** \\ \text{Fe(Tamm)} \text{ (mmol/kg)} &= 5.50 + 1.13\text{Fe(oxal. pH 4.2)} \text{ (mmol/kg)} & r &= 0.981*** \\ \text{Mn(Tamm)} \text{ (\mu mol/kg)} &= 55.98 + 1.10\text{Mn(oxal. pH 2.9)} \text{ (\mu mol/kg)} & r &= 0.984*** \\ \text{Mn(Tamm)} \text{ (\mu mol/kg)} &= 83.99 + 1.05\text{Mn(oxal. pH 4.2)} \text{ (\mu mol/kg)} & r &= 0.997*** \end{aligned}$$

The extractability of metals by 0.05 M oxalate at pH 4.2 was commonly < 100 % of

that extractable by Tamm's oxalate (Table 6). The relative extractability of aluminium was lower than that of iron and manganese, being at the lowest 43 % of the Tamm's oxalate-extractable aluminium (Table 6). In order for the extractability by 0.05 M oxalate to reach the same order of magnitude as that by Tamm's oxalate, the pH of the extractant must be lower than 4.2.

The lower extractability by oxalate at pH

4.2 is in agreement with the results of McKEAGUE and DAY (1966). They found that

Table 5. Extractable manganese,  $\mu\text{mol}/\text{kg}$  soil.\*

Soil No.	Mn extracted by				
	Tamm's oxalate	0.05 M oxalate pH 2.9	0.05 M oxalate pH 4.2	0.1 M $\text{Na}_4\text{P}_2\text{O}_7$	0.05 M $\text{K}_4\text{P}_2\text{O}_7$
1a	228 <sup>a</sup>	228 <sup>a</sup>	260 <sup>a</sup>	118 <sup>a</sup>	273 <sup>a</sup>
1b	410 <sup>c</sup>	408 <sup>c</sup>	346 <sup>bc</sup>	155 <sup>a</sup>	304 <sup>b</sup>
2a	419 <sup>d</sup>	355 <sup>bc</sup>	346 <sup>b</sup>	209 <sup>a</sup>	364 <sup>c</sup>
2b	346 <sup>c</sup>	346 <sup>c</sup>	260 <sup>b</sup>	151 <sup>a</sup>	315 <sup>c</sup>
3a	1 092 <sup>d</sup>	850 <sup>c</sup>	1 214 <sup>c</sup>	233 <sup>a</sup>	364 <sup>b</sup>
3b	160 <sup>cd</sup>	191 <sup>d</sup>	87 <sup>b</sup>	36 <sup>a</sup>	122 <sup>bc</sup>
4a	1 138 <sup>c</sup>	869 <sup>b</sup>	868 <sup>b</sup>	596 <sup>a</sup>	1 011 <sup>bc</sup>
4b	3 640 <sup>c</sup>	3 986 <sup>c</sup>	3 559 <sup>c</sup>	837 <sup>a</sup>	1 661 <sup>b</sup>
5a	301 <sup>c</sup>	282 <sup>bc</sup>	173 <sup>a</sup>	137 <sup>a</sup>	242 <sup>b</sup>
5b	956 <sup>d</sup>	784 <sup>c</sup>	824 <sup>c</sup>	346 <sup>a</sup>	513 <sup>b</sup>
6a	3 367 <sup>d</sup>	3 367 <sup>d</sup>	3 164 <sup>c</sup>	482 <sup>a</sup>	728 <sup>b</sup>
6b	1 911 <sup>d</sup>	1 531 <sup>b</sup>	1 734 <sup>c</sup>	164 <sup>a</sup>	242 <sup>a</sup>
7a	410 <sup>c</sup>	346 <sup>bc</sup>	303 <sup>bc</sup>	69 <sup>a</sup>	242 <sup>b</sup>
7b	273 <sup>c</sup>	164 <sup>b</sup>	173 <sup>b</sup>	87 <sup>a</sup>	152 <sup>b</sup>
8a	501 <sup>c</sup>	382 <sup>b</sup>	433 <sup>bc</sup>	190 <sup>a</sup>	274 <sup>a</sup>
8b	437 <sup>c</sup>	337 <sup>d</sup>	260 <sup>c</sup>	82 <sup>a</sup>	137 <sup>b</sup>
9a	1 211 <sup>c</sup>	1 008 <sup>bc</sup>	910 <sup>bc</sup>	301 <sup>a</sup>	637 <sup>ab</sup>
9b	528 <sup>c</sup>	497 <sup>d</sup>	433 <sup>c</sup>	100 <sup>a</sup>	137 <sup>b</sup>
10a	1 529 <sup>a</sup>	1 222 <sup>a</sup>	1 300 <sup>a</sup>	1 984 <sup>b</sup>	1 255 <sup>a</sup>
11a	4 004 <sup>d</sup>	3 640 <sup>c</sup>	3 553 <sup>c</sup>	1 766 <sup>b</sup>	1 183 <sup>a</sup>
12a	2 212 <sup>b</sup>	2 184 <sup>b</sup>	2 254 <sup>b</sup>	2 276 <sup>b</sup>	1 664 <sup>a</sup>
13a	2 821 <sup>c</sup>	1 671 <sup>c</sup>	2 340 <sup>d</sup>	1 183 <sup>b</sup>	698 <sup>a</sup>
14a	7 490 <sup>c</sup>	6 243 <sup>b</sup>	7 055 <sup>c</sup>	1 693 <sup>a</sup>	1 365 <sup>a</sup>
$\bar{x}$	1 538	1 343	1 385	574	604
s	1 753	1 562	1 664	697	502
range	160—7 490	164—6 243	87—7 055	36—2 276	122—1 664

\* Each soil tested separately. Values marked with the same letter do not deviate, with 5 % risk.

approximately equal amounts of iron and aluminium, respectively, were extracted by oxalate at pH 2 and 3, but that solution of pH 4.2 extracted somewhat less metals. The solutions of pH 2 and 3 also maintained their initial pH, whereas the solution of pH 4.2 was not buffered strongly enough to maintain a constant pH in extracts of soils rich in iron and aluminium.

The pH of oxalate was lowered to 2.9 because a preliminary experiment showed that the extractability of iron by 0.05 M oxalate at pH 3.3 was lower than that extractable by Tamm's oxalate (Table 7). In most soils, the extractability of aluminium and iron by oxalate at pH 2.9, unlike that of manganese, was not lower than the extractability by Tamm's solution (Table 6). The extractability of aluminium was exceptionally high in soil

1b, poor in aluminium.

Oxalate-extractable metals were not related to soil pH or organic carbon content. Only oxalate-extractable iron correlated weakly with the soil clay content. The linear correlation coefficients for the relationship between clay content and iron extracted by Tamm's solution and by oxalates of pH 2.9 and 4.2 were 0.55\*\*, 0.53\* and 0.52\*, respectively.

#### *Extractability by pyrophosphate*

In most of the soils, the values of aluminium and iron, respectively, did not deviate statistically in both pyrophosphate extractions (Tables 3 and 4), whereas the manganese values deviated in most soils (Table 5). The metals released in two pyrophosphate extractions correlated closely, the regression equa-

Table 6. Extractable aluminium, iron and manganese, % of Tamm's oxalate-extractable.

Soil No.	Metals extracted by															
	0.05 M oxalate pH 2.9				0.05 M oxalate pH 4.2				0.1 M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>				0.05 M K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>			
	Al	Fe	Mn		Al	Fe	Mn		Al	Fe	Mn		Al	Fe	Mn	
1a	110	127	100	114	55	85	114	45	38	52	32	35	120			
1b	171	132	100	84	47	71	84	12	18	38	24	18	74			
2a	104	126	85	83	78	117	83	57	55	50	47	60	87			
2b	109	127	100	75	46	82	75	36	27	44	36	46	91			
3a	89	112	78	111	67	91	111	50	39	21	42	38	33			
3b	108	103	119	54	43	71	54	48	26	23	41	26	76			
4a	93	114	76	76	75	84	76	86	63	52	75	96	89			
4b	101	125	110	98	72	80	98	100	61	23	98	46	89			
5a	103	135	94	58	68	83	58	68	48	46	65	52	80			
5b	105	118	82	86	69	92	86	79	57	36	76	67	54			
6a	102	120	100	94	70	86	94	53	34	14	40	38	22			
6b	104	113	80	91	65	75	91	29	22	9	21	18	13			
7a	94	91	84	74	84	83	74	47	20	17	39	24	59			
7b	90	91	60	63	84	96	63	30	17	32	21	18	56			
8a	104	103	76	86	83	86	86	65	49	38	65	56	55			
8b	110	117	77	60	71	88	60	48	41	19	48	46	31			
9a	117	140	83	75	92	83	75	78	43	25	78	50	53			
9b	89	122	94	82	106	97	82	52	31	19	54	28	26			
10a	97	109	80	85	85	68	85	69	53	130	52	50	82			
11a	95	102	91	89	80	62	89	53	27	44	36	20	30			
12a	87	98	99	102	85	68	102	50	45	103	44	38	75			
13a	84	78	59	83	72	71	83	68	35	42	47	25	25			
14a	94	102	83	94	68	70	94	51	27	23	39	21	18			
$\bar{x}$	103	113	87	83	72	82	83	55	38	39	49	41	56			
s	17	16	14	16	15	12	16	20	14	28	20	21	29			
range	84—171	78—140	59—119	54—114	43—106	62—117	54—114	12—100	17—63	9—130	21—98	18—96	13—120			

Table 7. Aluminium and iron extracted by 0.05 M oxalate pH 3.3, % of Tamm's oxalate-extractable.

Soil No.	Al	Fe
1a	94	88
1b	135	84
2b	99	74
3b	101	75
12a	68	69

tions and corresponding linear correlation coefficients being as follows:

$$\begin{aligned} \text{Al}(\text{Na}_4\text{P}_2\text{O}_7) \text{ (mmol/kg)} &= 0.99 + 1.14\text{Al}(\text{K}_4\text{P}_2\text{O}_7) \text{ (mmol/kg)} & r &= 0.968*** \\ \text{Fe}(\text{Na}_4\text{P}_2\text{O}_7) \text{ (mmol/kg)} &= 3.14 + 0.84\text{Fe}(\text{K}_4\text{P}_2\text{O}_7) \text{ (mmol/kg)} & r &= 0.945*** \\ \text{Mn}(\text{Na}_4\text{P}_2\text{O}_7) \text{ (\mu mol/kg)} &= -157 + 1.21\text{Mn}(\text{K}_4\text{P}_2\text{O}_7) \text{ (\mu mol/kg)} & r &= 0.872*** \end{aligned}$$

Pyrophosphate-extractable metals did not correlate statistically significantly with soil pH or clay content. In contrast, the pyrophosphate-extractable metals correlated with the oxalate-extractable metals. Regression equations describing the relationship between metals extracted by Tamm's oxalate and pyrophosphates and corresponding linear correlation coefficients were as follows:

$$\begin{aligned} \text{Al}(\text{Tamm}) \text{ (mmol/kg)} &= 13.37 + 1.40\text{Al}(\text{Na}_4\text{P}_2\text{O}_7) \text{ (mmol/kg)} & r &= 0.892*** \\ \text{Al}(\text{Tamm}) \text{ (mmol/kg)} &= 16.31 + 1.55\text{Al}(\text{K}_4\text{P}_2\text{O}_7) \text{ (mmol/kg)} & r &= 0.837*** \\ \text{Fe}(\text{Tamm}) \text{ (mmol/kg)} &= 5.39 + 2.76\text{Fe}(\text{Na}_4\text{P}_2\text{O}_7) \text{ (mmol/kg)} & r &= 0.756*** \\ \text{Fe}(\text{Tamm}) \text{ (mmol/kg)} &= 18.24 + 2.18\text{Fe}(\text{K}_4\text{P}_2\text{O}_7) \text{ (mmol/kg)} & r &= 0.670*** \\ \text{Mn}(\text{Tamm}) \text{ (\mu mol/kg)} &= 574 + 1.68\text{Mn}(\text{Na}_4\text{P}_2\text{O}_7) \text{ (\mu mol/kg)} & r &= 0.669*** \\ \text{Mn}(\text{Tamm}) \text{ (\mu mol/kg)} &= 27.97 + 2.50\text{Mn}(\text{K}_4\text{P}_2\text{O}_7) \text{ (\mu mol/kg)} & r &= 0.717*** \end{aligned}$$

The metals extracted by pyrophosphate, considered to describe the fraction bound by organic matter in soil (McKEAGUE et al. 1971) were, on the average, 38–56 % of the Tamm's oxalate-extractable metals (Table 6). The absolute values of pyrophosphate-extractable metals did not significantly correlate with the organic carbon content in soil. However, there was a low correlation between the organic carbon content and metals expressed as the percentages of Tamm's oxalate-extractable metals. The linear correlation coefficients for the relationship between soil organic carbon content and the percentages of  $\text{K}_4\text{P}_2\text{O}_7$ -extractable iron and  $\text{Na}_4\text{P}_2\text{O}_7$ -extractable iron and

aluminium were 0.49\*, 0.54\*\* and 0.47\*, respectively.

In pyrophosphate extracts of clay soils, metals are not exclusively in a dissolved form, but are also present in suspended material which is difficult to remove. This material may be fine particulate amorphous material, or it may have been formed by coagulation of solutes in the pyrophosphate extracts (BASCOMB 1968, McKEAGUE and SCHUPPLI 1982). The methods used for clarifying of pyrophosphate extracts are high-speed cen-

trifugation (McKEAGUE 1967) and the addition of Superfloc, a flocculating agent, followed by centrifugation at low speed (SHELDRIK and McKEAGUE 1975). The study of SCHUPPLI et al. (1983) shows that centrifugation at high speed or at low speed with Superfloc is inadequate to sediment suspended material completely. Adding a salt, such as  $\text{Na}_2\text{SO}_4$ , is not effective at low concentration, and at high

concentration it appears to precipitate dissolved metals. Ultrafiltration of the centrifugates through 0.025- $\mu\text{m}$  filters removes particulate material in a simple and effective way.

In this study, pyrophosphate extracts were cleared by precipitation of suspended clay and organic matter with acid or filtration through 0.2- $\mu\text{m}$  filters. The latter method seems to be more certain, as acidification of extracts may dissolve metals from suspended material or, on the other hand, metals may partially remain in precipitates.

$\text{K}_4\text{P}_2\text{O}_5$ , used by BASCOMB (1968), was used as an extractant because it was thought that

peptization of soil may be less than if  $\text{Na}_4\text{P}_2\text{O}_7$  were used. This opinion was based on the fact that the hydration sphere of  $\text{K}^+$ -ion is smaller than that of  $\text{Na}^+$ -ion. However, lowering the concentration of pyrophosphate from 0.1 M to 0.05 M hardly reduced dispersion of soil. According to ELONEN (1971), 0.05 M concentration of  $\text{Na}_4\text{P}_2\text{O}_7$  is high enough for peptization of soil in particle-size analysis.

## Conclusion

It seems possible to employ oxalate and pyrophosphate extractants, which are more dilute than conventional reagents. The amounts of metals released by dilute and traditional reagents are closely correlated. In general, extraction methods do not give absolute contents of elements. For example, the amounts extracted increase as the extraction time increases. However, the results obtained with a given method are valuable for soil comparisons.

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**Kivennäismaiden uuttuva alumiini, rauta ja mangaani**  
**II Uuttuvuus oksalaatti- ja pyrofosfaattiliuoksilla**

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Koska oksalaatti- ja pyrofosfaattiuutteiden analysoinnissa esiintyy vaikeuksia, tutkittiin tavanomaista laimeampien uuttoliuosten käyttöä. Kivennäismaiden alumiinia, rautaa ja mangaania uutettiin 0,05 M oksalaatti- ja pyrofosfaattiliuoksilla sekä vertailuliuoksilla: Tammin oksalaatilla ja 0,1 M natriumpyrofosfaatilla. Tammin oksalaatilla uuttui alumiinia, rautaa ja mangaania keskimäärin 67, 81 ja 1,5 mmol/kg maata. Keskimääräinen alumiinin, raudan ja mangaanin uuttuvuus 0,05 M oksalaatilla pH 2,9 ja 4,2 oli 103, 113 ja 87 sekä 72, 82 ja

83 % Tammin oksalaatilla uuttuvasta. Kunkin metallin uuttuvuudet Tammin oksalaatilla ja 0,05 M oksalaateilla korreloivat r:n arvojen vaihdella 0,967\*\*\*:stä 0,997\*\*\*:ään (n = 23). Alumiinia, rautaa ja mangaania uuttui 0,1 M natriumpyrofosfaatilla ja 0,05 M kaliumpyrofosfaatilla keskimäärin 38, 28 ja 0,6 sekä 33, 29 ja 0,6 mmol/kg maata. Kunkin metallin uuttuvuudet näillä liuoksilla korreloivat r:n arvojen vaihdella 0,87\*\*\*:stä 0,97\*\*\*:ään.