

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

RAINA NISKANEN

*Department of Agricultural Chemistry, University of Helsinki,
SF-00710 Helsinki, Finland*

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***.

Index words: amorphous oxides, complexing agents, soil organic carbon, soil extraction

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Traditional colorimetric, titrimetric and gravimetric techniques have commonly been superseded by atomic absorption spectrophotometry.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 CaCl₂ suspension (1:2.5 v/v) (RYTI 1965).

The soils were extracted by the methods given in Table 2. Na₄P₂O₇ extracts were clarified by the addition of 1 M HCl and then filtration through hard paper, K₄P₂O₇ ex-

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

Soil No.	pH(CaCl ₂)	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 ₄ P ₂ O ₇	10	1:20	4	McKEAGUE 1967
6. 0.05 M K ₄ P ₂ O ₇	10	1:100	3	

tracts by filtration through 0.2- μ m membrane filters. Aluminium, iron and manganese in filtrates were determined by atomic absorption spectrophotometry, iron and manganese with air-acetylene and aluminium with N₂O-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 ₄ P ₂ O ₇	0.05 M K ₄ P ₂ O ₇
1a	31 ^d	34 ^d	17 ^c	14 ^b	10 ^a
1b	17 ^b	29 ^c	8 ^a	2 ^a	4 ^a
2a	49 ^d	51 ^d	38 ^c	28 ^b	23 ^a
2b	11 ^b	12 ^b	5 ^a	4 ^a	4 ^a
3a	104 ^e	92 ^d	70 ^c	52 ^b	44 ^a
3b	63 ^c	68 ^d	27 ^a	30 ^b	26 ^a
4a	55 ^c	51 ^{bc}	41 ^a	47 ^{ab}	41 ^a
4b	81 ^b	82 ^b	58 ^a	81 ^b	79 ^b
5a	34 ^b	35 ^b	23 ^a	23 ^a	22 ^a
5b	58 ^c	61 ^c	40 ^a	46 ^b	44 ^{ab}
6a	53 ^d	54 ^d	37 ^c	28 ^b	21 ^a
6b	52 ^c	54 ^c	34 ^b	15 ^a	11 ^a
7a	79 ^d	74 ^d	66 ^c	37 ^b	31 ^a
7b	76 ^d	68 ^c	64 ^c	23 ^b	16 ^a
8a	23 ^c	24 ^d	19 ^b	15 ^a	15 ^a
8b	21 ^c	23 ^c	15 ^b	10 ^a	10 ^a
9a	59 ^b	69 ^c	54 ^b	46 ^a	46 ^a
9b	104 ^b	92 ^b	110 ^b	54 ^a	56 ^a
10a	67 ^d	65 ^d	57 ^c	46 ^b	35 ^a
11a	80 ^d	76 ^d	64 ^c	42 ^b	29 ^a
12a	186 ^c	161 ^b	158 ^b	92 ^a	82 ^a
13a	159 ^d	134 ^c	115 ^{bc}	108 ^b	74 ^a
14a	78 ^c	73 ^d	53 ^c	40 ^b	30 ^a
\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 ₄ P ₂ O ₇	0.05 M K ₄ P ₂ O ₇
1a	34 ^c	43 ^d	29 ^b	13 ^a	12 ^a
1b	28 ^c	37 ^d	20 ^b	5 ^a	5 ^a
2a	47 ^b	59 ^d	55 ^c	26 ^a	28 ^a
2b	11 ^{bc}	14 ^c	9 ^b	3 ^a	5 ^a
3a	107 ^c	120 ^d	97 ^b	42 ^a	41 ^a
3b	157 ^c	162 ^c	112 ^b	40 ^a	41 ^a
4a	49 ^{cd}	56 ^d	41 ^b	31 ^a	47 ^{bc}
4b	44 ^c	55 ^d	35 ^b	27 ^a	36 ^b
5a	23 ^c	31 ^d	19 ^b	11 ^a	12 ^a
5b	60 ^d	71 ^c	55 ^c	34 ^a	40 ^b
6a	79 ^c	95 ^d	68 ^b	27 ^a	30 ^a
6b	93 ^d	105 ^c	70 ^c	20 ^b	17 ^a
7a	211 ^d	192 ^c	174 ^b	42 ^a	50 ^a
7b	223 ^c	202 ^b	213 ^c	38 ^a	40 ^a
8a	140 ^c	144 ^c	121 ^b	69 ^a	78 ^a
8b	115 ^b	135 ^c	101 ^b	47 ^a	53 ^a
9a	30 ^c	42 ^d	25 ^b	13 ^a	15 ^a
9b	32 ^b	39 ^c	31 ^b	10 ^a	9 ^a
10a	34 ^c	37 ^c	23 ^b	18 ^a	17 ^a
11a	60 ^d	61 ^d	37 ^c	16 ^b	12 ^a
12a	53 ^d	52 ^d	36 ^c	24 ^b	20 ^a
13a	159 ^c	124 ^d	113 ^c	55 ^b	40 ^a
14a	84 ^d	86 ^d	59 ^c	23 ^b	18 ^a
\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 ^a	228 ^a	260 ^a	118 ^a	273 ^a
1b	410 ^c	408 ^c	346 ^{bc}	155 ^a	304 ^b
2a	419 ^d	355 ^{bc}	346 ^b	209 ^a	364 ^c
2b	346 ^c	346 ^c	260 ^b	151 ^a	315 ^c
3a	1 092 ^d	850 ^c	1 214 ^c	233 ^a	364 ^b
3b	160 ^{cd}	191 ^d	87 ^b	36 ^a	122 ^{bc}
4a	1 138 ^c	869 ^b	868 ^b	596 ^a	1 011 ^{bc}
4b	3 640 ^c	3 986 ^c	3 559 ^c	837 ^a	1 661 ^b
5a	301 ^c	282 ^{bc}	173 ^a	137 ^a	242 ^b
5b	956 ^d	784 ^c	824 ^c	346 ^a	513 ^b
6a	3 367 ^d	3 367 ^d	3 164 ^c	482 ^a	728 ^b
6b	1 911 ^d	1 531 ^b	1 734 ^c	164 ^a	242 ^a
7a	410 ^c	346 ^{bc}	303 ^{bc}	69 ^a	242 ^b
7b	273 ^c	164 ^b	173 ^b	87 ^a	152 ^b
8a	501 ^c	382 ^b	433 ^{bc}	190 ^a	274 ^a
8b	437 ^c	337 ^d	260 ^c	82 ^a	137 ^b
9a	1 211 ^c	1 008 ^{bc}	910 ^{bc}	301 ^a	637 ^{ab}
9b	528 ^c	497 ^d	433 ^c	100 ^a	137 ^b
10a	1 529 ^a	1 222 ^a	1 300 ^a	1 984 ^b	1 255 ^a
11a	4 004 ^d	3 640 ^c	3 553 ^c	1 766 ^b	1 183 ^a
12a	2 212 ^b	2 184 ^b	2 254 ^b	2 276 ^b	1 664 ^a
13a	2 821 ^c	1 671 ^c	2 340 ^d	1 183 ^b	698 ^a
14a	7 490 ^c	6 243 ^b	7 055 ^c	1 693 ^a	1 365 ^a
\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 ₄ P ₂ O ₇			0.05 M K ₄ P ₂ O ₇		
	Al	Fe	Mn	Al	Fe	Mn	Al	Fe	Mn	Al	Fe	Mn
1a	110	127	100	55	85	114	45	38	52	32	35	120
1b	171	132	100	47	71	84	12	18	38	24	18	74
2a	104	126	85	78	117	83	57	55	50	47	60	87
2b	109	127	100	46	82	75	36	27	44	36	46	91
3a	89	112	78	67	91	111	50	39	21	42	38	33
3b	108	103	119	43	71	54	48	26	23	41	26	76
4a	93	114	76	75	84	76	86	63	52	75	96	89
4b	101	125	110	72	80	98	100	61	23	98	82	46
5a	103	135	94	68	83	58	68	48	46	65	52	80
5b	105	118	82	69	92	86	79	57	36	76	67	54
6a	102	120	100	70	86	94	53	34	14	40	38	22
6b	104	113	80	65	75	91	29	22	9	21	18	13
7a	94	91	84	84	83	74	47	20	17	39	24	59
7b	90	91	60	84	96	63	30	17	32	21	18	56
8a	104	103	76	83	86	86	65	49	38	65	56	55
8b	110	117	77	71	88	60	48	41	19	48	46	31
9a	117	140	83	92	83	75	78	43	25	78	50	53
9b	89	122	94	106	97	82	52	31	19	54	28	26
10a	97	109	80	85	68	85	69	53	130	52	50	82
11a	95	102	91	80	62	89	53	27	44	36	20	30
12a	87	98	99	85	68	102	50	45	103	44	38	75
13a	84	78	59	72	71	83	68	35	42	47	25	25
14a	94	102	83	68	70	94	51	27	23	39	21	18
\bar{x}	103	113	87	72	82	83	55	38	39	49	41	56
s	17	16	14	15	12	16	20	14	28	20	21	29
range	84—171	78—140	59—119	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 Na_2SO_4 , is not effective at low concentration, and at high

concentration it appears to precipitate dissolved metals. Ultrafiltration of the centrifugates through 0.025- μm 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- μm 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 K^+ -ion is smaller than that of 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.

References

- ALEKSANDROVA, L.N. 1960. The use of sodium pyrophosphate for isolating free humic substances and their organic-mineral compounds from the soil. *Soviet Soil Sci.* 2: 190—197.
- BASCOMB, C.L. 1968. Distribution of pyrophosphate-extractable iron and organic carbon in soils of various groups. *J. Soil Sci.* 19: 251—268.
- ELONEN, P. 1971. Particle-size analysis of soil. *Acta Agr. Fenn.* 122: 1—122.
- GRAHAM, E.R. 1948. Determination of soil organic matter by means of a photoelectric colorimeter. *Soil Sci.* 65: 181—183.
- McKEAGUE, J.A. 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in Podzols and some other soils. *Can. J. Soil Sci.* 47: 95—99.
- , BRYDON, J.E. & MILES, N.M. 1971. Differentiation of forms of extractable iron and aluminium in soils. *Soil Sci. Soc. Amer. Proc.* 35: 33—38.
- & DAY, J.H. 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Can. J. Soil Sci.* 46: 13—22.
- & SCHUPPLI, P.A. 1982. Changes in concentrations of Fe and Al in pyrophosphate extracts of soil and composition of sediment resulting from ultracentrifugation in relation to spodic horizon criteria. *Soil Sci.* 134: 265—270.
- NISKANEN, R. 1989. Extractable aluminium, iron and manganese in mineral soils. I Dependence of extractability on the pH of oxalate, pyrophosphate and EDTA extractants. *J. Agric. Sci. Finl.* 61: 73—78.
- RYTI, R. 1965. On the determination of soil pH. *J. Scient. Agric. Soc. Finl.* 37: 51—60.
- SCHUPPLI, P.A., ROSS, G.J. & McKEAGUE, J.A. 1983. The effective removal of suspended materials from pyrophosphate extracts of soils from tropical and temperate regions. *Soil Sci. Soc. Am. J.* 47: 1026—1032.
- SCHWERTMANN, U. 1964. Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammoniumoxalat-Lösung. *Z. Pflanzenernähr. Düng. Bodenkd.* 105: 194—202.
- SEARLE, P.L. & DALY, B.K. 1977. The determination of aluminium, iron, manganese and silicon in acid oxalate soil extracts by flame emission and atomic absorption spectrophotometry. *Geoderma* 19: 1—10.
- SHELDRIK, B.H. & McKEAGUE, J.A. 1975. A comparison of extractable Fe and Al data using methods followed in the U.S.A. and Canada. *Can. J. Soil Sci.* 55: 77—78.
- SIMMONS, W.J. & PLUES-FOSTER, L.A. 1977. Improved method of analysing difficult soil extracts by flame atomic absorption spectrometry — application to measurement of copper in ammonium oxalate extracts. *Aust. J. Soil Res.* 15: 171—175.
- TAMM, O. 1922. Eine Methode zur Bestimmung der anorganischen Komponente des Gelkomplexes im Boden. *Statens Skogsförsöksanstalt, Medd.* 19: 387—404.
- WEBBER, M.D., McKEAGUE, J.A., RAAD, A.T., DeKIMPE, C.R., WANG, C., HALUSCHAK, P., STONEHOUSE, H.B., PETTAPEACE, W.W., OSBORNE, V.E. & GREEN, A.J. 1974. A comparison among nine Canadian laboratories of dithionite-, oxalate-, and pyrophosphate-extractable Fe and Al in soils. *Can. J. Soil Sci.* 54: 293—298.

Ms received January 12, 1988

Kivennäismaiden uuttuva alumiini, rauta ja mangaani

II Uuttuvuus oksalaatti- ja pyrofosfaattiliuoksilla

Raina Niskanen

*Helsingin yliopisto, Maanviljelyskemian laitos,
00710 Helsinki*

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.