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ON THE ANALYSIS OF MICRO NUTRIENTS OF FERTILIZED MOSS PEAT. THE ANALYSIS OF MOSS PEAT PART II

LANNOITETUN TURPEEN HIVENAINEIDEN ANALYSOINNISTA. KASVUTURPEEN ANALYSOINNISTA OSA II.

In the previous part of this work (Tummavuori et al. 1981) we have mainly concentrated on the analysis of unhydrolyzable water soluble major nutrients in moss peat. We compared the suitability of two most commonly used extraction methods, viz. the water extraction and ammonium acetate extraction (1M acetic acid and 0.5 ammonium hydroxide). Furthermore, we paid attention on the accuracy of sample taking and on the effect of shaking time (Tummavuori et al. 1980 c).

We have expanded this study to involve the following micro nutrients: copper, zinc, manganese, molybdenum and sulphur. Our aim was to find as simple analysis methods as possible so that they could easily be adopted in the routine work.

The first difficulty arises in searching the suitable extractant, because the extractant should equally extract the elements under investigation and eliminate the matrix effect. Neither water nor ammonium acetate is good due to the high pH value and moreover, ammonia and acetate ions are capable to form strong complexes with the ions under investigation (Sillén 1969, 1974). Since the metal ions are at the best form when they are in hydrated ion form, we decided to use strong acids as extractants. We selected hydrochloric acid, which on the other hand suffers from the complexing capability of chloride ion (Sillén 1969, 1974) and perchloric acid, which as a very strong acid is a weak complex forming agent.

As a comparative method we used ammonium acetate extraction to find out the differences between this and the acid extraction (Lakanen and Erviö 1971).

The peat material was supplied by the State Fuel Centre (VAPO) originating from Aitoneva production site. The degree of humification of this Sphagnum peat was H1-2 as expressed in von Post scale. The lime was dolomite lime and the fertilizer used was mixed fertilizer produced by Kemira Oy.

The samples to be investigated were prepared by mixing the components in portions of 2 dm^3 by the volume. The wetting and the determination of the moisture were carried out according to the method of Puustjärvi (Puustjärvi 1969, 1978).

The amount of the sample was 28 g which correpondes to 40 cm^3 of peat moistened to 80 % w/w. The volume of extractant was 90 cm^3 which after filtration was diluted to 250 cm^3 for further dilutions when necessary. The shaking time was 0,5 h (Tummavuori et al. 1981).

Copper, zinc, manganese and molybdenum were determined by means of atomic absorption spectrophotometry (Kirkbright and Sargent 1974, Mehlich and Bowling 1975, Scott and Thomas 1977, Shuman 1978, and Davis 1961). The standard solutions were always prepared using the corresponding extract solution.

The standard solution of copper was prepared from $Cu(NO_3)_2 \cdot H_2O$ ranging from 0.5 to 4 ppm. The standard solution of manganese was prepared from $Mn(NO_3)_2 \cdot 4H_2O$ ranging from 1 to 5 ppm.

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$ZnSO_4 \cdot 7H_2O$ was used to prepare the zinc standard solutions ranging from 0.5 to 4 ppm and $NaMoO_4 \cdot 2H_2O$ was used for molybdenum, the solutions were ranging from 0.5 to 7 ppm (Chao and Sanozolone 1973, David 1961). The increased sensitivity in the determination of molybdenum is achieved by making the solution to 2000 ppm with respect of Al^{3+} ions (David 1961).

Iron is determined by spectrophotometric means using 1.10 fenanthroline as a reagent. The standard solutions ranging from 0.5 to 2.5 ppm were prepared from $Fe(NO_3)_3 \cdot 9H_2O$. The measurements were made at 510 nm (Sandell 1978). Sulphur was also determined spectrophotometrically using turbimetric barium sulphate method. The standard solution ranging from 50 to 2000 ppm expressed as sulphate was prepared from Na_2SO_4. The results, however, are expressed as sulphur (Bolz and Honell 1977).

The calibration curves for each element were prepared corresponding to the concentration ranges mentioned previously. During the determinations, however, we did not use these standard curves but individually prepared the standards under the same condition as the samples were prepared.

The atomic absorption spectrophotometer used was Southern Analytical A 3000 and the spectrophotometer was Beckman DU 2.

The reagents were made by A. E. Merck AG and were pro analysi by the purity.

The error limits are given as deviations from the mean. Separate parallel determinations were carried out from 3 to 9 times depending on the element.

We started this work from the pH-measurement of peat-water suspension and the influence of the lime addition thereon. The results are depicted in Fig. 1, where the pH is expressed as a function of the lime addition (kg of lime/m³ of peat).

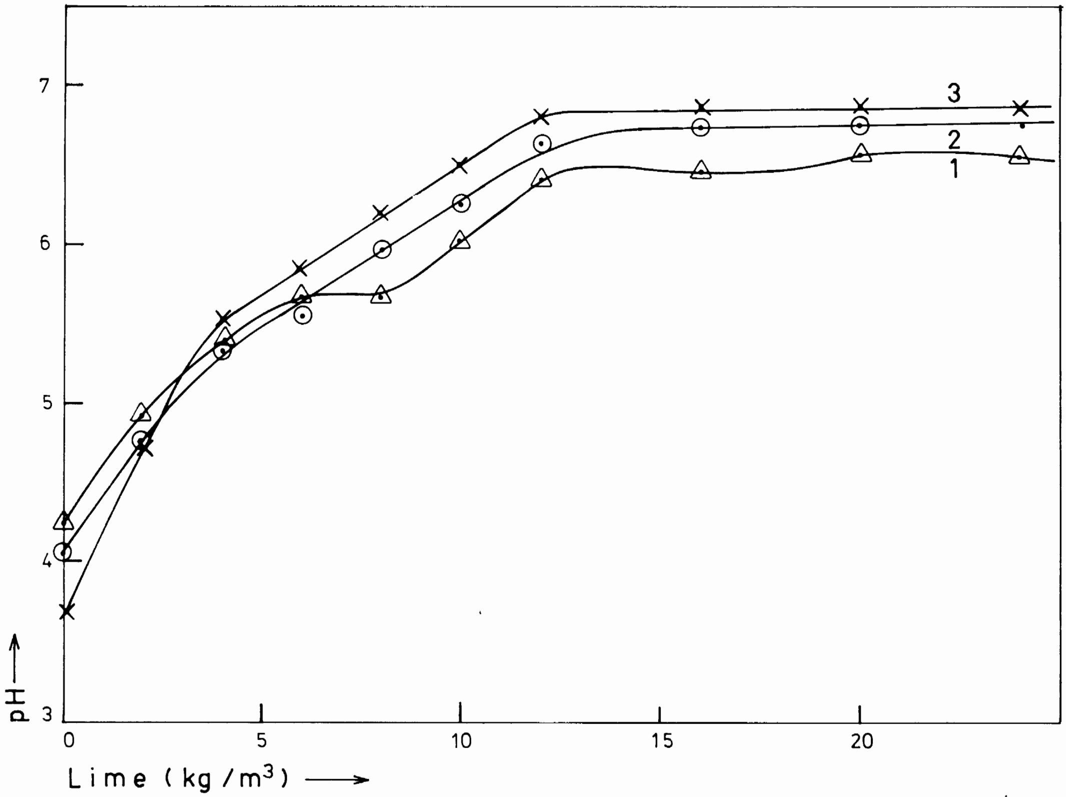

Fig. 1. The dependence on pH of the lime amount and the measuring time. Curve 1. Measurements immediately after shaking. Curve 2. Measurements five hours after two hours shaking. Curve 3. Measurements 24 hours after shaking.

Kuva 1. pH:n riippuvuus kalkitusasteesta ja mittausajasta. Käyrä 1. Mittaukset suoritettu välittömästi ravistelun jälkeen. Käyrä 2. Mittaukset suoritettu viisi tuntia kahden tunnin ravistelun jälkeen. Käyrä 3 24 h:n kuluttua ravistelun jälkeen.

Table 1. The results of the known addition experiment with metal ions. The amount of lime added was 8 kg/m³ and the fertilizer levels were ranging from 1.6 to 2.0 kg/m³.

Taulukko 1. Eri metalli-ioneilla määrälisäyksillä saadut tulokset. Turpeen kalkituspitoisuus on 8 kg/m³ ja lannoitustasona 1.6—2.0 kg/m³ yleislannoitetta.

Cu				Zn				Mn			
$HClO_4$		HCl		$HClO_4$		HCl		$HClO_4$		HCl	
Added	Found	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
0	31.9	0	36.1	0	14.2	0	21.1	0	25.7	0	36.4
5	37.1	5	41.2	5	16.5	5	26.1	5	31.4	5	41.6
10	41.0	10	45.9	10	19.3	10	30.3	10	35.0	10	46.8
40	72.3	40	56.1	15	27.8	20	40.7	15	42.0	20	55.7
$\pm\delta$	0.6	$\pm\delta$	±0.5	$\pm\delta$	±4.0	$\pm\delta$	0.4	$\pm\delta$	0.8	$\pm\delta$	0.5
Mo				Fe				S			
$HClO_4$		HCl		$HClO_4$		HCl		$HClO_4$		HCl	
Added	Found	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
0	3.3	0	6.3	0	27.8	0	111.3	0	99.3	0	157.8
5	7.9	2	7.9	10	37.8	10	121.1	10	109.5	10	166.4
30	34.0	5	11.2	15	42.8	20	129.4	15	115.0	20	177.8
45	47.0	10	17.0	20	48.2	30	138.3	20	120.1	30	191.9
$\pm\delta$	1.0	$\pm\delta$	0.5	$\pm\delta$	0.2	$\pm\delta$	1.4	$\pm\delta$	±0.4	$\pm\delta$	2.4

We can see, that if pH is measured immediately after 0.5 hours shaking we obtain too high pH for peat without lime and too low pH for peat with lime added. Also, the repeatebility of the measurements is poor, pH = ±0.3 pH units. The situation is illustrated by the curve 1 of the Fig. 1. The curve 2 on the same figure describes situation, where we first have shaken the samples for 2 hours and then allowed them to stand for 5 hours. The pH was frequently measured during the experiment. During the stand time and down to the lime amount of 4 kg/m³. the pH value decreases as a function of time about 0.3—0.4 pH units. When lime amount is 6 kg/m³ or more, the pH value remains constant during the stand time. The curve number 3 shows the situation after 24 hours. Compared with curve 2, the pH has further changed. Escpecially interesting feature is decrease of pH of peat without lime. This is due to the dissolution of slightly soluble acids in peat. Two distinct breakpoints can be observed in curve 3. At the first place, the pH is steeply ascending up to the value corresponding to 4 kg lime/m³ peat. Thereafter, the linear increase of pH is sloping until the saturation point (12 kg/m³). Sloping may be due to the atmospheric carbon dioxide as well as due to the increase of ionic strength. The particle size of lime plays an important role, too. The smaller the particle size is, the faster and larger solubility is achieved due to increased surface activity. The pH value over 7, however, can hardly be exceeded even with the smallest particle size if the sample is in contact with air. The contents of calcium and magnesium follow the changes of pH values presented.

The initial concentration of the extracting acids was 0.1 M during the trace element investigations. The acidity of the solutions (pH = 2—3) was not sufficient, which is shown by the large deviations of the results and by the changes of the composition of the solutions. Therefore, we choosed 1 M acid solutions which improved the accuracy of the determinations and better stabilized the sample solutions.

We investigated the accuracy and the suitability of the selected methods using known addition technique. The samples were separately prepared by weighing homogenized peat (28 g), lime (correspondint to 8 kg/m³) and mixed fertilizer corresponding to 1.6—2.0 kg/m³). The extraction was performed either with 1 M perchloric acid or with 1 M hydrochloric acid. The known addition was made using the standard solution of each element. The results are presented in Table 1. and they show almost as good accuracy as obtained with calibration curves for the standard solutions. Relatively largest deviations are shown by zinc. The results

Table 2. The results of the determination of metals after perchloric acid, hydrochloric acid and ammonium acetate extraction.

Taulukko 2. 1M perkloorihappo-, suolahappo- ja ammoniumasetaattiuutoilla (1 M HAc aj 0.50 M NH_3*) saadut tulokset.*

Sample		Cu			Zn			Mn			Mo		
		$HClO_4$	HCl	NH_4Ac	$HClO_4$	HCl	NH_4Ac	$HClO_4$	HCl	NH_4Ac	$HClO_4$	HCl	NH_4Ac
Unfertilized peat moss		4.7 ±0.1	0.6 ±0.4	0.2 ±0.05	3.9 ±0.5	3.1 ±0.05	1.2 ±0.5	5.6 ±0.2	8.5 ±0.5	4.4 ±0.3	2.0 ±0.1	2.2 ±0.4	0.8 ±0.5
Lime 8 kg/m³		—	0.1 ±0.5	—	0.1 ±0.05	0.5 ±0.3	0.2 ±0.1	1.8 ±0.05	3.6 ±0.1	0.9 ±0.1	—	1.5 ±1	0.7 ±0.2
Unfertilized peat + Lime 8 kg/m³		1.0 ±0.05	1.0 ±0.3	0.3 ±0.003	3.5 ±0.3	3.1 ±0.8	1.1 ±0.2	10 ±1	12 ±1	5.8 ±0.1	1.5 ±0.1	3.4 ±0.5	0.9 ±0.4
Fertilizer kg/m³	0.8	8.5 ±0.1	9.1 ±0.1	6.9 ±0.1	4.1 ±0.2	3.5 ±0.5	2.8 ±0.1	5.5 ±0.4	6.0 ±1.0	5.0 ±0.4	0.1 ±0.05	0.3 ±0.1	—
	1.2	12.5 ±0.4	12.9 ±0.5	11.5 ±0.5	6.0 ±0.1	6.1 ±0.1	5.8 ±0.1	9.0 ±1.8	11.0 ±1.0	7.5 ±0.1	0.3 ±0.1	0.7 ±0.1	0.1
	1.8	18.7 ±0.2	20.8 ±1	15.5 ±0.5	9.2 ±0.05	9.9 ±10.2	8.2 ±0.1	13.1 ±1.5	16.2 ±0.8	12.2 ±0.3	1.0 ±0.1	1.4 ±0.2	0.6 ±0.1
Peat + Lime 8 kg/m³ + Fertilizer	0.8	13 ±0.2	17 ±1.5	1.7 ±0.5	8.2 ±0.5	9.9 ±0.05	6.8 ±0.6	17 ±1	23 ±1	15.4 ±1.2	2.8 ±0.1	4.1 ±0.3	1.3 ±0.3
kg/m³	1.2	27 ±1	29 ±1	3.2 ±0.5	9.4 ±0.3	14 ±1	8.3 ±1.3	20 ±1	30 ±1	19 ±1.5	3.1 ±0.1	6.3 ±0.05	2.3 ±0.3
	1.8	41 ±1	31 ±2	6.9 ±0.3	25 ±1	18 ±1	13 ±1	32 ±1	34 ±	31 ±1	4.5 ±0.1	7.7 ±0.05	5.4 ±0.3

Sample		Fe			S			Moisture %		
		$HClO_4$	HCl	NH_4Ac	$HClO_4$	HCl	NH_4Ac	$HClO_4$	CHl	NH_4Ac
Unfertilized peat moss		20.6 ±0.3	8.3 ±2	1.6 ±0.5	8.3 ±0.05	20 ±3	22 ±4	82	80	80
Lime 8 kg/m³		12 ±1	17 ±0.5	14 ±1	0.7 ±0.5	1.7 ±0.05	11 ±2	—	—	—
Unfertilized peat + Lime 8 kg/m³		23 ±1	116 ±2	3.1 ±0.3	24 ±2	19 ±4	47 ±5	79	80	79
Fertilizer kg/m³	0.8	2.5 ±0.05	2.5 ±0.1	0.6 ±0.1	47.0 ±1.0	46 ±1	83 ±1	—	—	—
	1.2	5.8 ±0.05	3.8 ±0.1	0.9 ±0.1	70 ±2	69 ±1	104 ±5	—	—	—
	1.8	6.0 ±0.1	5.1 ±0.1	1.1 ±0.1	100 ±2	98 ±3	133 ±5	—	—	—
Peat + Lime 8 kg/m³ + Fertilizer	0.8	28 ±1	107 ±2	2.7 ±0.2	73 ±1	97 ±1	205 ±30	75	80	80
kg/m³	1.2	33 ±1.5	111 ±3	3.1 ±0.5	98 ±3	158 ±5	247 ±45	77	80	81
	1.8	37 ±2	122 ±1	3.0 ±0.3	136 ±1	230 ±10	408 ±25	77	79	80

of the actual determinations using 1 M perchloric acid, 1 M hydrochloric acid and ammonium acetate as ectracting agents are shown in Table 2. The samples investigated were as follows: untreated peat, lime, peat + 8 kg/m³ lime added, and peat + 8 kg/m³ lime + 0.8 or 1.2 or 1.8 kg/m³ mixed fertilizer added. The results show a noticeably larger deviation as given in Table 1, since the fertilizer is more inhomogenous as a source of ions to be added than pure standard solutions of the metal ions. The deviation is manifold larger than in known addition experiments with pure solutions.

The influence of the matrix on the cation binding capability can be illustrated by an example. The experiment was performed as follows: the initial copper content of the peat sample (28 g) was 27.5 ppm as determined with perchloric and hydrochloric acid extractions. The lime addition was 8 kg/m³ and the fertilizer level was 1.2 kg/m³. Then 5, 10, 15 and 20 ppm copper was added to samples and normal ammonium acetate extraction was carried

Table 3. The results of the experiment of copper adsorption on peat.

Taulukko 3. Kuparin adsorptiota turpeeseen kuvaavan kokeen tulokset.

Added Cu^{2+} ppm	From NH$_4$Ac extraction found ppm	From washing water/ ppm	From HCl extraction found ppm	Σ	Calculated background ppm
5	2.7	0.3	30.1	33.1	28.1
10	3.4	0.3	31.1	34.8	24.8
15	4.0	0.3	34.7	39.0	24.0
20	4.7	0.4	41.7	46.7	26.7

mean = 26 ± 2 ppm

out. Thereafter, the peat was thoroughly washed with water under filtration and finally, copper was extracted from peat with hydrochloric acid. At every stage of the experiment, the copper content was determined. The results are presented in Table 3. The background value of copper, 26. 2 ppm well corresponds to the original background value 27.5 ppm. Thus the copper contents given after ammonium acetate extraction are only about 10 % of total copper content of the system.

The contents of trace elements investigated in unfertilized peat and in lime are negligble. If we consider the demand of the fertilizer addition, the presence of manganese, molybdenum and iron may be of considerable importance. When the extraction solutions are compared, perchloric acid proved to be the best, because chloride ion disturbed the determination of copper, iron and sulphur. Ammonium acetate is unsuitable extraction agent for the determination of total cations. Comparing the adsorption of copper, zinc manganese and iron on peat as determined after stong acid and ammonium acetate extraction, we obtain values for the adsorption coefficients 7.6, 1.5, 1.2 and 11.2, respectively. These figures well correlate both by the order and the magnitude with the values resulted from our studies concerning the adsorption of ions on peat. Since the adsorption capacities of different peats appreciably vary it also increases the possibility of analytical errors if determinations are carried out with ammonium acetate extraction (Tummavuori and Aho 1980 a, 1980 b).

As a conclusion we note, that the pH determination of peat is readily influenced by the sample handling and the measuring time. The pH value of unfertilized peat decreases by about 0.5 pH units within 24 hours. The lime addition stabilized the pH value at relatively high concentrations.

As an extraction agent, perchloric acid is superior to hydrochloric acid because the chloride ion and its ability to form complexes disturb some determinations. The largest deviations are shown in the determinations of zinc and molybdenum. Peat is a very difficult matrix due to the variations in the ion adsorption capacities. This makes the ammonium acetate extraction unreliable in the total cation determinations.

Finally, the slowest stage of the procedure, the filtration cannot be speeded up by partial filtration and by neglecting washing because otherwise 30—75 % of the total contents are lost, depending on the ion to be determined.

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SELOSTE:

LANNOITETUN TURPEEN HIVENAINEIDEN ANALYSOINNISTA. KASVUTURPEEN ANALYSOINNISTA OSA II.

Turpeen pH:ta mitattaessa on huomioitava aika. Jos mittaamme pH:n liian nopeasti, saamme kalkitsemattomalle turpeelle liian korkean pH-arvon, kun taas kalkitulle turpeelle saamme liian alhaisen pH:n. Yleensä kalkitus stabiloittaa pH:n mittausta (kuva 1).

Metalli-ionien määrityksissä tarvitaan suhteellisen vahvat happoliuokset. Vasta 1M happoliuokset liuottavat ja irroittavat turpeesta kationiset hivenravinteet riittävän tehokkaasti. Vasta näin vahvoilla hapoilla voidaan myös eliminoida turpeen erilaiset ominaisuudet kationisten hivenaineiden pidättäjänä. Edellä esitetyistä syistä ei esim. ammoniumasetaatti sovellu uuttoliuokseksi nyt kyseessä olevia ioneja määritettäessä. (Vertaa taulukko 3).

Menetelmän hitainta työvaihetta (2—3 h) ei voida nopeuttaa sillä, että suodatuksesta otettaisiin vain osasuodos ennenkuin suodatettava on huolellisesti pesty. Totesimme, että osasuodoksista saadut metallimäärät olivat vain 25—70 % todellisista kokonaispitoisuuksista.