ON THE ANALYSIS OF BORON OF FERTILIZED PEAT MOSS THE ANALYSIS OF PEAT MOSS PART III

LANNOITETUN KASVUTURPEEN BOORIN MÄÄRITYKSESTÄ KASVUTURPEEN ANALYSOINNISTA OSA III

Boric acid is a weak trivalent acid, which protolysis in pure water as monovalent acid according to

 $H_3BO_3 + 2H_2O \rightleftharpoons B(OH_4)^- + H_3O^+$

giving a hydrated borate ion B(OH)₄ which is a weak complex forming agent. The protolysis constant of boric acid in water is $10^{-9.2}$ (Silen et al. 1964, 1971) thus at pH-value from 5 to 7 the neutral boric acid is the dominating form. As an element, boron is necessary for plants. It appears in plants as H₃BO₄ or as BO₇ ion (Philipson, 1953). The deficiency of boron is soon observed as disturbances in growth, but the mechanism of the chemical effect is unknown. Boron is known mainly to accumulate in the leaves of the plants (Philipson 1953). Since free principally exists in neutral form it is not adsorbed by peat because peat acts as cation exchanger. Further, boron does not form compounds with humic and flavo acids. This leads to the fact, that a boron overdose may easily happen, since boron available for plants may rise to excess fertilizer addition (Bolz during 1977. Philipson 1953, Puustjärvi 1973). Boron is relatively difficult to be analyzed from peat itself. When boron is determined from fertilized moss peat, the analysis disturbed by the elements present in fertilizer and lime. Usually, the amount of boron to be determined from the dry matter of moss peat is less than 0.1 per cent. Our aim during this work was to find

a method for the analysis of boron from peat which could be used routinely, would be accurate enough and could be performed using the extractants suitable for other nutrients, too.

As a research material we had moss peat produced by the State Fuel Centre (VAPO) from the Aitoneva production site. Also, some samples were delivered from Haukineva, Konnunsuo and Löyniönsuo production areas. The fertilizer was mixed fertilizer manufactured by Kemira Oy and the lime was dolomite lime.

The volume of an individual sample for the analysis was 40 cm³ having the moisture content of 80 % w/w. The preparation of the samples for the analysis was carried out as described previously. The volume of extractant was 90 cm³ and the shaking time was 30 minutes with 1 Hz frequency (Tummavuori et la. 1980). The ion exchange resin was Amberlite IR 20 and the flow velocity was 1 to 2 cm³ per minute per volume unit (cm3) of the ion exchange resin. The eluation was done with 2 M sodium hydroxide. The measurement were performed with Beckman DU-2 spectrophotometer. The cuvettes were Hellma 100 QS quatz cuvettes having the path length of 1.000 cm. The reagents were products of A.E. Merck and pro analysi grade by the purity.

Several methods for the determination of boron are presented in the literature (Ellis et al. 1949, Gorfinkel et al. 1952, Gupta et al. 1971, Kolthof et al. 1978, Maurice 1968 and Roth 1954).

We tested the majority of these methods and with slight modifications applied to our work the method presented by Boltz (Boltz and Howell 1977).

The main reagent of the method is 1,1-dianthra-amide dissolved in sulphuric

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acid. It forms with boron a compound, unknown by the structure, which absorbs at wavelengths ranging from 590 to 650 nm. We selected 635 nm for the analytical wavelength and water was well suited for the reference solution. The reagent solution was prepared by dissolving 150 mg of the reagent to the 1 dm3 of sulphuric acid. According to our experiments, the sulphuric acid must be at least 16 M by the strength. The relative amounts of the components used in the measurements have an effect on the absorbance. We tested several combinations of the mixtures of the solutions. The best combination proved to be the solution containing 1 part of the sample solution or reference solution, 2 parts of reagent and 2 parts of strong sulphuric acid.

We allowed the colour forming to take place at room temperature. The development of the constant colour took about 2.5 hours and the colour remained for 2 to 3 hours. The absorbances (A) of the standard solutions during that period obeyed the equation A = -0.019 + 1.35ppm when the amount of boric acid was ranging from 0.1 to 0.5 ppm. The regression coefficient of the fitting was 0.998. Some authors recommend the warming of the solution at 80 °C for 4.5 hours to speed up the colour formation (Bolz et al. 1977). At room temperature after 2.5 hours standing time we obtained for A the value 0.184 and at 80 °C after 4.5 hours standing time A increased to 0.243 when applied to 0.15 ppm solution. Considering the prolonged analysis time when warming and the concentration range

measured, we may note that the warming shows no significant improvement in the accuracy although the value of A increased after warming (it should be noted that absorbances of either solutions stabilized to the values of 0.542 and 0.539 after a two weeks stay time). Throughout the work the standard solutions were simultaneously prepared with the sample solutions at same conditions. When the concentration of interfering ions increases to the disturbing level the blue color formation does not develope instead a red precipitation is obtained. This phenomen on has also been observed with the plant analyses (Baron, 1954, Gorfinkel et al. 1952). In such case the ion exchange must be done (Tsutomer et al. 1971). Before making any attempt to investigate moss peat with fertilizer and lime added, we separately determined the boron contents of those components as well as the boron content of the extracting agents. We did not find boron in perchloric acid, hydrochloric acid and in ammonium acetate (0.5 M with respect of ammonia and 1.0 M with respect of acetic acid). Before boron could be determined, the ion exchange had to be done to the ammonium acetate solution and the acid solutions must be neutralized with 1 M sodium hydroxide. This was due to the increased cation concentration. Lime did not contain boron. The determination was performed from the water extract after the ion exchange. With the untreated peat the determinations could be done directly from the water extract without ion exchange. The results are presented in Table 1. Although our sample rather limited. amount is the

Table 1. The boron contents of different peat samples. The letters A, B and C refer to different production fields and lower indices to the different positions at the field. The degree of humification is expressed in von Post's scale (H 1-10).

Taulukko 1. Turvenäytteiden booripitoisuudet. A, B ja C viittaavat eri turvekenttiin ja alaindeksit vastaavasti kentän eri osiin. Maatumisaste on ilmaistu v.Postin asteikolla.

Moss	ppm	Moss	ppm	Moss	ppm
Haukineva H 1—3	2.1 <u>+</u> 0.1	Löyniö (H4—5) A1	0.15 <u>+</u> 0.05	Löyniö B3 H4—5	3.4 <u>+</u> 0.2
Kihniö H 1—3	0.8 + 0.2	A2 H 4—5	0.1 <u>+</u> 0	C1 H 4—5	2.7 <u>+</u> 0.2
Kihniö H 4—6	1.0 <u>+</u> 0.2	A3 H 4—5	0.03 + 0	C2 H 4—5	3.2 <u>+</u> 0.1
Kihniö H 4—6	5.7 <u>+</u> 0.1	B1 H 4—5	1.45 + 0.05	C3 H 4—5	3.5 <u>+</u> 0.4
Konnunsuo H 1—3	0.2 + 0	B2 H 4—5	0.2 + 0.1		

Table 2. The results of boron contents after known additions of boron at different fertilizer levels. The lime content was 8 kg/m³ (8 ppm). The basic boron content of peat was 2.3 ppm at all fertilizer levels and 3.5 ppm from fertilized peat in known addition experiments.

Taulukko 2. Booripitoisuus tulokset eri lannoitustasoilla annettujen tunnettujen boorilisäysten jälkeen. Kalkkipitoisuus oli 8 kg/m³. Puhtaan turpeen booripitoisuus oli 2,3 ppm kaikilla lannoitustasoilla ja lannoitetun turpeen vastaava pitoisuus oli 3,5 ppm.

Fertilizer level ppm	Measured boron content ppm	Boron added ppm	Measured boron content ppm
0.8	2.9 + 0.2	0.5	3.8 + 0.2
1.2	3.6 + 0.2	1.0	4.3 + 0.2
1.8	3.8 + 0.2	1.5	4.7 + 0.2

variation in the boron contents can be clearly seen.

With the fertilized peat, the lime addition was 8 kg/m³ and the fertilizer levels were 0.8, 1.2 and 1.8 kg/m³. Now the determinations could be carried out from the water extract since peat acts as on ion exchanger thus adsorbing the interfering cations. The boron content of "pure" peat was 2.3 ppm. The results are collected in Table 2. Additionally, we made experiments using the known addition method. Boron was added to the fertilized peat having 8 kg/m³ of lime and 1.2 kg/m³ of fertilizer added. The basic boron content of that peat was 3.5 ppm. The results are presented in Table 2. The results agree with sufficient accuracy with the boron content given by the manufacturer. Also, the known additions made with boric acid to the fertilized peat meet the accuracy demand set for the analysis.

Further, we determined boron after extraction with 1 M perchloric acid, 1 M hydrochloric acid and 0.5 M ammonium acetate. The basic level of boron was 2.3 ppm, lime and fertilizer additions wer 8 kg/m³ and 0,8 kg/m³, respectively. The results were 3.1 ± 0.1 , 7.7 ± 0.5 and 3.4 + 0.1 ppm of boron, indicating that the determination can not be done after hydrochloric acid extraction. An attempt was made to determine the total content of boron in peat by decomposing the sample using the wet digestion technique. We have successfully used this technique in the determination of total phophorus in peat (Tummavuori et al. 1978). The determination of boron did not succeed, however, due to the interference by the fluoride ion in the reaction.

CONCLUSION

The determination of boron can be carried out from water exract of moss peat with fertilizer and lime added. The other extracting agents (1 M HCLO₄ and 0,5 M CH₃COONH₄) require the ion exchange prior analysis and hydrochlorid acid can not be applied at all. The major interfering cations can be removed by ion exchange.

The large variations in the basic boron content of peat is very surprising. The amount of boron may be even zero or manifold compared with amount used in the fertilizers. The question is, whether the boron addition to the peat always is necessary and on the other hand, whether peat itself can contain an excess of boron available for the plants. In practice, the boron content of peat is very difficult to take into account, since the variations even on the same bog may be large. (see Table 1.) We conclude, that the accuracy of this method for determining the boron content of fertilized peat is good, because the error always is less than 10 %, even more so if we bear in mind the difficulties caused by the inhomogeniosity of peat and problems in taking samples. These both together cause deviations in the results (Tummavuori et al. 1980).

REFERENCES

Baron, H., 1954: Bestimnung der Bor in Pflansen mit 1,1-dianthrimid. — Z. Anal. Chem. 143: 339—349.

Bolz, P.F. and Howell, J., 1977: Colorimetric Determination of non-metals. — Vol. 8 Second Edition: 19—21.

Ellis, Q.H., Gates, D. and Bandish, O., 1949: Colorimetric Determination of Boron Using 1,1 dianthrimide as a Reagent. — Anal. Chem. 11: 1345—1348.

Gorfinkel, E. and Pollard, A.G., 1952: A Modified Procedure for Determing Boron in Plant Material and Soils Using 1,1-dianthrimide. — J. Sci. Food. Agic. 3: 622—624.

Gupta, H.K.L. and Bolz, D.F., 1971: 1,1-dianthrimide as a Reagent for the Spectrophotometric Determination of Boron. — Anal. Lett. 4: 161—167.

Kolthof, I.M. and Elving, P.J., 1978: Treatise on Analytical Chemistry. Part II Vol. 10. Section A.
— John Wiley and Sons, New York.: 1—101.

Maurice, J., 1968: Posage colorimetrigue du bore total des meneraux des roches et des sols au mougen du 1,1-dianthrimide. — Ann. Agron. 19: 699—704.

- Philipson, T., 1953: Boron in Plant and Soil Acta Agricultroe Scandinavica Vol: III 12: 121-242.
- Puustjärvi, U., 1973: Kasvuturve ja suon käyttö -Turveteollisuus Liitto rv. Julk. 1.: 87 and 142.
- Roth, H. and Beck, W., 1954: Die Bestimmung des Bors in borhaltingen Mineraldügern mit des Estermethode. — Z. Anal. Chem. 141: 404—414.
- Stability Constants of Metal-Ion Complexes, Complied by Sillén, L.G. and Martetell, A.E., 1964, 1971: The Chemical Society Special Publication No. 17 and Suplement No. 1, London.
- Tsutomer, F., Kazuo, Y., Shigeki, K. and Atsushi, M., 1971: Ion Exchange in Basic Media and it's Analytical Applications II. Determination of Traces of Boren in Sodium Metal and Sodium Hydroxide. — Japan Analyst 20: 193—200
- Tummavuori, J., Kaikkonen, R. and Nyrönen, T., 1981: On the Analysis of Majot Nutrients of Fertilized Moss Peat. The Analysis of Moss Peat. Part 1 - Suo 32 (1): 9-14.
- Tummavuori, J., Nyrönen, T. and Saastamoinen, M-L., 1978: Fosforin määrityksestä turpeesta. On the Determination on Phosphorus in Peat. - Suo 29: 89-92.

SELOSTE:

LANNOITETUN KASVUTURPEEN BOORIN MÄÄRITYKSESTÄ KASVUTURPEEN ANALYSOINNISTA OSA III

Boori voidaan määrittää spektrofotometrisesti suoraan lannoitetun turpeen vesiliuosuutosta. Jos uutto suoritetaan muilla reagensseilla, täytyy suorittaa ioninvaihto enlainkaan uuttoliuokseksi.

Boorin suhteellisen laajat pitoisuusvaihtelut eri turvekenttien välillä on hämmästyttäviä. Pitoisuus vaihtelee nollasta moni-

kertaiseen määrään verrattuna lannoituksen minimitarpeeseen. Tästä saattaa olla haittaa kasveilla (katso taulukko 1.).

Katsomme, että menetelmä on riittävän nen määritystä. Suolahappo ei sovellu tarkka boorin määritysmenetelmä, sillä ottaen huomioon käsiteltävänä olevan epähomogeenisen matriisin, saavutettua 10 %:n tarkkuutta voidaan pitää hyvänä.