

**THE USABILITY OF THE THERMOGRAVIMETRY IN FUEL RESEARCH
PART VII. ON THE SELF-HEATING PROPERTIES OF THE
MOSS PEAT OF LÄYNIÖNSUO**

**TERMOGRAVIMETRIAN KÄYTTÖMAHDOLLISUUDET POLTTO-
AINETUTKIMUKSISSA OSA VII. LÄYNIÖNSUON ITSEKUUMENEMIS-
OMINAISUUKSISTA**

We have continued investigations of the Läyniönsuo peat bog at Hankasalmi community to clarify the self-heating properties involved with peat. This work completes our previous investigations (Tummavuori et al. 1979, part VI). In the aforementioned, we took samples only from stockpiles in October after the production season. The results obtained were very promising both from thermogravimetric and IR analyses when predicting the self-heating tendency and rate of the stockpiles.

For the study at hand, we made an appreciably larger sample from the production field, approximately 100 samples. The sampling was made before the production season in May and also thereafter, in late September. During the last sampling, we collected samples not only from the layer of the production field but also from the depths of 0.5 m and 1.0 m. The samples from the stockpiles were taken both in August (denoted I) and in October (denoted II). The research methods applied were thermogravimetry, IR spectroscopy and X-ray fluorescence, the latter being used for the determination of the amounts and distribution of some metals (Mn, Fe, Cu, Zn). The samples were dried without any pretreatment at 105° and at 140° centigrades. They were then milled with a blade mill (Franz Morat, Type A 70).

The experimental part of thermogravimetry was carried out as described previously (Tummavuori et al. 1978, part I) and calculations were performed with ABC 80 microcomputer as described earlier using modified methods of Broido (Broido 1969), method I and Coats-Redfern (Coats and Redfern 1964), method II (Balarin 1977, Tummavuori et al. 1979). The infrared spectrophotometer was Perkin-Elmer model 283. The powdered samples were diluted with potassium bromide to 2 % w/w. The reagent was a product of A.E. Merck A.G., trademark Uvasol. The röntgenspectrophotometer was Spark 1 and the peat samples were prepared as previously described (Tummavuori and Aho, 1980). The humic acid was a product of Fluka A.G. Initially all samples were dried both at 105° and at 140° centigrades for 24 hours. According to IR analyses we observed that some acids with a small molecular weight evaporated. We decided to make further dryings at 105° centigrades. Some moisture was adsorbed by the samples after drying and that could be seen both in TG and IR spectra. The moisture adsorbed, however, remained constant at 3 % w/w. We also tried to accelerate self-heating with nutrient solution (Kuster et al. 1972) but the use of this solution very seriously disturbed the interpretation of TG and IR data, thus we gave up this trial. We determined the contents of four different metals by means of röntgenfluorescence in order to establish their distribution. The distribution, however, was surprisingly small at different fields. The contents varied within the following ranges: manganese 35 ± 5 µg/g, iron 800—4000 µg/g, copper 3.8 ± 0.5 µg/g

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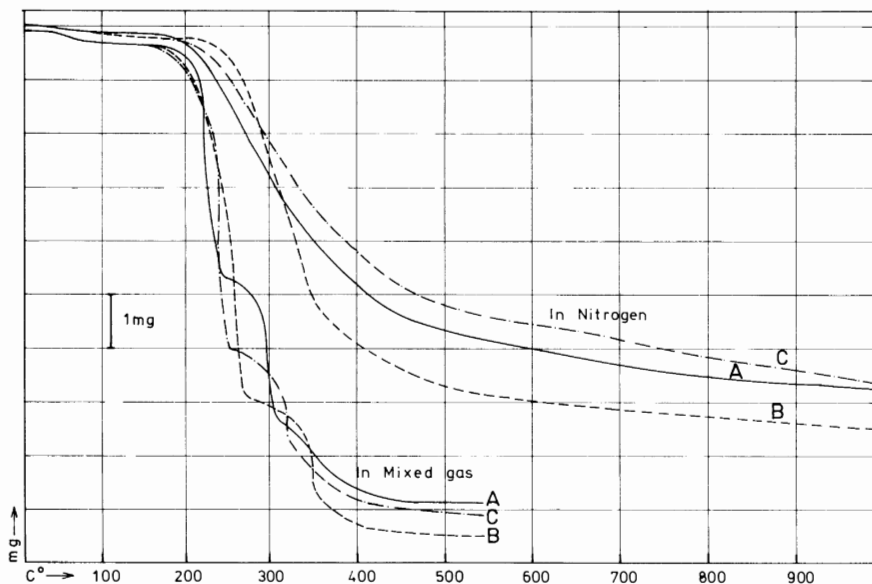


Figure 1. Some typical thermogrammes of different samples from the production fields A, B and C in nitrogen and in mixed gas atmospheres.

Kuva 1. Tuotantokentän eri osien (A, B ja C) tyypillisiä termogrammeja sekä typpi- että seoskaasuatmosfäärissä.

and zinc $18.03 \pm 3 \mu\text{g/g}$. The ash content rang from 5.5 to 6.5 % w/w. Thus these relatively small variations had no influence on the interpretation of IR spectra.

Figure 1. shows typical thermogrammes of the samples taken from different production fields run both at nitrogen and at mixed gas atmospheres.

Differences between production fields can be seen in the thermogrammes. Table 1. collects the kinetic quantities calculated from the thermogrammes for the first actual reaction. During this reaction, cellulose is mainly decomposed and its amount varies at different fields. The present values of E^* and $\log A$ correspond well to those obtained in previous investigations (Tummavuori et al., part II 1979). Now, on this occasion the reaction orders have also been taken into account. They are 1.0 for nitrogen and less than unity a mixed gas. The reaction orders have only a minor, diminishing influence on the values of E^* . Before this study, we frequently used the assumed value 1.0 for all reaction orders.

Table 2. shows the mean values of E^*

and $\log A$. The computed values indicate a straight forward direction of the self-heating tendency of the field samples. The values of $\log A$ and E^* change with respect to this tendency. Peat in field A possesses a very great tendency to self-heating, whereas peat in field C has a lower tendency and peat field B only slightly. This is reflected in the values of $\log A$ and E^* , the samples from field A show the smallest and samples from field B the largest values both in mixed gas and in nitrogen atmospheres. The samples taken from the stockpiles in July (I), and corresponding to the fields B and C, show similar values of $\log A$ and E^* , but the samples from the stockpiles in field A exhibited noticeably lower values. Further, the samples taken in October (II) from stockpiles give the smallest values for $\log A$ and E^* in the case of field A, but now the samples from the stockpiles in field B give the largest values. The storing in stockpiles gives rise to the values of $\log A$ and E^* especially in field A, whereas the values of samples from other fields show a minor decrease. Fig. 2. shows the decomposition reaction

Table 1. The initial temperature (Ti), the final temperature (Tf), the mass change (ΔW , w/w %), the values of kinetic quantities and regression coefficients of the main reaction as calculated by two different methods. The thermogrammes are recorded both in nitrogen and in mixed gas (80 % N₂, 20 % O₂) atmospheres.

Taulukko 1. Pääreaktion alkulämpötila (Ti) loppulämpötila (Tf), massanmuutos (ΔW , w/w %), kineettisten suureiden arvot sekä regressiokerroin kahdella eri menetelmällä laskettuna. Termogrammit on ajettu sekä typpi- että seoskaasuatmosfäärissä (80 % N₂ ja 20 % O₂).

	In nitrogen			Method I			Method II				
	W _{obs} (%)	Ti	Tf	n	E*	logA	R	n	E*	log A	R
A1	60.1	434	576	0.01	87	5.7	0.999	0.07	79	5.0	0.999
A2	55.1	447	562	0.37	106	7.9	0.995	0.48	100	7.3	0.996
A3*	45.0	449	573	0.37	138	11.7	0.997	0.32	128	10.7	0.998
B2**	73.5	464	590	0.60	130	9.8	0.996	0.71	124	9.2	0.996
B3	47.9	435	578	0.82	102	7.6	0.997	0.77	93	6.6	0.999
C1	55.2	440	589	0.75	106	7.6	0.999	0.79	98	6.8	0.999
C2	54.1	445	555	0.00	99	7.2	0.993	0.04	6.5	6.5	0.994
C3	42.1	448	589	0.63	89	6.1	0.999	0.68	82	5.3	0.999
Stock piles											
A1	44.4	430	565	0.00	68	4.1	0.99	0.07	61	3.3	0.999
B1	44.6	429	585	0.69	99	7.2	0.99	0.67	91	6.3	0.999
C1	57.0	425	571	0.13	100	7.2	0.999	0.05	90	6.2	0.999
AII	56.9	433	564	0.52	83	5.7	0.999	0.63	77	5.1	0.999
BII	51.2	428	566	0.22	98	7.0	0.999	0.12	87	6.0	0.999
CII	39.7	434	575	0.55	93	6.6	0.999	0.53	85	5.7	0.999
In mixed gas											
A1	48.3	431	691	1.00	59	2.7	0.997	1.00	50	1.4	0.994
A2	52.8	440	705	1.00	60	2.7	0.989	0.99	50	1.7	0.983
A3	49.8	454	751	1.00	52	1.7	0.991	1.00	42	0.4	0.985
B1	53.1	435	686	1.00	65	3.4	0.991	1.00	56	2.1	0.986
B2	62.6	469	683	0.99	80	4.7	0.987	0.99	71	3.8	0.982
B3	53.2	435	655	0.99	72	4.2	0.994	0.99	63	3.3	0.993
C1	47.6	440	683	0.99	71	3.9	0.990	0.99	61	2.9	0.986
C2	46.8	449	696	0.99	65	3.3	0.974	0.99	55	2.3	0.963
C3	47.0	429	691	1.00	57	2.6	0.991	1.00	48	1.3	0.987
Stock piles											
A1	53.0	420	727	0.99	46	1.4	0.991	0.99	36	0.5	0.985
B1	54.4	435	692	0.99	66	3.4	0.980	0.99	56	2.5	0.972
BI	45.4	428	705	0.99	65	3.3	0.986	0.99	56	2.4	0.979
AII	50.4	445	730	0.99	59	2.5	0.989	0.99	49	1.6	0.983
BII	51.2	445	685	0.99	66	3.5	0.988	0.99	57	2.6	0.982
BIII	48.8	436	707	1.00	61	2.8	0.993	1.00	52	1.5	0.990

* ditch side

** ditch bottom

of the cellulose fraction of the samples A₁, B₁ and C₁ expressed as -ln k vs. 1/T. The curves clearly depict the exception of the "hot" stockpile from others both in mixed gas and nitrogen atmospheres.

Fig. 3 shows the IR spectra of some samples and Table 3 collects the absorbance values and the relative intensities of these spectra. The IR spectrum of humic acid (HA) was used as a reference.

Consider the differences between the "hot" stockpile from field A and the "cold" stockpile from field B. The region from 3400 to 3429 cm⁻¹ shows no significant differences. The absorbance is mainly due to the water content. At the region from 2918 to 2860 cm⁻¹ the concentration of aliphatic hydrocarbons of the sample A is clearly higher than that of sample B and humic acid. The most significant absorption

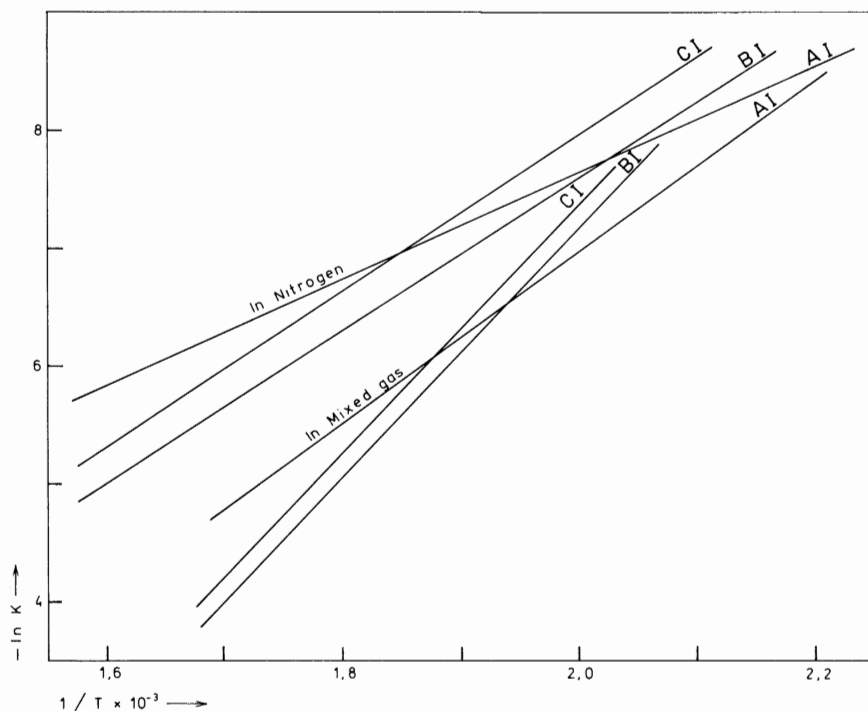


Figure 2. The rate constant of the main reaction, expressed as $-\ln k$ vs. $1/T$, of the samples from the stockpiles A_1 , B_1 and C_1 .

Kuva 2. Aumojen (A_1 , B_1 ja C_1) näytteiden pähajoamisreaktion reaktionopeusvakio $-\ln k$ $1/T$:n funktiona.

Table 2. The mean values of the kinetic quantities of the main reaction as obtained from several samples.

Taulukko 2. Pääreaktion useamman näytteen keskiarvoina saadut kineettisten suureiden arvot.

Sample	Method I				Method II			
	In mixed gas		In Nitrogen		In mixed gas		In Nitrogen	
	E^*	$\log A$	E^*	$\log A$	E^*	$\log A$	E^*	$\log A$
A	97	6.80	60	2.7	90	6.1	50	1.6
B	101	7.55	69	3.8	92	6.6	60	2.7
C	98	6.95	64	3.2	90	6.2	55	2.2
A_1	69	4.1	46	1.4	61	3.3	37	0.5
B_1	100	7.2	66	3.4	91	6.3	57	2.5
C_1	100	7.2	66	3.4	91	6.2	57	2.4
A_{II}	83	5.7	59	2.5	77	5.1	50	1.6
B_{II}	98	7.0	66	3.5	87	6.0	57	2.6
C_{II}	93	6.6	61	2.8	85	5.7	52	1.5

at 1708–1727 cm^{-1} is caused by free carboxylic groups. The content of free carboxylic groups in sample A is negligible if compared with that of sample B and humic acid. The content of bound carboxylic (through tight hydrogen bonds) in relation with free groups is largest in sample A. The aromatic $C=C$ bonds are missing from the humic acid as can be seen

from the absorptions at 1509–1522 cm^{-1} . The region 1030–1083 cm^{-1} is important, because some functional groups of alcohols, phenols and saccharides show absorption here. In humic acid their share is negligible. In sample B, however, their absorption is considerably stronger than in sample A.

We observed, that if we join points

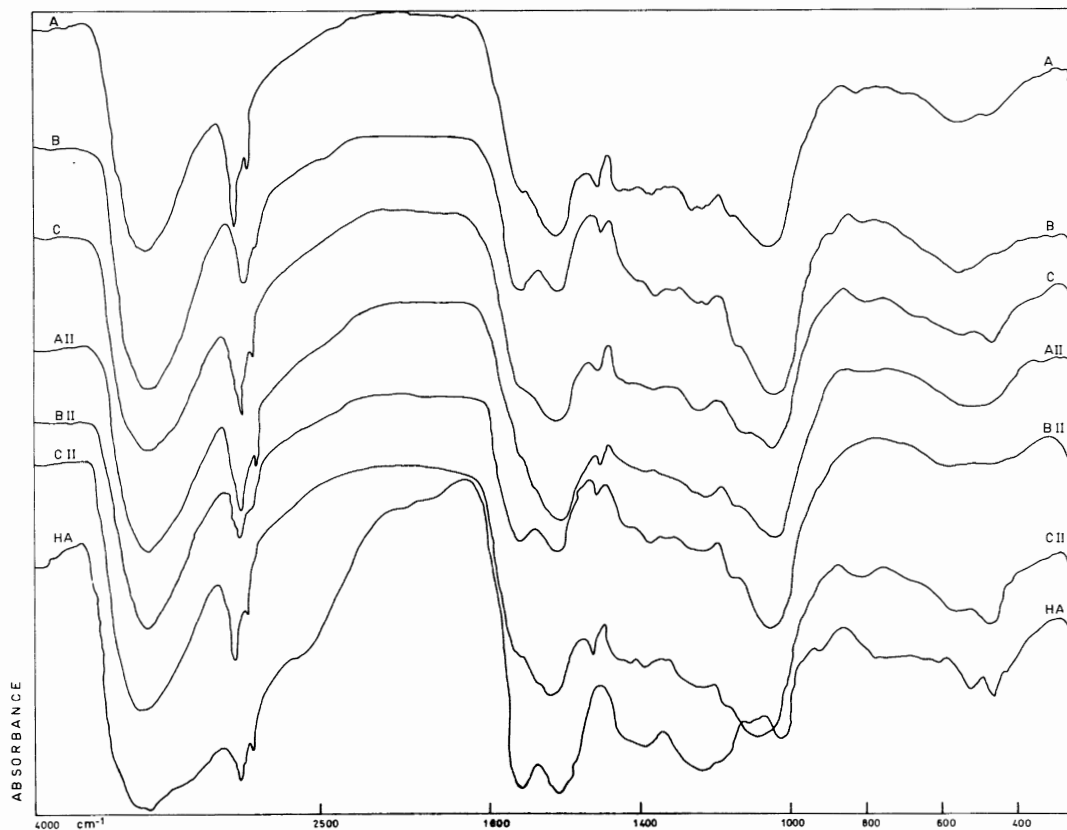


Figure 3. The IR spectra of some sample at the wavenumber region from 4000 to 350 cm^{-1}

Kuva 3. Eräiden näytteiden IR-spektrejä aaltolukualueella 4000–350 cm^{-1} .

Table 3. The wave numbers (cm^{-1}) of the most significant absorptions of the IR spectra and the relative intensities (VS = very strong, S = strong, M = medium, W = weak, vw = very weak).

Taulukko 3. Infrapunaspektrien merkittävimpien absorptioiden aaltoluvut (cm^{-1}) ja suhteelliset intensiteetit (VS = hyvin voimakas, S = voimakas, m = keskinkertainen, w = heikko ja vw = hyvin heikko).

Band range cm^{-1}	Production tracts			Stock piles			HA	Assignments of vibrations	References
	A	B	C	A II	B II	C II			
3400—3429	3400 vs	3400 vs	3400 vs	3418 vs	3417 vs	3422 vs	3410 vs	H-bonded-OH, H	Mondal 1978 Theng 1966, Mathur 1978 Adhikari 1978
2918—2924	2919 m	2919 m	2918 m	2924 m	2918 m	2918 m	2920 m	alifatic-CH stretch	Mondal 1978, Theng 1966 Mathur 1978, Adhikari 1973
2850—2860	2860 w	2855 vw	2858 w	2858 w	2855 vw	2855 w	2850 v	alifatic-CH	Theng 1966, Mathur 1978
1708—1727	1714 vw	1727 m	1715 vw	1712 vw	1720 m	1708 vw	1713 m	C = O of COOH and ketones	Adhikari 1978, Schnitzer 1972, Theng 1966 Mathur 1978
1611—1632	1621 s	1632 s	1632 s	1611 s	1625 s	1621 s	1612 s	aromatic C = C H-bonded C = O of COOH double bond conjugated with C = O, COO ⁻	Adhikari 1978, Schnitzer 1972, Theng 1966, Mathur 1978, Adhikari 1973
1509—1522	1509 w	1512 w	1522 w	1511 w	1511 w	1509 w	—	aromatic C = C	Adhikari 1973 Theng 1966
1369—1380	1376 vw	1369 w	1370 vw	1378 w	1369 w	1376 w	1380 w	alifatic-CH COO ⁻	Adhikari 1973 Schnitzer 1972 Mathur 1978
1220—1263	1263 w	1233 w	1226 w	1232 w	1220 w	1220 w	1235 w	C = O stretch, OH deformation of COOH	Adhikari 1973, 1978
1030—1083	1061 s	1055 vs	1070 s	1051 s	1059 ws	1083 ws	1030 m	C = O in cyclic alifatic esters and alcohols CHOH, CH ₂ OH	Adhikari 1973, 1978 Weast 1977

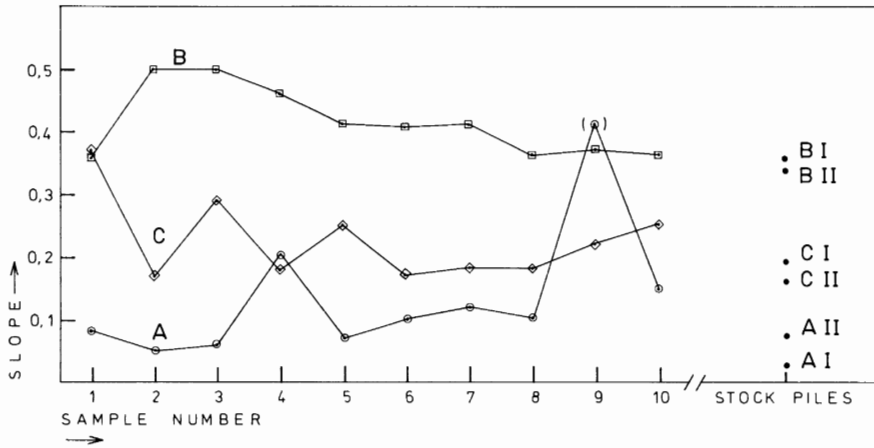


Figure 4. The slopes of the lines between the absorptions at 1060 and 1620 cm^{-1} . The slopes have been determined to the samples from the production fields and to the samples from corresponding stockpiles.

Kuva 4. Näytteiden suoran kulmakerroin, joka on saatu yhdistämällä näytteiden aaltolukujen 1060 cm^{-1} ja 1620 cm^{-1} absorptiomaksimit tuotantokenttien eri pisteissä ja vastaavissa aumoissa.

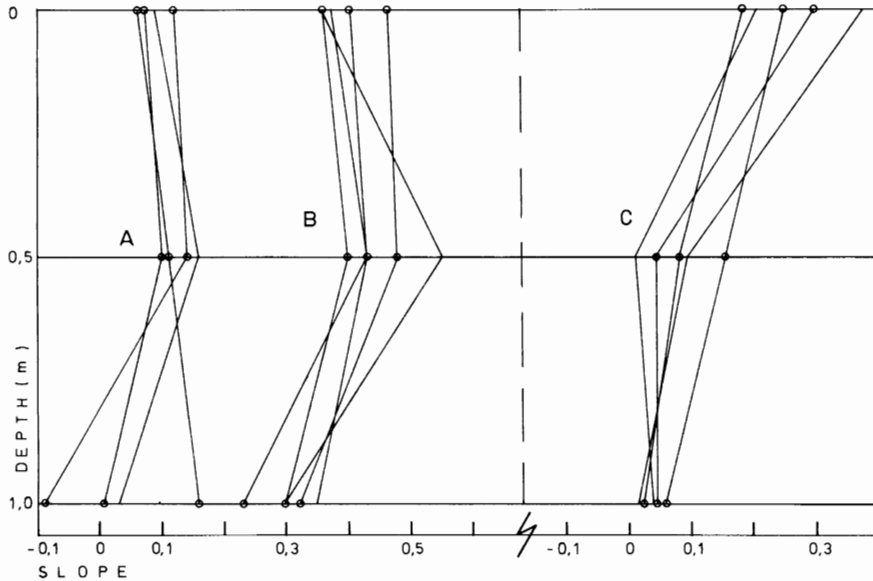


Figure 5. Some slopes of the lines between the absorptions at 1600 and 1620 cm^{-1} . The slopes have been determined to the samples from different part of production fields and from different depths.

Kuva 5. IR-spektreistä laskettujen näytteiden kulmakertoimien arvoja tuotantokentän eri osista ja syvyyksistä.

1060 cm^{-1} and 1620 cm^{-1} together with a line and calculate the slope of the line, it will indicate the self-heating tendency of the sample. The less the value of the slope is, the more sensitive peat is toward self-heating. This is illustrated in figure 4, where the slope has been presented as a function of sampling points. The lowest values are shown by sample A and the

highest by sample B. This order of self-heating tendency corresponds well to the practical experience on the Läyniönsuo production fields. (The sample from point 9 is clearly a random sample, since it appreciably deviates from the others). Figure 5 shows the slopes of the vertical samples as a function of the depth. The figure gives reason to predict that no

changes take place in the peat from field A. Furthermore, the self-heating tendency of peat in field B decreases at the first place but thereafter will increase. In field C, the self-heating tendency will steadily increase as a function of depth. Figure 5 also illustrates the noticeable difference between A and B fields.

CONCLUSION

The IR spectrum of peat and the interpretation we suggest realizes a rapid handling of even large amount of samples. The interpretation involves the determination of the slope of the line between the absorptions of two wave numbers (1060 and 1620 cm^{-1}). Although the results obtained

with thermogravimetric methods are parallel with this interpretation, the thermogravimetry is considerably slower and the calculation of the results more tedious. Since the IR method is fast and sensitive, it is easily employed by the qualitative analysis of peat and humic substances with respect of different purposes. The IR analysis can be applied to the prediction of the self-heating tendency of different peat species and thus money can be spared during the production season by taking this tendency into account in determining e.g. the transportation order of stockpiles. The IR analysis also gives a basis for further investigations of the self-heating process and for the elimination of this harmful phenomenon.

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TERMOGRAVIMETRIAN KÄYTTÖMAHDOLLISUUDET POLTTO-
AINETUTKIMUKSISSA OSA VII. LÄYNIÖNSUON ITSEKUUMENEMIS-
OMINAISUUKSISTA

Infrapunaspektrien ajaminen ja ehdottamamme tulkintamenetelmä, jossa määritetään yksinkertaisesti kahden aaltoluvun (1060 cm^{-1} ja 1620 cm^{-1}) absorptioiden välisen suoran kulmakerroin, on huomattavan nopea ja mahdollistaa suurenkin näytemäärän analysoimisen. Vaikkakin termogravimetriset tulokset ovat yhdensuuntaiset ja niistä on saatavissa lähes samat tiedot kuin IR-analyyseilläkin se on käytännössä huomattavasti hitaampi ja tulosten laskenta on suhteellisen monimutkainen.

Koska IR-menetelmä on nopea ja herkkä, sitä voidaan helposti käyttää lähinnä kvantitatiiviseen turpeen ja humusaineen luokittamiseen eri käyttötarkoituksia varten.

Analyysin soveltaminen tuotantokenttien aumojen itsesyttymisalttiuden ja palamisjärjestyksen selvittämisellä saavutetaan taloudellista säästöä. Lisäksi IR-analyysi antaa selkeän lähtökohdan turpeen itsekuumenemisen selvittämiseen sekä sen haittojen vähentämiseen.