TRACE ELEMENT ANALYSIS OF SOUND AND DECAYED NORWAY SPRUCE (PICEA ABIES) BY XRF AND NAA METHODS

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SELOSTE:

TERVEEN JA LAHON KUUSEN HIVENAINEANALYYSEJÄ RÖNTGENFLUO-RESENSSI- JA NEUTRONIAKTIVOINTIMENETELMILLÄ

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Ashed tree samples from sound and decayed Norway spruce were studied by means of fast neutron activation analysis (neutron energy 14 MeV) and, for comparison, also by X-ray fluorescence analysis. In fast neutron activation analysis the following elements were detected: (Na), Mg, Al, Si, K, Ca, Mn, Rb, Sr and Ba, and according to the results of the X-ray fluorescence method the elements present in the wood samples were: K, Ca, Mn, Rb, Sr and Ba. A general diminishing was revealed by both methods in most elemental concentrations, with the exceptions of K and Rb, when going from a sound tree to a decayed one. The use of the ratio of the amounts of potassium to calcium as an indicator of the degree of decayedness is therefore proposed.

1. INTRODUCTION

worst, can result in about one third of the thickness of the tree's bark. trees in spruce forests being discarded in importance.

Internal decay in growing trees, at its reliable and their sensitivity depends on the

Other methods are therefore being looked the timber industry. As this obviously into for measuring the condition of trees. has unfavourable economic consequences, A large selection of nuclear methods has an early indication of the presence and been utilized during recent years in the extent of decay in growing trees is of investigation of various environmental problems. Amongst the methods using Of the devices which exist for measuring radiation is activation analysis by neutrons, the internal decay, only few are completely which is worth examining in the context nondestructive. Examples of the non- of tree inspection. In this method neutrons destructive methods are those using ultra- are used to excite characteristic radioactivity sonic equipment or X-ray photography. in the sample nuclei by nuclear reactions These methods, however, have serious and the radioactivity is measured by radisadvantages, as they are for instance not diation detectors. This radioactivity reveals the elements present in the sample. If the These X-rays can be identified by suitable chemical composition correlates with the radiation detectors. In this work gamma state of the tree, activation analysis by neutrons could serve as a rapid inspection isotopes were employed for to create the method. Fast or thermal neutrons can be employed for the activation; in this work fast neutrons were employed.

neutron activation in elemental analysis another nuclear method was also checked. Thus tree samples were studied using the X-ray fluorescence method, whereby characteristic X-rays of the elements in the sample are excited by gamma radiation or Physics, University of Helsinki, and the Academy by energetic, charged particles. In the of Finland for financial support. The English of excitation process vacancies in the inner orbitals of the sample atoms are first Sundström, and the typing completed by Ms. created, and as these vacancies are imme- Tuula Gustafsson, for who we express our warm diately filled by a series of electron transitions, emission of X-ray photons follows.

and X-ray radiation from long lived radioexcitation.

Technical details of these two independent investigations and the results obtained for In order to compare the effectiveness of elemental concentrations in sound and decayed tree samples are presented herein. The spruce samples for the examinations were cut from spruce forests in Virrat, Central Finland.

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2. EXPERIMENTAL TECHNIQUES

2. 1. Sample characteristics

were burned to ash at low temperature (about 200-300 C) and the cooled ash strained with a 0.5 mm sieve.1) For use in the neutron activation approximately halfgram samples of ash were weighed accurately respectively. In a sample consisting preand put in small polyethylene irradiation dominantly of potassium $\left(Z=19\right)$ the boxes. The area of the prepared samples maximum attenuation would be 2 and 0.7 was 3.61 cm² with a thickness of about 1 mm. As this sample thickness (~1 mm) about 97 per cent of the y-radiation is left does not affect much the penetration of energetic neutrons (in our case 14 MeV energy) in the samples, no serious absorption problems arise. This makes the use of neutrons in the decay studies favourable.

of elements in neutron activation analysis appear at energies above 200 keV (in this Samples of decayed and sound spruce study all of them), which also means that γ -ray absorption is negligible. The maximum attenuation of γ -rays of 100 keV and 500 keV energy would in 1 mm of carbon (Z = 6) sample be 3 per cent and 2 per cent, per cent, respectively. In our case then, unabsorbed in the sample material.

For the analysis by X-ray fluorescence, thin pellets of 1 mm · 3.14 cm² size were prepared from the ash by using a pressure of 4500 kg/cm². In X-ray fluorescence Almost all γ -rays used in identification analysis the sample thickness (~1 mm) has a more pronounced effect, the extent of which depends on the energy utilised for excitation as well as on the energy of the radiation excited. The attenuation of 5.9 keV X-rays (i.e. the exiting radiation from a Fe-55 source) is 91 per cent and diation from an Am-241 source) is 3 per cent in 1 mm of carbon sample. Respecation would result in 1 mm thick samples

¹⁾ As it was considered possible that quantities of chemical compounds of some elements might have been evaporated during the ashing process, which could lead to erroneous conclusion as to the mineral contents, the melting and boiling points of that of 59.6 keV y-rays (the exciting rathe most probable mineral compounds were checked. Those were found to be too high to allow vaporisation at the low burning temperatively, ~ 100 and 5.5 per cent attenutures used.

of potassium. Absorption effects must measurements can thus be performed in therefore be carefully taken into account a 7-10 minute sequence, which means when X-rays are used for identification. that approximately 50 samples can be Only in the case of thin samples, such as investigated in one day. air particulate matter with a few tenths of milligrams per square centimeter on thin filters, can the absorption be almost negligible. Even then other factors such as sample composition should be equally accurately known.

2.2. Sample analysis

2.2.1. Neutron activation

MeV neutrons from a SAMES T 400 neutron generator at the Department of Physics, position and transported manually to the a 5 minute irradiation should be enough to employed here. Four to five samples could be irradiated simultaneously, but usually limitations in detecting capacity make this al. 1978). impracticable.

using a coaxial 43 cm³ Ge(Li) semiconductor for measuring environmental samples. The detector and a 4 K ADC connected to the PDP 9/L computer of the Department of Physics, University of Helsinki. An experimentally determined response curve for the efficiency to detect γ-rays of different energy was used. The experimental detector resolution was 3 keV for 1333 keV 60Co γ-rays. Standard IAEA sources and a 152Eu source were used for energy calibration. Measuring times were 5 and 15 minutes. the former starting about one minute after irradiation, and the latter one minute after the first measurement.

In routine work only one measurement Kuva 1. Spektrometrin toimintaperiaate, per sample is needed and can be performed 1. Näyte 2. Lähde 3. Ilmaisin 4. Be-ikkuna during the first five minutes. Sample 5. Rajoitin.

2.2.2. X-ray fluorescence

In the X-ray fluorescence method the particle size effects might be seriously sample measurements each took 4 minutes involved (Räisänen et al. 1978), and the in the XRF spectrometer facility at the Department of Physics, University of Helsinki. Characteristically for this method. excitation and detection were made simultaneously. As no separate irradiation and detection periods are needed, noticeable reduction in the investigation time results.

Each sample pellet to be analysed was In neutron activation analysis the samples placed on thin mylar foil supported by a were irradiated for 15 min with 14-15 metal ring. X-ray spectra of the samples were measured using a 5 mm thick intrinsic germanium X-ray detector with 25 mm² University of Helsinki. The average neutron sensitive area. The energy resolution of this flux used was $5 \cdot 10^9$ n/cm²·s. Shorter detector for Mn KX-rays was 150 eV. irradiations were performed in identifying A module based pulse processing system short lived activities. After irradiation the and a 4 096 channel pulse height analyser samples were removed from the irradiation with paper and magnetic tape registration devices were used in data collection. These measuring apparatus. The transport time instruments are routinely employed in from irradiation to measurement was about nuclear spectroscopy. When using the Feone minute. According to the present results 55 excitation, the low energy X-radiation can best be detected in vacuo. A brief enable the same identification procedure as description of the spectrometer characteristics is given below with a more detailed account reported elsewhere (RAUNEMAA et

The XRF spectrometer employed in The gamma spectra were measured by this study had been constructed specially radiations used for the excitation of X-rays

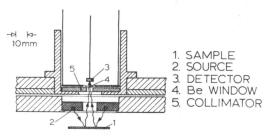


Figure 1. An overview of the spectrometer.

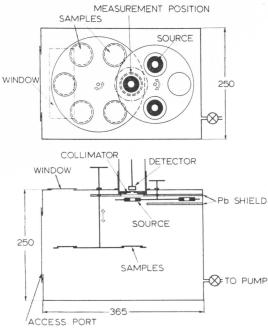


Figure 2. The fluorescence chamber characteristics. The dimensions are given in mm.

Kuva 2. Mittauskammion rakenne ylhäältä ja sivulta.

originate from radioisotopes of Fe-55, Cd-109 and Am-241. In this study only the Fe-55 and Am-241 sources were used. The

sources, which have annular shape, have an activity level of 1-4 GBq, i.e. they show about 109 decays/s.

Figure 1 presents an overview of the experimental arrangement of the spectrometer with the sample, radioisotopic source and radiation detector.

The samples, the sources and the detector are enclosed in a »fluorescence» chamber shown in Figure 2. The chamber is vacuumtight and can be evacuated or filled with a chosen gas. The chamber material is aluminum, as this material does not cause interferences in the measurements.

An efficiency calibration of the detector, which is usually necessary, can be avoided by using single element standards (GIAUQUE et al. 1975).

2.2.3. Data manipulation

Data manipulation was carried out using the computer program VIPUNEN (PAATERO 1977) in a Burroughs 6 700 computer. A least-squares fit of a polynomial to calibration points yields in this program the energy-channel response, which is used to calculate the needed information i.e. the energies and intensities. The program is constructed useroriented and can very well be adapted to analysis of any spectroscopic data.

3. RESULTS

3. 1. Neutron activation analysis

Characteristic gamma spectra resulting from neutron activation of sound and decayed tree ash samples, respectively, $\Delta N = \text{intensity of the gamma peak}$ prepared as described above, are reproduced in Figure 3. Reaction channels, reaction cross sections and characteristics of the $t_{1/2}$ = radioactive half-life of the reaction product reaction products used in elemental iden- t_w = waiting time tification are presented in Table 1.

To determine the relative abundances of different elements in the samples one has to calculate normalised intensities for peaks in the spectra. The number of atoms Ni of element i in the sample is then

$$N_{j} = \frac{\lambda \Delta N e^{\lambda t_{w}}}{\sigma \varnothing} (1 - e^{-\lambda t_{a}})^{-1} (1 - e^{-\lambda t_{m}})^{-1}$$

 λ = radioactive decay constant = en $2/t_{1/2}$

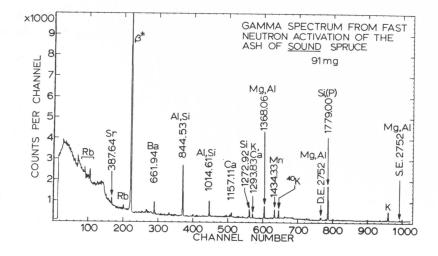
 \emptyset = neutron flux

 σ = reaction cross section

t_a = activation time

t_m = measuring time

The photopeak efficiency of the gamma detector, the variation of the neutron flux and the differences in dry weights of the sam-



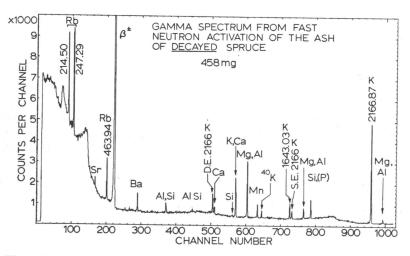


Figure 3. Gamma spectra from fast neutron activation of the ash of sound and decayed spruce samples. Gamma-ray energy and/or the element in question are shown by the keV value and/or the chemical symbol, respectively, in each relevant case.

Kuva 3. Gammaspektrit terveestä (yllä) ja lahosta (alla) kuusinäytteestä neutroniaktivointimenetelmällä. Gammasäteilyn energia-arvot ja piikkien alkuperä on merkitty kuvioon.

ples were taken into account via correction compatible as between sound and decayed factors. By using the reaction cross sections trees and within the two groupings. (LEPPÄMÄKI and KANTELE 1970) and half-

In calculating the errors of relative lives of the reaction products (Tannila abundances, two main error sources should and Kantele 1969), the relative abunbe mentioned: the errors in peak areas, as dances of the elements were finally found. given by the error analysis of the computer The results presented in Table 2 correspond program VIPUNEN, and the uncertainties to the data collected in the 15 min measure- in the timing. For the waiting time a ment periods. The values obtained are rather large uncertainty of ± 0.5 min

Table 1. Identification data used in neutron activation analysis. Taulukko 1. Tunnistukseen käytetty aineisto neutroniaktivointianalyysissä.

		Mai	n γ-ray			1	
Product	Half-life	Energies	Intensities	Reaction	Abundance	Cross Section	
nucleus Tuoteydin	Puoliintumis- aika	γ-s Energiat keV	äteilyn Intensiteetit	Ydinreaktio	Runsaus %	Vaikutusala mb	
$^{23}\mathrm{Ne}$	37.6 s	440	0.33	²³ Na(n,p)	100	40	
²⁴ Na	15.03 h	1 368.5	1.00	24Mg(n,p)	79	40 170	
		2 753.9	1.00	$^{27}\text{Al}(n,\alpha)$	100	114	
$^{27}{ m Mg}$	9.45 m	843.8	0.72	²⁷ Al(n,p)	100	83	
		1 014.4	0.28	$^{30}\mathrm{Si}(\mathrm{n},a)$	3	86	
²⁸ A1	2.24 m	1 778.9	1.00	²⁸ Si(n,p)	92	250	
			-	31P(n,a)	100	125	
²⁹ A1	6.52 m	1 273.3	0.94	²⁹ Si(n,p)	5	92	
38C1	37.18 m	2 167.5	0.55	$^{41}\mathrm{K}(\mathrm{n},a)$	7	35	
		1 642.4	0.40				
$^{41}\mathrm{Ar}$	1.82 h	1 293.6	0.99	$^{44}Ca(n,a)$	2	35	
				$^{41}{ m K(n,p)}$	7	74	
38K	7.71 m	2 166.8	1.00	$^{39}K(n,2n)$	93	5.1	
$^{44}\mathrm{K}$	22.15 m	1 156.9	0.58	44Ca(n,p)	2	42	
		2 151.3	0.23				
52V	3.76 m	1 433.9	1.00	$^{55}\mathrm{Mn}(\mathrm{n},\alpha)$	100	39	
				$^{52}Cr(n,p)$	84	110	
84mRb	20.40 m	247.9	0.65	85 Rb(n,2n)	72	640	
		215.4	0.37				
96 T) 1		463.7	0.32				
86mRb	1.02 m	556.1	0.98	87 Rb(n,2n)	28	930	
87mSr	2.81 h	388.4	0.89	88Sr(n,2n)	83	200	
137mBa	2.55 m	661.6	0.85	138 Ba(n,2n)	72	1250	

(i.e. 8 per cent) was taken, as this time was 3.2. X-ray fluorescence analysis not regularly checked. Fairly large errors therefore result in the abundances when short lived reaction products (eg. 137Ba) are considered. In the analysis based on very long lived activities (eg. 87mSr) rather large errors are due to the short ferent elements in the samples the KX-line irradiation-measurement sequence.

The following elements were detected in fast neutron activation analysis (NAA): (Na), Mg, Al, Si, K, Ca, Mn, Rb, Sr and Ba. Furthermore the presence of P is probable, but due to interfering activities was difficult to resolve unambiguously.

X-ray spectra resulting from excitation using Fe-55 and Am-241 sources are presented in Figures 4 and 5.

In calculating the abundances of difintensity was used. This intensity depends on the flux of the exciting radiation (I_O), the cross section for production of photoelectrons (τ) , the probability for deexcitation by X-rays ($\omega = \omega_K$) and on the weight fraction (W) of the fluorescent elements in the sample. The exciting as

Table 2. Relative number of atoms of elements and their ratios in sound tree ash sample (1) and decayed tree ash sample (5) normalised to equivalent dry weight.

Taulukko 2. Samaan kuivapainoon normitetut alkuaineiden suhteelliset määrät ja niiden suhde terveessä ja lahossa puussa.

Stable	Reaction used in	Relative number o	Ratio Suhde N(D)/N(S)	
isotope Alkuaine- isotooppi identification Ydinreaktio		Sound tree Terve puu N(S)		
$^{24}{ m Mg}$	(n,p)	18.3 ± 0.9	16.0 ± 0.4	0.87 ± 0.07
27A1	(n,a)	3.61 ± 0.16	0.155 ± 0.003	0.043 ± 0.003
27A1	(n,p)	3.5 ± 0.2	0.16 ± 0.02	1.146 ± 0.008
28Si, 31P	(n,p), (n,α)	21 ± 4	1.8 ± 0.4	0.09 ± 0.04
²⁹ Si	(n,p)	1.8 ± 0.2	0.05 ± 0.02	0.030 ± 0.016
³⁰ Si	(n,α)	1.20 ± 0.07	0.032 ± 0.005	0.027 ± 0.006
$^{39}\mathrm{K}$	(n,2n)	11.1 ± 1.0	21.9 ± 1.3	2.0 ± 0.3
$^{41}\mathrm{K}$	(n,a)	0.84 ± 0.20	1.75 ± 0.09	2.1 ± 0.6
44Ca	(n,p)	1.25 ± 0.16	0.35 ± 0.04	0.28 ± 0.07
55Mn	(n,α)	7.8 \pm 1.3	1.8 ± 0.3	0.23 ± 0.08
85Rb	(n,2n)	0.022 ± 0.007	0.040 ± 0.006	1.8 ± 0.5
88Sr	(n,2n)	0.18 ± 0.05	0.076 ± 0.012	0.42 ± 0.20
¹³⁸ Ba	(n,2n)	0.27 ± 0.06	0.08 ± 0.02	0.29 ± 0.13

Note: Reaction ²³Na(n,p)²³Ne is not included here because of the short half-life of the reaction product. Error values shown are due to statistical and systematic errors in the measurements of only one sample, the sound tree sample (1) and the decayed tree sample (5), respectively.

Huomautus: Natriumin tunnistamiseen on käytetty reaktiota 23 Na(n,p) 23 Ne. Virhearviot sisältävät statistiset ja systemaattiset mittausvirheet.

absorptive processes. The X-ray intensity is therefore decreased by a factor F, the attenuation factor, given by

$$F = \frac{1 - e^{-(\mu + \mu') m}}{(\mu + \mu') m}$$

where μ and μ ' are the mass attenuation coefficients for exciting and fluorescent radiation, respectively, and m is the mass of the sample (g/cm²).

Fluorescent intensity Ii for a homogeneous sample can now be expressed in the form (Räisänen et al. 1978).

$$I_{j} = \frac{I_{o}G\tau wW}{\mu + \mu'} (1 - e^{-(\mu + \mu')m})^{\mu},$$

well as the fluorescent radiation are in- where the geometry factor G takes into fluenced by the sample matter, due to account the differences in experimental arrangements. From this equation the amount of an element j, $m_i = W \cdot m$, in the sample can be determined. The values of ω , τ for different elements can be found in the literature (Bambynek et al. 1972, Veigele 1973, FREUND 1975).

If the factor $(\mu + \mu')$ m is ≥ 4 in the intensity equation, the sample is said to be thick, and total absorption is at least 75 per cent. If, on the other hand, total absorption is less than 5 per cent, the sample is said to be thin with respect to that radiation. The thin sample criterion is in the present work true only for BaKX-rays when using Am-241 excitation. The thick sample criterion is correspondingly fulfilled only for KX-rays of Mn or of any lighter element. The elements in between Mn and

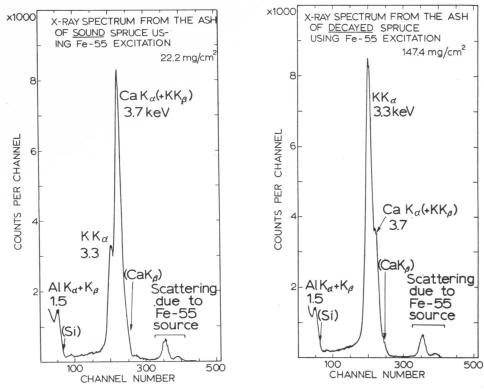


Figure 4. X-ray spectra from the ash of sound and decayed spruce samples obtained by XRF method. Fe-55 excitation.

Kuva 4. Röntgenspektrit terveestä (vasemmalla) ja lahosta (oikealla) kuusinäytteestä röntgenfluoresenssimenetelmällä. Fe-55 viritys.

Table 3. Attenuation factor F using Fe-55 excitation. Taulukko 3. Vaimennuskertoimen F arvot Fe-55 virityksessä.

Sample — <i>Näyte</i>	Mass	Fluorescent radiation Röntgensäteily			
Origin — Alkuperä	Massa (mg/cm²)	$\begin{array}{c} \text{Ca} \\ \text{E}_{\text{KX}} = 3.7 \text{ keV} \end{array}$	$\mathrm{E_{KX}} = 4.8~\mathrm{keV}$		
Sound (1) — <i>Terve</i>	22.2 147.4	F = 0.278 F = 0.043	F = 0.402 F = 0.068		

Ba fall within these extreme cases, and lations are based on the mass absorption must be considered with more care.

The attenuation factors F for Am-241 excitation, as applied to the samples studied in this work, are illustrated in Figure 6 by

coefficients for the most probable tree ash sample compositions.

When one uses the Fe-55 excitation, the theoretical »thick sample» criterion is always the solid curves drawn through the points fulfilled. The values of the attenuation calculated for some elements. These calcu- factors for the fluorescent radiations of Ca

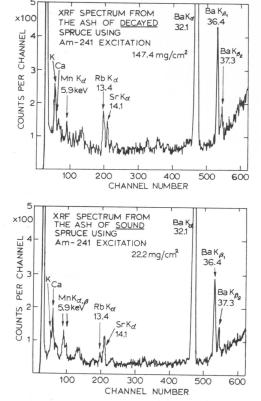


Figure 5. X-ray spectra from the ash of sound and decayed spruce samples obtained by XRF method. Am-241 excitation.

Kuva 5. Röntgenspektrit terveestä (alla) ja lahosta (yllä) kuusinäytteestä röntgenfluoresenssimenetelmällä. Am-241 viritys.

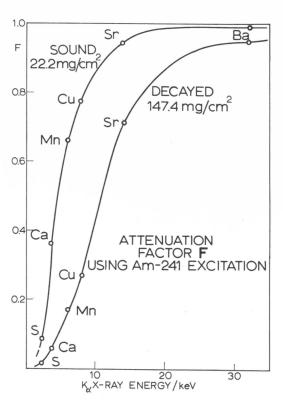


Figure 6. Attenuation factor using Am-241 excitation.

Kuva 6. Vaimennuskerroin Am-241 viritystd käytettäessä.

Table 4. The amounts of different elements in sound (1) and decayed (5) tree ash samples. Taulukko 4. Alkuaineiden pitoisuudet terveessä ja lahossa kuusinäytteessä.

	55 Excitatio Fe-55 viritys	n	Am-241 Excitation Am-241 viritys					
Element Alkuaine	K (%)	Ca (%)	Mn (%)	Rb (ppm)	Sr (ppm)	Ba (ppm)		
Sound (1) Terve	6.6 ± 0.7	7.5 ± 0.8	0.9 ±0.3	310 ± 50	970 ± 120	3700 ± 100		
Decayed (5) Laho	13.2 ± 1.3	2.7 ± 0.3	0.3 ±0.1	350 ± 110	190±75	790± 65		
Element Alkuaine	K	Ca	Mn	Rb	Sr	Ва		
Decayed — sound Laho — Terve	2.0 ± 0.3	0.36 ± 0.05	0.33 ± 0.15	1.1 ± 0.4	0.20 ± 0.08	0.21 ± 0.02		

and V excited by the Fe-55 radiation are 3.3. Comparison of the results obtained given in Table 3.

The quantitative results of the X-ray fluorescence analysis for the samples (1), sound tree, and (5), decayed tree, are are relatively consistent with each other presented in Table 4. The error limits were calculated by taking into account uncertainties in standardisation, in geometry and in absorption correction. Statistical errors of the peak areas, as given by the computer program VIPUNEN, are included. Differences in absorption correction as various thicknesses and compositions of sample (due to developments in the ashing technique) were also considered.

The quantitative values are based on single element standards which are normally used in our laboratory for thin sample determinations. Systematic errors may thus exist, but on the relative abundances (at least of neighouring elements) and on the decayed to sound ratio this will have only is much faster and easier to accomplish a minor effect.

The elements K, Ca, Mn, Rb, Sr, and Ba were found to be present in the ashed tree X-ray fluorescence analysis (XRF). In addition, trace amounts of the elements Al, Ti and probably Cr were seen. Short investigation periods (4 min) and relatively thick samples (tenths of mg/cm²) prevented

with NAA and XRF methods

The results obtained by NAA and XRF in that which concerns the number of elements found and their relative amounts. Matrix effects which are of importance in XRF applied on thick sample studies can affect systematic differences between the NAA and XRF results. Both methods reveal a general diminishing in most elemental concentrations in going from a sound tree to a decayed one. The striking exceptions, the elements K (potassium) and Rb (rubidium), whose concentrations increase, were also similarly obtained by both methods.

In both investigations roughly equal time sequences were employed in the analysis. Experimentally, routine analysis with XRF than with NAA. Other factors. however, limit the usefulness of XRF.

Of the main elemental components in samples, according to the results of the Norway spruce (Jalava 1952), i.e. calcium, manganese, potassium, magnesium, silicon, sulphur, phosphorus, and sodium, the presence of all elements other than sulphur and phosphorus was distinctly revealed in fast neutron activation analysis. In X-ray clear detection of other possible elements. fluorescence analysis, the lightest elements

Table 5. Relative amounts of potassium and calcium in sound (1) and decayed (5) tree ash samples by different methods.

Taulukko 5. Kaliumin ja kalsiumin suhteelliset määrät terveessä ja lahossa kuusinäytteessä eri menetelmillä.

		NAA	7
Sound (1) — Terve	K Ca	12.0 ± 1.4 63 ± 8	$\frac{(K)}{(Ca)} = 0.19 \pm 0.04$
Decayed (5) — Laho	K Ca	24.3 ± 1.0 17 ± 2	$\frac{(K)}{(Ca)} = 1.4 \pm 0.2$
		XRF	* 12
Sound (1) — Terve	K Ca	6.6 ± 0.7 7.5 ± 0.8	$\frac{(K)}{(Ca)} = 0.9 \pm 0.2$
Decayed (5) - Laho	K Ca	$13.2\pm1.3 \\ 2.7\pm0.3$	$\frac{(K)}{(Ca)} = 4.9 \pm 1.0$

sodium and magnesium cannot be observed due to severe absorption effects, as mentioned earlier; the other elemental components listed above are observable, but only K and Ca were detected in greater can be chosen to illustrate the drastic amounts.

Some elements not included in the main list were also detected. For example, aluminum was observed with NAA and trace elements rubidium, strontium and barium were observed with both NAA and XRF. The amounts of the other elements above fluorine (Z = 9) except those mentioned above seem to be low in the wood samples reported in this work. This same feature was found characteristic also in the samples

originating in southern Finland for which only preliminary study was applied (JARTTI 1978).

The elements K (Z = 19) and Ca (Z = 20) differences in the amounts of some elements observed in the samples studied here. In sound tree samples the element Ca dominates, whereas in decayed tree samples the amount of K clearly exceeds that of Ca. The ratio of the amounts of these elements, i.e. the potassium to calcium ratio K/Ca, is presented in Table 5. Both methods clearly produce the apparent increase in this

4. DISCUSSION

The distribution of the elements found in here to be quantitatively increased as this investigation can be illustrated in terms of the periodic table (Figure 7).

based on studies on only few samples preliminary investigation of samples from other part of Finland showed quite similar results. The results herein may thus be used to point out some effects of more general importance. Both elements found

I	п											${\rm 1\!\!\!\!I}$	V	∇	V	VII	VIII /0
н																	Не
Li	Ве	200										В	С	N	0	F	Ne
Na	Mg			7								Al	Si	Р	S	CI	Ar
K	Ca	Sc	Ti	٧	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	12	Υ	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	J	Xe
Cs	Ва	La	Hf	Та	w	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Ро	At	Rn
Fr	Ra	Ac															

THE PERIODIC TABLE OF ELEMENTS

Fig. 7. The distribution of the elements found in the investigations of the ash of sound and decayed spruce samples by XRF and NAA methods. Elements found are shown by thick frames. Kuva 7. Terveen ja lahon kuusinäytteen tutkimuksissa havaittujen alkuaineiden sijainti jaksollisessa järjestelmässä.

comparing a sound tree to a decayed one, namely, potassium and rubidium, belong Although the results presented here are to the chemical group I in the periodic system. Thus the increase of minerals containing the group I alkali metals in decaying tree might indicate the advancement of the decay. This increase can hypothetically be thought to arise from ionic exchange processes which are correlated with such other factors as temperature and humidity. The enrichment of alkali minerals in a tree may also be due to a decrease of organic matter in the decayed region of the tree, but then the noticeable decrease of other minerals requires some other explanation.

> The results show, that the amounts of potassium and calcium, or their ratio, might serve as indication of whether the tree is decaying or not. Besides the K/Ca ratio, also other ratios might be considered for this purpose. Adopting potassium for the element of comparison and using the results obtained with the NAA method the following values can be found:

Ratio In	sound tree	In decayed tree
K/Ca	0.19	1.4
K/A1	3.4	154
K/Si	3.2	22

If the largest possible change in going carried out in field conditions, therefore a from sound to decayed tree is preferred, the K/Al ratio may thus be thought to be used instead of the K/Ca ratio: the increase is six times that obtained for the K/Ca ratio. The chemical properties of aluminum and silicon differ, however, from those of calcium, which is moreover a more probable element in respect of ionic exchange processes.

If the internal decay of a spruce tree is caused by Fomes Annosus, as is often the case, the decay generally starts in the roots and advances upwards through the trunk even to the top of the tree. The final stage is usually a hollow tree. If one wishes to investigate the condition of a tree in situ, 2 167 keV gamma peak. If the energy the NAA method should be recommended. because the attenuation of X-rays already in the bark of the tree makes the XRF method incapable of probing the centre of the trunk, where the decay is actually taking place.

Experiments were conducted during this work also with unashed spruce wood samples using the NAA method, and those showed that e.g. potassium and calcium are advancement of decay in a tree in situ. still detectable, which implies that the results obtained in this work for tree ash countered due to the water content of a are to some extent applicable also to ungrowing tree, as water causes interfering burned dry treematter.

Inspection of the growing trees must be

small unit consisting of a miniature neutron generator and field detecting instruments should be employed. For gamma ray counting, NaI(Tl) scintillator detectors instead of semiconductor detectors can then be employed, since these scintillators are easier to handle, cheaper and more field resistant. They are also very efficient and selective enough to reveal the K and Ca contents of a tree. For instance, the determination of K is favoured by spectrosopic data of the spruce samples. The most intense radioactivity produced in potassium with short irradiation times is that due to 39K (and to 41K) with the intense range in the data registering is biased to 1900 keV and above, the K-activity is seen to form the main component. Small interferences originating from Mg and Al can, if necessary, be eliminated by other discriminator settings. As the element Ca can similarly be analysed, these delicate, but simple, measurements could perhaps, with appropriate calibrations, estimate the Serious problems, however, might be enabsorption.

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SELOSTE:

TERVEEN JA LAHON KUUSEN HIVENAINEANALYYSEJÄ RÖNTGEN-FLUORESENSSI- JA NEUTRONIAKTIVOINTIMENETELMILLÄ

Tutkimuksessa on selvitetty neutroniaktivointianalyysin (NAA) ja röntgenfluoresenssianalyysin (XRF) käyttöä kuusipuun lahoisuuden mittaamiseen. Pääosa tutkituista puunäytteistä oli peräisin kuusimetsiköstä Virroilta, Keski-Suomesta. Näytteet poltettiin tuhkaksi ja tuhka jauhettiin.

NAA-analyysissä säteilytettiin n. 0,5 g:n tuhkanäytteitä nopeilla 14 MeV:n neutroneilla 15 minuutin ajan, minka jälkeen syntynyt gammasäteily mitattiin koaksiaalisella 43 cm³:n (GeLi) puolijohdeilmaisimella. Säteilytykset suoritettiin Helsingin yliopiston fysiikan laitoksen neutronigenaattorilaboratoriossa. Mittausajat vaihtelivat 5 ja 15 min välillä. Tyypilliset mittauksissa havaitut spektrit terveestä ja lahosta puunäytteestä on esitetty kuvassa 3. Alkuaineiden tunnistamisessa käytetyt tiedot on luetteloitu taulukossa I. Neutroniaktivointianalyysissä löydettiin tutkittujen puiden tuhkasta seuraavia alkuaineita: (Na), Mg, Al, Si, K, Ca, Mn, Rb, Sr ja Ba. Näiden alkuaineiden suhteelliset osuudet terveessä ja lahossa puussa on esitetty taulukossa II.

Röntgenfluorenssianalyysiä varten puristettiin jauhetusta tuhkasta n. 1 mm:n paksuisia tabletteja. Analyysissä käytetty energiadispersiivinen laitteisto, joka on rakennettu Helsingin yliopiston fysiikan laitoksella, on esitetty kuvassa 2. Röntgensäteilyn virittämiseen käytettiin radioaktiivisia isotooppeja Fe-55, Cd-109 ja Am-241. Säteilyn ilmaisu suoritettiin Ge-röntgenilmaisimella, jonka energian erotuskyky oli noin 150 eV mangaanin röntgenenergialle. Röntgenspektrit Fe-55 ja Am-

241 virityksillä on esitetty kuvissa 4 ja 5. Röntgenfluoresenssianalyysin tulosten perusteella puun tuhkassa on seuraavia alkuaineita: K, Ca, Mn, Rb, Sr ja Ba. Näiden alkuaineiden prosentuaaliset osuudet terveessä ja lahossa puussa on esitetty taulukossa IV.

Tuloksia vertailtaessa havaitaan eri menetelmillä saatujen tulosten olevan sopusoinnussa keskenään. Molemmilla menetelmillä voitiin selvästi todeta samansuuntaiset alkuainekonsentraatioiden muutokset siirryttäessä terveestä puusta lahoon puuhun. Kun pitoisuudet yleensä pienenevät muille alkuaineille, muodostavat jaksollisen järjestelmän ryhmän I alkuaineet K ja Rb poikkeuksen niiden määrien lisääntyessä. Pitoisuuksien suhteellista muutosta on pyritty selvittämään vertaamalla kalium/kalsium -suhdetta sekä terveessä että lahossa puussa (taulukko V). K/Ca -suhteen voidaan todeta voimakkaasti suurenevan puun lahotessa. Näin ollen saattaisi olla mahdollista käyttää K/Ca-suhdetta puun lahonneisuusasteen määrittämiseen.

Kun esimerkiksi tyvilahon eteneminen halutaan määrittää kasvavasta puusta, on NAA-menetelmä suositeltavampi kuin XRF-menetelmä, sillä röntgensäteily vaimenee jo puun kuorikerroksessa. NAA-menetelmästä on mahdollista kehittää kenttäkäyttöön soveltuva versio; laitteiston muodostaisivat pienikokoinen kannettava neutronilähde ja tuikeilmaisin lisälaitteineen. Ilmaisu olisi mahdollista välittömästi mittaushetkellä.