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DETERMINATION OF TRACE ELEMENTS IN ANNUAL RINGS OF SPRUCE

Concentrations of seventeen elements in annual rings of spruce (*Picea abies*) were measured by the ICP-AES method. Samples were taken from trees growing in the Stołowe Mountains National Park, south-west Poland. The age of trees ranged from 27 to 76 years. The dependence of measurement accuracy on a mass of sample was investigated. The correlations between elements were discussed.

1. INTRODUCTION

Trace analysis of wood samples is a complex and difficult task. Wood samples can be considered as strongly unhomogeneous due to the differences between young and mature wood, as well as the differences in miscellaneous types of wood cells of various composition, shape and size. Furthermore the elements, which mainly interest environmental investigators, occur in trees at very low levels [1].

Despite the aforementioned difficulties a growing interest in a trace analysis of inorganic components of tree samples has been aroused since the eighties. Parts of trees (bark, leaves) can serve as bioindicators in environmental and geochemical investigations [2]–[4]. Attention paid to pollution episodes or ecological characteristics of sites results in advancing elemental analysis of annual rings of tree (see, e.g. [5]–[8]). Some papers have been devoted to the studies of seasonal variations in metal concentrations in annual rings [9]. In spite of the attention given to such studies, only few elements such as lead, cadmium, copper, iron, zinc, potassium and calcium have often been investigated [5], [6]. Sulphur, phosphorus, nickel, sodium and barium can serve as examples of the elements rarely studied. Often a small mass of an annual ring group sample is analysed only once. Furthermore the quality of measurements is rarely verified by a certified reference material analysis.

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This paper has been devoted to the analysis of a possibly wide range of elements in annual rings of spruce from the Stołowe Mountains National Park, Poland, by means of inductively coupled plasma atomic emission spectrometry. The accuracy of results was verified using a certified reference material analysis. The relation between the mass of a sample and the accuracy of measurements was also established. The correlation between the element changes were investigated.

2. MATERIAL AND METHODS

2.1. SAMPLES

Wood samples of seven spruce trees (*Picea abies*) from the Stołowe Mountains National Park, south-west of Poland, were collected. The age of the trees analysed ranged between 27 and 76 years. Bark and phloem were carefully removed and the samples were divided into the groups of rings (each five-year old). Because bark and phloem could be contaminated, an outer ring was removed.

2.2. DIGESTION PROCEDURE

Each group of the annual rings was divided into three parts, then every part was digested and analysed separately. The digestion method described by FERRETTI [7] was used. About 1 gram of a sample – exactly weighed – was mixed with 5 cm^3 of nitric acid (65%) in a glass beaker. Then the beaker was covered with glass and allowed to stand overnight. Next, another 5 cm^3 of nitric acid was added and the mixture was heated for 60 min in such a way that the rise of temperature was slow. When the solution temperature reached 100 °C, the increase in heating was stopped. Such conditions were kept for few hours until a clear solution was obtained. After digestion a sample solution (about 4 cm^3) was filled up to the volume of 25 cm^3 with deionized water in a glass flask. Blank sample solutions were prepared in the same way as the wood sample solutions.

The same digestion method was used for preparation of wood and reference material samples.

2.3. REAGENTS AND APPARATUS

Chemicals of analytical grade and deionized water (18.3 MΩ · cm) were used in all solutions. Multielemental solutions of the standards applied in analysis were prepared from the ICP-SPEX standard solutions. Measurements of the element concentrations were performed using the Jobin Yvon sequential inductivly coupled plasma atomic emission spectrometer (ICP-AES JY38S). Experimental conditions were reported elsewhere [10].

3. RESULTS AND DISCUSSION

3.1. CERTIFIED REFERENCE MATERIAL ANALYSIS

Lack of wood certified reference materials inclined us to make use of the IAEA V5-cotton cellulose certified material in order to test the accuracy of measurements. Such a material was also used in earlier studies devoted to annual ring analysis [8]. Six independent samples of the cellulose were separately digested and subjected to measurements. The element concentrations obtained are shown and compared with the certified values in table 1. Confidence limits were calculated at the significance level of 0.05. A good agreement between measured and certified values has been obtained.

Table 1

Analysis of a certified reference material IAEA V5-cotton cellulose. Confidence level is 0.05 ($N = 6$)

Elements	Determined value [µg/g]			Certified value [µg/g]		
	Mean	Confidence limits		Mean	Confidence limits	
Al	25	24	26	44*	13*	53*
Ba	9.1	9.0	9.2	9	6	12
Ca	214	210	218	240	220	260
Cr	0.12	0.03	0.21	0.11	0.08	0.14
Cu	0.60	0.52	0.68	0.59	0.47	0.94
Fe	11.7	10.8	12.7	11*	7*	15*
Mg	60	58	63	53	46	67
Mn	0.17	0.16	0.19	0.15	0.12	0.21
Na	61	58	64	56	49	64
Sr	0.60	0.56	0.63	0.65	0.54	0.96

* Information values.

3.2. RELATION BETWEEN MASS OF WOOD SAMPLE AND MEASUREMENT ACCURACY

Often in annual ring analysis, samples are collected using increment borer. Such a procedure is the least damaging to trees, but it involves a serious disadvantage, i.e. very small sample mass which is well below 0.2 g in the case of one group of annual rings. Due to a complex structure of wood, such a small mass of samples can cause unreproducible results. In order to establish a relation between the mass of a sample and the accuracy of trace element measurements, the following experiment was carried out. One sample of spruce tree (about 10 gram) was divided into very small pieces, less than 10 mm × 1 mm × 1 mm, and carefully mixed. From such a sample three groups of six samples were taken. Masses of the samples in groups were 0.5 g, 1.0 g and 2.0 g. Each sample exactly weighed was digested and subjected to measurements separately. The accuracy of measuring the concentrations of selected elements is presented in figure 1.

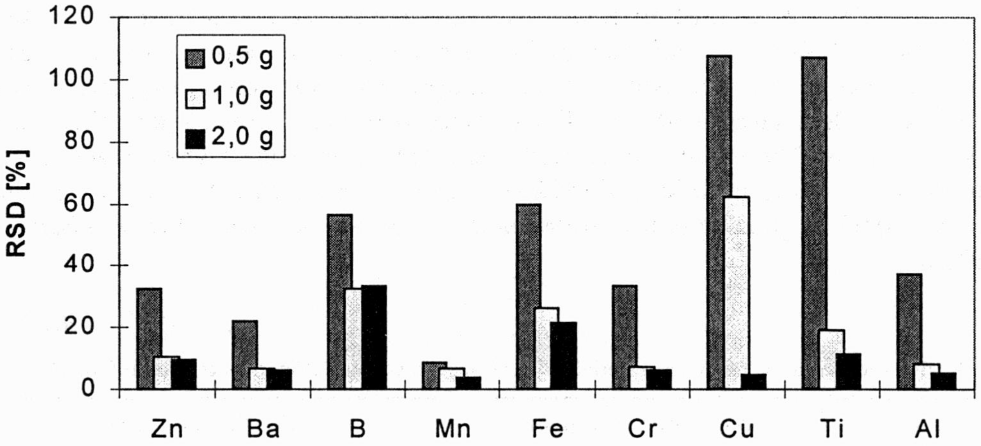

Fig. 1. Dependence of the accuracy of analytical measurements on the sample mass

As can be seen, 0.5 g mass of the sample results in a poor accuracy of the concentration measurements, while 1.0 g mass of the sample allows more accurate measurement. Subsequent increase in a sample mass improves the quality of analytical results only for copper. In the case of other elements investigated here, an inessential change in accuracy of measurement was observed. Therefore in all subsequent experiments performed, the sample of 1 g mass was taken.

3.3. ELEMENTAL ANALYSIS OF ANNUAL RINGS

The concentrations of seventeen elements in the groups of annual rings were measured using the ICP-AES method. The five-year old annual rings were analysed in triplicate for each tree under investigation. The ranges of element concentrations measured in all seven trees are shown in table 2.

In all wood samples in the youngest groups of annual rings (since 1989), the concentrations of chromium, cadmium and lead were found to be below their detection limits. The concentration of cadmium could be measured in samples of four trees, and that of lead in the samples of three trees. The concentration of chromium above its limit of detection was measured in the samples of three trees. All samples with measurable chromium content were dated from 1975 to 1989. The concentrations of nickel, cobalt and titanium in all tree samples were below the limits of detection, i.e. 0.62, 0.40 and 0.20 μg/g, respectively.

Table 2

Ranges of element concentrations [μg/g] measured in the trees analysed

	Al	B	Ba	Cd	Cr	Cu	Fe	Mn	P
Min	2.1	1.0	4.2	< 0.25	< 0.37	0.4	1.7	13	1.4
Max	8.8	15	15	0.28	0.41	6.0	23	120	110
	Pb	**S**	**Zn**	**Sr**	**Ca**	**K**	**Mg**	**Na**	
Min	< 2.4	130	6.1	1.9	380	44	43	4.0	
Max	5.1	270	16	3.5	780	630	110	61	

From each of three trees six samples were taken and examined for the level of sulphur. The concentrations of this element reached 220, 137 and 129 μg/g with a standard deviation of 27, 13 and 6.0, respectively.

Results of the annual ring analysis of the oldest tree are reported in tables 3a, b, c.

Table 3a

Concentrations of elements [μg/g] in groups of annual rings for 76 years-old spruce

Years	Al		B		Ba		Cu		Fe	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1990–1994	3.0	0.8	2.35	0.16	2.6	0.3	1.10	0.00	5.21	0.77
1985–1989	3.2	1.8	3.75	2.09	7.1	1.0	0.84	0.01	4.99	1.70
1980–1984	3.2	0.9	4.77	0.20	6.0	2.4	1.15	0.06	3.83	0.98
1975–1979	3.1	1.6	5.33	0.75	7.1	1.1	0.39	0.03	2.64	0.64
1970–1974	3.9	0.4	6.03	0.26	4.2	2.0	0.69	0.02	2.12	0.46
1965–1969	4.2	2.8	8.93	0.22	5.7	1.3	0.85	0.01	5.86	3.30
1960–1964	3.6	0.3	4.19	0.13	5.1	2.1	0.74	0.02	2.31	0.24
1955–1959	2.7	0.5	3.47	0.14	4.6	0.7	0.73	0.01	2.86	0.45
1950–1954	3.3	0.4	4.37	0.40	5.6	0.4	1.29	0.02	3.02	0.43
1945–1949	3.0	1.2	3.19	0.25	6.7	2.9	0.87	0.22	4.03	3.44
1940–1944	2.4	0.2	3.88	0.63	9.1	0.6	1.00	0.01	1.70	0.16
1935–1939	3.3	1.0	7.00	0.24	9.3	1.9	1.31	0.06	2.21	0.89
1930–1934	3.2	0.5	3.03	0.87	9.7	0.6	0.84	0.05	5.08	3.18
1925–1929	3.1	0.4	3.91	0.16	10.5	1.1	1.36	0.00	4.99	1.75
1920–1924	3.6	0.3	6.30	0.37	12.0	2.4	1.66	0.01	5.21	0.69

Table 3b

Concentrations of elements [μg/g] in groups of annual rings of spruce

Years	Mn		P		Pb		Sr		Zn	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1990–1994	15.9	1.0	76.8	1.0	*		1.90	0.05	8.20	1.04
1985–1989	15.3	0.6	36.6	4.5	*		3.51	0.40	6.13	1.28
1980–1984	15.7	0.1	31.1	3.5	*		3.25	0.40	8.13	1.31
1975–1979	19.4	1.1	51.3	2.4	*		3.43	0.42	9.36	0.16
1970–1974	20.1	1.4	52.2	2.0	4.4	0.2	2.41	0.66	11.71	2.33
1965–1969	17.4	1.3	37.2	1.8	*		2.86	0.07	8.10	1.88
1960–1964	17.6	1.1	22.3	4.0	*		3.08	0.82	10.72	4.31
1955–1959	19.7	0.6	5.7	2.0	*		2.71	0.54	11.98	2.09
1950–1954	21.1	1.4	5.3	1.6	*		2.63	0.43	11.87	1.55
1945–1949	22.3	0.0	1.6	0.8	*		2.46	0.80	8.71	0.95
1940–1944	23.9	0.4	1.7	0.3	*		3.04	0.08	8.72	0.24
1935–1939	25.5	0.7	1.4	0.6	*		2.85	0.10	9.93	0.65
1930–1934	23.6	1.4	8.2	0.9	*		2.85	0.15	8.73	0.84
1925–1929	23.7	1.5	7.9	2.2	*		2.84	0.14	9.33	0.30
1920–1924	33.7	1.9	9.2	1.8	*		3.31	0.12	13.26	0.94

* Below 2.42 μg/g.

Table 3c

Concentrations of elements [μg/g] in groups of annual rings of spruce

Years	Ca		K		Mg		Na	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1990–1994	452	25	367	29	65.7	1.91	41.0	5.9
1985–1989	576	22	52.3	34	48.5	0.21	31.4	2.7
1980–1984	561	18	71.4	30	49.9	2.8	19.9	5.4
1975–1979	645	17	66.0	7.6	43.1	3.4	32.3	7.8
1970–1974	624	5.0	89.4	13	68.6	0.21	27.1	7.6
1965–1969	545	105	81.3	7.7	68.8	1.7	22.9	0.1
1960–1964	601	6.5	106	32	77.6	1.9	28.9	7.0
1955–1959	625	24	174	15	105	0.79	22.9	4.3
1950–1954	655	39	252	38	93.9	3.8	22.5	3.3
1945–1949	564	181	187	51	74.4	1.2	21.8	4.2
1940–1944	665	12	257	45	82.8	5.8	19.4	4.2
1935–1939	637	21	317	16	88.3	4.8	20.5	2.8
1930–1934	595	29	443	208	84.4	0.51	23.0	2.9
1925–1929	612	24	339	34	86.0	2.6	30.2	8.3
1920–1924	785	47	414	146	108	4.2	33.5	6.7

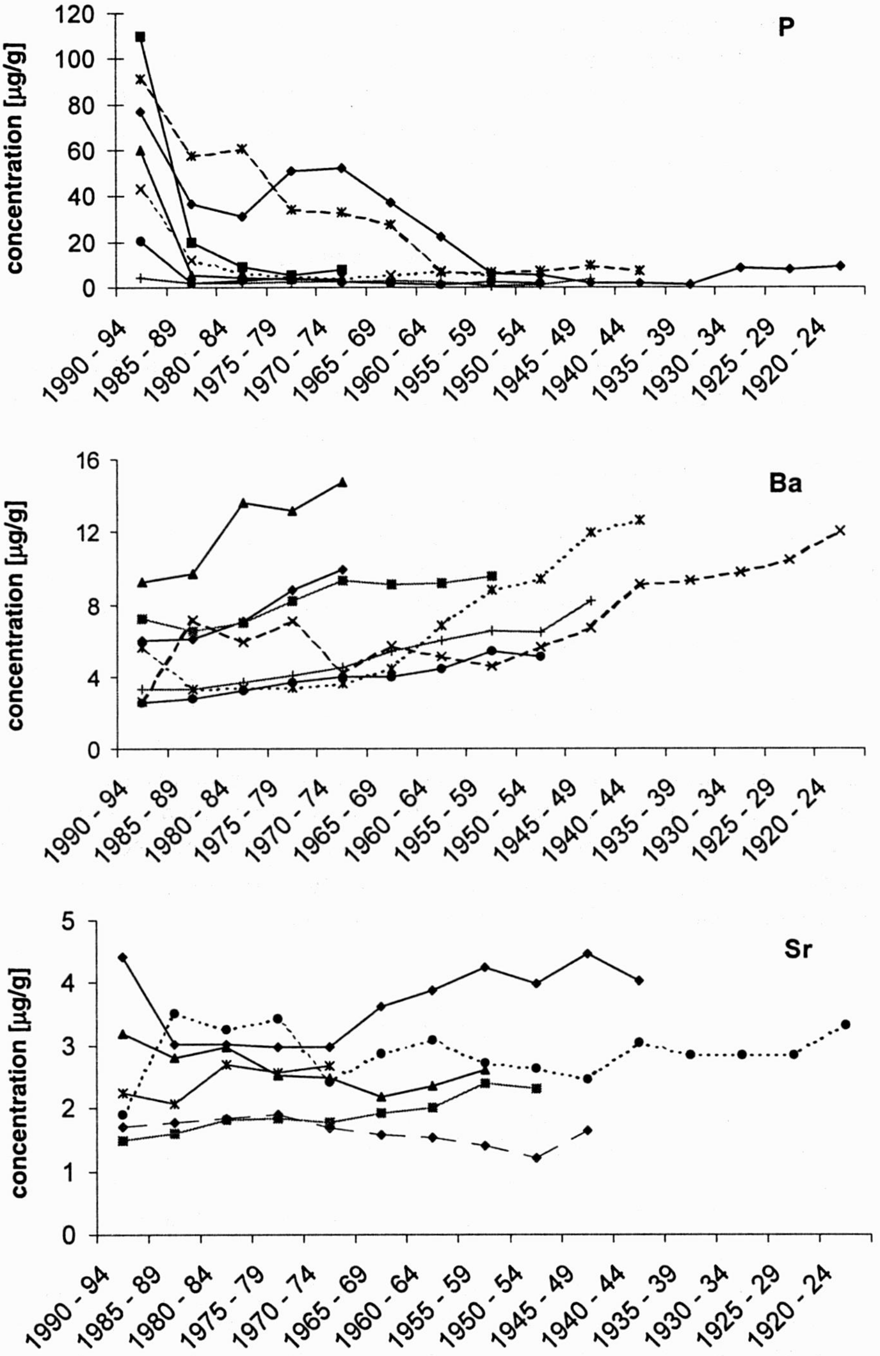

Fig. 2. Concentrations of phosphorus, barium and strontium versus age of annual ring groups

In all trees examined, the concentration of barium increased with the age of an annual ring, while the concentration of phosphorus decreased with the age of annual rings. The concentration of strontium in the groups of annual rings can be considered as constant in all trees (figure 2). Generally the concentrations of other elements in annual rings did not show any constant tends.

3.4. CORRELATION BETWEEN ELEMENTS

In order to assess the relations between each pair of elements, the Pearson correlation coefficient was calculated for all of them in each tree. A significant correlation between zinc and magnesium concentrations was found. For the data presented in table 3a, b, c the correlation coefficient amounted to 0.83 ($N = 15$). Only in one of the seven trees no such a correlation was found.

The Pearson test allowed us to check whether there was a correlation between the concentrations of magnesium and zinc in the tree wood investigated by other authors. In the wood samples of both spruce and maple from Canada [8], the concentrations of these two elements were highly correlated – the correlation coefficients were respectively equal to 0.64 ($N = 19$) and 0.75 ($N = 12$). For the trees from Italy [7] a strong positive correlation was found for spruce ($r = 0.85$ for $N = 12$), but the was no correlation in the case of stone pine ($r = -0.19$ for $N = 7$).

The concentrations of elements measured in the spruce samples are, with the exception of phosphorus, in good agreement with the results obtained by other researchers [8], [11], [12]. The highest phosphorous concentration reported in the spruce wood samples was 70 μg/g [12], while in some samples from the Stołowe Mountains National Park concentration of this element exceeded 90 μg/g.

4. SUMMARY

The concentrations of seventeen elements were measured in the annual rings of spruces from the Stołowe Mountains National Park. In wood samples, the concentrations of such rarely measured elements as boron, phosphorus and strontium were determined. The correlation between zinc and magnesium concentrations in annual ring is reported for the first time.

The dependence of the sample mass on the accuracy of trace elements measurements proves that the sample mass affects the reliability of the concentrations determined. Therefore the way the wood is sampled is of a prime importance.

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ANALIZA PIERWIASTKÓW ŚLADOWYCH W SŁOJACH ŚWIERKA

Oznaczono stężenia siedemnastu pierwiastków w słojach świerka (*Picea abies*) za pomocą ICP-AES. Próbki drewna pochodziły z Parku Narodowego Gór Stołowych. Wiek badanych drzew mieścił się w przedziale 27–76 lat. Zbadano zależność precyzji pomiarów od masy próbki. Określono korelacje występujące między badanymi pierwiastkami.