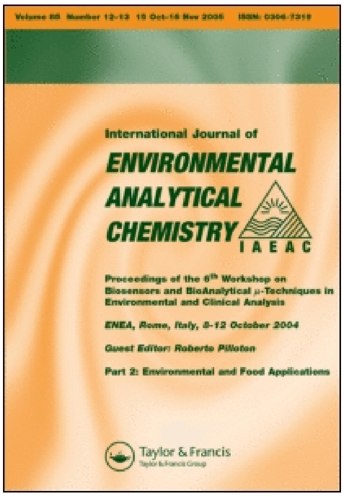

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MULTIELEMENTAL ANALYSIS OF YEW, PINE AND SPRUCE NEEDLES BY ICP-AES

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Concentrations of 22 trace and nutritional elements in yew, pine and spruce needles collected from urban and industrial areas were determined by inductively coupled plasma atomic emission spectrometry. Dependence of concentrations of trace elements in conifers species on sampling site was investigated. Various procedures of sample digestion (different acids, conventional hot plate and microwave digestion methods, dry ashing) were examined and discussed.

Keywords: Trace and nutritional elements; multielemental analysis; ICP-AES; yew; pine; spruce needles

INTRODUCTION

Heavy metals inputs to the biosphere from anthropogenic activities are increasing. Metals enter the biological cycle through the roots and leaves of plants and are enriched in various plant organs. They can directly affect plant growth and an excess dietary intake of contaminated plants is dangerous for the health of humans and animals. The chemical composition of plants is related to the elemental composition of the soil and the contamination of the plant surface indicates the presence of noxious environmental contaminants in ambient air. Surface contamination is ascribed to aerosol deposition[1].

One of the methods of environmental monitoring is assessment of the pollution grounds on chemical composition of plants. For biomonitoring are used: mosses, lichen, grass, cultivated plants, deciduous plants and conifers. Different tissues of trees such as wood, bark, shoots, buds, cones and needles have been analysed.

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Among conifers Norway spruce *(Picea abies)* [2–19] and Scots pine *(Pinus sylvestris)* [4,17,20–23] have most often been investigated. Tissues of black pine, loblolly pine, white spruce, red spruce, black spruce, Fraster fir and silver fir [11,24,25, 27–31] have been also studied. Some published papers have been devoted to chemical composition of epicultural waxes and dew from the needles [2,3,5,7,9,32 and 33]. Sampling areas were very different. Samples were collected from open territories [2,3,5,7,8,9,12,16,17], industrial districts, national parks and mountain forests [6,11, 22,24,29,31] and small areas located around industrial cites, steel mills or generating stations [4,20,27,28]. Nutritive elements (Ca, Mg, K, Na and P), heavy metals (mainly: Fe, Cd, Cu, Pb and Zn) and non-metals (S, As, Br and I) have been usually determined. Concentrations of rare-earth elements have also been measured. The INAA [2,3,5,7,9,12,24,30,34], AAS [6,16,22,24,25,31,35,36,37], XRF [8,17], ICP-MS [11] and ICP-AES [7,11,17,20,22,28,29,36,38,39] methods have been employed for determination of elements in needles. Needle samples have been prepared for measurements using as a rule wet digestion method. Microwave-assisted method, pressurised decomposition in Teflon bombs and conventional hot-plate digestion in open vessels has been employed. Usually samples are digested in nitric acid [11,36,37,38], nitric acid and hydrogen peroxide [17], nitric acid and perchloric acid [20,28], nitric acid and hydrochloric acid [31,39], nitric acid and sulphuric acid [31] mixtures. Comparison and evaluation of various digestion procedures was performed for some biological and environmental samples, but there is a lack of such a studies for foliage.

The aim of this work was the analysis of trace and nutritional elements in needle samples of yew (not studied so far), pine and spruce from different sites. Various digestion procedures for needle samples were examined and evaluated. The ICP-AES method was applied for measuring element concentrations.

EXPERIMENTAL

Sampling

Sampling of yew (*Taxus boccata*), pine (*Pinus sylvestris*) and spruce (*Picea abies* and *Picea galuca*) needles was carried out in November and December in four locations in Lower Silesia (Poland) Wrocław (a city – 1), Oława (an industrial town – 2 and 3) and Siechnice (a village 4 -). At each site samples were taken from 3 to12 trees (depending on number of trees growing in selected location) by cutting branches from the middle of the crown, as described in other studies (see e.g. refs. 7, 8, 10, 12 and 16).

Sample pre-treatment

Dust and deposits were removed from the surface of needles by washing in tap and distilled water (see [28]). The cleaned needles were dried in the room temperature (as in Ref. 20, 29, 40) and removed from twig axis. Needles from trees growing at one site were mixed into one laboratory sample (e.g. [12, 40]) and stored until analysis in bags.

Reagents

Aqueous standard solutions were prepared by dilution of the stock standard (SPEX Industries) solutions. The following chemicals of analytical grade were used for sample preparation: 65% Nitric Acid – Merck KGaA, Darmstad, Germany; PPH "Standard", Lublin, Poland; 35 – 38% Hydrogen Chloride – PPH "Standard", Lublin, Poland; 95 – 97% Sulphuric Acid – TZPN "Polchem", Toruń, Poland; 30% Hydrogen Peroxide – PPH-PoCh, Gliwice, Poland.

Deionized water (specific resistivity – 18,3 MΩcm) was prepared with the aid of an Easy pure RF (series 703, Barnstead, Thermolyne Corporation, USA) water purification system.

Glassware and plastic bottles were cleaned by soaking them for two days in 10% nitric acid and rising with deionized water.

Sample digestion procedures

Conventional digestion

A portion of 10 g (weighted exactly) of needles was placed in a clean, glassy baker. 100 ml of concentrated nitric acid was added and the baker (covered with a watch glass) was left overnight. The next day, the solution was gently heated on the conventional hot plate. Next portions of nitric acid were added and sample was heated again. The solution was evaporated to a small volume. After cooling hydrogen peroxide was added dropwise and the solution was heated – this step was repeated until the solution was colourless. Finally, the digestion residues were diluted with deionized water to 50 ml in the calibrated flask.

Microwave-assisted digestion

About 500 mg of powdered spruce needles were accurately weighed into a Teflon digestion vessel. 6 ml of concentrated nitric acid and 1 ml of hydrogen peroxide were added. Decomposition of samples was carried out in a microwave digestion system (Milestone, MLS-1200, MEGA). The following program was applied to the examined material: step 1- 2 min, 250 W; step 2- 2 min, 0 W; step 3- 6 min, 250 W; step 4- 5 min, 400 W; step 5- 5 min, 600 W; step 6- 5 min, ventilation. After cooling the sample solutions were quantitatively transferred into 25 ml volumetric flask and filled up with deionized water to the mark.

Dry ashing

A 10-gram of air-dried needle sample was weighted to a porcelain crucible. Six crucibles were placed in a microwave furnace (MAS 7000, CEM Corporation) and ashed in three steps with the following times corresponding to the temperature rise and heating at the selected constant temperature: step 1- 100 °C, 30 min, 5 min; step 2- 300 °C, 30 min, 5 min; step 3- 550°C, 45 min, 12 h. The totally ashed sample was moistured with deionized water and dissolved in 6 ml of concentrated nitric acid. Finally, the crucible content was transferred into 50 ml flask.

In the described above digestion procedures, before analysis all the solutions were filtered through the hard filter paper. All investigated sample solutions were prepared in 5% nitric acid.

Instrumentation

The element concentrations in needle samples were measured using atomic emission spectrometry with inductively coupled argon plasma as the excitation source. A Jobin-Yvon 38S spectrometer working under conditions shown in Table I was used.

For all measurements blank solutions were prepared and taken into account.

RESULTS AND DISCUSSION

Sample homogeneity

The homogeneity of the examined material was studied by analysis of ten replicate samples digested in nitric acid with addition of hydrogen peroxide. The mass of every sample was 10 gram. The results of the study are presented in Table II in the form of relative standard deviations for individual elements. As can be observed the RSD values for most of the elements are low, indicating that the examined material is quite homogenous.

TABLE I Instrumental and operating conditions for ICP-AES

Discharge parameters:			
Forward power	1000 W		
Plasma gas flow rate	13 L min^{-1}		
Sheath gas flow rate	0.20 L min^{-1}		
Nebulizer gas flow rate	0.3 L min^{-1} (cross-flow nebulizer)		
Sample uptake	1.5 mL min^{-1}		
Mnochromator:			
	1 m Czerny-Turner type: HR 1000		
Gratings	4320 and 2400 grooves mm^{-1}		
Slit width (entrance/exit)	20 μm/ 50 μm		
Analytical lines (wavelengths in nm):			
Al 226.922, 396.152		Mg	279.553, 285.213
B 249.773		Mn	257.610, 259.373, 294.920
Ba 233.527, 455.403		Na	588.995
Ca 317.933, 393.366		Ni	221.647, 231.604, 232.003
Cd 214.438, 226.502, 228.802		P	213.618
Co 228.616		Pb	220.353
Cr 205.552, 206.149, 267.716		Sr	407.771
Cu 224.700, 324.754		Ti	334.904, 334.941
Fe 238.204, 259.940		V	292.402
K 766.490		Zn	202.548, 206.200, 213.856, 334.502

TABLE II Sample homogeneity obtained for ten replicates

RSD [%]	*Elements*
<2	Al, Ca, Fe, B, Cu, Ti, Cd, Cr, V
2 – 4	K, Mg, Ba, Mn, Pb, Zn
4 – 6	Co, Ni, P, Sr

Evaluation of applicability of various acids for digestion

The effectiveness of different acid mixtures for the digestion of needle samples was investigated. To test the influence of different oxidant mixtures five replicate samples of each material were digested with the following concentrated acid mixtures: nitric acid, nitric and hydrochloric acids, and nitric and sulphuric acids.

The element concentrations measured in solutions obtained after digestion in various acids were compared. For most of the elements their concentrations were found to be consistent as shown, for example, for Fe, Mg and P in Figure 1. For a few elements (B, Ba and Pb) different concentrations were obtained (see Figure 1). Meaningful differences have been found for Ba and B. In the case of Ba it can be explained by the formation of hardly soluble $BaSO_4$. The low concentration of B measured in the solutions digested in the $HNO_3 + H_2SO_4$ mixture was rather unexpected. It can be due to various reasons. In addition, for the mixture of nitric and sulphuric acids, the RSD values of the concentrations of almost all elements were higher then for other acids. The highest concentrations were measured in the solutions digested with the aid of nitric acid. Therefore, the nitric acid was employed for the next experiments.

Comparison of different digestion methods

Selected results of the determination of trace and mineral elements in grounded spruce needles digested by three different methods are shown in Figure 2. For inorganic matrix elements (Ca, Mg, P) and for most of the other elements (e.g. Ba, B, Cu) the three methods have led to consistent results. However, for Mn, Al, Ti and Cr dry ashing has been found to be an ineffective method of needle sample digestion. This can be due to the formation of compounds only partially or hardly soluble, as reported by Hoenig et al. [41].

The microwave-wet decomposition in a high-pressure system has been found to be the most efficient method for digestion of such a plant material as tree needles. Small amounts of reagents were used. An additional advantage of this method is the very short time of digestion (about 25 min.) if one compares the conventional hot-plate digestion and dry ashing methods.

Trace and nutritional elements in needles

Using multielemental standard solutions for calibration, concentrations of Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sr, Ti, V and Zn were simultaneously measured. During all measurements the argon line Ar I 356.766 nm was monitored to control the stability of plasma excitation conditions.

For Al, Ca, Cd, Cr, Cu, Fe, Mn, Mg, Ni, Ti and Zn in yew, spruce and pine samples, concentrations were measured from a few analytical lines. Results of the element concentration measurements from different emission lines are given

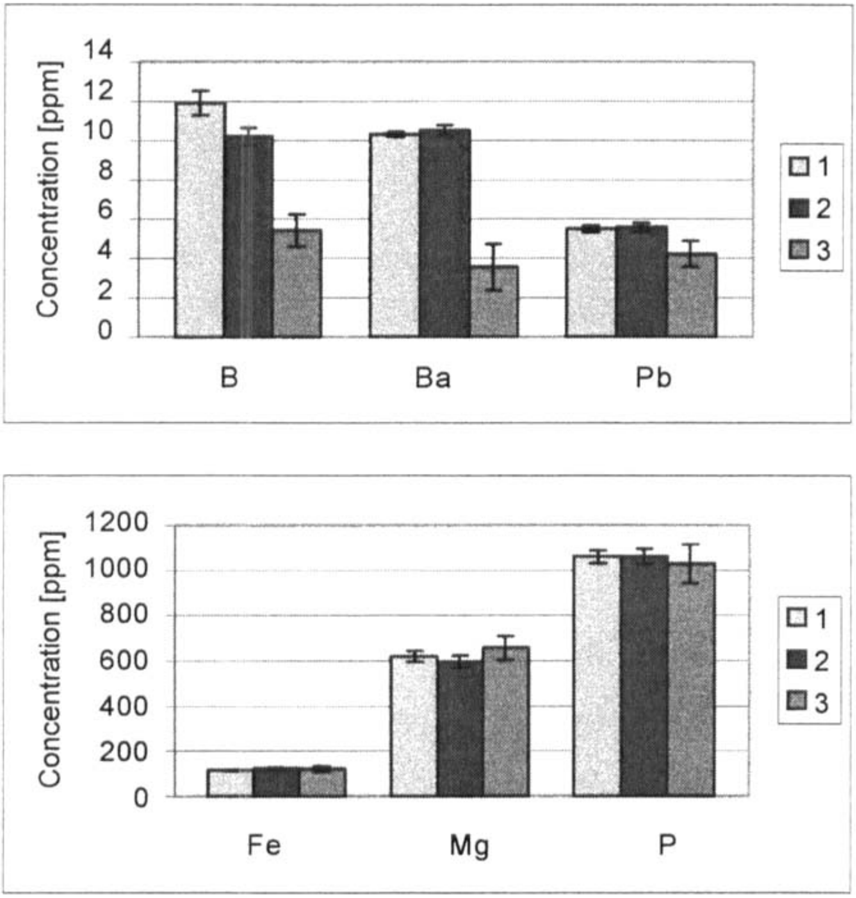
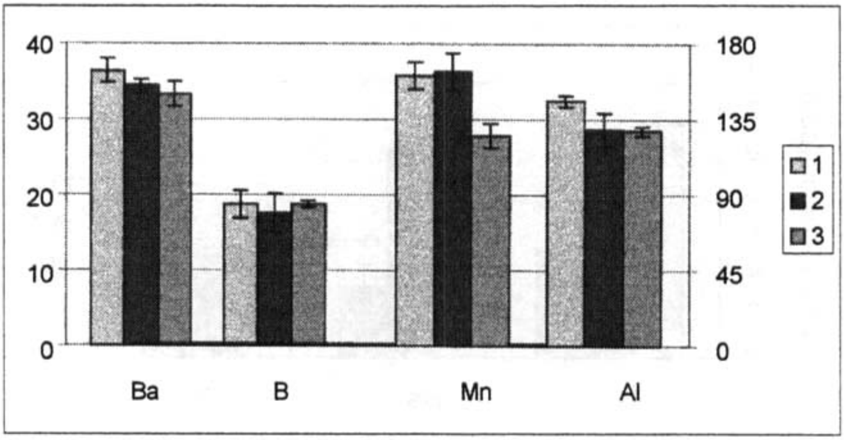


FIGURE 1 Comparison of needle digestion in various acid mixtures (1- HNO_3, 2- HNO_3 + HCl, 3- HNO_3 + H_2SO_4)

in Figure 3. For most of the elements measured consistent concentration values were obtained. Only for Al and Cr significant differences in the concentrations were observed. As it has been reported for Al [42,43] it can be explained by spectral interferences of the Al 396.2 nm line. The selection criteria of lines for final measurements were signal to background ratio, detection limit and spectral interferences.

The final measurements of aluminium and chromium were based on Al 226.9 nm and Cr 205.5 nm lines.

The matrix effects in the analysis of yew and spruce needles by the ICP-AES method were evaluated by comparison of calibration curve and standard addition



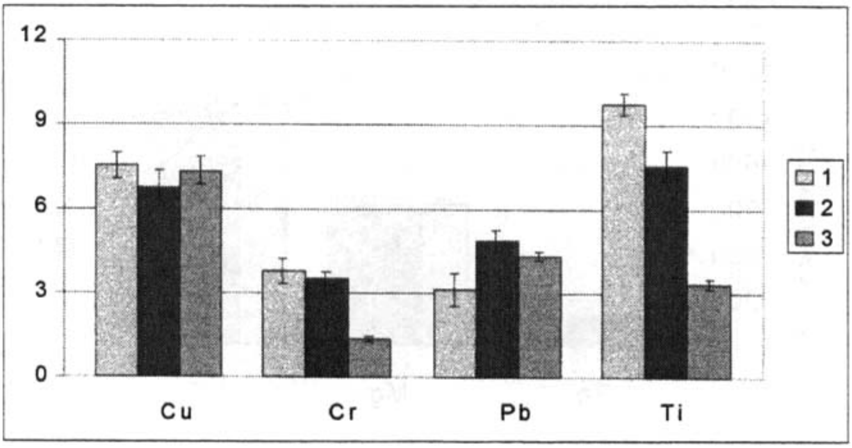


FIGURE 2 Concentrations of elements [in µg/g] – comparison of different digestion procedures: 1 – microwave-assisted, 2 – conventional hot-plate and 3 – dry ashing

methods. The standard addition method was performed for the detemination of Al, B, Ba, Cd, Cr, Cu, Fe, Ni, Pb, Sr, Ti, V and Zn. It was found that at appropriate dilutions of the measured solutions the matrix effects are lower than the standard deviation uncertainties of the concentrations.

Analysis of yew needles collected from three different sites was carried out. The results obtained (Table III) demonstrate dependence of the elemental composition of needles on the trees growing site. The very high levels of zinc in needle samples from Oława (Stations 2 and 3) were connected with the presence of the mill in the town. Generally, in samples from urban areas (both Wrocław and Oława), the concentrations of Al, B, Ba, Cr, Cu, Fe, Mg, Pb, Ti and V were

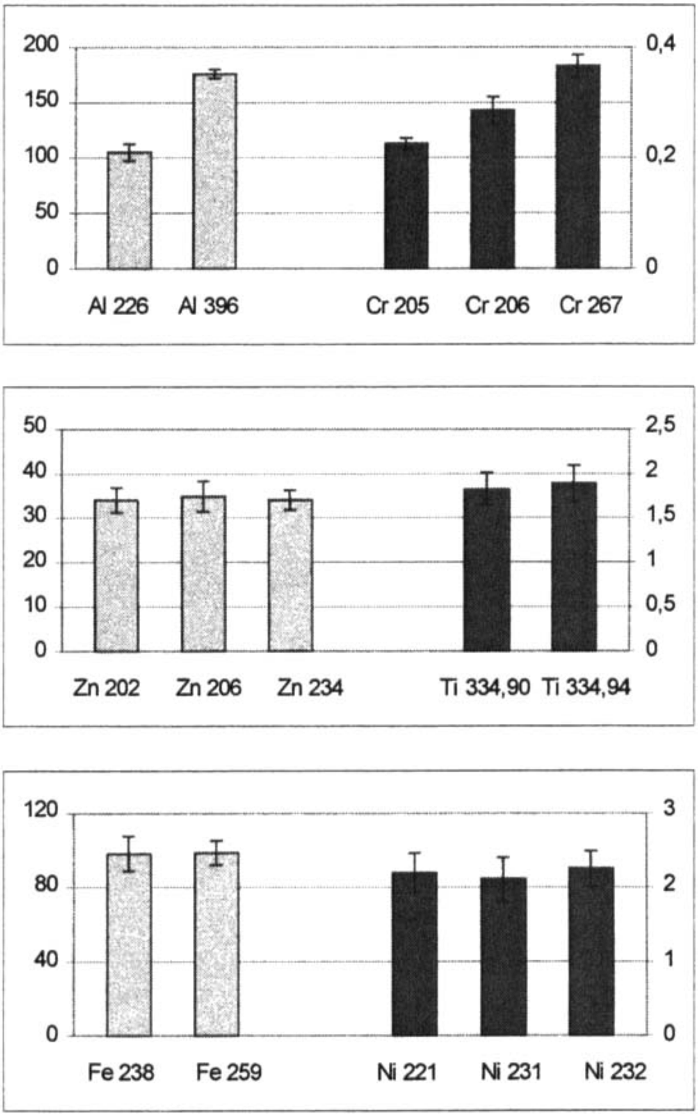


FIGURE 3 Concentration of selected elements measured from various lines in µg/g

higher than those found in needles from the place located outside the town, while the lowest concentration of Mn was found in town samples (Stations 1 and 2). In the samples from the centre of Oława (2) the highest concentrations of Al, Fe, Mg, Pb, and Ti are observed. The concentration levels of the trace (B, Ba, Cr, Cu, Sr and V) and nutritional (Ca, K, Na, P) elements are the highest in the samples from Wrocław.

TABLE III Concentrations of elements in needles in μg/g

	YEW (1)[a]	*YEW (2)*[a]	*YEW (3)*[a]	*NORWAY SPRUCE (3)*[a]		*WHITE SPRUCE (3)*[a]	*PINE (4)*[a]	
				Measured	*Literature data*		*Measured*	*Literature date*
Al	126	133	41.8	87.7	6.8–319	141	105	194–1001
B	37.6	25.4	14.3	23.8	17–63	18.8	23.6	11.3–33.6
Ba	23.9	19.9	12.0	42.5	1.0–53.2	47.8	2.15	0.13–7.2
Ca	7250	5980	5520	3700	600–8078	3200	3000	1498–6400
Cd	0.50	0.16	0.47	0.51	0.064–0.19	0.53	0.25	0.081–0.753
Co	0.43	0.24	0.33	0.33	0.1–0.336	0.42	–	0.074–0.36
Cr	1.74	1.42	0.84	1.22	0.312-<1.0	1.41	0.23	0.145–67.1
Cu	9.40	5.53	3.68	3.52	1.75–5.09	4.60	3.73	1.2–207.3
Fe	432	461	135	235	16.3–150	387	98.7	20–431
K	11800	7200	6970	7560	3400–9000	7610	7210	1800–8973
Mg	810	869	550	451	220–1500	533	465	751–2000
Mn	59.5	65.3	376	17.7	33–3474	48.5	765	25–2555
Na	612	288	190	494	–	521	191	46–500
Ni	1.29	1.38	1.37	0.94	1.2–3.5	3.38	2.11	0.1–395.6
P	1810	–	1320	1630	1500–1600	1720	1450	530–2200
Pb	15.4	19.6	6.92	11.8	0.8-<10	17.6	3.23	0.12–10.8
Sr	29.2	–	18.8	26.2	<10–99	21.5	3.84	1.5–16
Ti	9.99	13.9	4.75	9.16	–	15.2	1.89	2–5
V	0.98	0.86	0.36	0.58	<1	0.88	0.17	0.5–0.9
Zn	47.2	77.7	93.0	71.7	6.9–80	63.3	36.9	13–480

[a] Numbers in brackets correspond to the locations described in the text.

Results of the analyses carried out on needle samples of three species of conifers picked in the same place in Oława (3) are also included in Table III. The comparison of concentrations of the elements in yew and two spruce samples from one site and yew needle samples collected from three locations indicates different metal uptake by the examined species. The results obtained here indicate that the species have different characteristics for monitoring pollution. Differences in concentrations for B, Cd, Co, Cu, K, Mg and P are smaller than for Al, Ba, Ca, Fe, Mn, Ni, Pb, Sr, Ti, V and Zn. The highest quantities of trace (Al, Ba, Cd, Co, Cr, Cu, Fe, Ni, Pb, Ti and V) and main (K, Na and P) elements in needles of white spruce were measured. The amounts of Ca, Mg, and Zn in yew needles are considerably higher than in spruces. The results obtained for spruce and pine needles are comparable with literature data. Only the concentrations of cadmium, chromium, iron, phosphorus and lead in the Norway spruce needles are greater.

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