Environment Protection Engineering

Vol. 25 1999 No. 4

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STUDY OF SELECTED MAJOR AND TRACE METALS IN VARIOUS TREES FROM URBAN AREA

Samples of the oak, maple, willow, lime tree and birch trees growing in a Wrocław urban area have been analysed. Major and trace elements (Zn, Cr, Pb, Ni, Cd, Fe, B, Mn, Cu, Ti, Al, Ba, Mg, Ca, Na, K) have been determined using the ICP-AES method. Some analytical problems such as matrix effects and homogeneity of wood samples have been discussed.

1. INTRODUCTION

Recently, a growing interest has been paid to the analysis of inorganic components of tree samples [1]. Concentrations of various elements in trees have been used for monitoring environmental pollution [2], [3]. Parts of trees can serve as bioindicators in environmental and geochemical investigations [4], [5]. Some papers have been devoted to seasonal variations of metal concentrations in trees [6].

Several analytical methods have been employed to study inorganic contents of trees. For many years, the graphite furnace atomic absorption spectrometry (GF-AAS) method has been the most popular analytical technique. Some investigators have used flame atomic absorption spectrometry (FAAS) as well as neutron activation analysis (NAA) and other techniques. Nowadays the inductively coupled plasma (ICP) atomic emission spectrometry (AES) or mass spectrometry (MS) is frequently used in such studies. The ICP method is advantageous because it offers the possibility of measuring simultaneously a number of elements. Recently, papers describing successful application of X-ray fluorescence (especially EDXRF) without the necessity of sample digestion were published [7], [8].

Tree rings are of exceptional interest as a chronological record of element concentration changes with time due to internal and external events. Some variations of ecosystems and environment as well as metabolism of inorganic components of plants may be studied via tree rings. As a rule, one or two tree species have been the subject of a study. Usually such trees as oak, maple or fir have been examined. In some pa-

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pers devoted to the analysis of wood samples, close attention is also paid to a homogeneity of such a type of material as wood [9].

In this paper, the main attention and interest have been focused on multielemental analysis of five species of trees, using the ICP-AES method. In addition, such analytical problems as matrix effects and homogeneity of the material have been investigated.

2. MATERIALS AND METHODS

2.1. SAMPLES AND SAMPLING

Samples of the five trees: oak (*Quercus petraea* (Matt.) Liebl.), maple (*Acer platanoides* L.), willow (*Salix caprea* L.), lime tree (*Tilia cordata* Miller) and birch (*Betula pendula* Roth) were investigated. The first kind of material analysed here consisted of the samples collected from the above tree species growing on the same site in the city of Wrocław (the southwest Poland). The samples taken from three lime trees located on various sites in the same city were the second kind of the material. The distance between these sites was longer than 5 km. All trees were of similar age.

Each type of the sample consisted of three 3-year-old branches, growing 2 meters above the ground. Only one tree of each species was analysed because it was difficult to find such a place where many trees of different species were growing.

2.2. SAMPLE PREPARATION

After collection of the samples both bark and phloem were carefully removed from the branches. Then, the samples were dried in an oven at 80 °C to a constant weight. Wood of each type was divided into very small pieces and mixed to obtain samples as homogeneous as possible. Each sample was digested and analysed three times separately.

The digestion method described by FERRETTI et al. [10] was used. Approximately 1 g of a sample – exactly weighed – was mixed with 5 cm^3 of nitric acid (65%) in a glass beaker. The beaker was covered with bull glass and allowed to stand overnight. Next, another 5 cm^3 of nitric acid was added, and the mixture was heated for 60 min with simultaneous slow rise in temperature. The solution was heated up to a temperature of 100 °C. Such conditions were kept for few hours until a clear solution was obtained. Maple and lime tree wood required an additional 5 cm^3 of nitric acid to obtain nearly colourless solutions.

After digestion, the sample solution (about 4 cm^3) was brought up to 25 cm^3 with deionized water in a glass flask. Blank sample solutions were prepared in the same way as the wood sample solutions.

2.3. REAGENTS AND APPARATUS

Chemicals of analytical grade and deionized water were used for the sample solution preparation. Multielemental standard solutions were prepared using the ICP -SPEX standards. Element concentrations were measured by means of the Jobin Yvon sequential inductively coupled plasma atomic emission spectrometer (ICP-AES JY38S) under conditions given in table 1. Elements and their lines measured are pre-

Table 1

Instrumental and operating conditions
– ICP-AES sequential system JY 38S

Plasma and sample introduction system	
Generator frequency	40 MHz
R.F. power	1.0 kW
Nebulizer	cross-flow
Spray chamber	Scott type
Argon flows	outer gas, 12.0 $dm^3 \cdot min^{-1}$
	intermediate gas, 0.3 $dm^3 \cdot min^{-1}$
	sheath gas, 0.2 $dm^3 \cdot min^{-1}$ (0.8 for alkaline)
Sample uptake	1.0 $cm^3 \cdot min^{-1}$
	Monochromator
Focal length	1 m
Grating	double, 4320/2400 groves mm^{-1}

Table 2

Elements and their analytical spectral lines

Element	λ [nm]		Element	λ [nm]	
Zn	202.5	213.8	Cu	224.7	324.7
Cr	205.5	267.7	Ti	334.9	
Pb	220.3		Al	226.9	396.1
Ni	221.6		Ba	233.5	
Cd	214.4	228.8	Mg	279.5	
Fe	238.2	259.9	Ca	393.4	
B	249.8		Na	589.0	
Mn	257.6		K	766.5	

sented in table 2. Choice of spectral lines of the elements was based on recommendations in published papers and composition (matrix elements) of the analysed material. The differences in the concentrations of the elements measured on the basis of two lines never exceeded 4%.

3. RESULTS AND DISCUSSION

Matrix effects and homogeneity of wood material, which are considered to be important if a quality assurance of analytical measurements is taken into account, have been investigated before final determination of metals in tree samples.

3.1. MATRIX EFFECTS

Interelement effects can have a significant influence upon the results of analysis of the samples. In the ICP-AES method the matrix effects are usually small, especially in comparison to those obtained by means of other methods (e.g. atomic absorption spectrometry or X-ray fluorescence).

In the case of inductively coupled plasma atomic emission spectrometry, one could expect some matrix effects from such elements as natrium, potassium, calcium and magnesium present in the wood material. In order to study the influence of the matrix on trace element analysis, the measurements obtained using a calibration curve and a standard addition method were carried out and the results were compared. The concentrations of five elements measured using the two methods are presented in table 3.

Table 3

Comparison of the results of wood analysis obtained with two different methods ($mg \cdot kg^{-1}$)

Element	Calibration curve		Standard addition	
	Average	S.D.	Average	S.D.
Zn	0.323	0.053	0.334	0.066
Cu	0.035	0.010	0.036	0.008
B	0.136	0.004	0.131	0.066
Mn	3.39	0.04	3.56	0.11
Fe	4.98	0.04	5.26	0.06

As can be seen from the table the results obtained are in a good agreement. This indicates that the matrix effects are not significant here.

3.2. HOMOGENEITY OF WOOD MATERIAL

Two experiments have been performed to examine the homogeneity problem. In the first experiment, a piece of lime tree branch, 20 cm in length, was divided into three parts (samples) and each sample was analysed separately. Concentrations of the elements measured in these samples were well comparable for most of the elements, and the relative standard deviations (RSD) of the mean concentrations calculated were small. Examples of the RSD values calculated for the trace elements are shown in figure 1. The biggest standard deviations were noted for iron and copper. For zinc and aluminium, the RSD values were about 10%, and for the others – up to a few percent.

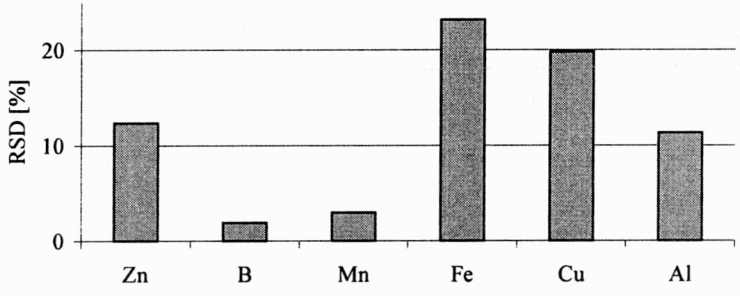

Fig. 1. The RSD values of the concentrations obtained as arithmetic means for the selected elements in one branch of lime tree

In the second experiment, six branches of one lime tree were collected during one day from different points of the tree and analysed. The concentrations of trace ele-

Table 4

Concentrations of elements in six different branches of one lime tree ($mg \cdot kg^{-1}$)

Element	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Zn	22.4	3.9	27.7	1.6	38.9	2.1	40.3	3.2	28.7	1.5	35.9	1.2
Ni	0.669	0.333	1.45	0.39	1.15	0.40	1.55	0.60	1.79	0.82	1.44	0.43
Fe	20.0	1.9	21.1	2.2	17.5	1.7	22.3	1.6	29.5	2.4	17.0	0.88
B	8.37	1.96	6.94	1.21	8.42	1.01	10.9	0.5	7.58	0.83	9.16	0.08
Si	63.2	47.3	77.0	64.2	64.0	49.7	58.2	43.0	56.4	41.0	55.5	34.2
Mn	33.2	2.7	34.9	3.0	36.3	0.5	24.2	0.8	19.6	0.9	20.6	1.5
Cu	3.05	0.41	3.73	0.08	3.14	1.04	3.95	0.48	4.45	0.47	4.05	0.34
Ti	0.29	0.03	0.254	0.033	0.230	0.080	0.271	0.093	0.278	0.054	0.542	0.268
Al	8.33	1.51	12.2	2.8	12.9	1.9	12.2	1.7	7.21	1.48	11.2	0.6

ments are given in table 4. As can be seen, there is no consistency in the concentrations measured, which indicates that wood is not a homogeneous material and problem of sampling is crucial in the analysis of such a material. Up till now, in the literature on the wood analysis an insufficient attention has been paid to the problem of sample representativeness.

3.3. MAJOR AND TRACE ELEMENTS IN VARIOUS TREES

Wood samples of oak, maple, willow, lime tree and birch growing at one location have been analysed. Because of the fact that wood is not a homogeneous material, the samples have been taken from each tree in the same way. Matrix effects have been found to be insignificant here, therefore final concentrations of the elements in various trees were measured using the calibration curve method. Results of the measurements with their standard deviations are shown in table 5. As can be seen from table 5, the concentrations of boron, manganese and titanium in the trees investigated

Table 5

Concentrations of elements in 3-years-old branches of trees growing on the same site ($mg \cdot kg^{-1}$)

Element	Oak		Willow		Maple		Birch		Lime	
	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.
Zn	8.19	1.44	18.3	2.8	16.4	1.2	33.4	6.3	30.5	1.4
Cr	0.62	0.29	0.13	0.03	ND		0.29	0.01	0.59	0.07
Pb	0.64	0.15	ND		0.43	0.10	0.2	0.18	0.49	0.43
Ni	4.51	1.47	0.21	0.04	ND		ND		ND	
Cd	ND		0.22	0.05	0.12	0.06	ND		ND	
Fe	29.2	7.3	15.2	1.1	15.0	2.6	6.9	0.2	39.7	17.8
B	12.8	5.1	5.86	1.07	6.72	0.57	4.46	0.76	7.59	0.87
Mn	5.82	0.37	5.10	1.06	4.63	0.71	6.53	1.34	1.65	0.16
Cu	5.06	0.95	3.35	1.44	2.61	2.64	0.30	0.09	1.54	0.36
Ti	0.43	0.07	0.04	0.02	0.38	0.02	0.41	0.05	0.45	0.06
Al	8.87	3.43	2.56	0.75	2.89	0.60	4.86	5.38	2.99	0.79
Ba	2.81	0.4	1.23	0.23	1.89	0.10	5.13	0.36	4.82	0.34
Mg	338	34	110	8	172	53	297	4.6	684	92
Ca	1160	186	681	233	986	165	1594	243	2327	649
Na	148	52	43.4	6.7	38.1	3.2	79.4	5.4	361	60
K	2143	316	977	333	542	58	705	26	4785	730

ND – not detected.

were similar with one exception in each case. For other elements, the differences in their concentrations found in the trees being analysed were noticeable. This was true

for both inorganic matrix elements (Na, K, Mg, Ca) and the trace elements. Differences in trace element concentrations were observed for copper and iron, where the ratios of the maximum to minimum values were 17 and 6, respectively. The relative standard deviations for the concentrations measured were as follows: for zinc, manganese, and barium smaller than 20% and for iron, boron, and titanium – up to 50%. For copper and aluminium the RSD values were comparable with mean values. Accuracy of the concentration measurements is comparable or even better than those published in other papers. For instance, ZAYED and LORANGER [11] reported for many elements standard deviations bigger than mean values. In a number of papers devoted to wood analysis, relative standard deviations have not been reported.

It is worthwhile to note that for some elements correlation could be observed, for example an increase in calcium concentration is positively correlated with magnesium concentration.

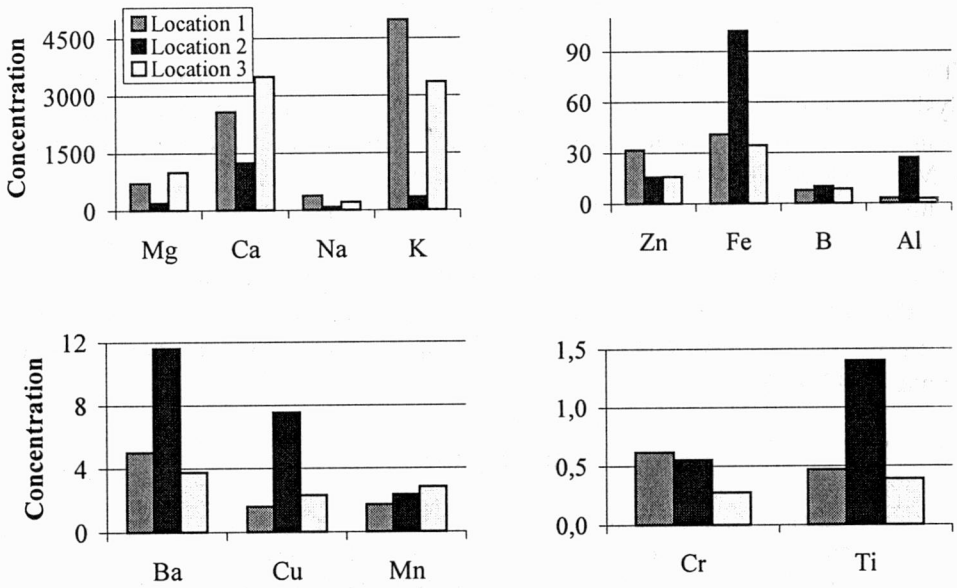

Fig. 2. Concentrations of elements in lime trees growing at various locations of urban area. All concentrations in $mg \cdot kg^{-1}$

Three lime trees growing on different urban sites were investigated. The concentrations of the trace elements in wood of these trees have been measured and compared (figure 2). The boron, manganese, and chromium concentrations in the lime trees analysed are similar if one takes into account the RSD values. Similar distributions of metal concentrations (with a distinct maximum corresponding to the second location) were observed for such trace elements as iron, aluminium, barium, copper, and titanium. Significant differences in the concentration were found for the matrix

elements, i.e. natrium, potassium, magnesium, and calcium, but for all elements similar distributions with a minimum at the second location were recorded as shown in figure 2. The relationship between the changes in the concentrations of natrium, potassium, magnesium, and calcium on the one hand and trace element levels (iron, aluminium, copper, titanium and barium) on the other hand can be seen in the figure. The decrease in alkali and alkaline earth metal contents in wood of lime trees is correlated with the increase in the concentrations of the mentioned trace elements in this material.

The zinc, nickel, cadmium, iron, manganese, copper, aluminium, magnesium, calcium, and natrium concentrations measured are comparable with the data reported by other researchers. Information on the measurement of boron concentration in trees has not been found in an available literature.

4. CONCLUSIONS

The ICP-AES method is a suitable analytical technique for a fast multielemental analysis of such a material as wood samples. Concentrations of many elements in trees are high enough to be measured by the ICP-AES method without preconcentration. Matrix effects have proved to be insignificant.

Although the element concentrations in various tree species differ meaningfully, it is rather difficult to arrive at definite statements about metal concentrations changes because wood samples cannot be considered a homogeneous material. This also means that tree sampling is a crucial analytical problem. Some correlation between the elements in trees have been stated and it can be interesting from both biological and analytical viewpoints.

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ANALIZA WYBRANYCH METALI W RÓŻNYCH GATUNKACH DRZEW Z OBSZARU ZURBANIZOWANEGO

W próbkach drewna dębu, klonu, wierzby, lipy i brzozy pochodzących z drzew rosnących na obszarze miejskim (Wrocław) oznaczono stężenia wybranych głównych i śladowych pierwiastków (Zn, Cr, Pb, Ni, Cd, Fe, B, Mn, Cu, Ti, Al, Ba, Mg, Ca, Na, K). Oznaczeń dokonano za pomocą atomowej spektrometrii emisyjnej indukcyjnie sprzężonej plazmy. Zbadano i omówiono efekty matrycowe występujące podczas analizy próbek drewna tą metodą oraz problem jednorodności badanego materiału.