Determination of As, Bi, Sb and Sn in conifer needles from various locations in Poland and Norway by hydride generation inductively coupled plasma atomic emission spectrometry

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DETERMINATION OF As, Bi, Sb AND Sn IN CONIFER NEEDLES FROM VARIOUS LOCATIONS IN POLAND AND NORWAY BY HYDRIDE GENERATION INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

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Hydride generation inductively coupled plasma atomic emission spectrometry (HG-ICP-AES) in the system with aerosolised sample introduction has been employed for the first time for analysis of conifer needles. Arsenic, bismuth, antimony and tin along with other trace elements were simultaneously determined in pine, spruce, yew and thuja foliage sampled from various locations in Poland and Norway. Quality of the measurements was assured by examination of two attested plant reference materials. The application of different analyte introduction techniques and interference effects from matrix elements, i.e. Na, K, Mg, Ca and transition metals in the analysis of needles are discussed.

Keywords: Conifer needles; Trace elements; As; Bi; Sb; Sn; Hydride generation; ICP-AES

INTRODUCTION

The use of coniferous trees as bio-indicators of atmospheric deposition in environmental studies is very common owing to the high prevalence of these tree species in European countries, e.g. Croatia, France, Germany, Italy, Lithuania, Poland, Russia, Slovakia, Sweden, Switzerland [1–14], and North America, i.e. Canada and United States [15–23]. Elemental composition analysis or examination of extrafoliar material deposited on the surface of spruce and pine needles is very suitable for assessment of environmental pollution. Environment degradation studies of conifer foliage focus mainly on the determination of nutritive elements (Ca, Mg, K, Na and P), heavy metals (Cd, Cu, Fe, Pb and Zn) and some non-metals (As, Br, I and S) [1,6].

The bio-dynamics of elements such as arsenic, bismuth, antimony, selenium and tin are much less well known since these pollutants are often present in conifer needles at

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levels below the detection limit of many analytical techniques [8,11]. Arsenic, being the most often investigated element in that group, has been determined so far in pine, spruce and fir needles using instrumental neutron activation analysis (INAA) [6–9,19], atomic absorption spectrometry with graphite furnace (GF-AAS) [11], inductively coupled plasma atomic emission spectrometry (ICP-AES) [16] and inductively coupled plasma mass spectrometry (ICP-MS) [14]. However, special procedures for the separation and pre-concentration of that element, e.g. extraction with Zn-diethyldithiocarbamate [6,8,9], or optimisation of the analytical method used (see Ref. [11]) were needed prior to the analysis. There are a few reports regarding the determination of Sb in pine, spruce and fir needles using NNA [6,7,12,19] and ICP-MS [14], Se in pine and spruce needles by ICP-AES [16] or ICP-MS [14] and Bi and Sn in pine and spruce needles by ICP-MS [14].

In the case of analysis of space needles, hydride generation has been used so far only with AAS for As and Se [10]. The advantage of ICP-AES over AAS measurements is the possibility of the simultaneous determination of a larger number of elements. To the best of the authors' knowledge, hydride generation inductively coupled plasma atomic emission spectrometry (HG-ICP-AES) has not been previously used for the analysis of conifer needles, although the technique is considered to be the most suitable for determination of As, Bi, Sb, Se and Sn [20–22] in biological and environmental samples.

Recently, we have examined some aspects of sample pre-treatment in the multi-element analysis of conifer foliage [2,3]. Results presented in this study are the extension of our previous studies devoted to the determination of major and trace elements in conifer needles. In the present study, ICP-AES with the hydride generation technique was used for the determination of As, Bi, Sb, and Sn in pine, spruce, yew and thuja needles and the system also allowed the introduction of the sample as an aerosol. The material was collected at different sites in south-western Poland and central Norway. Different techniques of analyte introduction, i.e. hydride generation, the simultaneous introduction of hydrides and aerosolising the sample using pneumatic nebulisation, were compared and discussed in relation to the accuracy and precision of measurements, possible interference effects and application to the multi-element analysis of conifer needles.

EXPERIMENTAL

Instrumentation

The experiments were performed using a JY 38S (Jobin Yvon, France) ICP spectrometer equipped with a hydride generation system consisting of a glass cyclone spray chamber (Jobin, Yvon, France) with PTFE delivering tubes and a Meinhard-type concentric nebuliser placed in a tangential tube of the chamber. Operating conditions for the ICP-AES instrument and for continuous flow hydride generation as well as wavelengths of analytical lines are given in Table I. Atomic and ionic emission lines that were sensitive and free from spectral interferences were selected for measurements.

For sample decomposition, a microwave digestion system MLS-1200 (Milestone, Italy) with a microwave digestion rotor (MDR-1000/6/100/110) were used.

TABLE I   Operating conditions for continuous flow hydride generation inductively coupled plasma atomic emission spectrometry measurements

Supplied power	1000 W
Plasma Ar flow rate	13 L min^{-1}
Intermediate Ar flow rate	0.25 L min^{-1}
Nebulising (carrier) Ar flow rate	0.25 L min^{-1}
Pressure on nebuliser	3.0 bar
Slit widths (entrance/exit)	20 μm/50 μm
Observation height	12 mm above load coil
Background correction	± 0.025 nm
Wavelengths of analytical lines (nm)	As 193.759, Zn 202.548, Cd 214.438, Pb 220.353, Ni 221.647, Bi 223.061, Co 228.616, Sb 231.147, Mn 259.373, Fe 259.940, Cr 267.716, Sn 283.999, Cu 324.754, Sr 407.771
NaBH$_4$ flow rate	1.0 mL min^{-1}
NaBH$_4$ concentration	1.0% (m/v) in 0.50 M NaOH
HCl flow rate	0.50 mL min^{-1}
HCl concentration	6.0 M
Sample flow rate	1.0 mL min^{-1}
Drain flow rate	4.2 mL min^{-1}

Reagents and Solutions

Bulk (1000 μg mL^{-1}) single-element standard solutions (Johnson Matthey GmbH, Germany) were used to prepare a series of working standard solutions containing As, Bi, Sb and Sn at concentrations of 0.10, 0.20, 0.50 and 1.0 μg mL^{-1} along with a series of solutions containing Cd, Co, Cr, Cu, Fe, Mn, N, Pb, Zn and Sr at concentrations of 1.0, 2.0, 5.0 and 10 μg mL^{-1}. A 1.0% (m/v) sodium tetrahydroborate solution was prepared by dissolution of solid NaBH$_4$ (Serva Feinbiochemica GmbH & Co., Germany) in 0.50 mol L^{-1} solution of NaOH (Polish Chemical Reagents, Poland). The solution of the reducing agent was filtered before measurements. A 6-M solution of HCl was prepared by dilution of concentrated HCl (Merck KGaA, Germany). For sample digestion, concentrated HNO$_3$ (Merck KGaA, Germany) was used. For sample digestion, concentrated HNO$_3$ (Merck KGaA, Germany) and 30% (m/v) H$_2$O$_2$ (Polish Chemical Reagents, Poland) were applied. De-ionised water obtained from an EASY pure$^{®}$ model D7033 (Barnstead, USA) was used for dilution.

Sites and Sampling

Needles were collected from trees growing in an urban area of Wroclaw (yew, thuja) – a city in south-western Poland (Lower Silesia region), and villages nearby: Bystrzyca (pine), Olawa (spruce) and Siechnice (pine). Two other sites were located in Trondheim (pine, spruce) – a city in central Norway. Sampling at each site was carried out by cutting branches from the middle of the crown from three trees, as described previously [4,7,10]. The samples were collected after completion of a growth period, i.e. during November and December.

Sample Preparation and Analysis

Dust and deposits were removed from the surface of needles by washing with tap water and then de-ionised water (see Refs. [2,3,10,16]). Cleaned needles collected at one site were used to prepare a laboratory sample as reported in Refs. [2,5,17].

Three independent 1.0-g sub-samples from one sampling site were taken and decomposed in a mixture of concentrated HNO_3 (8.0 mL) and 30% (m/v) H_2O_2 (3.5 mL) using a microwave-assisted digestion system. For this purpose needle samples were exactly weighed and placed in high-pressure Teflon vessels. The reagents were added and the vessels were covered and left overnight. Then the samples were digested using a seven-step programme described previously [2]. After digestion and cooling of the samples, solutions were quantitatively transferred to 25-mL calibrated flasks and made up to the volume. Before measurement the sample solutions were filtered. The procedure given above was also used for the decomposition of two certified reference materials: Oriental Tobacco Leaves (CTA-OTL-1) and Virginia Tobacco Leaves (CTA-VTL-2). For each analysis of needles and reference materials a blank solution was prepared and then taken into account in calculating the final results.

To avoid differences in acid concentration and oxidation state of analytes in sample and standard solution (especially important in the case of hydride-forming elements), working standard solutions described above were also processed in the microwave digestion system. For that purpose, appropriate volumes of bulk standard solutions were added to the vessels followed by the addition of 1.5 mL of de-ionised water, 8.0 mL of concentrated HNO_3 and 3.5 mL of 30% (m/v) H_2O_2. The vessels were covered and the microwave digestion procedure was completed. After cooling, the solutions were quantitatively transferred to the calibrated flasks and filled with water up to 25 mL.

Hydride-generation Procedure

Two systems of sample introduction into plasma have been tested. For simultaneous hydride generation and pneumatic nebulisation, $NaBH_4$ and HCl solutions were introduced separately to the bottom of the chamber, while samples and standards were nebulised into the chamber. Drops of the aerosol deposited on the wall of the chamber ran down and mixed with the incoming reagents, i.e. $NaBH_4$ and HCl. The gaseous products liberated in the reaction, along with the sample aerosol, were transported into the plasma by argon as a carrier gas. Wastes were drained from the chamber.

A slightly modified system was used for hydride generation, without introduction of an aerosolised sample into the plasma. Solutions of $NaBH_4$, HCl and the sample were introduced in three separate streams to the bottom of the chamber where they merged and the reaction occurred. Evolved gases were swept by the stream of carrier argon, introduced *via* the gas inlet of the nebuliser (the sample inlet was choked), and transported to the plasma. The post-reaction waste was drained continuously.

RESULTS AND DISCUSSION

Analysis of Certified Reference Materials

The lack of certified reference materials of conifer needles and elements being certified in them has been reported previously [3,6]. There are two commercial reference materials without certified values of As, Bi, Sb and Sn, i.e. CRM 101 (spruce needles from Europe) and CLV 2 (spruce needles from Canada), and one, SRM 1575 (pine needles), with amounts of As and Sb lying outside the range of concentrations found in the present contribution. Therefore, we analysed two plant reference materials,

TABLE II Concentrations of As, Sb, Sn, Cr, Ni and Pb in certified reference materials of plants in $\mu g \, g^{-1}$ of dry sample

Element	CTA-OTL-1		CTA-OTL-1	
	Determined	Certified	Determined	Certified
As	0.54 ± 0.06	0.539 ± 0.060	0.98 ± 0.07	0.969 ± 0.072
Sb	0.98 ± 0.02	–	0.33 ± 0.02	0.312 ± 0.025
Sn	10.8 ± 1.1	–	6.98 ± 2.20	–
Ba	72.1 ± 3.6	84.2 ± 11.5	33.2 ± 4.0	42.7 ± 6.6
Cd	1.45 ± 0.02	1.12 ± 0.12	1.67 ± 0.10	1.52 ± 0.17
Co	0.93 ± 0.01	0.879 ± 0.039	0.36 ± 0.01	0.429 ± 0.026
Cr	2.45 ± 0.26	2.59 ± 0.32	1.33 ± 0.09	1.87 ± 0.16
Cu	15.6 ± 1.7	14.1 ± 0.5	19.0 ± 0.7	18.2 ± 0.9
Fe	892 ± 73	–	1053 ± 51	1083 ± 33
Mn	3.68 ± 49	412 ± 14	60.4 ± 12	79.7 ± 2.6
Ni	6.23 ± 0.61	6.32 ± 0.65	2.58 ± 0.14	1.98 ± 0.21
Pb	4.69 ± 0.22	4.91 ± 0.80	24.1 ± 0.4	22.1 ± 1.2
Sr	204 ± 5	201 ± 20	110 ± 5	110 ± 12
Zn	50.3 ± 1.7	49.9 ± 2.4	42.2 ± 1.9	43.3 ± 2.1

–, no certified value.

Oriental Tobacco Leaves (CTA-OTL-1) and Virginia Tobacco Leaves (CTA-VTL-2), with As and Sb contents similar to those in the investigated needles.

The results of the analysis of reference materials carried out by HG-ICP-AES with simultaneous introduction of aerosolised sample are given in Table II. Concentrations of As, Sb and Sn are presented as mean values of three replicate samples with one standard deviation. Certified values of As and Sb are given for comparison. Good agreement between measured and certified concentrations was achieved for both elements.

Other (non-hydride-forming) trace elements, i.e. Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn, were also measured. The results of their determination, exemplified in Table II for Cr, Ni and Pb, demonstrate the very good accuracy of the present technique not only for analysis of hydride-forming elements but for others as well.

The precision of measurements obtained with HG-ICP-AES was good. The relative standard deviations ranged from 1 to 11% for most of elements.

Analysis of Needles

The influence of experimental conditions on the analytical response of hydride-forming elements was investigated in our previous study [23], where HG-ICP-AES was used along with the introduction of an aerosolised sample. In the present work, HG-ICP-AES was tested with needles of different conifer species growing at various locations in Poland and Norway.

The results of As, Sb and Sn determination in pine, spruce, yew and thuja needles are given in Table III. The concentrations of As and Sb are comparable in all analysed needle samples. The effects on elemental concentrations of site location and tree species were relatively minor. The concentrations of As and Sb varied in the range 0.33 to 1.94 $\mu g \, g^{-1}$ and 0.02 to 2.37 $\mu g \, g^{-1}$, respectively. The concentrations of As and Sb determined in this study are comparable to those reported in the literature [1,6,8–12,14,16]. No literature data has been found for a comparison of the results obtained for yew

TABLE III   Concentrations of As, Sb and Sn in pine, spruce, yew and thuja needles in $\mu g\,g^{-1}$ of dry sample

Tree species/location	As	Sb	Sn
Pine			
Trondheim	0.34 ± 0.09	0.55 ± 0.10	3.29 ± 0.67
Bystrzyca	0.33 ± 0.02	< 0.02	8.80 ± 0.80
Siechnice	1.04 ± 0.25	1.09 ± 0.13	27.6 ± 3.8
Literature data	$0.3–4.1$	$0.001–7.0$	$12–25$
Spruce			
Trondheim	0.36 ± 0.12	0.50 ± 0.14	7.55 ± 2.08
Olawa	0.81 ± 0.28	0.95 ± 0.23	11.8 ± 3.0
Literature data	$0.003–0.68$	$0.001–0.006$	$0.01–0.02$
Yew[a]			
Wroclaw	0.71 ± 0.16	0.58 ± 0.21	12.0 ± 4.3
Thuya[a]			
Wroclaw	1.94 ± 0.69	2.37 ± 0.53	90.1 ± 27.4

[a]No data available in the literature.

and thuja. To our knowledge this is the first report on As, Sb, Bi and Sn concentrations in these tree species.

The Sn concentrations determined in all needle samples were significantly (from 10 to almost 50 times) higher than those observed for As and Sb. The highest Sn concentration was found in thuja needles. A similarly high concentration of Sn was also observed by Hüttle and Wisniewski [4] in pine needles. However, Sn concentrations two to three orders of magnitude lower than those determined in this study have also been reported in pine and spruce foliage [14].

Bismuth was also measured here, but its concentrations in all analysed needle samples were lower than the detection limit estimated to be $0.02\,\mu g\,g^{-1}$. The low concentrations of Bi observed here are in agreement with ICP-MS measurements performed previously for pine and spruce [14].

The precision of the As, Sb and Sn measurements, expressed as a relative standard deviation, ranged mostly from 10 to 15%. Quite similar RSD values were obtained in other studies [7,11,12,19] where the precision varied from 10 to 30%.

Assessment of Different Sample Introduction Techniques

Different techniques of sample introduction into the plasma were compared here for the analysis of the conifer needles. The advantage of hydride generation with the introduction of aerosolised samples was the possibility of simultaneous determination of As, Bi, Sb and Sn and other (non-hydride-forming) elements without any change of sample introduction technique. To estimate the capability of such a multi-element technique, concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn in pine, spruce, yew and thuja needles were measured using the hydride generation system. Then the results were compared with those obtained earlier in our laboratory [2,3] using ICP-AES with pneumatic nebulisation (PN) for spruce and yew needles. The material was collected in Poland and Norway at the same locations and for the same growth period as in the present study. Satisfactory correspondence between the results was achieved as

TABLE IV Concentrations of Cr and Cu in spruce and yew in $\mu g\,g^{-1}$ of dry sample by HG-ICP-AES and ICP-AES

Tree species/location	HG-ICP-AES[a]		ICP-AES	
	Cr	Cu	Cr	Cu
Spruce, Trondheim	0.71 ± 0.05	2.41 ± 0.49	1.23 ± 0.07[b]	2.11 ± 0.31[b]
Spruce, Olawa	1.64 ± 0.22	4.68 ± 0.14	1.22 ± 0.15[b]	3.52 ± 0.30[b]
Yew, Wroclaw	1.26 ± 0.06	8.76 ± 0.15	1.59 ± 0.11[c]	9.40 ± 0.10[c]

[a]This work. [b]Ref. [3]. [c]Ref. [2].

illustrated by Table IV with the outcomes exemplified by Cr and Cu (the concentrations are the mean values obtained for three replicate samples and standard deviations of the means are indicated). Good precision of measurements has been achieved. For most of the determined elements relative standard deviations varied from 0.6 to 9%.

For comparison of the results of As, Sb, Bi and Sn measurements, hydride generation without the introduction of sample aerosol in the same system was also used in this study. The concentrations of As, Sb and Sn in all examined samples of needles were very similar for both techniques applied. The differences between the values were in the range of measurement error and the maximum difference was 25%.

Interference Effects

Despite the rich matrices of the samples examined here, no matrix interferences in the plasma were observed. This was in agreement with our earlier results [23] concerning the influence of Na, K, Mg and Ca on the analytical signals of hydride-forming elements in the investigated system. Concentrations of major elements, i.e. Na, K, Mg and Ca, in analysed needles and reference materials were not very high and did not suppress the analytical signals of As, Sb and Sn. On the other hand, relatively low concentrations of metals such as Cd, Co, Cu, Fe and Ni in the foliage samples and reference materials did not cause chemical interferences in the liquid phase during the hydride generation reaction.

CONCLUSIONS

Inductively coupled plasma atomic emission spectrometry with on-line hydride generation in the system and the introduction of aerosolised sample into the plasma was found to be very suitable for the examination of conifer needles. Good sensitivity, accuracy and precision are the principal advantages of this technique for complete multi-element analysis. The possibility of determination of both elements forming volatile hydrides (As, Sb, Bi and Sn), whose contents in environmental samples are lower than the detection limits found for pneumatic nebulisation, and simultaneously other trace elements, constitutes another benefit. Here, concentrations of As, Bi, Sb and Sn determined in the needles of pine, spruce, yew and thuja followed the sequence: $Sn \gg As \approx Sb \gg Bi$.

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