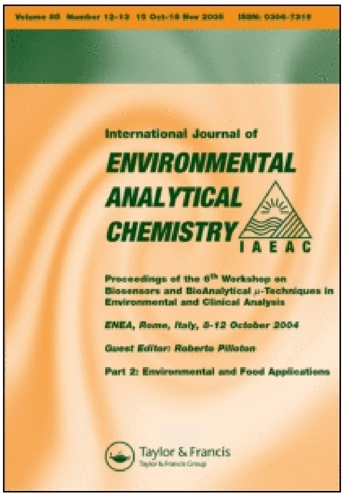

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of mineral and trace element concentrations in pine needles by ICP-OES: evaluation of different sample pre-treatment methods

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To cite this Article Väisänen, Ari , Laatikainen, Paula , Ilander, Aki and Renvall, Sanna(2008) 'Determination of mineral and trace element concentrations in pine needles by ICP-OES: evaluation of different sample pre-treatment methods', International Journal of Environmental Analytical Chemistry, 88: 14, 1005 — 1016

To link to this Article: DOI: 10.1080/03067310802308483

URL: http://dx.doi.org/10.1080/03067310802308483

Intern. J. Environ. Anal. Chem.
Vol. 88, No. 14, 10 December 2008, 1005–1016

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Determination of mineral and trace element concentrations in pine needles by ICP-OES: evaluation of different sample pre-treatment methods

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(*Received 11 March 2008; final version received 23 June 2008*)

In the present study, the determination of mineral and trace elements (Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn) from pine needles using three sample pre-treatment methods followed by inductively coupled plasma optical emission spectrometry, was examined. Sample pre-treatment methods tested were microwave digestion, ultrasound-assisted digestion and dry ashing. The new ultrasound-assisted digestion method was optimised by the analysis of the standard reference material (SRM) 1575a (pine needles) sample. The speed of dry ashing method was significantly increased by ultrasound dissolution after ashing. All the ICP-OES measurements were performed in robust plasma conditions which were tested by measuring the Mg II 280.270 nm/Mg I 285.213 nm line intensity ratios. The microwave digestion resulted generally in slightly higher element concentrations than ultrasound-assisted digestion. B, Cu and Na resulted in such low concentrations that they could not be accurately determined by using the microwave digestion method. The *t*-tests found no significant differences between the certified and the determined element concentrations of the SRM 1575a using the dry ashing method followed with ultrasound dissolution.

Keywords: ultrasound; microwave; dry ashing; pine needles; trace elements

1. Introduction

It is well known that plants play a significant role in both nutrient and trace element cycling in the environment. Biomonitoring of trace elements is essential to access ecosystem health, in particular in landscapes influenced by human activity [1–3]. The impact of human activity can vary from harmful to essential for plants and the whole ecosystem [4]. Harmful effects are produced by traffic [3], industrial activity [4] and energy production [5] whereas essential effects include liming and fertilizing of soils [6].

Pine needles have been evaluated as good biomonitors of airborne trace element pollution by industry [4,7–9] and traffic [8]. The concentrations of trace elements originate both from soil and atmospheric aerosols and dry particles [9], which increase the uptake of these elements. According to this, the determination of trace element concentrations in pine and spruce needles can be used for the evaluation of the need of fertilizing [10,11] and long-term pollution even at low levels of concentrations [7]. Some researchers

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802308483
http://www.informaworld.com

suggest the use of mosses instead of pine needles as bioindicators in areas with low pollution levels [12].

Dissolution of sample is usually needed when trace element concentrations in pine needles as well as other plant samples are determined. The determination of trace element concentrations in pine needles has mainly been done by flame atomic absorption spectrometry (FAAS) [13], electrothermal atomic absorption spectrometry (ETAAS) [14–16], hydride generation atomic absorption spectrometry (HGAAS) [17,18] or inductively coupled plasma optical emission spectrometry (ICP-OES) [19–24] depending on the analyte elements and concentrations. Such instrumental technique as direct current plasma atomic emission spectrometer (DRC-AES) [25] has successfully been used in the analysis of selected element concentrations in pine needles. When extremely low-element concentrations are determined, inductively coupled plasma mass spectrometry (ICP-MS) has been found to be the most attractive technique [26,27]. Most of those techniques use liquid sample introduction; however, slurry sample [14,28] and solid sample introduction [29] can be used for ETAAS. Slurry sampling hydride generation microwave induced plasma optical emission spectrometry (SS-HG-MIP-OES) has been introduced by Matusiewicz and Ślachciñski [30] for trace element analysis of biological and environmental materials, including pine needles. Instrumental neutron activation analysis (INAA) has also been used for the analysis of pine needles for environmental monitoring [31,32].

Two principles of the sample pre-treatment of plant materials are mineralisation and dissolution [33]. Sample pre-treatment methods used for plant samples are based on the use of concentrated mineral acids at elevated temperatures. The total dissolution of samples with organic material and silicates, such as plant materials are, is usually not achieved when one mineral acid is used alone. The widely used digestion solutions for the dissolution of pine needles include HNO_3–HCl [22,25], HNO_3–HBF_4 [24], HNO_3–H_2O_2 [21,26,34], HNO_3–HF [35] and HNO_3–HCl–HF [14].

Sample pre-treatment methods used for dissolution of pine needles include microwave digestion [21,22,24–26,35], microwave extraction using diluted acids [34], hot plate digestion [23] and ultrasound-assisted extraction using an ultrasonic probe or water bath [34,36]. The microwave accelerated dissolution has become the main sample pre-treatment method for elemental analysis of pine needles and other kinds of environmental samples [21,22]. An alternative, faster and cost effective sample pre-treatment method for microwave digestion is ultrasound-assisted extraction, which has been validated for several sample matrices [37]. In the ultrasound-assisted sample pre-treatment, a high-energy field is focussed to the sample solution using an ultrasonic water bath or ultrasonic probe [37,38]. Energy intensities on the order of $5\,\mathrm{W\,cm^{-2}}$ can be achieved in an ultrasonic water bath, whereas extremely high intensities ($100\,\mathrm{W\,cm^{-2}}$) can be produced with an ultrasonic probe [37]. Ultrasound-assisted sample pre-treatment is typically performed during 20 min, which is quite a short time when compared to conventional digestion methods [38]. The major advantages of the ultrasound-assisted sample pre-treatment over other methods are the possibility to use low sample weights, small reagent usage and high sample treatment capacity, especially when an ultrasonic water bath is used [39].

One of the most useful methods of mineralisation of plant samples is dry ashing, which ensures the effective removal of carbon from the samples. After dry ashing, the residue can be dissolved in mineral acids [33]. Dry ashing is rather tedious and requires a substantial amount of time; however, it results in the total destruction of organic material and pre-concentrates the analyte elements in the sample. Dry ashing is usually performed at temperatures of about 450 or 500°C. When such high temperatures are used, some analyte elements, especially As, Hg, Cd, Pb and Se, can volatilise. The loss of analyte elements can be minimised by using a slow temperature ramp rate and ashing aids, the most common of which are nitrates of Mg, Ca or Al [40].

The determination of mineral and trace element concentrations in pine needles was subjected to interferences. The determination of B, Cu and Na in standard reference material (SRM) 1575a (pine needles) using microwave digestion (USEPA method 3051) followed with ICP-OES failed to obtain the certified concentrations at the 95% level of confidence using the significance tests. Due to this an ultrasound-assisted digestion method for the analysis of element concentrations in pine needles was developed. The speed of commonly used dry ashing method was also increased with the ultrasound dissolution of the residue. Nowadays, one of the most important elements in Finnish forest research is B due to its effects on growing. The correlation between height growth of coniferous trees and concentrations of B has been noticed [11]. The B deficiency is observed when concentrations are 5 mg kg^{-1} (d.w.) or lower in needles [11].

2. Experimental

2.1 *Instrumentation*

All the measurements were performed with a Perkin-Elmer (Norwalk, CT, USA) model Optima 4300 DV ICP-OES. A Scott-type double-pass spray chamber and a cross-flow nebulizer were used throughout. The determination of element concentrations was optimised using different default parameters of the instrument (nebulizer flow 0.5–1.0 L min^{-1}, auxiliary gas flow 0.2 L min^{-1}, plasma gas flow 15 L min^{-1} and plasma power of 1300 or 1400 W). Two wavelengths for each of the elements investigated were tested by radially viewed plasma. Due to low concentrations of B, Cu, P and Na, axially viewed plasma was used for the determination of these elements. The wavelengths with the plasma viewing used in the determinations are shown in Table 1.

2.2 *Reagents and samples*

All the reagents used were of analytical grade and ultrapure water of 18.2 MΩ cm^{-1} resistivity (ELGA Maxima, Elga Ltd., Bucks, GB) was used throughout. Nitric acid (65%, p.a.) and hydrochloric acid (36–38%, p.a.) were both supplied by Riedel-de-Haën. The standard stock solutions (1000 mg L^{-1}) for the ICP-OES measurements were supplied by Merck. The working concentration ranges used are shown in Table 1.

The method validation was based on the analysis of pine needles SRM 1575a, certified by the National Institute of Standards and Technology (NIST). Seven pine needle samples collected from forest in Central Finland were analysed. It is known that plants have their maximum nutrient content in early summer [3]; the sampling was performed at that time in order to maximise their nutrient concentrations. The sampling was performed using polyethylene gloves and a sharp stainless steel knife. Each sample contained at least 200 g of fresh pine needles collected all around the tree. Samples were collected so that needles were exposed to sunlight and were not damaged. The samples collected were loosely placed into 5000 mL polyethylene bags for a couple of hours only. The samples were washed two times with water to ensure that they were not contaminated by dust. They were then dried in an oven at 60°C for seven days, after which they were ground in a sample preparation

Table 1. Calibration data of the determination of samples by ICP-OES.

Element	Wavelength (nm)	Atom/Ion I/II	LOQ[a] (mg kg^{-1})	Calibration ranges (mg L^{-1})
Al	**308.215 Radial**	I	5.40	0.2–20.0
	396.153 Radial	I	3.00	
B	249.677 Axial	I	2.40	0.1–10.0
	249.772 Axial	I	2.40	
Ca	**315.887 Radial**	II	11.0	1.0–100.0
Cu	**327.393 Axial**	I	0.32	0.05–5.0
	324.752 Axial	I	0.32	
Fe	**238.204 Radial**	II	2.60	0.20–20.0
	239.562 Radial	II	3.00	
K	**766.490 Radial**	I	38.00	2.0–200.0
Mg	279.077 Radial	II	13.00	0.50–50.0
	285.213 Radial	I	11.60	
Mn	259.372 Radial	II	4.40	0.20–20.0
	257.610 Radial	II	4.00	
Na	**589.592 Radial**	I	2.40	0.20–20.0
P	**213.617 Axial**	I	4.80	0.40–40.0
	214.914 Axial	I	4.00	
Zn	**206.200 Radial**	II	2.20	0.05–5.0
	213.857 Radial	I	2.60	

Notes: Bold = Appropriate wavelength for the accurate analysis of pine needle samples.
[a] LOQ = Limit of quantification when 250 mg sample was pretreated with dry ashing method and filtrate diluted to a volume of 50 mL. Calculated by substituting the intercept and its standard deviations multiplier ($a + 10s_a$) into the calibration line $y = bx + a$.

mill (Cyclotec 1093, Foss Tecator, Hilleroed, Denmark). After grinding samples were transferred into dark wide neck glass storage bottles.

2.3 *Ultrasound-assisted digestion*

An efficient and cost effective method of digestion for the determination of element concentrations in pine needles was developed. Different digestion solutions (Figure 1) and sonication times were tested. A SRM or real sample of about 250 mg was accurately weighed into a 100 mL plastic screw-top bottle into which 10 mL of the digestion solution was added. The bottle was closed and placed into a 650 W, 35 kHz, Model Transsonic 820/H ultrasonic water bath (ELMA, Singen, Germany). The optimised sonication procedure lasted 9 min and was carried out at a temperature of about 50°C using a mixture of 5 mL of ultrapure water and 5 mL of *aqua regia* as a digestion solution. After digestion the sample solution was filtered (Whatman No. 41) into a 50 mL volumetric flask and the filtrate diluted to volume with ultrapure water.

2.4 *Microwave digestion*

A SRM or real sample of about 250 mg was accurately weighed into a 100 mL TFM (tetrafluormethaxil) vessel into which 10 mL of 65% HNO_3 or 10 mL of *aqua regia* was added. After 1 h, the sample was placed into an ETHOS PLUS microwave digestion system (Milestone, Sorisole, Italy) and heated with a digestion program containing (step 1)

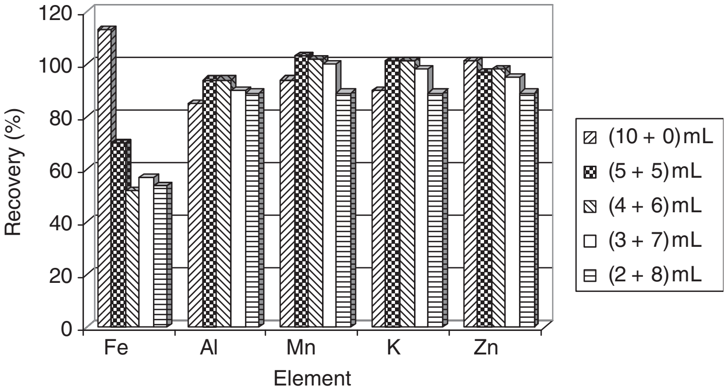

Figure 1. Recovery rates (%) of element concentrations, when different volumes of *aqua regia* and ultrapure water were used as digestion solutions.

power of 1000 W for 5.5 min (175°C) and (step 2) power of 1000 W for 10 min (175°C). The digestion program was adapted from the EPA methods which suggest the use of HNO_3 as a digestion solution [41]. The same digestion program was also used with *aqua regia* for a comparison between these two digestion solutions. After digestion the sample solution was filtered (Whatman No. 41) into a 50 mL volumetric flask and the filtrate diluted to volume with ultrapure water.

2.5 *Dry ashing*

A SRM or real sample of about 250 or 500 mg was accurately weighed into a crucible. The crucible was placed into a muffle furnace (25°C) and heated during 1 h to a temperature of 500°C and left to stand for 4 h [33]. After cooling, the sample ash was placed into a 50 mL plastic wide-neck screw-top bottle into which a digestion solution of 2.5 mL of ultrapure water and 2.5 mL of *aqua regia* was added. The bottle was closed and placed into a 650 W, 35 kHz, Model Transsonic 820/H ultrasonic water bath (ELMA, Singen, Germany). After 3 min of sonication, the total dissolution was obtained.

3. Results and discussion

3.1 *Calibration*

All the ICP-OES measurements were carried out using a four-point calibration. Multi-element calibration standards were used for all elements (Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn). The optimisation of elements determination was performed by taking two emission lines. The quantification limits of the determination of element concentrations can be seen in Table 1.

3.2 *Optimisation of an ultrasound-assisted digestion procedure*

The ultrasound-assisted digestion procedure was optimised by the analysis of two replicate samples of about 250 or 500 mg of the SRM or real sample. The optimisation was carried out by the determination of the Al, Fe, K, Mn and Zn concentrations by ICP-OES. These elements were selected because they represent different kinds of dissolution trends. The concentrations determined for Al and Fe are normally used as an indication of successful sample pre-treatment of plant materials [40]. The efficiency of different digestion solutions was evaluated. Digestion solutions of 10 mL of *aqua regia* and different volumes of *aqua regia* and ultrapure water were tested. The effects of the concentrations of digestion solutions on element recoveries are presented in Figure 1.

The optimisation procedure showed that concentrated *aqua regia*, as a digestion solution is, surprisingly, not as powerful as the digestion solution of 5 mL of *aqua regia* and 5 mL of ultrapure water. The determination of Al, K and Mn was carried out successfully when diluted *aqua regia* was used as digestion solution for SRM 1575a. The element concentrations determined decreased significantly when a smaller volume of *aqua regia* was used.

Different sonication times were also tested. The sonication time varied from 3 to 21 min with and without dividing it into steps. The sonication time did not significantly influence on the element concentrations determined. Slightly higher concentrations were determined when a sonication time of 9 min was used and the sonication was divided into three equal steps, including shaking by hand between each steps. The sonication time of 9 min has been used also for the analysis of toxic elements in soil samples [39].

3.3 *Optimisation of plasma conditions*

It is well known that the ICP-OES measurements may be subject to matrix interferences. Interferences can be significantly reduced by optimising the plasma properties and using the appropriate emission lines for each element. Robust plasma conditions are usually obtained using high plasma energy and low nebulizer gas flow; however, the correct parameters should be tested. In this study, correct plasma conditions were obtained by determining the Mg II/Mg I line intensity ratios [42]. The Mg II 280.270 nm/Mg I 285.213 nm line intensity ratios were determined by the analysis of synthetic mixture of matrix elements containing a concentration of 2 mg L^{-1} of Mg. The concentrations of the main matrix elements of Al, Ca, K, Mn and Na were 20, 50, 150, 10 and 5 mg L^{-1}, respectively.

The values of the diagnostic ratio [43,44] showed the efficiency of a plasma power of 1400 W (Figure 2). According to the highest values, the robust plasma conditions were obtained with 0.5 or 0.6 L min^{-1} nebulizer gas flow and a plasma power of 1400 W for both axially and radially viewed plasmas. The nebulizer flow of 0.6 L min^{-1} was chosen instead of 0.5 L min^{-1} for measurements because of the higher emission intensities produced by the radial plasma. A lower precision was also obtained when nebulizer flow of 0.5 L min^{-1} was used.

3.4 *Evaluation of wavelengths and plasma viewing*

The selection of the plasma viewing and analytical wavelengths was based on the analysis of real pine needle sample with and without the standard addition method at two levels of concentrations. The element concentrations added were 100 and 200% of the concentration determined. The standard addition method consisted of pre-treating six replicate samples of a real pine needle sample with the ultrasound-assisted

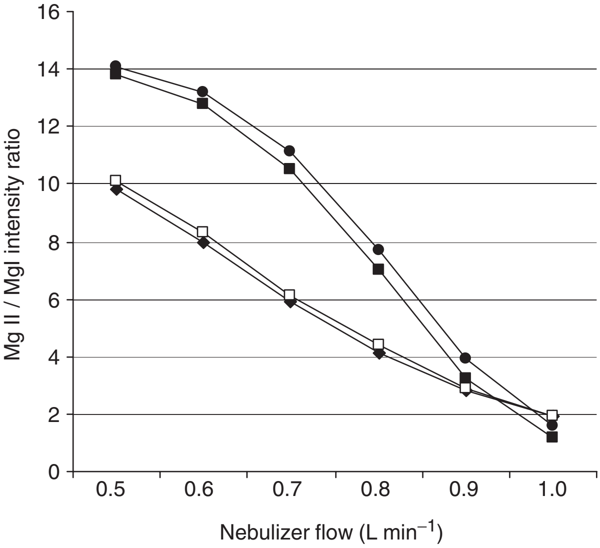

Figure 2. Values of Mg II 280.270 nm/Mg I 285.213 nm line intensity ratios for synthetic mixture of the matrix elements containing 2 mg L^{-1} of Mg by different nebulizer gas flow rates with plasma power of 1300 W using (◆) axial and radial (■) plasma viewing and 1400 W using (□) axial and (●) radial plasma viewing.

digestion method, after which 100 or 200% standard addition was made to four samples. Two replicate samples without the standard addition were used as a baseline for recovery. The standard addition method was performed repeatedly and no significant differences between the recovery rates were observed.

The recovery rates of the selected wavelengths varied from 92% (Zn) to 108% (Na). The determination of concentrations of Al, B, K, Mg and P can be performed with a high accuracy, resulting in recoveries of 100 ± 2% at wavelengths 308.215, 249.772, 766.490, 285.213 and 213.617 nm, respectively. The concentrations determined for Ca, Cu, Fe and Mn showed slightly higher recoveries at wavelengths 315.887, 327.393, 238.204 and 257.610 nm, respectively. The recoveries of Na and Zn were 102 and 96%, but with a low precision.

According to the recovery rates of the standard addition method, the axial plasma viewing was valid for B, Cu and P only. Ca and K were present in such high concentrations that the most sensitive emission lines were not appropriate for the measurement.

3.5 *Analysis*

One SRM sample and seven pine needles samples collected from Central Finland were analysed. The element (Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn) concentrations determined were highly comparable with the certified concentrations of the SRM 1575a (pine needles), as can be seen in Table 2. The element concentrations determined with both ultrasound-assisted and microwave digestion followed with the ICP-OES was also statistically tested; significant differences were found for couple of elements. It should be noted that the SDs of the certified concentrations are not taken into consideration when the *t*-test is used for method validation with SRM [45]. The calculated *t*-tests showed that

Table 2. Analytical results (mg kg^{-1}; d.w.) for the composition obtained with SRM 1575a (mean of four replicate samples with the confidence limits of the mean, $p = 0.05$).

Element	Wavelength (nm)	Ultrasound (*aqua regia*)	Microwave (65% HNO_3)	Microwave (*aqua regia*)	Dry ashing[a]	Certified
Al	308.215 (Radial)	550 ± 30	560 ± 20	584 ± 10	550 ± 30	580 ± 30
B	249.772 (Axial)	9.6 ± 1.2	21 ± 5	16 ± 3	10.7 ± 1.5	9.6 ± 0.2
Ca	315.887 (Radial)	2410 ± 40	2600 ± 120	2600 ± 40	2520 ± 80	2500 ± 100
Cu	327.393 (Axial)	3.5 ± 0.3	5.7 ± 0.5	4.4 ± 0.6	3.1 ± 0.1	2.8 ± 0.2
Fe	238.204 (Radial)	32 ± 3	47 ± 2	41 ± 2	43 ± 5	46 ± 2
K	766.490 (Radial)	4230 ± 120	4240 ± 120	4360 ± 30	4070 ± 120	4170 ± 70
Mg	285.213 (Radial)	1000 ± 20	1010 ± 30	1030 ± 10	990 ± 40	1060 ± 170
Mn	257.610 (Radial)	452 ± 8	493 ± 15	493 ± 6	477 ± 14	488 ± 12
Na	589.592 (Radial)	85 ± 9	210 ± 60	200 ± 30	67 ± 6	63 ± 1
P	213.617 (Axial)	700 ± 30	970 ± 40	1010 ± 20	1080 ± 40	1070 ± 80
Zn	206.200 (Radial)	34 ± 3	37 ± 2	37 ± 2	37 ± 3	38 ± 2

Note: [a]Dry ashing method followed with the ultrasound-assisted dissolution using a digestion solution of ultrapure water and *aqua regia*.

the determination of concentrations of Al, Ca, Mg and Zn only can be performed with all sample pre-treatment methods investigated.

According to the statistical tests, the most suitable sample pre-treatment method is dry ashing followed with the ultrasound dissolution. The determination of element concentrations with dry ashing was performed successfully, resulting in significant differences between the determined and certified concentrations of Cu only. The concentrations determined for Cu were slightly high, which correlates with the recoveries in the standard addition method. This is due to the low concentrations of Cu in pine needles.

The determination of Mn by ultrasound-assisted digestion followed with ICP-OES resulted in slightly lower concentrations; significantly lower concentrations were observed for Fe and P only. The Cu and Na determinations resulted in too high concentrations in all the sample pre-treatment methods investigated.

Microwave digestion methods with the same digestion program but with different digestion solutions were highly comparable. Better analytical results for P were obtained by microwave digestion with *aqua regia*, whereas HNO_3 resulted in better concentrations for Fe. Both methods were unsuitable for the determination of B, Cu and Na at this level of concentrations. The significant contamination of B, Cu and especially Na by TFM vessels was observed. It did not disappear even when a multi-step clean up procedure was used; however, the contamination of B and Cu was slightly reduced. On the basis of the element concentrations determined in SRM, the microwave digestion with *aqua regia* was valid for the comparison of real samples.

The ultrasound-assisted digestion, microwave digestion using *aqua regia* as a digestion solution and dry ashing followed with ultrasound dissolution were also compared using two real pine needle samples (Table 3). The element concentrations determined compared well except of the concentrations of Na and P. Significantly low concentrations of P were found in ultrasound-assisted digestion, and also in the analysis of the SRM sample. The determination of Na using microwave digestion resulted in significantly high concentrations in sample Pine 1 but not in Pine 2. The determination of B was performed

Table 3. Determined concentrations (mg kg^{-1}; d.w.) of two pine needle samples by ultrasound-assisted and microwave digestion and dry ashing method (mean of four replicate samples with the confidence limits of the mean, $p = 0.05$) followed with ICP-OES.

	Pine 1			Pine 2		
Element	Ultrasound (*aqua regia*)	Microwave (65% HNO_3)	Dry ashing[a]	Ultrasound (*aqua regia*)	Microwave (65% HNO_3)	Dry ashing[a]
Al	163 ± 9	207 ± 14	191 ± 6	178 ± 5	230 ± 30	210 ± 12
B	18.1 ± 1.2	20.0 ± 1.0	19.7 ± 1.4	11.5 ± 1.3	11.5 ± 1.0	11.0 ± 2.0
Ca	1950 ± 50	2000 ± 100	2070 ± 50	2460 ± 60	2490 ± 30	2570 ± 40
Cu	4.7 ± 0.2	7.7 ± 1.4	5.5 ± 0.7	5.7 ± 0.3	6.3 ± 0.7	6.0 ± 0.5
Fe	35 ± 3	66 ± 7	39 ± 2	38 ± 3	53 ± 3	40 ± 7
K	5600 ± 200	6100 ± 300	6100 ± 200	4730 ± 70	5090 ± 40	4800 ± 300
Mg	920 ± 30	1000 ± 30	1020 ± 30	733 ± 10	798 ± 14	800 ± 30
Mn	970 ± 20	1000 ± 50	1020 ± 30	770 ± 20	780 ± 20	800 ± 20
Na	40 ± 5	100 ± 20	44 ± 14	56 ± 7	57 ± 3	40 ± 7
P	1170 ± 20	1530 ± 100	1720 ± 10	830 ± 20	1090 ± 30	1210 ± 30
Zn	48 ± 1	60 ± 6	50 ± 1	48 ± 1	52 ± 1	47 ± 3

Note: [a]Dry ashing method followed with the ultrasound-assisted dissolution using a digestion solution of ultrapure water and *aqua regia*.

well with all the methods tested and surprisingly significant contamination was not observed with microwave digestion. It should be noted that the concentrations determined for B were higher than the concentration in the SRM sample.

When the element concentrations obtained for SRM (Table 2) and two real pine needle samples (Table 3) were compared, the dry ashing method followed with ultrasound dissolution resulted in highest accuracy for trace element analysis in pine needles but, however, all the sample pre-treatment methods tested can be used. When real pine needle samples were compared, the ultrasound-assisted digestion resulted in too low concentrations for Al and P, whereas, microwave method resulted in too high concentrations for Cu, Fe and Na. All the other elements resulted in concentrations highly comparable. Ultrasound-assisted digestion resulted in sample pre-treatment method highly comparable with the microwave method, but with lower time and power used. The same effect has been observed also for the analysis of toxic element concentrations in soils [39] and ash samples [44]. The ultrasound-assisted digestion has two advantages over other methods which are the high sample treatment capacity and the possibility to use new sample vessels for all samples. The usage of new plastic screw-top bottles or centrifuge tubes as sample vessels minimises the risk of contamination significantly.

The concentrations determined for Al, Cu, Fe, K and Zn did not vary significantly between the pine needle samples (Tables 3 and 4). However, the concentrations determined for B, Ca, Mg, Mn, Na and P, some of which are known to be essential elements for the growth and division of a cell, varied significantly so that the highest concentrations were two or even three times higher than the lowest ones. This shows that the variations between the essential element concentrations can be significant.

Boron resulted in concentration range from 11.5 to 24.0 mg kg^{-1}, which is high enough for efficient growth. A strong dependency has been found between the height growth and needle concentrations, when the concentrations of B decreases lower than 5 mg kg^{-1} [11].

Table 4. Analytical results (mg kg^{-1}; d.w.) for the composition obtained with five pine needle samples and average composition in Central Finland adapted from the literature.

Element	Pine 3	Pine 4	Pine 5	Pine 6	Pine 7	Literature data[a]
Al	96 ± 4	127 ± 4	147 ± 14	205 ± 4	96 ± 5	258 ± 117
B	18.0 ± 2.0	19.0 ± 2.0	24.0 ± 1.0	18.0 ± 2.0	15.8 ± 0.6	15.2 ± 3.8
Ca	6600 ± 200	4740 ± 50	5090 ± 90	1600 ± 30	2000 ± 80	2200 ± 470
Cu	5.7 ± 0.2	6.7 ± 0.3	6.4 ± 0.6	8.3 ± 0.9	4.8 ± 0.4	2.58 ± 0.48
Fe	46 ± 2	50 ± 3	59 ± 4	32 ± 3	15 ± 1	47.2 ± 9.74
K	4190 ± 120	4710 ± 120	4600 ± 100	6200 ± 200	4500 ± 200	5670 ± 770
Mg	1040 ± 30	1220 ± 30	1280 ± 30	1110 ± 20	670 ± 30	850 ± 150
Mn	1700 ± 40	1130 ± 10	573 ± 10	381 ± 7	315 ± 14	536 ± 178
Na	48 ± 15	26 ± 2	33 ± 8	66 ± 15	81 ± 5	32.6 ± 10.8
P	1510 ± 60	1490 ± 60	1490 ± 40	2200 ± 40	1220 ± 60	1670 ± 190
Zn	45 ± 2	37 ± 2	46 ± 4	35 ± 4	36 ± 1	46.8 ± 8.7

Note: [a]Reference [10].

In this work, the concentration level of B is in the same line with the average concentrations (Table 4) determined in Central Finland 10 years ago [10].

The determination of mineral and trace elements in pine needles resulted in concentrations comparable (Table 4) with average concentrations determined 10 years ago. As the concentration levels of these elements are used for the evaluation of the need of fertilizers, a more extensive analysis program is needed. This can be performed effectively with the ultrasound-assisted digestion or dry ashing method followed with ICP-OES. The usage of microwave digestion method may be subjected to significant increase in B concentrations.

4. Conclusion

The analysis of Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn concentrations in pine needles was performed successfully. The effectiveness of ultrasound-assisted and microwave digestion and dry ashing followed with ultrasound dissolution were demonstrated (Tables 2 and 3). The sample pre-treatment methods tested were comparable, although dry ashing followed with ultrasound dissolution was found the most accurate. The determination of all elements in SRM 1575a by ICP-OES using a dry ashing followed with ultrasound dissolution as a sample pre-treatment method obtain the certified concentrations at the 95% level of confidence using the *t*-tests. The exception is Cu which resulted in low concentrations. The major advantages of the dry ashing method over other methods investigated are the total destruction of the sample matrix, which resulted in lower matrix effects in the measurements and the capability to increase sample weights, which enabled lower detection limits to be attained. The major advantages of the ultrasound-assisted digestion are the speed of digestion and the possibility to use new contamination free sample vessels for all samples but with low costs.

All the concentrations determined were obtained at robust plasma conditions which were thoroughly optimised. The optimisation of the ICP-OES nebulizer gas flow and plasma power was based on the Mg II 280.270 nm/Mg I 285.213 nm line intensity ratios. The observed line intensity ratios showed that the sample matrix of pine needles had a significant influence on the atomisation and excitation conditions of the plasma. The Mg II 280.270 nm/Mg I 285.213 nm line intensity ratios decreased dramatically (Figure 2) when the nebulizer flow was increased up to 0.8 L min^{-1}. The robust plasma conditions were reached with a nebulizer flow of 0.6 L min^{-1} and a plasma power of 1400 W for both axially and radially viewed plasmas. The axially viewed plasma was used for the determination of B, Cu and P concentrations. B and Cu were found in such low concentrations that measurements using radially viewed plasma could not be performed. The standard addition method was applied at two levels of concentrations to show the efficiency of the analysis. The element recovery rates of the selected wavelengths varied from 92% (Zn) to 108% (Na). The determination of Al, B, K, Mg and P was performed with high accuracy and precision resulting in recoveries of $100 \pm 2\%$.

The analysis of two real pine needle samples was performed with three sample pre-treatment methods and the remaining five samples were analysed using the dry ashing method followed with ICP-OES. A comparison of three sample pre-treatment methods resulted in results similar as to those of the SRM sample. One exception was the concentrations determined for B, which did not increase in the microwave digestion. This was due to higher concentrations of B in real samples but, however, when low concentrations of B are determined, the microwave digestion method should not be used. B is one of the key elements in growth of height of coniferous trees and needs to be accurately determined.

Acknowledgements

This research has been carried out under the auspices of the European Union COST D32 Action (Working Group WG005/04: Microwaves and ultrasound activation in chemical analysis).

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