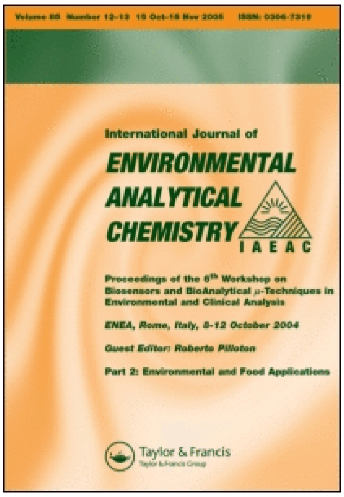

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Comparison of Conventional, Ultrasound- and Microwave-Assisted Extraction Techniques Applied for the Determination of Metals in Spruce Needles

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COMPARISON OF CONVENTIONAL, ULTRASOUND- AND MICROWAVE-ASSISTED EXTRACTION TECHNIQUES APPLIED FOR THE DETERMINATION OF METALS IN SPRUCE NEEDLES

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In the present study the extraction of trace and major elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sr, Ti, V and Zn) from spruce (*Picea*) needle samples under various experimental conditions, i.e., extractant, temperature and time of extraction, was examined. The effectiveness of conventional, ultrasound- and microwave-assisted extraction techniques was investigated. The replacement of a sample decomposition procedure by leaching prior to multielemental analysis by ICP-AES as well as the aspect of fractionation analysis is discussed. Standard Reference Material (CRM 101-Norway spruce needles) was used for validation of the applied analytical procedures.

Keywords: Conventional extraction; Ultrasound-assisted extraction; Microwave-assisted extraction; Spruce needles; Metals; ICP-AES

INTRODUCTION

Extraction is most often used to separate the analyte from the matrix or to concentrate the analyte up to a detectable concentration level [1]. Increasing attention has been paid lately to the application of extraction procedures as sample preparation methods prior to elemental analysis. Trace metal measurements in environmental samples are mainly focused on the determination of the total elements composition. However, the information about the total metal concentration is often insufficient, and different forms of heavy metals must be determined.

Solid–liquid extraction (leaching) has become a well-developed tool for determination of metal fractionation and speciation in sediments and soil samples (see, for example, [2–6]). Few papers have been devoted so far to leaching elements from

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biological materials, especially bioindicators used for assessment of environmental pollution. Solid–liquid phase extraction has been used as a method of sample preparation for determination of B, Cd, Cu, Pb in various samples, i.e., plant materials, animal tissues and sediments [7–9].

An evaluation of extraction techniques for metal species from biological materials has also been performed [10]. So far the effectiveness of solid–liquid extraction from plant materials has been studied, as a rule, for only a few elements simultaneously [11–14]. Main group elements (Ca, K, Mg, Na) and anions (HPO_4^{2-}, NO_3^-, SO_4^{2-}) have been removed from corn, cabbage leaves, peach leaves, and cotton leaves by water [11]. The metals Cr, Cu, Fe, Mn, Ni and Zn have been extracted from tea leaves by boiling water [12]. Metal-binding carbohydrates have been extracted from plant roots by ammonium acetate [13]. Concentrations of Ca, K, Mn, Mg, Ni and Zn have been determined in isolated low-molecular-weight fractions of plant extracts, which have been obtained after extraction by 0.5 M ammonium acetate at different pH values. A pressurized liquid extraction procedure using water and water/methanol mixtures has been applied to extract organoarsenic compounds from plant materials [14].

Most of the procedures developed for metal leaching are based on the conventional extraction technique, where a very long time (up to 24 h for a single process) is essential. Recently some papers have reported the use of microwave energy and ultrasound for acceleration of the extraction process. Conventional shaking was replaced by microwave- or ultrasound energy assistance, which allows the extraction time to be shortened. The microwave technique was used to extract trace elements (i.e., Al, B, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V and Zn) from spinach leaves and onion [15]. Microwave energy was used for boron leaching from biological materials [9]. Leaching of Ca, Cu, Fe, K, Mg, Mn, Ni and Zn with diluted nitric acid from plant samples was performed and reported by Zhou *et al.* [16], where extraction parameters such as the nitric acid concentration, pressure, extraction time and sample mass were investigated. A few metals (Cu, Pb, Mn and Zn) have been separated from an aquatic plant matrix by ultrasound energy [17]. Ultrasound-assisted extraction of Cd, Cu and Pb by diluted nitric acid from biological samples was carried out [8]. Quantitative extraction by diluted nitric acid and determination of Cd and Pb in mussel tissue was performed using the ultrasound technique [18]. Compared with conventional shaking, sonication significantly improved the extraction process of biologically active substances from raw plant materials [19]. Solvent extraction with sonication using various aqueous and aqueous/solvent mixtures was employed for extraction of arsenic species from freeze-dried apples [20]. Ethylenediaminetetraacetic acid in alkaline medium was used for ultrasound-assisted solubilization of trace and minor metals from plant samples [21].

Extraction methods for such a plant material as coniferous needles have been reported in detail only in [22–25]. The extraction of Al, Ca, Cu, Fe, Mg, Pb and Zn by concentrated hydrochloric and diluted (1 : 5) nitric acids at 90°C from pine needles (*Pinus sylvestris*) was studied by Wieteska and co-workers [22,23]. From red spruce needles (*Picea rubens* Sarg.) major inorganic cations (i.e., Ca, Mg, Mn and K) were leached by 0.01 M HCl [24]. Six extraction media (acetic acid, EDTA, tetrabutylammonium hydroxide, NaOH, MeOH/H_2O and acetonitrile/H_2O) extracted Sb and As from freeze-dried pine and spruce shoots as well as from poplar leaves and a peat matrix [25].

A study devoted to a comparison of various solid–liquid extraction techniques, i.e., conventional, ultrasound- and microwave-assisted leaching methods, applied to plant materials has not been reported so far.

The main purpose of this study was the comparison of the effectiveness of conventional, microwave- and ultrasound-assisted element extraction from spruce needles. The influence of various experimental conditions, such as the extractant, the concentration of the extractant, temperature and leaching time on the extraction efficiency was investigated. Concentrations of Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Sr, Ti, V and Zn extracted from spruce (*Picea*) needles were measured using the ICP-AES method.

EXPERIMENTAL

Samples

Extraction procedures were applied to spruce (*Picea*) needle samples collected in urban areas. Dust and deposits were removed from the surface of needles by washing in tap and distilled water. The cleaned needles were dried at room temperature, removed from the twig axis and milled. Needles were stored in bags until preparation.

The Reference Material – BCR CRM 101 (spruce needles) was used for quality control and assurance.

Reagents, Glassware and Plastics

Standard calibration solutions were prepared by dilution of 1000 ppm stock standard solution (ICP Multi Element Standard; Merck KGaA, Darmstadt, Germany). Deionized water (18.3 MΩ cm) was prepared by water purification system Easy pure RF (series 703, Barnstead, Thermolyne Corporation, USA) and used throughout preparation and analysis.

Glassware and plastic bottles were cleaned with 10% nitric acid in an ultrasonic bath and rinsed several times with deionized water.

The extractant solutions were prepared from analytical-grade reagents (Merck kG&A, Darmstad, Germany and PPH-POCh, Gliwice, Poland). The hydroxylammonium chloride solution was prepared in 0.05 M HCl prior to use.

Sample Preparation Procedures

Microwave-assisted Digestion

About 500 mg of powdered spruce needles was accurately weighed into a teflon digestion vessel. 6 mL of concentrated nitric acid and 1 mL of hydrogen peroxide (30%) were added. Decomposition of samples was carried out in a microwave digestion system (Milestone, MLS-1200, MEGA). After cooling, the sample solutions were quantitatively transferred into 25-mL volumetric flask and made up to the volume.

Conventional Extraction (CE)

20 mL of extractant was added to 2 g of dry needles in a glass tube, and the tube was shaken on a mechanical shaker at a speed of 200 r/min.

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	0.2 L min^{-1}	
	Nebulizer gas flow rate	0.3 L min^{-1}	
	Sample uptake	0.8 mL min^{-1}	
Monochromator:			
		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, 280.270, 285.213
B	249.773	Mn	257.610, 259.373
Ba	233.527	Ni	221.647, 231.604
Ca	317.933, 393.366	P	213.618, 214.914
Cd	214.438, 226.502, 228.802	Pb	220.353
Co	228.616	Sr	407.771
Cr	205.552, 267.716	Ti	334.941
Cu	224.700, 324.754	V	292.402
Fe	238.204, 259.940	Zn	202.548, 213.856

Ultrasound-assisted Extraction (UE)

An accurately weighed 2 g of a sample was placed in a polyethylene tube and 20 ml of extractant solution was added.

Microwave-assisted Extraction (ME)

About 2 g of dry material was weighed into a PTFE extraction vessel. After adding 20 mL of extractant solution, the vessel was capped and placed in the oven.

After extraction, the supernatant was separated from the solid residue by filtration through hard filter paper.

With each set of leached and digested samples a blank sample was prepared and used for the correction of results.

Apparatus

Atomic emission spectrometry with inductively coupled argon plasma was used for elemental concentration measurements in digests and extracts. A Jobin-Yvon 38S spectrometer equipped with a cross-flow nebulizer and Scott-type spray chamber was used. The operating parameters and wavelengths used are listed in Table I.

RESULTS AND DISCUSSION

Extraction efficiency was calculated as the ratio of the metal amount leached by an extractant to the total metal content, determined using microwave digestion. Precision of the measurements was determined by the analysis of three, individually prepared, sub-samples and the RSD values were found to be lower than 5% for the digests and 15% for the extracts.

Total Concentration of Elements

The total metal concentrations in the needle samples were determined in digests obtained by using the microwave decomposition procedure. This technique was validated using the standard reference material (CRM 101-Norway spruce needles, *Picea abies*). A good agreement with certified values was obtained. The details of the standard reference material analysis were reported in our previous work [26].

Effect of Extractant

Six extraction media were tested to investigate extraction of metals from dry spruce needles. Deionized water and solutions of ammonium acetate (1 M), ethylenediamine tetraacetic acid trisodium salt (0.1 M), hydroxylamine hydrochloride (0.1 M), hydrochloric and nitric acids (1 M) were used as extractants. The listed chemicals have been commonly used in fractionation analysis of solid environmental samples, e.g., sediments and soils. Water removes the water-soluble (exchangeable) metal fraction; ammonium acetate separates metals bonded to carbonates; EDTA chelating (complexing) agent extracts the bioavailable metal fraction (metals nominally associated with carbohydrates); the amine removes the reducible fraction (forms associated with oxides and hydroxides of Fe, Al and Mn; dilute HCl leaches acid-soluble metals and HNO_3 is an oxidizing agent, which removes the fraction of oxidizable elements (oxidizable species bound to organic matter and sulfides)).

The efficiency of the conventional extraction for selected elements is presented in Fig. 1. As can be seen, the efficiency of the extraction strongly depends on the extractant solution and the element. Medium efficiency of all extractants, i.e., close to or over 50% were obtained for magnesium, manganese and zinc (in all examined extractant solutions). The extraction process was least effective for Cr and Ti (not shown). These metals seem to be hardly mobile.

Generally, water, an agent removing the exchangeable metal fraction, has extracted the least amounts of all examined elements. Analysis of the water-extractable fraction shows that a significant part of Cu, Mg, Mn and Zn (30–40%) occurs in plant material in water-soluble forms. Very small concentrations of Al, Cr, Fe, Ni, Pb and Ti were found in water-soluble forms. The extraction efficiency of ammonium acetate was similar or higher than that found for water. The highest extraction efficiency with EDTA (over 50%) was obtained for Cu, Mg, Mn, Ni, Pb and Zn. The highest efficiency of 75% was obtained for phosphorus. Hydroxylamine efficiently released Ba, Cu, Mg, Mn and Zn. There was a very small amount (less than 10%) of Al, Cd, Cr and P detected in amine extracts. 1 M HCl was found to be an efficient extractant for most of the elements. Close to 100% efficiencies were observed for Ba, Ca, Cu, Fe, Mg, Mn, Pb and Zn. 1 M HNO_3 removed a significant proportion (up to 100%) of Ba, Ca, Cd, Mg, Mn, Pb and Zn.

Large differences in the efficiency of the employed extractants indicated the possibility of applying the extraction process in speciation and/or fractionation analysis of the plant material. For some of the examined elements, i.e., Ba, Cu, Mg, Mn and Zn, extraction with the dilute acids can replace a conventional mineralization procedure by concentrated acids. None of these elements seems to be bonded to silicates and therefore none requires full decomposition of a sample.

Ultrasound and microwave extraction revealed a similar dependence of the extraction efficiency on the extractant solution.

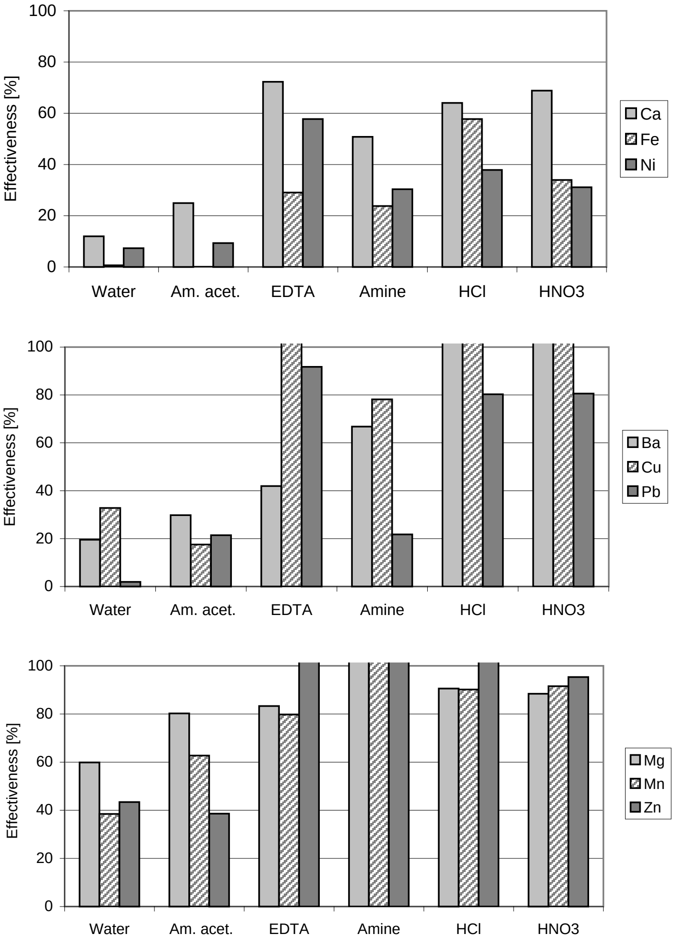

FIGURE 1 Conventional extraction (CE) effectiveness for various elements and extractants ($t = 24$ h; $T = 30$°C).

Effect of Extraction Temperature

Temperature Influence in Conventional and Ultrasound-assisted Extractions

Conventional and ultrasound-assisted extractions were carried out at five different temperatures: room temperature, 40, 50, 60 and 70°C (in some cases at 80°C). Temperatures higher than room temperature were achieved in a water bath controlled by a thermostat.

Results of determinations of selected elements in solutions obtained by extraction at different temperatures are shown in Figs 2 and 3. Usually, for conventional extraction, a rise in temperature causes increased leaching effectiveness, but this relationship is different for the various elements examined here. The largest differences were obtained for Fe, Cr and P concentrations. A general increase of the Al, Ni, Pb, Sr, Ti and V concentrations in all extractants with temperature was also observed. No meaningful differences were found between the concentrations of B, Ba, Ca, Mg, Mn and Zn

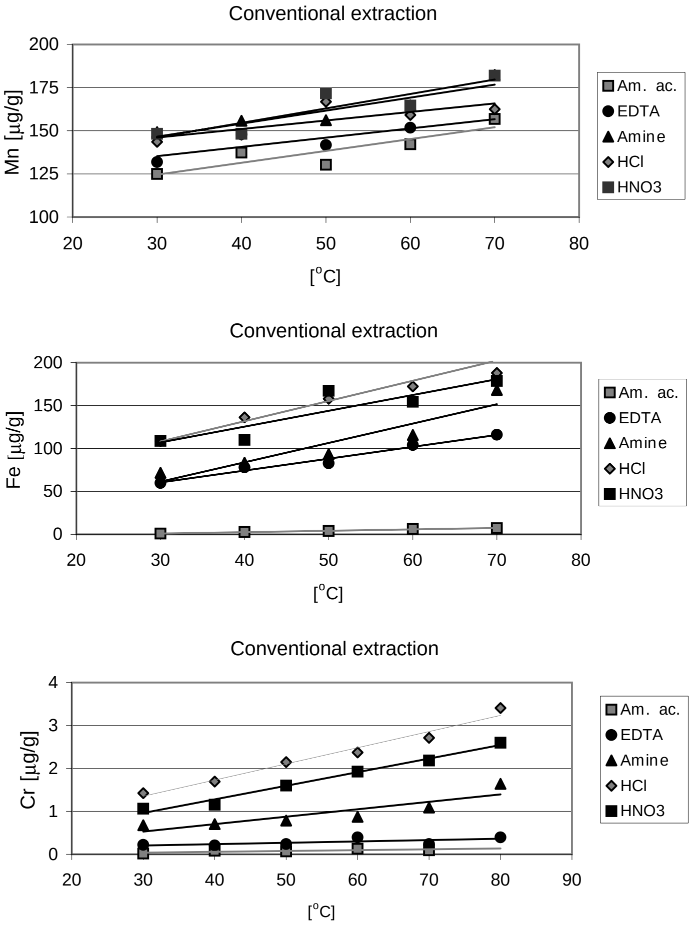

FIGURE 2 Extraction efficiency *versus* temperature for conventional extraction (CE: $t = 24\,\mathrm{h}$).

released at the temperatures used. Considering the results obtained it can be said that the strongest changes with temperature were observed for acids and amine.

For ultrasound-assisted extraction (and likewise for conventional shaking) temperature increase produced an increase in the leaching process efficiency for Al, Cr, Fe, Mn, Ni and Sr. For the rest of the elements analyzed here, only a small increase of the leaching efficiency with the temperature or even no effect was noticed.

Effect of Radiation Power in Microwave-assisted Extraction

To study the influence of microwave power on extraction process, the power varied from 100 to 300 W (i.e., 100, 150, 200 and 300). The relationship of the microwave radiation power and the leaching process effectiveness for selected elements is presented in Fig. 4. For all the elements studied here an increase in power increased the leached metal contents in the extraction solvents. The greatest concentration growth with power was observed for Al, Cr and Fe leached by HCl. However, extraction power did not

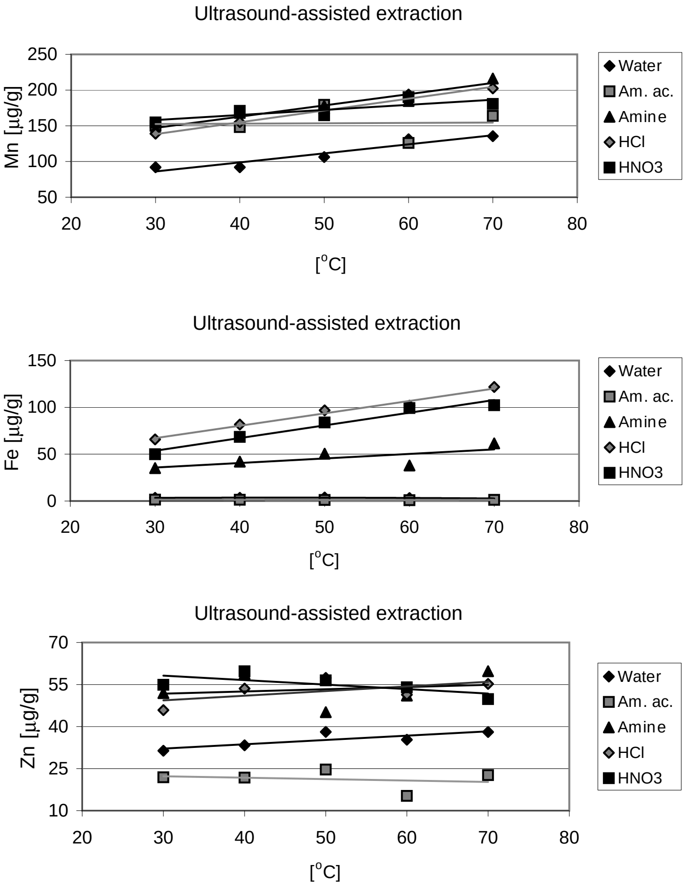

FIGURE 3 Extraction efficiency *versus* temperature for ultrasound-assisted extraction (UE: $t = 10\,\mathrm{min}$).

have an effect for B (in HNO_3 and ammonium acetate), Ba (in HNO_3 and water), Ca (in HNO_3), Cu (in amine, HNO_3 and ammonium acetate), Mg (in HNO_3 and ammonium acetate), Mn (in amine), Pb (in HNO_3, water, ammonium acetate and amine), Sr (in HNO_3 and ammonium acetate) and Zn (basically for all extractants). A relatively low power was sufficient for quantitative leaching of the elements mentioned or of the metal species occurring in the examined material. We have noticed that increasing the radiation power and lengthening the leaching time caused changes in the extractants' colour. Ammonium acetate and amine solutions became turbid, and HCl extracts dark brown. Solutions of nitric acid became lighter and clear. This is probably due to the transfer of various organic matrix components into the extractant solutions.

Effect of Extraction Time

To evaluate the effect of leaching time needle samples were agitated: from 2 to 24 h (2, 4, 8, 12 and 24 h) for a conventional method, from 10 to 120 min for an ultrasound-assisted method and from 2 to 15 min for a microwave-assisted method.

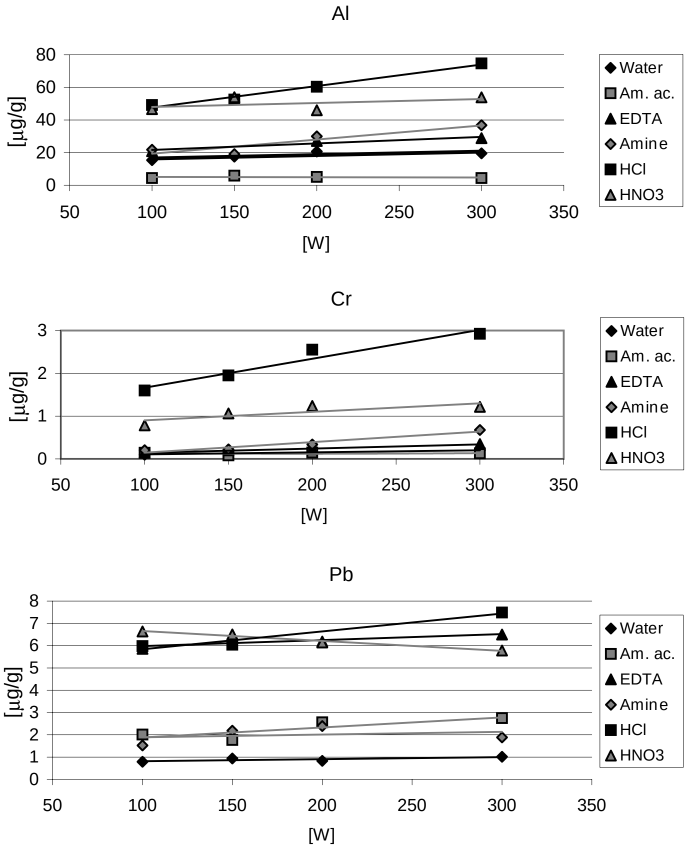

FIGURE 4 Microwave-assisted extraction efficiency *versus* radiation power ($t = 10\,\text{min}$).

Results of the determinations for the selected elements in extracts obtained for various leaching times are presented in Figs 5 and 6.

For conventional extraction a significant increase of concentrations with time was noticed only for Al and Fe. For some elements (Cu, Ni, Pb, Sr and V) a small but definite content increase was found in some extraction solutions. For B, Ba, Ca, Cd, Cr, Mg, Mn and Zn conventional extraction efficiencies did not increase with time (for $t > 2\,\text{h}$).

After the application of ultrasound concentrations of Al and Fe (in EDTA, amine and both acid solutions), Ca (in amine and EDTA), Cu (in amine), and Ti and V (in amine and both acids) showed a significant increase with the leaching time. For some elements (e.g., Zn, see Fig. 6) for most extractants no relation between metal content and time was observed.

In comparison to the conventional and ultrasound extractions, in microwave-assisted extraction the growth of the element concentration with time was much higher. A considerable increase of leaching effectiveness with lengthening of time for Al, Cr, Cu, Fe and Sr was observed in all extractants. The same dependence was noticed for B (water, EDTA, amine and nitric acid), Ba (in water, ammonium acetate, EDTA and amine) and Ca (extracted with water, ammonium acetate, EDTA and amine). The increased

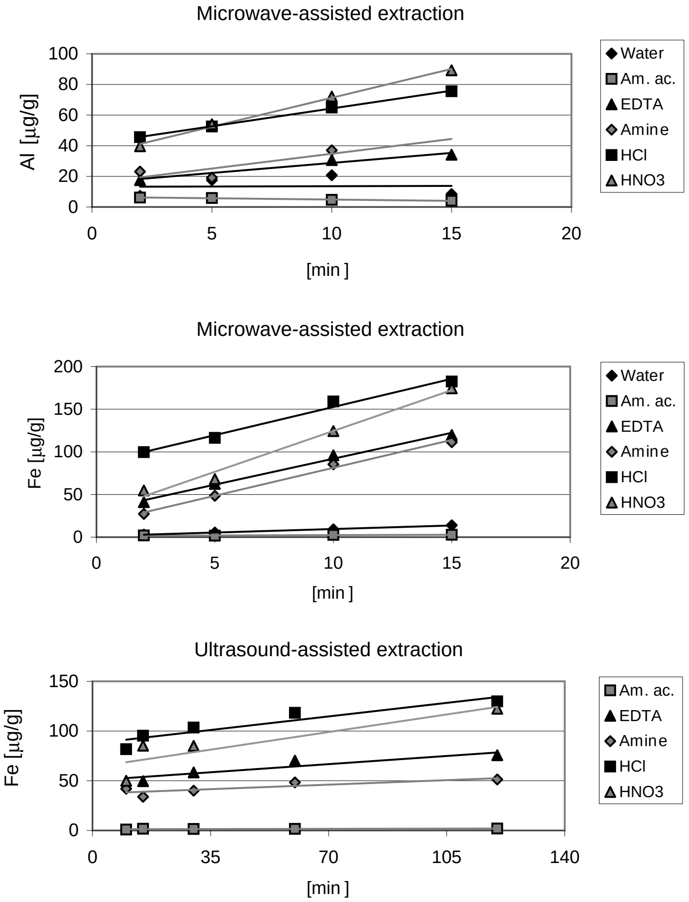

FIGURE 5 Extraction process efficiency *versus* leaching time (ME: $t = 10$ min; UE: $t = 15$ min, $T = 30$°C).

extractability of the analyzed metals may be due to a partial decomposition of the sample.

Comparison of Three Extraction Procedures

Conventional, ultrasound- and microwave-assisted extraction techniques were compared, selecting the following operation conditions: for conventional extraction (CE) – 2 h shaking; for ultrasound-assisted extraction (UE) – sonication for 2 h and 10 min; and for microwave-assisted extraction (ME) – 10 min. Figures 7 and 8 show a comparison between concentrations of selected elements determined here in the extracts. Significant differences are observed between the results obtained using conventional extraction and the extraction with ultrasound and microwave assistance. The use of ultrasound and microwave energy treatment leads to a remarkable shortening of the leaching time. The highest differences between the examined extraction techniques were observed for such elements as Al, Ca, Cr, Ni and Pb, for which, in addition to time

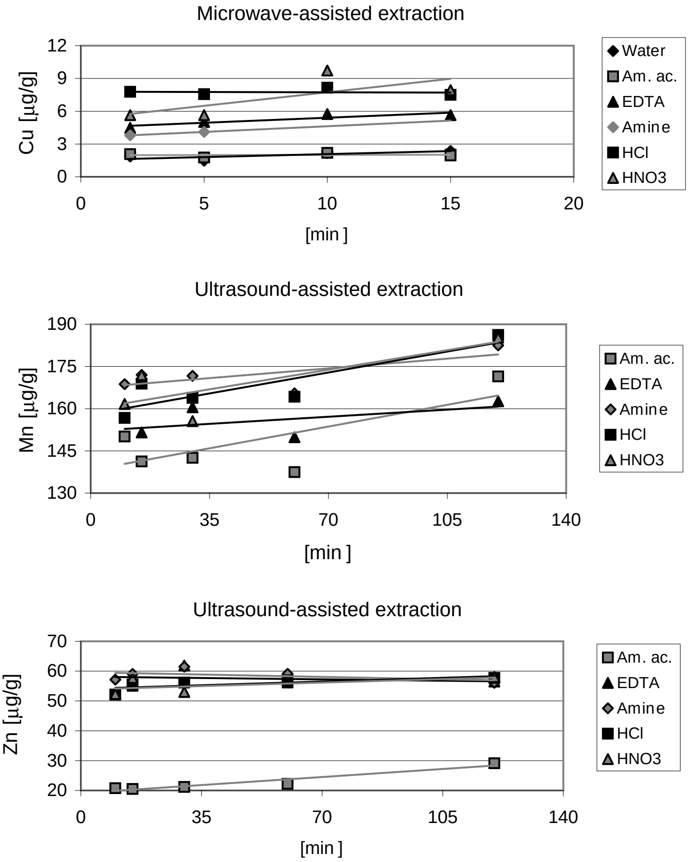

FIGURE 6 Extraction process efficiency *versus* leaching time (ME: $t = 10$ min; UE: $t = 15$ min, $T = 30°C$).

shortening, a growth of the efficiency was found. For elements such as Mg, Sr or Zn about 100% extraction effectiveness was obtained in every type of extraction, so the considerable shortening of the leaching time is the main benefit of the use of ultrasound and microwave energy.

Ultrasonic extraction (compared with conventional for two hours) gives higher efficiency for Al (EDTA and HCl solutions), B and Ba (EDTA, amine and hydrochloric acid), Cr (in hydrochloric and nitric acids), Cu (ammonium acetate, EDTA and both acids), Fe (EDTA and both acids), Mg, Pb, Sr and Zn (EDTA), Mn (ammonium acetate and EDTA, Ni (ammonium acetate, EDTA and both acids).

Microwave treatment caused an additional increase in extraction efficiency. After 10 min of microwave-assisted leaching, higher concentrations of all examined elements were obtained in acid solutions (both hydrochloric and nitric). Higher recoveries were also noticed for B, Fe, Mg and Ni in amine and Mg in ammonium acetate. A small growth of extraction efficiency was found in amine for Al, Ca and Cr and in ammonium acetate for B, Ba, Ca, Cr and Zn.

An accurate quantitative comparison between conventional, ultrasonic- and microwave-assisted extraction techniques is difficult. For example, microwave radiation

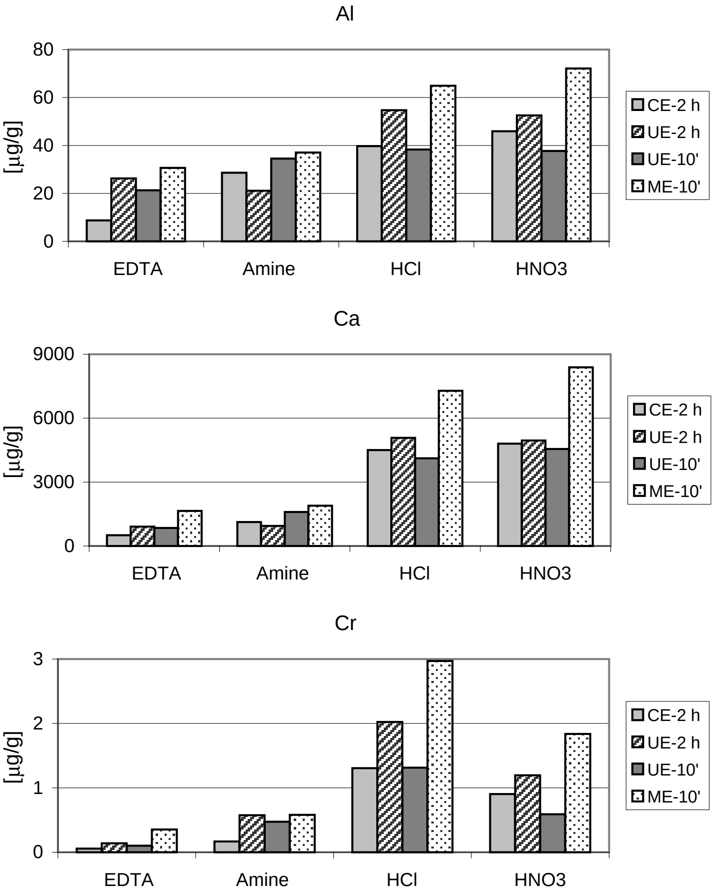

FIGURE 7 Comparison between conventional (CE), ultrasound- (UE) and microwave-assisted (ME) extraction effectiveness.

causes a rise of extractant temperature with time. Nevertheless, the considerable advantages of ultrasound- and microwave-assisted leaching methods applied to plant materials are very clear.

CONCLUSIONS

Microwave and ultrasound extraction techniques can be used to improve the leaching process of trace elements from spruce needles. The replacement of traditional shaking by microwave heating or ultrasound acceleration always causes a reduction of treatment time, and for some elements a considerable increase of leaching effectiveness is an additional benefit. It was found here that diluted acids (HCl and HNO_3) could quantitatively leach Ba, Cu, Mg, Mn and Zn from spruce needles. For those elements one-stage solid–liquid extraction procedure can be easily and successfully applied as an alternative method to the traditional digestion of such plant material as spruce needles. The different amounts of metals released by different extraction solvents indicate that it

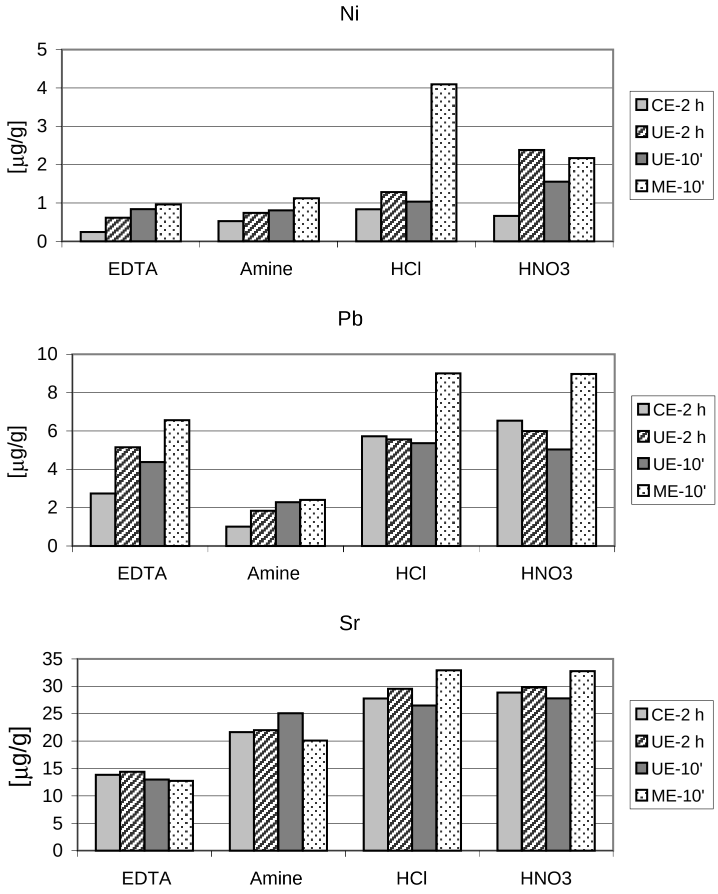

FIGURE 8 Comparison between conventional (CE), ultrasound- (UE) and microwave-assisted (ME) extraction effectiveness.

should be possible to distinguish various element species by fractionation analysis, but for this purpose more experimental work, including sequential extraction, is required.

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