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Comparison of non-destructive techniques and conventionally used spectrometric techniques for determination of elements in plant samples (coniferous leaves)

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Abstract: Conventionally used spectrometric techniques of inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma optical emission spectrometry (ICP-MS) usually involve time-consuming sample preparation procedure of a sample dissolution which requires the usage of aggressive and toxic chemicals. The need for suitable and sustainable analytical methods for direct multi-elemental analysis of plant samples has been increased in recent years. Spectrometric techniques for direct sample analysis, instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF) have been applied in environmental studies and various fields of screening tests. Nevertheless, these techniques are not commonly used for plant sample analysis and their performances need to be evaluated. This research aimed to assess how reliable non-destructive techniques are in the determination of elements in plants compared to conventionally used spectrometric techniques. A total of 49 plant samples of four conifer species (*Pinus nigra*, *Abies alba*, *Taxus baccata* and *Larix decidua*) were measured using two conventionally applied (ICP-MS, ICP-OES) and two non-destructive techniques (wavelength dispersive XRF (WD-XRF), INAA). The comparison was performed by investigation of relative ratios of concentrations and by correlation analysis. Moreover, precision of the techniques was examined and compared. The quality control included analysis of NIST pine needles certified reference material (1575a) using all examined techniques. Our results suggest that addit-

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ional analytical and quality control steps are necessary for reaching the highest accuracy of multi-elemental analysis.

Keywords: multi-element determination; WD-XRF; standardless analysis; INAA; ICP-OES; ICP-MS.

INTRODUCTION

The chemical composition of plant matrices has been conventionally determined by spectrometric techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS).[1–4] The usage of these techniques usually involves demanding sample preparation procedures for sample dissolution. For total destruction of the sample matrix, wet mineralization (digestion) with strong acids has been commonly used.[5,6] Digestion of the sample can be performed in closed or open systems using a wide choice of reagents and their mixtures. The complete digestion in open systems (at atmospheric pressure) usually requires a long time for some plant materials (up to 10 h or even more), and also there is a problem of the loss of volatile compounds. Digestion in a closed system implies the usage of microwave ovens which shortens the time required for dissolution, reducing the volume of corrosive and environmentally non-friendly reagents, and avoiding analyte losses and contamination.[7] However, the required time, equipment, the use of aggressive and toxic chemicals during the sample preparation procedure are the main drawbacks of those conventionally used techniques.[8–11]

In recent years, the need for suitable, sustainable, or more diverse analytical methods for direct and multielemental analysis of plant samples has been increased. Such need arises from the necessity to comply with the principles of green chemistry, but also in order to overcome the shortcomings of multiple conventionally used techniques, related to the analysis of certain elements (*e.g.*, quantification of Na and K using ICP-OES, and Ni using ICP-MS).

The instrumental neutron activation analysis (INAA) is one of the techniques that do not require previous mineralization of samples.[12] This technique requires thermal neutrons produced within a nuclear reactor for the activation of sample elements to form radioactive isotopes. High costs of equipment and maintenance, the long time needed for analysis (several days), and the limited availability of a nuclear reactor are the greatest shortcomings of the INAA technique. INAA has been previously applied in environmental studies (soils, sediments, biological samples), nevertheless, it is not a commonly used technique especially for the vegetal samples, and therefore it is worth to further explore its potential and limitations for plant analysis.[13–16]

X-ray fluorescence (XRF) is another nondestructive technique that has also been used for plant material analysis.[17–21] XRF spectrometry provides the possibility of performing direct multielement analysis of solid samples with a wide dynamic range and low cost per measurement.[22–29] Using the XRF technique, it is possible to perform qualitative, semiquantitative, and quantitative determinations within a short time of analysis (high throughput). The limitations for more frequent usage of XRF spectrometry in environmental studies are higher detection limits for some environmentally important elements (*e.g.*, Pb and Cd).[2,30] The general characteristic of analytical techniques discussed in this study are described in research of Frontasyeva and Orlić *et al.*[31,32]

Conifers have been proven to be passive biomonitors of atmospheric pollution because of their characteristics (thick epicuticular waxy layer) and their distribution all over the world, in urban and industrial environments, in natural forests, as well as in maintained habitats.[33–36]

Although several well-known analytical techniques which require wet digestion are successfully applied to multielemental analysis of plant samples, it is still necessary to explore the potential of the other analytical options for numerous reasons. Either because some elements cannot be accurately analyzed by one or more conventionally used analytical techniques or because total sample digestion can not be easily accomplished (*e.g.*, matrices with high Si content). Non-destructive techniques not only preserve samples for further analysis, but may also save a significant amount of resources and time. Investigated non-destructive techniques (WD-XRF and INAA) are still not routinely used for the analysis of plant samples, therefore it is important to compare their strengths and limitations to conventionally used analytical techniques (ICP-OES and ICP-MS), as well as the potential to replace or complement them. Another goal was to compare the standardless semiquantitative XRF method to other investigated techniques since it is expected that it has lower accuracy, but it also has the highest potential for fast screening studies, because it neither requires digestion of the sample nor any calibration standards.

EXPERIMENTAL

A total of 49 plant samples of four conifer tree species, black pine (*Pinus nigra*), white fir *(Abies alba)*, European yew (*Taxus baccata*), and larch (*Larix decidua*), were measured using four instrumental techniques (WD-XRF, ICP-MS, ICP-OES and INAA). Conifer needles were collected during spring (April and May) on four locations: Belgrade, Pančevo, Banatski Brestovac, and Šar Mountains. The studied locations represent urban and rural areas. The collected needles were up to one year old.

Needles samples were placed into plastic bags and delivered to the laboratory. In the laboratory, samples were air-dried for several days. Conifer needles were then grounded and drying was continued in the oven at 60 °C until a constant mass was reached.

Within WD-XRF analysis, the grounded and dried plant samples were pressed into 32 mm diameter pellets using Retsch PP25 hydraulic press with 15 tons pressure applied for 5 min. The prepared pellets contained around 4 g of plant samples and 20 wt. % of binder (Hoechst wax C micropowder, Merck, C.A.S. number: 110-30-5).

For INAA analysis, approximately 0.3 g of grounded conifer samples was pelletized in 10 mm diameter pellets. For short-term irradiation purposes, plant pellets were heat-sealed in polyethylene foil bags, whereas for long-term irradiation the samples were packed in aluminium cups. Further, polyethylene foils bags and aluminium cups were transferred by pneumo-transport system to the reactor for irradiation.

For ICP-OES and ICP-MS analysis, conifer powder samples (approximately 200 mg) were subjected to microwave digestion with 5 mL of 65 vol. % HNO_3 (Merck) and 2 mL of 30 vol. % H_2O_2 (Merck).[32] A microwave oven Berghof (Speedwave, Berghof, Germany) was used for the sample digestion. After a cooling period, the samples were quantitatively transferred into a volumetric flask of 25 mL and diluted with ultra-pure water (Millipore Simplicity 185 system).

Instrumental techniques

Wavelength dispersive X-ray fluorescence spectrometry (WD-XRF). An ARL™ PERFORM’X sequential X-Ray fluorescence spectrometer (Thermo Fisher Scientific, Switzerland) equipped with a 4.2 kW Rh X-ray tube with a 50 μm Be window was apllied. A primary beam spot size of 29 mm in diameter was used. The spectrometer was equipped with seven different crystals (AX16, AX03, AX09, Ge111, LiF200, LiF220 and PET), four collimators (0.15, 0.4, 1.0 and 2.6), and a tandem of detectors (flow proportional counter and scintillation counter). The analysis was performed in a high vacuum atmosphere (< 1 Pa). For qualitative analysis, spectral recording, and data processing, a software program Thermo Scientific™ OXSAS was used.[37] Two different types of quantitative analysis were used during the experimental work in this study, empirical calibration and standardless method. Empirical calibration was performed using artificial spiked cellulose standards (in further text WD-XRF). The procedure of cellulose standard preparation and calibration was described in the previous paper.[32] Table S-I (Supplementary material to this paper) shows the analytical lines and parameters for the analyzed elements. UniQuant (ThermoFisher Scientific, Integrated version), a standardless semi-quantitative to quantitative method for XRF analysis was used.[38]

Instrumental neutron activation analysis (INAA). INAA was performed using the pneumo-transport facility REGATA at the IBR-2 reactor (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research FLNP, JINR, Dubna, Russia). The IBR-2 pulsed nuclear reactor has an average power of 2 MW and installed a pneumatic system.[39] Short-lived elements (Mg, Al, Cl, Ca, Ti, V, Mn and I) were irradiated for 3 min and measured for 15 min. Another aliquote of plant sample was irradiated for 3 days in the Cd-screened channel under the neutron flux of 1.8×10^{11} cm^{-2} s^{-1} to determine long-lived isotopes. The first group of long-lived isotopes (LLI 1; Na, K, As, Br, Mo, La, Sm, W, Au and U) were measured for 30 min after 4 days of decay, while the second group of long-lived isotopes (LLI 2; Sc, Cr, Fe, Co, Ni, Zn, Se, Rb, Sr, Zr, Sb, Cs, Ba, Ce, Nd, Eu, Tb, Yb, Hf, Ta and Th) were measured for 90 min after 20 days of decay. HPGe detector with a resolution of 2.5–3 keV for the 1332 keV line of the ^{60}Co was used for gamma spectra measurement. To display, analyze and store the gamma spectra Genie 2000 software was used.

Inductively coupled plasma mass spectrometry (ICP-MS). For plant samples analysis ICP-MS (iCAP Q, Thermo Scientific X series 2) was used. The entire system of ICP-MS is controlled with Qtegra Instrument Control Software. The analysis was carried out at the following operating parameters for the instrument: 1.548 kW radio frequency power, 13.9 $L\cdot min^{-1}$ plasma gas flow, 1.09 $L\cdot min^{-1}$ auxiliary gas flow, 0.80 $L\cdot min^{-1}$ carrier gas flow, and 3.50 s acquisition time.

Inductively coupled plasma optical emission spectrometry (ICP-OES). Analysis of digested plant samples was carried out by an ICP-OES instrument (iCAP 6500 Duo; Thermo Scientific, Loughborough, UK). For data processing, the specialized iTEVA software was used. The quantification of 19 elements (Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Ag, Cd, In, Tl, Bi and Pb) was carried out in axial mode and at the following operating parameters for the instrument: 1.150 kW radio frequency power, 12.0 $L \cdot min^{-1}$ plasma gas flow, 0.50 $L \cdot min^{-1}$ auxiliary gas flow, 0.50 $L \cdot min^{-1}$ carrier gas flow.

Quality control

For the purpose of quality control, NIST pine needles certified reference material (1575a) was analyzed using all examined techniques. Table S-II of the Supplementary material shows the certified values and the measured ICP-MS, ICP-OES, INAA, UQ and WD-XRF concentrations in mg kg^{-1} for investigated and detected elements. The measured concentrations were in good accordance with the certified for all investigated techniques.

RESULTS AND DISCUSSION

Elements in the analyzed real sample set are present in a wide concentration range, as can be seen in Table S-III (Supplementary material), which sums up descriptive statistics of all investigated elements measured using different analytical techniques. Thereby, the results are shown as relative concentration ratios. The relative ratio values were calculated by dividing the element concentration measured, using the investigated analytical techniques with the concentration determined by ICP-MS and multiplied by 100. ICP-MS is the most commonly used technique within plant analysis, which possesses a very wide linear range, low detection limits, good accuracy, and precision. For that reason, the ICP-MS was used as the basis for comparisons of other investigated techniques in this research. Fig. 1 shows the median of the relative ratios of concentrations obtained using different analytical techniques compared with ICP-MS results for the same sample. Minimum, maximum, median, average, and standard deviations of relative ratios are presented in Table S-IV (Supplementary material).

The comparison of investigated techniques presented in Fig. 1 shows that concentrations of most of the analyzed elements are in good accordance, except for Na. UQ method is most often not in agreement with other techniques, which was expected, since this is a semi-quantitative method. Ratios of some elements were not presented for the WD-XRF technique because they were below the detection limit. The results also show that Na is a very difficult element for quantification, regardless of the type of the used technique.

The results obtained using ICP-OES were underestimated compared to ICP-MS for all analyzed samples, except for Na. On the contrary, the concentrations obtained using UQ method were overestimated compared to ICP-MS for all the analyzed elements, except for Mg. UQ as a standardless method for direct analysis shows a positive systematic error. Ratios of WD-XRF and ICP-MS did not show any trend of systematic errors (they are neither dominantly positive nor negative).

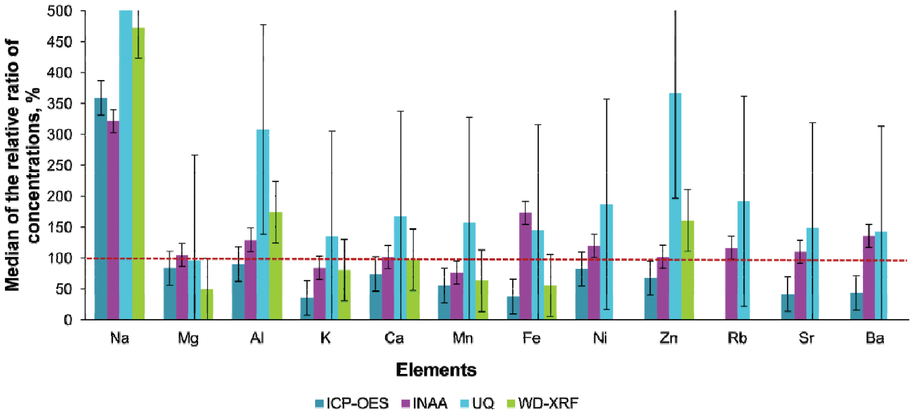

Fig. 1. Median values of the relative ratios of concentrations obtained using different techniques compared with ICP-MS concentration. The error bar represents ± standard deviation the relative ratio values.

Relative ratios of INAA concentrations were always in the range of 70–130 % compared to ICP-MS concentrations, except for Na (332 %), Fe (173 %) and Ba (136 %), which indicated that this non-destructive technique produced results that were most similar to ICP-MS results.

The relative ratios of concentration of P and S, measured using only ICP-MS and UQ, are presented in Fig. 2. UQ method produces results that were in good accordance with ICP-MS for these two elements.

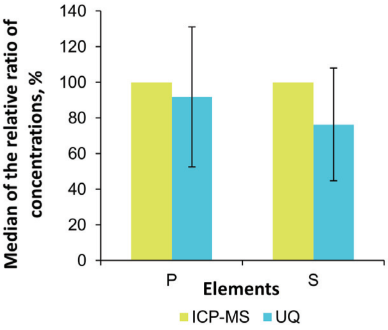

Fig. 2. Median of the relative ratio of concentrations of P and S obtained using ICP-MS and UQ.

Comparison of the techniques based on paired t-*test*

Paired *t*-test was applied in order to objectively estimate whether the difference among applied techniques is statistically significant. Table I shows the analyzed elements which were divided into three groups, according to the results of the paired *t*-test. The first group in the table gathered the elements whose concentrations did not show a statistical difference when investigated analytical techniques were compared, while in the other two groups ("Difference*" and

"Difference**") difference was statistically significant at 0.05 and 0.01 levels, respectively.

TABLE I. Grouping of elements according to results of paired *t*-test applied to the compared analytical techniques. Boundaries between groups of elements are based on P values of the paired *t*-test (P = 0.05 and P = 0.01); * – significant at the 0.05 level; ** – significant at the 0.01 level

Compared techniques	Without difference	Difference*	Difference**
ICP-MS and INAA	Mg, Ca, Mn, Rb, Sr	Ba	Na, Al, K, Fe, Ni
ICP-MS and UQ	Mg, P	Mn	Na, Al, K, Ca, S, Fe, Zn, Rb, Sr
ICP-MS and WD-XRF	Na, Ca	Mn	Mg, Al, K, Fe, Zn
ICP-OES and INAA	Na, Mn, Ni, Zn	Mg, Ba	Al, K, Ca, Fe, Sr
ICP-OES and UQ		–	Na, Mg, Al, K, Ca, Mn, Fe, Zn
ICP-OES and WD-XRF	Na, Mn	–	Mg, Al, K, Ca, Fe, Zn
INAA and UQ	Mg	Mn, Fe	Na, Al, K, Ca, Zn, Rb, Sr
INAA and WD-XRF	Na, Al, K, Ca, Mn	Zn	Mg, Fe
UQ and WD-XRF	–	–	Na, Mg, Al, K, Ca, Mn, Fe, Zn

From Table I it is possible to notice that ICP-MS did not show a statistically significant difference within the analysis of Mg, Ca, Mn, Rb and Sr compared with INAA; Mg and P compared with UQ; Na and Ca compared with WD-XRF. There was a statistically significant difference between ICP-MS and non-destructive techniques for all rest elements. ICP-OES did not show a statistically significant difference within the analysis of Na, Mn, Ni and Zn when compared with INAA; Na and Mn compared with WD-XRF. There is a statistically significant difference between ICP-OES and UQ for all analyzed elements. In comparison with XRF techniques, INAA did not show a significant difference within the analysis of Mg compared with UQ, and Na, Al, K, Ca and Mn compared with WD-XRF. There was a statistically significant difference between UQ and XRF methods for all analyzed elements.

According to the results of paired *t*-test, Fe showed a statistically significant difference within all compared techniques. UQ method differed from other techniques for the largest number of elements. Na, Mn, and Ca most frequently showed parity among compared techniques. Nevertheless, one must be careful during the interpretation of the *t*-test results, since some elements such as Na might show the absence of statistically significant differences not because the investigated techniques produce similar results, but because they all have low precision and large random error related to the analysis of this element.

Comparison of the techniques based on correlation

In the previous section, it was observed that investigated techniques may produce results with a statistically significant difference for a number of elements. The next logical question is to establish whether these measurements, obtained from compared techniques, are correlated or not. Because if the results are well correlated then the difference between compared techniques is a consequence of systematic error related to one or both of compared techniques, which means that it can be more thoroughly described and corrected.

The correlations of concentrations of analyzed elements measured by investigated techniques were compared by nonparametric Spearman's correlation coefficients (ρ) which are presented in Table II.

TABLE II. Spearman's correlation coefficient (ρ) for elements of all compared techniques; * – significant at the 0.05 level; ** – significant at the 0.01 level; *** – significant at the 0.001 level

Element	ICP-MS and INAA	ICP-MS and UQ	ICP-MS and WD-XRF	ICP-OES and INAA	ICP-OES and UQ	ICP-OES and WD-XRF	INAA and UQ	INAA and WD-XRF	UQ and WD-XRF
Na	0.836***	0.354*	0.182	0.424*	0.041	0.168	0.455**	0.159	0.081
Mg	0.714***	0.334*	0.641***	0.622***	0.437**	0.681***	0.263	0.526***	0.194
Al	0.884***	0.753***	0.823***	0.818***	0.786***	0.833***	0.720***	0.801***	0.932***
K	0.938***	0.707***	0.813***	0.681***	0.611***	0.774***	0.729***	0.855***	0.837***
Ca	0.873***	0.690***	0.845***	0.880***	0.855***	0.970***	0.764***	0.900***	0.877***
P	–	0.723***	–	–	–	–	–	–	–
S	–	0.412**	–	–	–	–	–	–	–
Mn	0.766***	0.607***	0.711***	0.734***	0.731***	0.835***	0.669***	0.786***	0.822***
Fe	0.417***	0.535***	0.770***	0.472***	0.500***	0.586***	0.269*	0.434***	0.646***
Ni	0.779***	–	–	0.470*	–	–	–	–	–
Zn	0.647***	0.267	0.097	0.621***	0.361*	0.164	0.334*	-0.017	0.631***
Rb	0.767***	0.814***	–	–	–	–	0.814***	–	–
Sr	0.936***	0.753***	–	0.979***	0.688**	–	0.802***	–	–
Ba	0.930***	0.5	–	0.864**	–	–	–	–	–

The statistically significant correlation at the 0.001 level was found for all elements within ICP-MS and INAA comparison. The correlation between the ICP-MS and XRF techniques (UQ and WD-XRF) was statistically significant at the 0.001 level for the most of the investigated elements, except for Na and Mg ($P < 0.05$) and S ($P < 0.01$) with UQ method (Table II). There was no statistically significant correlation for Zn within ICP-MS and WD-XRF, and for Zn and Ba within ICP-MS and UQ comparisons.

The comparison of ICP-OES with non-destructive techniques showed similar results as when they were compared to ICP-MS. The statistically significant correlation at the 0.001 level was observed for most of the investigated elements. The correlation between ICP-OES and INAA was statistically significant at the 0.01 level for Ba, at the 0.05 level for Na and Ni. The correlation between ICP-OES and UQ was statistically significant only at the 0.01 level for Mg and Sr, only at the 0.05 level for Zn, and it was without statistical significance for Na.

The comparison with WD-XRF method did not show a statistically significant correlation for Na and Zn.

The statistically significant correlation between the INAA and UQ was found for Al, K, Ca, Mn, Rb and Sr ($P < 0.001$); Na ($P < 0.01$); Fe and Zn ($P < 0.05$), while for Mg there was no statistically significant correlation. For INAA and WD-XRF comparison the statistically significant correlation at 0.001 level was found for all observed elements, except Na and Zn, for which there was no statistically significant correlation.

Comparison of the results of two XRF methods showed statistically significant correlation at the 0.001 level for all observed elements, with exception of Na and Mg (no statistically significant correlation).

Results in Table II demonstrated that measurements of the investigated techniques were well correlated, but not for all elements and all instrumental techniques. Sometimes instrumental techniques have difficulties producing accurate results due to technical reasons: *e.g.*, some ICP-MS instruments have sampler and skimmer cones created from Ni, which hinders quantification of this element by ICP-MS, while XRF instruments may have problems to accurately quantify Zn if the sample holder contains this element *etc*. On the other side were elements that are immanently difficult for quantification for one or even more techniques. The best example was Na which is inconvenient for ICP-OES because it had a small number of lines that were often burdened with spectral interferences, while XRF techniques suffer from very low sensitivity when they analyze spectral lines of Na. Fe was another element in our research without very good agreement among applied techniques results which could be attributed to lower concentrations compared to other macro elements (Al, Mg, Ca, K), but this cannot be the only reason for the discordance among applied techniques since other elements with low concentrations were very well correlated (*e.g.*, Sr, Br, Ni).

The fact that measurements from compared techniques were well correlated (Table II) and that some techniques had lower (ICP-OES *vs.* ICP-MS) or higher (UQ *vs.* ICP-MS) correlation coefficients for all investigated elements implied that the systematic error significantly affects observed discrepancies among investigated instrumental techniques. Nevertheless, a systematic error can be corrected if it is properly characterized.

Comparison of techniques' precisions

Every plant sample was analyzed multiple times with each of the investigated techniques, therefore it was possible to calculate the relative standard deviation (*RSD*) for every measurement, which was used for comparisons of techniques' precisions. The Medians of relative standard deviations of repeated measurements of all investigated techniques are presented in Fig. 3. Minimum, maximum, average, and medians of *RSD* are presented in Table S-V (Supplementary material). Measurements of all investigated analytical techniques were performed with low *RSD* values. Except for Ni, *RSD* of ICP-MS was lower than 5 % for all analyzed elements. *RSD* of non-destructive techniques (INAA, UQ and WD-XRF) was sometimes lower than *RSD* of ICP-MS and *RSD* medians are for the most elements lower than 10 %.

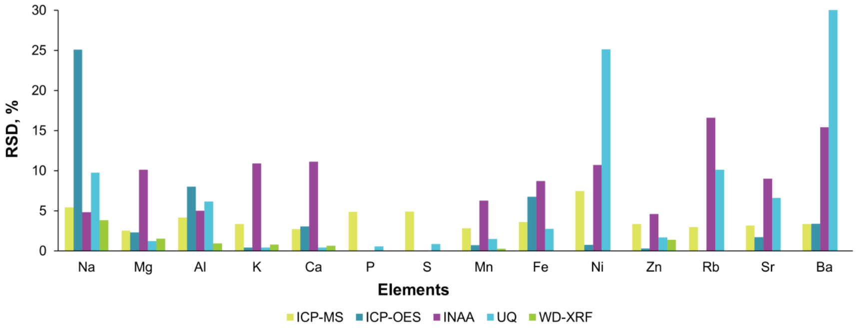

Fig. 3. Medians of relative standard deviations of repeated measurements of elements content, obtained using all investigated techniques.

CONCLUSION

Comparisons in this study confirmed that the non-destructive spectroscopic techniques (INAA, WD-XRF, UQ) can be successfully applied to the analysis of plant samples which is valuable because sample preparation for these techniques can be fast and in good accordance with the principles of green chemistry. Even the semi-quantitative UQ method can produce either similar or at least well-correlated results, when it is compared to other techniques based on calibration standards. Although all investigated techniques have had comprehensive QC programs which included analysis of certified reference materials (CRM), their results have in some cases demonstrated discrepancies. Studies like ours, which analyze a large number of elements in samples from the environment (with potentially difficult matrices), rely on multi-element standards for calibration. The multi-element standards may have some interfering elements in much higher concentrations than in the analyzed samples and *vice versa*. On the other side, CRMs may not be enough similar to all analyzed samples within one research (either by the composition or by concentration) which limits their ability to control the accuracy of the technique. Our results suggest that if the highest possible accuracy is a priority for the analysis, the additional analytical and QC steps must be taken, such as the use of internal standards or standard addition.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/11186, or from the corresponding author on request.

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ИЗВОД

ПОРЕЂЕЊЕ НЕДЕСТРУКТИВНИХ И КОНВЕНЦИОНАЛНО КОРИШЋЕНИХ СПЕКТОМЕТРИЈСКИХ ТЕХНИКА ЗА ОДРЕЂИВАЊЕ ЕЛЕМЕНАТА У БИЉНОМ МАТЕРИЈАЛУ (ИГЛИЦЕ ЧЕТИНАРА)

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Конвенционално коришћене спектрометријске технике (ICP-OES, ICP-MS) обично подразумевају дуготрајну процедуру припреме узорка која захтева коришћење агресивних и токсичних хемикалија за минерализацију. У последњих неколико година расте потреба за погодним и одрживим аналитичким методама за директну мулти-елементарну анализу биљних узорака. Спектрометријске технике за директну анализу (INAA, XRF) се већ примењују у еколошким истраживањима и у различитим пољима скрининг испитивања. Ипак, ове технике нису уобичајено коришћене за анализу биљака и њихове перформансе морају бити процењене. Циљ овог истраживања је био да се процени колико су недеструктивне технике поуздане код одређивања елемената у биљном материјалу, у односу на рутински коришћене спектрометријске технике. Укупно 49 узорака четири врсте четинара (*Pinus nigra*, *Abies alba*, *Taxus baccata* и *Larix decidua*) су анализиране помоћу две рутински коришћене (ICP-MS и ICP-OES) и две недеструктивне технике (WD-XRF и INAA). Технике су упоређене испитивањем релативних односа концентрација и помоћу корелационе анализе. Поред тога, испитана је и упоређена прецизност техника. Програм контроле квалитета је обухватао анализу сертификованог референтног материјала, иглица бора (NIST 1575a) помоћу свих коришћених техника. Резултати нашег истраживања сугеришу да су неопходни додатни аналитички и кораци контроле квалитета како би се постигла максимална тачност мулти-елементарне анализе.

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