ANOTATION

of the materials according to the Article 65 of the Regulations on the Development of the Academic staff of the Paisii Hilendarski University of Plovdiv.

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in regard to the competition for the academic position of "Associate Professor" in the Field of higher education 4. Natural Sciences, Mathematics and Informatics, Professional field 4.2. Chemical Sciences (Analytical Chemistry), announced in the State Gazette, issue 98 of 19.11.2024.

Fourteen scientific publications and one chapter of a collective monograph were submitted for the competition, and these materials do not repeat those used for previous procedures for obtaining a PhD. The numbering of the materials used corresponds to that in the list of publications and the table of scientific indicators submitted for the competition.

The topics in the published research can be summarized in two main areas. The first area encompasses the development and application of inductively coupled plasma mass spectrometry for the characterization of nanosized materials (publications under indicator B). The second area encompasses the development and evaluation of sample preparation approaches and spectrochemical methods for the analysis of essential and potentially toxic elements in environmental objects (publications under indicator Г).

1. The publications falling under **indicator B** pertain to habilitation work, specifically scientific publications that have been indexed and peer-reviewed, and are included within internationally recognized databases, such as Web of Science and Scopus

The paper "**B3**" offers a critical review of the application of inductively coupled plasma mass spectrometry (ICP-MS) for the characterization of nanoscale materials. It discusses the principles of the method when operated in single particle registration mode (spICP-MS), as well as the main factors influencing its capability to characterize nanoparticles. The text devotes particular attention to the influence of the sample introduction system on the analytical performance of the method, and a critical review is made on the variations in the systems used so far for the introduction of nanocolloid suspensions, published in the scientific periodicals, as well as on the guidelines for future possibilities for the development of sample introduction systems in order to improve the analytical performance of the method.

In the studies published in B1, the factors affecting the performance of inductively coupled plasma mass spectrometry (ICP-MS) operating in single particle registration mode (spICP-MS) for the characterization of silver nanoparticles (Ag NPs) are investigated. A distinct characteristic of this registration mode is that to acquire sufficient data regarding particle size and concentration, the recorded peak signals must be attributable to the sequential detection of individual particles. This inherent feature of the method presents several challenges, namely: i) the necessity of appropriate dilution to ensure the separation of signals generated by individual particles, ii) the stabilization of the introduced nanocolloid suspension, and iii) the capacity to record fast peak signals. To address the first challenge, a theoretical model has been proposed to calculate the dilution factor, thereby providing the optimal peak detection frequency. The proposed model is based on the fundamental relationships between particle mass, material density, composition, and diameter (assuming spherical shape of the nanoparticles). For the optimal dilution factor calculations, it is necessary to introduce prior information for the analyte into the theoretical model, such as nanoparticle size and mass concentration, and specific instrumental parameters as well. The capability of applying electron spectroscopy in the visible and ultraviolet region of the spectrum (UV-Vis) to obtain preliminary information on the size of AgNPs was verified.

The present study evaluated the influence of the solvent on the stability of the nano-colloid suspension and the equilibrium between the presence of Ag in ionic or particulate form. To this end, dilute suspensions of Ag NPs were prepared in three different media: i) ultra-pure water, ii) solution of non-ionic surfactants (TX-100 and TX-114), and iii) citrate buffer. The study also investigated the potential for eliminating the "memory effect" caused from the introduction of the nanocoloid suspension by washing the nebulization system with surfactant solutions, citrate buffer, and dilute nitric acid. The analysis of samples with AgNP by the spICP-MS method included the evaluation of several parameters under optimal conditions. These parameters encompass the particle number concentration (Particles L^{-1}), the mass concentrations of the ionic and particulate forms of silver present in the suspension, and the mass fraction of nanoparticles in the suspension. The method was applied to the analysis of three nano-colloid suspensions: one synthesized in our laboratory and two commercial products.

In paper B2, the theoretical model is further developed by the incorporation of two new modules. The first module facilitates the dynamic calculation of the probability of occurrence of single and double events over the integration time. The second module enables the calculation of the concentrations of homogeneous standards that would deliver a specific mass of analyte (corresponding to a particle of a given diameter) for a given integration time.

The following research is presented: an investigation of the factors affecting the noise of the time-segmented steady-state signal obtained when homogeneous ionic standards of Ag are introduced and its contribution to the size uncertainty of individual silver nanoparticles (AgNPs) recorded by spICP-MS. The experimental evidence demonstrates the capability of introducing homogeneous ionic standards to consistently generate silver with masses ranging from 0.045 fg to 5.4 fg, corresponding to nanoparticle diameters from 20 nm to 100 nm, for a single measurement. The behavior of the time-segmented signals was investigated for five different Ag masses measured over four integration times (td) in the range from 3 ms to 10 ms. The results show that both the sensitivity and reproducibility of the signals are independent of the single measurement time chosen. The homogeneity of variance hypothesis was confirmed by Bartlett's test, and in all cases, the calculated values of Bartlett's criterion (B_{exp}) were much lower than B_{crit}. This finding indicates that the noise in the recorded signal is solely dependent on the introduced Ag mass. Consequently, it can be utilized as a reliable estimate of the contribution of ionization processes in the plasma and ion flux transport to the uncertainty of the nanoparticle diameter determined by spICP-MS. The proposed approach to calculate the uncertainty of the diameters is flexible and applicable to characterize the sizes of nanoparticles of different compositions. The consistency of the two calibration strategies: using reference materials with certified diameters or introducing ionic standards of silver confirm that the signals are comparable, regardless of whether Ag is introduced via homogeneous solutions or directly as nanoparticles. The combined uncertainty (RSDc%) was calculated for the introduced Ag masses corresponding to nanoparticles with different sizes and the contribution of different noise sources on the size uncertainty of individual nanoparticles was evaluated. Confidence intervals for the diameters of AgNPs were calculated (1σ, P = 68%). Two main trends are observed: i) as the size decreases, the combined uncertainty (Uc) increases and ii) due to the cubic relationship between the mass and the diameter of the nanoparticles, the two half-intervals are asymmetric. The developed approach has been applied to calculate the size uncertainty (U_c) of silver-containing nanoparticles of AgCl, AgI, Ag_2O and Ag_2S. The determination of these types of nanoparticles is of environmental interest; however, reference materials with certified sizes are not currently available. It has been demonstrated that the average uncertainty interval is dependent upon the physical properties of the nanoparticles and ranges from

3.4 nm for Ag to 5.5 nm for AgI. This enables the experimental evaluation of the resolution of spICP-MS and the proposal of a criterion for cluster size selection when defining the size distribution. The method was applied to the analysis of AgNPs in a commercial pharmaceutical product, and the proposed approach to calculate the uncertainty of diameters was found to be flexible and applicable to the characterization of sizes of nanoparticles with different compositions.

The spICP-MS method, which has been developed and optimized, has been applied to characterize Ag nanoparticles in order to explore the possibility of their application in nanomedicine. The objective of the studies outlined in publications B4 and B5 is to synthesize drug-loaded Ag NPs and to investigate the release of the drug component from their surface. In particular, publication B4 investigated the potential of mebeverine precursor-modified Ag nanoparticles for drug delivery into the body to treat inflammation of the gastrointestinal tract. A "green" synthetic method was employed to prepare the silver nanoparticles with galactose as a reactant, which exhibits the properties of a surface-modifying reagent in addition to being a reducing agent. The efficacy of the modification of Ag nanoparticles with mebeverine precursor has been demonstrated. The release of the drug component from the surface of the modified Ag NPs was found to be between 80 and 85%.

In publication B5, the potential application of Ag nanoparticles as a carrier for phenindione was examined. This pharmaceutical agent has limited application due to its anticoagulant properties, which completely prevent coagulation and could lead to potentially life-threatening complications. The objective of the present study was to synthesize Ag NPs whose surface was modified with the drug component to delay the coagulation process. The study also sought to ascertain the potential for drug release from Ag NPs. To this end, density functional theory (DFT) calculations were performed for the first time to indicate the nature of the interaction between the phenindione and the nanostructures. The DFT results indicate that galactose-modified nanoparticles have the potential to be utilized for the delivery of phenindione. The drug-modified Ag NPs were characterized in vitro for their antimicrobial, cytotoxic, and anticoagulant activity, and ex vivo for their antispasmodic activity. The findings substantiated the outcomes pertaining to the release of the drug component from the surface of the modified nanoparticles. The investigation further revealed that the prothrombin time (PT, seconds) and activated partial thromboplastin time (APTT, seconds) exhibited approximately 1.5 times the standard value, while the direct anticoagulant action of PID resulted in a complete cessation of coagulation. This finding suggests that PID-modified Ag NPs have the potential to be utilized as more effective therapeutic anticoagulants.

In both studies the obtained Ag nanoparticles were characterized in terms of composition, size, size distribution, and surface charge by electron microscopic (TEM) and spectral methods, among which were inductively coupled plasma mass spectrometry in single particle registration mode (spICP-MS), electron spectroscopy in the visible and ultraviolet region (UV-Vis), X-ray diffraction (XRD), etc. The results obtained from the spICP-MS analysis, in terms of the size of the Ag nanoparticles, demonstrate that they possess an asymmetric size distribution, shifted towards particles with small sizes, which are close to the size detection limit of the method. The reported results for the size of the Ag core are comparable to those obtained by other methods.

2. Publications under indicator Г - Scientific publications in journals that are refereed and indexed in world-renowned databases of scientific information (Web of Science and Scopus), outside the habilitation thesis

Development and evaluation of sample preparation approaches and spectrochemical analysis methods for the determination of essential and potentially toxic elements in environmental objects

2.1 Development and evaluation of sample preparation approaches for elemental analysis (papers Г2, Г3 and Г5).

Research in this field can be categorized into two distinct groups. The first group encompasses studies that examine the impact of varying energy input mechanisms (Г2 and Г3) and reaction mixture composition (Г3) on the efficiency of the sample pretreatment by acid mineralization. In paper Г5, the capability of employing dispersive solid-phase extraction using modified magnetic nanoparticles as a sorbent for the extraction of elements from aqueous samples is investigated.

In the study published in paper Г2, the potential of ultrasound-assisted extraction as a sample preparation approach for the determination of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn by inductively coupled plasma optical emission spectrometry (ICP-OES) in sewage sludge samples was investigated. Alternatively, samples were prepared for analysis by microwave-assisted acid mineralization. Multivariate optimization of the parameters of both sample preparation methods was performed and different experimental designs were applied. The microwave-assisted mineralization conditions were optimized by a $2^{(5-1)}$ fractional factorial experiment. The optimal conditions for the microwave treatment were determined to be as follows: a pressure of 120 psi, a treatment time of 30 minutes at this pressure, the use of an acid mixture containing 3 milliliters of HNO_3, 1 milliliter of HF, and 1 milliliter of HCl. The conditions for ultrasonic extraction were optimized through the implementation of three distinct experimental designs. Initially, a Plackett-Burman design was used to screen the behavior of the main factors influencing the extraction process. The main factors identified through this experiment included US-amplitude, treatment time, temperature, and acid mixture volume. Subsequently, a full factorial design was employed to ascertain the optimal values for amplitude, treatment time, and acid mixture composition. The optimal conditions for ultrasonic treatment were determined to be 80% ultrasonic field amplitude, energy (400 W), treatment time (20 minutes), temperature (90 °C), acid mixture (5 ml HNO_3 and 5 ml HCl), and 10 minutes of homogenization by magnetic stirrer. The validation of both sample processing approaches was carried out using reference material BCR No. 146R (bottom sewage sludge of industrial origin), and their application was subsequently extended to the preparation of three sewage sludge samples. Microwave-assisted acid mineralization yielded quantitative recoveries for all elements tested, whereas ultrasonic treatment only quantitatively recovered Cd, Cu, Pb, and Zn. For elements Cr, Mn, and Ni, analytical recoveries of 75%, 84%, and 81%, respectively, were obtained. However, Co could not be extracted. The reproducibility and total analysis time were found to be similar for both sample preparation approaches. Despite certain limitations, ultrasound-assisted extraction emerges as a promising alternative to the conventional microwave-assisted acid mineralization method due to its inherent safety features, such as its operation at atmospheric pressure and the absence of the use of HF acid. Furthermore, the necessary instrumentation required for ultrasound-assisted extraction is significantly more affordable than that of the commercially available microwave systems.

In publication Г3, a comparative review of different approaches for the preparation of soil samples for the determination of total and plant extractable phosphorus content is presented. The survey encompassed soils of varying composition and phosphorus content. The initial stage of the study is centered on the quantification of total phosphorus in five certified reference materials. The study compared three sample preparation approaches: 1) perchloric acid treatment, 2) treatment with aqua regia (ISO 11466) on a thermal plate, and 3) microwave-assisted acid mineralization with aqua regia (EPA Method 3052). The ensuing analysis yielded the following findings: (i) The mode of energy input to the reaction system during the treatment of the samples with aqua regia did not affect the phosphorus recovery efficiency, with the analytical recoveries obtained ranging from 73% to 103%; (ii) The treatment of the samples with perchloric acid resulted in an increase in the analytical recoveries obtained of up to 10%. In the subsequent phase of the study two methodologies for extracting plant extractable phosphorus from soil samples were comparatively evaluated. The initial method (BDS ISO 11263:2002) is founded on extraction conducted in a $NaHCO_3$ medium (0.5 mol L^{-1}) at a pH of 8.5. Conversely, the Egner-Riehm (ER) method employs Ca-lactate (0.04 mol L^{-1}) as the extraction medium, with the extraction process being carried out in an acidic medium. The efficacy of these methods was evaluated through a comparative analysis of phosphorus extraction from twenty soil samples of varying compositions. A comparative analysis of the sample preparation approaches reveals that, in general, the Egner-Riehm method resulted in a higher extracted quantity of phosphorus compared to the BDS ISO method.

Research published in Г5 is focused on a comparative study of the sorption efficiency of magnetic manganese-ferrite nanoparticles ($MnFe_2O_4$) prepared by two synthetic approaches (precipitation and solution combustion). The two types of particles were investigated as sorbents for dispersive solid-phase extraction of Co, Cu, Zn, Mo, Cd, Tl, Pb, and Bi from model solutions and aqueous samples. The synthesis approaches yielded magnetic nanoparticles (MNPs) with distinct size distributions: i) monodisperse with an average size of ~13 nm for MNPs synthesized by solution combustion and ii) bimodally for NPs produced by precipitation with major fraction sizes of 2 nm and 25 nm. These physical parameters imply a difference in the nanoparticle surfaces that may affect the solid-phase extraction efficiency. To enhance the selectivity and stability of the sorbents in acidic media, a two-step magnetic core modification approach was proposed. This approach entailed two steps: (i) coating with a protective silica layer to prevent dissolution in acidic media, and (ii) impregnation with a complexing agent, ammonium pyrrolidine dithiocarbamate (APDC), to improve selectivity. In the initial stage of modification, the amount of Si-reagent required for the effective creation of the protective layer was optimized for both types of MNPs investigated. A single-factor optimization of the experimental conditions was also performed. These conditions included the solution pH and sorbent mass, which affect the sorption efficiency of the investigated elements on the surface of $MnFe_2O_4@SiO_2$-APDC NPs. The elution conditions for the analytes from the solid phase after extraction were also examined, and the following compromise conditions were selected for batch solid-phase extraction of all elements under investigation: pH = 5; sorbent mass = 30 mg NPs; elution with 1 mol L^{-1} HNO_3 at elevated temperature for 15 min. The solid-phase extraction of Co, Cu, Zn, Mo, Cd, Tl, Pb, and Bi on $MnFe_2O_4@SiO_2$-APDC NPs has been demonstrated to be both reproducible and applicable for the analysis of the aforementioned elements in aqueous samples by ICP-MS.

2.2 *Application of spectrochemical methods for the determination of essential and potentially toxic elements in environmental objects (publications Γ1, Γ3, Γ4 and Γ6 to Γ10)*

The prevailing focus of research in this area entails the implementation of spectrochemical methodologies for the assessment of essential elements (Γ1 and Γ3) and potentially toxic elements (Γ4, Γ6 to Γ10) in soil (Γ3, Γ7 and Γ8) and plant (Γ1, Γ4, Γ6, Γ8, Γ9 and Γ10) samples. The following spectroscopic methods were employed: Flame Atomic Absorption Spectrometry (FAAS) (Γ1), UV-Vis spectroscopy (Γ3), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Γ6 to Γ9) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (publications Γ1, Γ3, Γ4 and Γ6 to Γ10) were used to determine the content of the target analytes in studied samples.

2.2.1 *Application of spectrochemical methods in soil analysis*

A comparative discussion of the capabilities of UV-Vis (Murphy and Riley's method and Merck's Spectroquant phosphate test) and ICP-MS methods for the detection of total and plant extractable phosphorus in soil samples of different composition and phosphorus content is presented in Publication Γ3. When analyzing the total phosphorus content in certified reference materials, the different detection methods give statistically comparable results. However, in the determination of extractable phosphorus, the results obtained by the ICP-MS analysis were found to be higher than those obtained by the spectrophotometric methods in both approaches of soil sample preparation for the determination of plant available phosphorus. Furthermore, there was a tendency for the relative differences between the two methods to increase with decreasing phosphorus content. One potential explanation for this phenomenon is that the ICP-MS method detects all forms of phosphorus present in the sample extracts, whereas the spectrophotometric methods primarily detect phosphorus if it is in the form of orthophosphate. To test the hypothesis that the discrepancy in results obtained by the two spectral methods was attributable to the varying forms of phosphorus present, the extracts obtained by the BDS ISO method underwent an additional treatment with peroxydisulphate in an acidic medium to oxidize the different forms of phosphorus to orthophosphates (APD method). Following this additional treatment step, the results obtained by the two spectral methods were statistically comparable, thereby confirming the hypothesis proposed.

In paper Γ7, the accumulation of macro- (N, P, K) and trace elements (Co, Cu, Mn, Zn) in urban soils was investigated. The study focused on the upper soil horizon of samples from large park areas and next to the main boulevards in the city. The study was conducted in Plovdiv, Bulgaria. The trace element concentrations were determined after microwave-assisted extraction of soil samples with subsequent detection by plasma spectrochemical methods (ICP-OES and ICP-MS). The developed methods were validated by analysis of certified soil reference material (Loam Soil ERM - CC141). The obtained data demonstrated significant variations in the contamination levels among the investigated soil samples. The majority of the roadside soils exhibited higher trace element loading compared to park soils from the same area. The coefficients of variation (CV) in the different soil groups were used to determine the likely sources of these loadings. The CVs were found to be less than 0.40 for all elements investigated, suggesting that the loadings are primarily of natural origin. However, anthropogenic contributions should be considered for the results recorded for Co, Cu, and Zn. The potassium (K) and phosphorus (P) contents were found to be high in all soil samples, ranging from 292 to 825 milligrams per kilogram (mg/kg) for potassium and from 411 to 1,220 mg/kg for phosphorus, respectively. Nitrogen content ranged from low/insufficient (14.2 - 19.4 mg/kg) in some park soils to average (20.9 - 31.4 mg/kg) in the remaining samples.

In Publication Г8, plasma spectrometry methods (ICP-OES and ICP-MS) were employed to ascertain potentially toxic elements (As, Cd, Co, Cu, Mn, Mo, Ni, Pb, U, and Zn) in soils from urban areas (in residential and non-residential areas, roadsides, etc.) undergoing remediation through the planting of various crops. The methods developed for the determination of target analytes were validated by analysis of a certified soil reference material (Loam Soil ERM-CC141).

2.2.2 Application of Spectrochemical Methods in the Analysis of Plant Samples

An automated, rapid, and reliable method for the analysis of Ca, Fe, and Mn in mosses by flame atomic absorption spectrometry was developed by the authors and reported in publication Г1. This method is suitable for routine analysis of large numbers of moss samples and allows sequential determination of the three elements in the same solution. To mitigate the impact of calcium on the analysis and to standardize the influence of the sample matrix, lanthanum (La) was added to the moss sample solutions and standard solutions at a concentration of 1%. An integrated system for the discrete introduction of the sample solution, separated from the carrier stream by air segments, in combination with the flame atomic absorption detection method (ASDI-FAAS), was successfully applied. The system operates in a solvent-air-sample-air-solvent mode that allows the introduction of solutions with high-salt content, reduces reagent and sample consumption, and enables the application of data processing models to pseudo steady-state signals to improve repeatability. With respect to investigated elements, the ASDI-

FAAS method is proposed as a cheaper, easier, more reliable, and with better precision alternative to inductively coupled plasma mass spectrometry (ICP-MS). The ASDI-FAAS results were used to select appropriate isotopes and to determine spectral and non-spectral matrix correction procedures for ICP-MS analysis of the same elements. It was observed that both methods yielded comparable results for Ca, Fe, and Mn against the certified values in the analyzed certified moss reference materials.

The study published in paper Г6 examined the potential of moss and mussel bag transplants for monitoring water quality in three standing water bodies potentially exposed to anthropogenic pollution. For this purpose, moss and mussel species that are not naturally distributed in the three water bodies were selected. The moss and mussel samples were collected from areas unpolluted by human activity and placed in cages in the three water bodies for a period of 30 days. The alterations in the levels of 12 elements (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn) and priority organic substances (six polybrominated diphenyl ethers (PBDEs) and short-chain chlorinated paraffins (SCCPs)) in the mosses and mussels before and after exposure in the potentially polluted pools, as well as in water samples taken from the studied water bodies, were monitored.

The content of the studied elements in the biota was determined after microwave-assisted acid mineralization (HNO_3 and H_2O_2 in a ratio of 4:1) of the samples, by ICP-MS and ICP-OES methods. The separation of the determined elements between the two spectral methods was tailored to the concentration levels in the sample solutions, as well as to the potential spectral interferences specific to each of the methods. The efficacy of the developed methods was validated by analysis of certified reference material NCS DC 73348—"Bush Branches and Leaves," with the recoveries ranging from 93.8% for Cr to 109% for Al. A high level of accumulation of the studied substances was established in the applied combined transplants in all studied sites, and a different accumulation pattern was demonstrated for mosses and mussels with respect to elements and organic pollutants.

ICP-OES and ICP-MS methods of analysis were also employed to assess the ecological status of mountain river water basins in Bulgaria (Г9) based on the accumulation of Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn in aquatic plants (three moss species and two vascular plant species). The plant samples were prepared for subsequent instrumental analysis by the microwave-assisted acid mineralization procedure in closed PTEE vessels. Two types of reference materials, moss RM (M2 and M3) and CRM "Bush Branches and Leaves" (NCS DC 73348), were treated according to the same protocol. The tested elements were divided into two groups according to their concentration levels in the sample solutions. The concentrations of Al, Fe, and Mn were determined by ICP-OES in the radial mode of observation, while the axial plasma monitoring mode was employed for the determination of Zn. The trace elements As, Cd, Co, Cr, Cu, Hg, Ni, and Pb were determined by ICP-MS. To assess the risk of spectral matrix interferences, two emission lines were observed in the ICP-OES method and two isotopes per element in the ICP-MS analysis, except for the monoisotopic elements (^{75}As, ^{59}Co). Furthermore, the ICP-MS analysis was conducted in collision gas measurement mode (He 4.8 mL min^{-1}) to mitigate the risk of matrix-induced polyatomic ions interfering signals of the isotopes of As, Cr, Cu, Co, and Ni. Utilizing the obtained results for the elemental composition, contamination factors (CF) and metal pollution index (MPI) were calculated, which were then employed to evaluate the ecological status of the studied river basins.

In the study described in paper Г8 the ICP-OES and ICP-MS methods were employed to evaluate the bioremediation capacity of diverse plant species by monitoring the content of potentially toxic elements (As, Cd, Co, Cu, Mn, Mo, Ni, Pb, U, and Zn) in roots and shoots. The study encompassed four separate plant species and one mixture of these species. The suitability of a given plant for phytoremediation was assessed by the bioaccumulation and translocation factors, calculated respectively as the ratio of the element contents in roots to soil and the ratio of the contents in shoots to those determined in the roots. The results demonstrated that all studied plants exhibited different potential for phytoremediation with respect to the studied elements, with the most promising results obtained for mixed species.

The findings presented in paper Г4 characterized the composition of four types of wild forest fruits occurring on the territory of Bulgaria in terms of concentration of carbohydrates, some essential and potentially toxic elements and moisture content,. The study included fruits of bilberry (*Vaccinium myrtillus*), lingonberry (*Vaccinium vitisidaea*), cornel (*Cornus mas*) and howthorn (*Crataegus laevigata*). To ascertain the elemental composition of the berries, a set of 12 elements (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Pb) was selected, and the concentrations of these elements were determined after acid mineralization (HNO_3+H_2O_2) by inductively coupled plasma mass spectrometry (ICP-MS). The content of As, Se, V, and Co was below the determined methodological limits of quantification (MLOQ) in all studied samples. The lead concentration was below the European regulatory norm of 0.2 mg kg^{-1} (EC) 1881/2006, BG 31/29 July 2004. The content of Fe, Zn, Cu, and Mn in 100 g of fruit was compared with the recommended dietary intake specified in Directive 2008/100/EC, and the results indicated significant variation. Specifically, the content of Zn in hawthorn varied from 1.4% to 100% for Mn in bilberry. The established statistically significant difference in the content of these elements allows for their separation into distinct groups based on the determined elemental profile, as facilitated by discriminant analysis.

The ICP-MS method was also employed to ascertain the concentrations of essential and potentially toxic elements in 29 samples of linden blossom and infusions prepared from them (Г10). This approach was used to evaluate the influence of the urban environment on their elemental profile and to assess the associated health risks. To this end, the results obtained from the determination of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, V, and Zn in samples purchased from the local market, collected from different locations in the city of Plovdiv and from two presumably unpolluted areas were compared. The sampling points in the urban environment were selected to cover locations near busy intersections, low-traffic roads, parks, and gardens.

The total content of the target analytes was determined in the linden blossom samples after microwave-assisted acid mineralization with an acid mixture HNO_3 + H_2O_2. The method was validated by analysis of CRM "Bush Branches and Leaves" (NCS DC 73348), and the obtained recoveries ranged from 92% (Mn) to 113% (V). The content of the elements extracted in the infusions was determined after treating the linden blossom in hot water, according to the manufacturer's recommendations for infusion preparation. The findings indicate that the concentrations of regulated elements (Cd, Cu, Hg, Ni, and Pb) in the linden blossom samples are below the limits established by regulatory authorities for medicinal herbs. Arsenic (As) concentrations in three samples exceeded the most restrictive norm ($0.5\ \mathrm{mg\ kg^{-1}}$) specified in pharmacopoeias for medicinal plants. The concentrations of elements detected in the infusions are below the maximum permissible levels established for regulated elements in teas and general beverages. A comparison with the maximum permissible contents of elements regulated in drinking water reveals that only the content of manganese (Mn) in the samples approaches the specified levels, and in two samples it exceeds the established limits, which could potentially pose a health risk. The study demonstrated that the consumption of infusions prepared from linden blossom contributes negligibly to the permissible daily limits established by the European Food Safety Authority (EFSA). The degree of extraction of the studied elements in the infusions is below 20%, with the exception of Zn, Cu, Mn, and Ni. To the best of our knowledge, there are no published systematic studies in scientific literature assessing the degree of extraction of elements from linden blossom in the respective infusions. In most cases studies are focused on the content of elements in different medicinal plants, teas and/or infusions prepared from them, and linden is included among the studied plant species. Comparison with previously published data shows that the efficiency of extraction strongly depends on the chemical forms of the elements in the plants and the extraction conditions.

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