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Dispersed particle extraction—A new procedure for trace element enrichment from natural aqueous samples with subsequent ICP-OES analysis

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ABSTRACT

A novel sample pre-treatment method for multi trace element enrichment from environmental waters prior to optical emission spectrometry analysis with inductively coupled plasma (ICP-OES) is proposed, based on dispersed particle extraction (DPE). This method is based on the use of silica nanoparticles functionalized with strong cation exchange ligands. After separation from the investigated sample solution, the nanoparticles used for the extraction are directly introduced in the ICP for measurement of the adsorbed target analytes. A prerequisite for the successful application of the developed slurry approach is the use of sorbent particles with a mean size of 500 nm instead of commercially available μm sized beads. The proposed method offers the known advantages of common bead-injection (BI) techniques, and further circumvents the elution step required in conventional solid phase extraction procedures. With the use of 14.4 mL sample and addition of ammonium acetate buffer and particle slurry limits of detection (LODs) from 0.03 $\mu g\,L^{-1}$ for Be to 0.48 $\mu g\,L^{-1}$ for Fe, with relative standard deviations ranging from 1.7% for Fe and 5.5% for Cr and an average enrichment factor of 10.4 could be achieved. By implementing this method the possibility to access sorbent materials with irreversible bonding mechanisms for sample pre-treatment is established, thus improvements in the selectivity of sample pre-treatment procedures can be achieved. The presented procedure was tested for accuracy with NIST standard reference material 1643e (fresh water) and was applied to drinking water samples from the vicinity of Vienna.

1. Introduction

Trace metals are ubiquitous constituents of environmental liquid samples such as sea water, river water, rain or snow as well as drinking water. The accurate determination of individual trace metals in those samples is a very challenging task. Low concentration levels of the metal traces combined with matrix induced interferences are major difficulties even for the most sensitive analytical techniques such as mass spectrometry with inductively coupled plasma (ICP-MS). Although in the last years the objectives of methodological work was focused on the development of sample pre-treatment procedures for pre-concentration of target analytes and quantitative separation of interfering matrix there is still a demand for improved techniques [1].

Among the many pre-concentration techniques available, solid-phase extraction (SPE) has become increasingly popular in trace element pre-concentration because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of solvents and the ability to combine with different detection techniques in on-line or off-line mode [2–6]. In SPE trace metal analytes are adsorbed on a specifically designed sorbent material and subsequently eluted under selected conditions (e.g. pH, polarity). Conventionally, the sorbent column is being used repeatedly for many sample loading/elution sequences, and is replaced or repacked only after long term operation.

Nevertheless trace metal analysis using conventional SPE with sorbent columns represents some inherent limitations. Indeed, due to repetitive use, the performance of the columns is often deteriorated by the build-up of flow resistance or back pressure caused by progressive tighter packing of the column [7,8]. Moreover, considering long term operation, the surface properties of the column material, ensuring the retention efficiency and the kinetics during the elution process, might be irreversibly altered through contamination, deactivation, or even loss of functional groups or active sites [9,10]. Such alteration can have highly detrimental consequence, mostly manifesting in results below the actual values. Trace metal analysis was improved by implementing the renewable surfaces scheme (also referred to as bead-injection (BI) technique). In the BI technique the content of the packed column is renewed with fresh beads after each single analytical run. Renewing the column effectively eliminates the flow resistance and any potential changes or malfunctions of the surface properties encountered in the traditional SPE approach [11–15].

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Table 1
Instrumental parameters used for ICP-OES analysis.

Parameters	Values	Parameters	Values
Rf power	1500 W	Nebulizer flow	0.6 L min^{-1}
Sample flow rate	0.60 mL min^{-1}	Auxiliary flow	0.8 L min^{-1}
Observation height	10 mm	Coolant flow	12 L min^{-1}
Integration time	8 s		
Background correction	Constant shift from analytical line		
Number of replicates	4		

Elements	Wavelength [nm]		Elements	Wavelength [nm]	
	λ 1	λ 2		λ 1	λ 2
Al	308.215	396.152*	Fe	238.204*	259.940
Be	234.861*	313.107	Mn	257.610*	294.920
Cd	214.438*	228.802	Ni	231.604*	341.476
Co	228.616*	238.892	Pb	216.999	220.353*
Cr	267.716	283.563*	Ti	308.802*	323.452
Cu	224.700*	324.754			

* Wavelengths used for analyte quantification, the other lines were applied for quality control

Another problem of conventional SPE as well as the renewable surfaces approach is the need of eluents such as organic solvents or concentrated mineral acids for sample elution. The use of these reagents often results in solution matrices that present compatibility problems with plasma based detection techniques like ICP-OES or ICP-MS, requiring the removal or adjustment of the matrix prior to analysis [14]. The applied harsh elution conditions can drastically reduce the lifetime of the column material [16,17]. Furthermore is has to be considered that this elution step represents a major limitation for the selection of the sorbent material, since only reversible processes can be used for retention of the analyte on the stationary phase.

To overcome the problems related with the elution of analytes, the concept of “on-bead detection” was developed. In on-bead detection the analyte loaded beads, replacing the packed column, could be directly transported into the detection device for measurement. “On-bead detection” is used predominantly in the field of drug confirmation [18] and bio-analysis [19–21]. Considering the analysis of trace metals until now mostly electro thermal atomic absorption spectrometry (ET-AAS) [10,22] and electro thermal vaporization (ETV)-ICP-OES [23] have been used for element specific analysis of analyte containing beads. However, the ETV-based approach requires special instrumentation normally not available in routine laboratories and the use of ET-AAS does not fulfil the requirements for modern analytical tools where a large number of elements have to be determined in various samples with an unknown and/or variable matrix composition (e.g. water framework directive [24]).

In this work we present a procedure where the on-bead-approach is coupled with ICP-OES for the analysis of trace elements in aqueous sample solutions. To the best of our knowledge, a method combining these approaches has not been reported. In this procedure self-prepared functionalized silica particles were used as sorbent material to extract trace metals from aqueous sample solutions. The functional groups anchored on the silica surface are strong cationic exchange groups (SCX) to target multiply charged metal ions. After extraction the particles are separated from the sample solution and analyzed with ICP-OES using a slurry approach.

The applicability of the procedure has been demonstrated by analysis of NIST SRM 1643e and finally has been implemented by analysis of drinking water samples collected in Vienna (Austria).

2. Experimental

2.1. Chemicals and consumables

High purity water was obtained by purifying de-ionized water (reverse osmosis/ion exchange combination Euro 20 plus, SG Water Systems, Germany) with an Easypure 2 system (Thermo Barnstead, USA). Nitric acid, ethanol and ammonium acetate were purchased with analysis grade form Merck Germany. Certipur(R) multi-element (VIII/100 mg/L) ICP-standard (Merck, Darmstadt, Germany) was used for method development and quantification of sample signals. A stock solution with a concentration of 10 mg L^{-1} was prepared in 2.5% nitric acid (v/v) by dilution of Certipur(R) multi-element standard. Working solutions were prepared by dilution of the stock solution just before use. All chemicals used for the synthesis of functionalized particles were of highest available quality. Conical polypropylene vials were precleaned with 5% nitric acid for 12 h and rinsed with high purity water prior to use.

NIST Standard Reference Material 1643e (trace elements in water) was used for method verification.

2.2. Instrumentation

ICP-OES analysis was carried out with an iCAP 6500 from Thermo scientific, USA. Measurements were performed using radial observation. The samples were introduced with a Thermo high-solid-kit containing an aerosalt nebulizer and a cyclone spray chamber with ascension pipe. Transportation of sample solutions was performed by the peristaltic pump of the iCAP 6500 applied with a Cetac ASX-520 auto sampler. Per element two sensitive and noninterfered emission lines were used, one for measurement (highlighted by *), second for quality control. For detailed instrument parameters see Table 1.

2.3. Synthesis and characterization of functionalized nanoparticles

To overcome problems related with the elution of the analytes from the sorbent material, the concept of the slurry approach for direct measurement of analytes bound to sorbent particles has been applied in this study. Preparation of stable slurries requires particle diameters in the range of some μm (or below). Thus, due to the limited commercial availability of exchange beads with diameters around 500 nm, self-synthesis of surface functionalized nanoparticles was necessary for the procedure. Further reasons for the use of self-prepared nanoparticles are their advantages in the separation of target analytes from aqueous sample solutions. Compared with micrometer-sized particles used for conventional SPE, nanoparticles offer a significantly higher surface area-to-volume ratio, resulting in high extraction capacity, rapid extraction dynamics and high extraction efficiencies. In addition less precursor has been needed to synthesize the same number of particles and makes the synthesis more cost effective in a large scale.

Synthesis of spherical porous silica particles with an average diameter centred on 500 nm was carried out following a previously reported method [25]. Spherical porous silica particles were chosen as particle basis because of their simple synthesis route, the large surface areas provided by the porous structure and the metal free basis, which is essential for analysis of trace metals.

At first n-Cetyl-tri-methyl-ammonium bromide (CTAB) was dissolved in water before adding tetra-ethyl-ortho-silicate (TEOS) in the presence of aqueous ammonia and ethanol. The white precipitate was filtered, dried and calcined for 5 h at 550 °C. With the appointed mass ratios (Table 2) 1.3 g of porous-particles were synthesized.

Table 2
Amounts and molar ratios for particle synthesis.

Chemical	Mass [g]	Amount [mol]
CTAB	2.50	0.0069
De-ionized water	50.0	2.78
Aqueous ammonia	13.2	0.25
Ethanol	60.0	1.3
TEOS	4.67	0.024

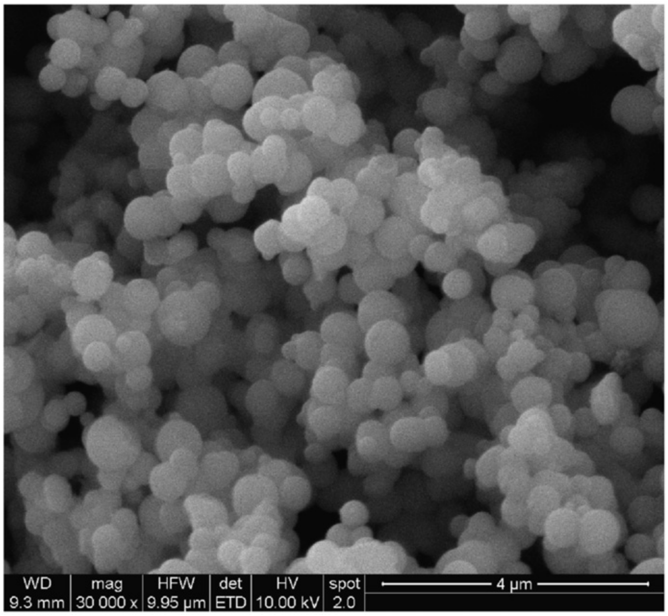

Fig. 1. SEM image of functionalized porous silica particles.

The SCX surface modification was done as suggested by Lianbing and Ruijun [26]. The surface of the prepared particles was activated with HCl (50%, v/v) and after filtration the particles were dried overnight at 110 °C. Then 1.5 mL 3-mercaptopropyltriethoxysilane was added to a dispersion of 1 g of particles in toluene abs. and refluxed under argon atmosphere. The material was extracted by filtration and dried at 110 °C. To finalize the modification, 30 mL acetonitrile and 1.1 mL trifluoroacetic anhydride as well as 1.55 g urea hydrogen peroxide was added to the particles. After mixing these components the particles were filtered and dried.

Particle shape and diameter were verified by scanning electron microscopy (Quanta 200 MK2, FEI, USA) after synthesis and after post-functionalization. For SEM analysis, standard conditions promoted by the manufacturer have been used. The diameters of the spherical particles measured on SEM micrographs were ranging from 300 to 700 nm (Fig. 1).

Surface area und pore diameter were characterized using N_2-sorption at 77 K (ASAP 2000, Micromeritics, USA). The BET surface area was 715 ± 15 $m^2\,g^{-1}$ which is comparable to commercially available SCX materials like Chromabond® HR-XC (specific surface area 800 $m^2\,g^{-1}$) from Magerey-Nagel [27]. The average pore diameter was estimated to 3.6 ± 2 nm from the BJH equation on the desorption branch of the isotherm.

2.4. Sample pre-treatment and analysis

The principle of the proposed method is the retention of multiple charged cations on meso-porous particles, which surfaces were modified with SCX functionalities. To ensure quantitative recovery, the pH-milieu has to be carefully adjusted according to retention properties of the surface groups. Thus in a first step the aqueous sample is treated with buffer solution. Afterwards the particles are added in form of slurry solution, prepared by dispersing the synthesized product in high purity water. Ultrasonic agitation is applied for a certain time (minutes) in order to disperse the particles throughout the sample and to ensure quantitative reaction. Then the particles, including the retained analytes, are separated from the solution by centrifugation (Hettich-EBA 20, Germany). The supernatant, particle free solution is removed by pipette withdrawal; the remaining particles were used for ICP-OES analysis.

To avoid the elution step required in conventional SPE we applied the concept of slurry analysis for measurement of analytes including the sorbent particles. Slurry initiation was achieved by re-suspension of the centrifuged particles in a small volume of liquid using a shaker (Vortex Genie 2, Scientific Industries). Analyte enrichment is determined by the volume ratio of applied sample volume and the final slurry volume. For ICP-OES measurement the slurry is directly introduced into the plasma where first the particles are disintegrated and second the target analytes are atomized and excited. Nitric acid (1% v/v) was utilized as purge liquid between measurements.

3. Results and discussion

3.1. Optimization of the enrichment procedure

To optimize the designed procedure several factors were isolated from the different stages (sample-preparation, analyte extraction, analyte separation, slurry state and ICP-OES measurement) and carefully investigated with synthetic aqueous sample solutions. For method development initial conditions with a sample volume of 10 mL and an analyte concentration of 50 $\mu g\,L^{-1}$ for each element has been used. Regarding the amount of applied particles, 100 µL of a suspension containing 50 mg nanoparticles per mL were added to the sample solution, corresponding to 5 mg particle mass per sample. All investigations were carried out with fourfold replication ($n=4$).

3.1.1. Effect of sample pH

Under strong acidic conditions the retention of trace element analytes on strong cation exchangers is insufficient and under neutral or basic conditions precipitation and sedimentation losses are possible. Usually the optimum working range for SCX sorbents is in the pH range 3–6. If the sample pH is out of this range it has to be regulated by adding a buffer solution. To optimize adsorption properties of target trace metal analytes the pH-milieu was adjusted with ammonium acetate. The buffer concentration in the sample was varied between 0.05 and 0.005 $mol\,L^{-1}$ by addition of 500 µL buffer with a concentration of 1.0 $mol\,L^{-1}$. For metals with an oxidation state of 2 (e.g. Cu, Mn) a buffer concentration of 0.01 $mol\,L^{-1}$ corresponding to a pH of 5.1 delivered best results. For metals with an oxidation state of 3 (e.g. V) a concentration above 0.01 $mol\,L^{-1}$ lead to a drop in the ICP-OES signal by 40%. No significant differences in the reproducibility given as the relative standard deviation (RSD) could be observed. Thus, further investigations were carried out with a buffer concentration of 0.01 $mol\,L^{-1}$.

3.1.2. Reaction time

To ensure a sufficient adsorption, the reaction between particles and target metal species was carried out under ultrasonic agitation. The time dependency of particle dispersion and quantitative adsorption was investigated by monitoring different agitation times varying from 2 to 10 min. Observed signal differences were not significant, but improved RSDs were found

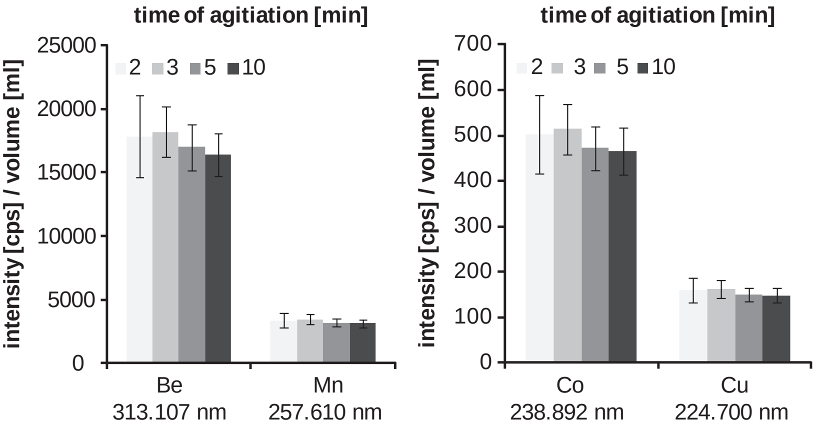

Fig. 2. Observed signal intensities measured after different reaction times ($n=4$, analyte concentration: 10 μg L^{-1}).

with increased agitation time, as shown in Fig. 2. These results imply that analyte retention works very fast, within 2 min of reaction time the target analytes are adsorbed quantitatively at the particle surface. The decreasing RSDs can be explained by a better particle distribution due to the longer period for establishing equilibrium. Hence an agitation time of 10 min was selected for further measurements.

3.1.3. Particle amount

To achieve an optimum between particle amount, necessary for quantitative enrichment, and signal suppression during ICP-OES analysis due to decrease of plasma excitation capabilities, the introduced amount of particles was varied from 1.25 to 10 mg per sample. Investigated solutions contained 50 μg L^{-1} of target analytes and 0.01 mol L^{-1} ammonium acetate buffer. Obscured emission signals increased steadily until a content of 5 mg particles per sample and decreased afterwards. Exemplary for Cu the intensity was raised from 1200 counts s^{-1} for samples treated with 1.25 mg to 1500 Cts s^{-1} for samples treated with 5 mg particles. A further increase of the particle amount resulted in a decrease of the emission signals. The enhancement can be explained by the increasing number of surface functionalities available for analyte adsorption due to escalating the particle number in the sample thus analyte ions were retained more efficiently. At some point the retention of analyte ions reaches a maximum, thus a further increase in particle mass resulted only in a negative influence on the plasma excitation capabilities reducing the signal intensities for the investigated elements. RSDs of the performed replicates ($n=4$) were in the order of 2.5% for up to 2.5 mg particle addition. Reduced values of 1.0–1.2% were observed for the remaining range. All further investigations were carried out with a particle amount of 5 mg/sample.

3.1.4. Volume of the final slurry solution

To increase the enrichment potential of the procedure the volume of the final slurry required for ICP-OES measurement has been reduced as much as possible—necessitating careful optimization of sample pre-treatment and ICP-OES analysis. On the one hand the final slurry volume, as well as the centrifugation step and the separation of supernatant liquid, were optimized to minimize particle losses during sample pre-treatment. On the other hand the ICP-OES parameters like sample flow rate and instrument rinsing time were adapted to enable the analysis of the required replicates with reduced sample volumes. In the experiments mentioned before, after centrifugation, 8 mL of supernatant solution were removed from the initial sample volume of 10 mL, thus 2 mL sample were left after pipette removal. When decreasing this volume, sample utilization as well as enrichment potential can be improved. But at the same time sample handling becomes more difficult and the probability of removing analyte loaded particles alongside the supernatant solution is enhanced. Thus conical-end sample tubes were used further on to improve sample pre-treatment. Based on an initial sample volume of 15 mL the tested volumes of the final slurry ranged from 0.5 to 2 mL. With a remaining volume of 1 mL the optimal conditions were found, achieving the highest signal intensities and lowest RSDs indicating reproducible sample pre-treatment and only negligible losses of analytes under these conditions. Thus for all further investigations a final volume of 1 mL has been used, resulting in a theoretical enrichment factor of 15 (15 mL sample reduced to 1 mL).

3.1.5. Amount of applied sample solution

Since the primary target of this research was the development of an enrichment method, the effects due to variation of sample volume and analyte concentration had to be investigated. The volume of metal containing solution with a concentration of 10 μg L^{-1} was varied from 7.5 to 30 mL to test linearity of the enrichment procedure with a constant particle mass of 5 mg per sample and a final volume of 1 mL after pre-treatment. Between measured signal intensities and applied sample volumes a linear correlation was observed for all investigated elements (with r^2 varying from 0.958 for Al to 0.999 for Cu), indicating that the retention capabilities of the nanoparticles were not limited up to a sample volume of 30 mL.

In a further experiment various concentrations of aqueous multi-element standards were investigated, ranging from blank level to 50 μg L^{-1}. The applied sample volume was 15 mL and all measurements were carried out under optimized conditions. Throughout the whole investigated range a linear correlation was found between applied analyte mass and derived ICP-OES signal for all investigated elements. Thus significant losses of analyte could be excluded up to a concentration of 50 μg L^{-1}. However, by increasing analyte concentrations beyond the tested concentration range, there is a possibility of reduced recoveries for the investigated elements since the retention capabilities of the functionalized nanoparticles might be insufficient. Nevertheless, derived results indicate that with an applied amount of 5 mg sorbent material a corresponding minimum exchange capacity of 0.025 meq (milliequivalents) could be reached. Considering the sample volume used in this experiment (15 mL) a capacity of 1.65 meq L^{-1} has been achieved, which should be appropriate for retention of multiply charged cations in natural environmental liquids.

3.1.6. Slurry stability

With the use of self-synthesized nanoparticles the preparation of stable slurries is enabled. However in addition to slurry stability, good control on the particle size is also critical for ICP-OES measurement. Indeed the particle diameter is directly affecting the sample introduction efficiency as well as excitation capabilities in the plasma. A crucial point for routine application of the proposed procedure is the stability of the prepared slurries, in particular if the use of an autosampler is desired.

Slurry stability was analyzed with different holding times after the ultrasonically agitation. For this investigation the slurry solutions derived from the simultaneous preparation of 10 identical aqueous standard solutions (with a nominal concentration of 10 μg L^{-1} for each investigated element) were combined to create a total sample volume of 10 mL slurry solution. Prior to measurement the combined slurry sample was elaborately mixed to ensure a sufficient homogeneity, placed in the autosampler and consecutively analyzed 6 times with 5 replicates each (every 2.5 min) without re-suspension steps. The measurement has been started immediately after thoroughly mixing of the pooled sample. The results shown in Fig. 3 point out that after the first measurement the analytical signal is decreased by around 10% and remained constant for the following measurements (period up to 12.5 min). Furthermore it was observed that for all elements the RSD of the first measurement is distinctly elevated compared to the successive measurements. These findings are explained by fast sedimentation of agglomerates or larger particles which were present at the beginning of the first replicate and settled down during analysis of the remaining other replicates of the first measurement. In consequence, for all further experiments the analysis was carried out 2 min after slurry preparation to overcome the influence of larger particles.

3.1.7. Signal quantification

For accurate quantitative analysis of target analytes with the proposed procedure, external calibration with aqueous standards has been found to be defective, since the results derived with this strategy underestimated the true contents. This is caused by its inability to account for differences to the sample introduction efficiency of the slurry approach and the particle impact on plasma excitation capabilities. Furthermore it has to be considered that the recovery of the enrichment procedure is not quantitative (e.g. retention of analytes on the sorbent material is incomplete, causing losses during sample pre-treatment). Both effects can be circumvented by applying the enrichment procedure to aqueous standards which were prepared and measured in the same way as the samples. The observed signal intensities of standards with concentrations from 0 to 20 μg L^{-1} were used to create a calibration function for the whole procedure.

The effects of the nanoparticles during enrichment and measurement become obvious when comparing the slopes of different calibration approaches. Fig. 4 presents the results achieved for Co—comparable findings were derived for all other investigated elements. The calibration function in the centre was deduced from analysis of conventional aqueous standard solutions. It was achieved by preparing aqueous standard solutions in 1% nitric acid with concentrations of 25, 50, 100 and 250 μg L^{-1}. The function with the remotest slope on the right is resulting from calibration with aqueous standards in the presence of buffer and particles. Therefore solutions were prepared analogue to the previous calibration and then each concentration level was treated with 5 mg particles and 500 μL of buffer (1.0 mol L^{-1}). In this example the negative particle impact on plasma excitation capabilities leads to a drop in the functions slope by a factor of 1.4. The steepest slope to the left was obtained from application of the proposed procedure to another set of aqueous standard solutions with initial concentrations of 2.5, 5, 10 and 20 μg L^{-1}. Due to the enrichment process the slope is increased by a factor of 11.4 compared to the findings for aqueous standard solutions containing buffer and nanoparticles which demonstrates, that negative plasma effects are more than compensated by the enrichment capabilities.

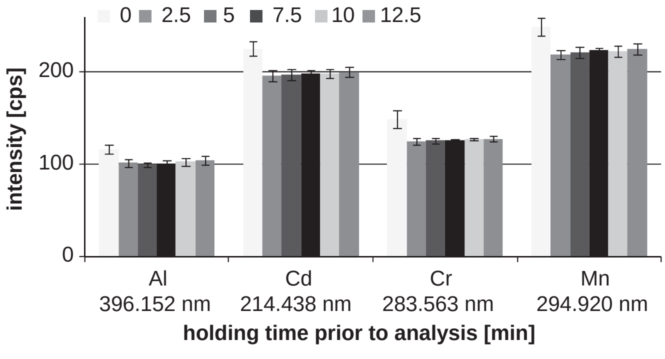

Fig. 3. Observed signal intensities measured after different holding times prior to analysis, each measurement presents the average of 5 replicates ($n=4$, analyte concentration: 10 μg L^{-1}).

3.2. Figures of merit

The intention of the thorough optimization was to achieve the operational conditions regarding a maximized sensitivity and reproducibility for the whole procedure. The resulting parameters are listed in Table 3. For all experiments regarding figures of merit, validation or application this method alignment was applied.

For the determination of LODs a calibration function was prepared with 15 mL aqueous standard solutions with the following concentrations: 10 μg L^{-1}, 20 μg L^{-1} and 40 μg L^{-1}, respectively. The detection limits of this method for the investigated elements, based on three times the standard deviation of four blank solutions, ranged from 0.03 μg L^{-1} for Be to 0.48 μg L^{-1} for Fe. The relative standard deviation (RSD) of this method, obtained for six determinations of a 10 μg L^{-1} multi-element solution ranged from 1.7% for Fe to 5.5% for Cr. The most often used criterion for the evaluation of pre-concentration procedures is the enrichment factor. This factor is defined either as the ratio between the analyte concentration in the enriched solution and in the original sample, or, since these concentrations are often hard to obtain, as the ratio of the slopes of the linear section of their calibration functions. By applying this approximation [28] a theoretical enrichment factor (ef$_t$) of 14.4 was calculated considering an initial sample volume of 14.4 mL and a residual volume of 1 mL. Concerning already described intensity losses due to signal suppression through slurry introduction a reduced practical enrichment factor (ef$_p$) is anticipated. The calculated ef$_p$ ranged from 8.8 for Ni to 12.0 for Cr, which corresponds to total yields of 61% and 83% of the theoretical enrichment. It can be noted that in general the ef$_p$ are higher for triple charged cations than for double charged cations. The enrichment factor is strongly depending on the sample volume applied for pre-treatment but is not indicative for efficiency of sample utilization. Therefore we used another important parameter, the consumptive index (CI) [29] for comparing our results with literature data. The CI is defined as the ratio of the used sample volume in mL and the achieved ef$_p$. It represents the sample volume expressed in mL necessary to obtain a unit of enrichment factor. For the proposed procedure it ranged from 1.2 to 1.6 depending on the element.

The analytical performance of the present work was in good agreement with enrichment procedures reported in the literature, for example Gawin et al. reported a LOD of 0.11 μg L^{-1} and a RSD of 6.3% for Cd extracted through bead injection (BI) and analyzed with flow injection flame atomic absorption spectrometry (F-AAS).

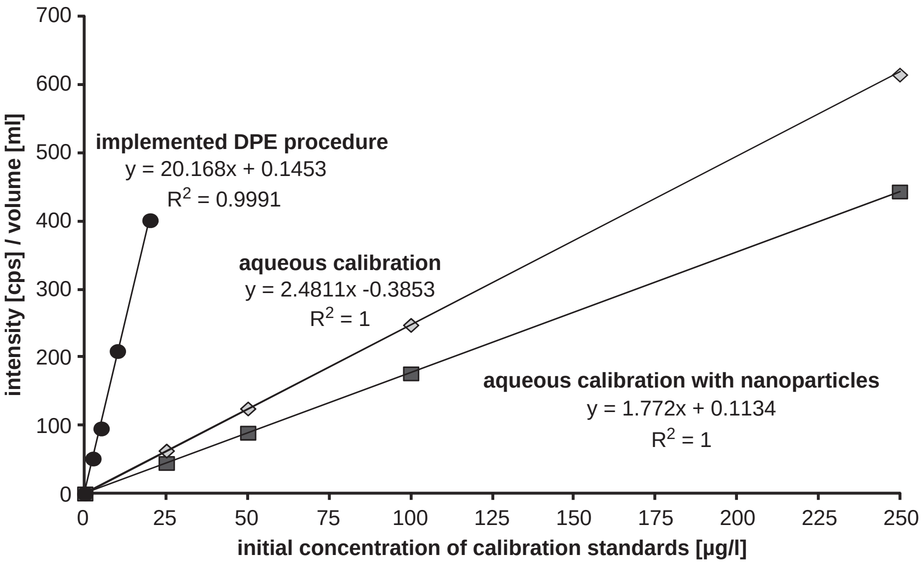

Fig. 4. Comparison of calibration slopes for Co originating from aqueous calibration, aqueous calibration in the presence of nanoparticles and application of the final DPE procedure.

Table 3
Final conditions derived via method alignment with synthetic aqueous standards.

Parameter	Value
Sample volume	14.4 mL
Buffer solution (ammonium acetate)	0.1–0.5 mol L^{-1} (500 μL, 1.0 mol L^{-1})
Particle addition	100 μL (of a 50 mg/mL particle suspension) corresponding to 5 mg per sample
Reaction time for analyte adsorption	10 min (ultrasonic agitation)
Centrifugation	4000 rpm, 3 min
Final volume of slurry	1 mL
Time for re-suspension of particles	2 min (ultrasonic agitation)
Number of prepared replicates	$n=4$

An ef_p of 200 was achieved by employing 1000–2000 mL sample volume, gaining a CI of 5–10 [30]. Mengwei et al. published comparable findings of 0.08 μg L^{-1} and a RSD of 4.9% for Pb using SPE coupled to graphite furnace (GF-)AAS. They reached an ef_p of 100 and, considering the sample volume of 100 mL a CI of 1 [31]. Liang et al. used multiwall carbon nanotubes SPE coupled with ICP-OES to investigate Cd, Mn and Ni. They achieved LODs of 0.05, 0.02 and 0.04 μg L^{-1} for Cd, Mn and Ni with RSDs of 3.5%, 2.6% and 2.2% respectively. By using 50 mL sample volume an ef_p of 25 was obtained, corresponding to a CI of 2 [32]. Sereshti et al. combined ultrasound-assisted emulsification microextraction with ICP-OES to investigate trace metals (Al, Bi, Cd, Co, Cu, Fe, Ga, In, Ni, Pb, Tl and Zn) in water. They achieved LODs from 0.13 to 0.52 μg L^{-1} for Al and Tl with RSDs from 1.9% to 5.7% and an average ef_p of 18.75 by using 10 mL of the sample yielding an CI of 0.53 [3].

Table 4
Results ($n=4$) for the application of the proposed procedure on fresh water (NIST SRM 1643e).

Element	Measured concentrations [μg/l]	Certified values/5 [μg/l] for 1:5 dilutions
Al	28.3 ± 1.10	28.4 ± 1.72
Be	2.79 ± 0.11	2.80 ± 0.03
Cd	1.31 ± 0.19	1.31 ± 0.02
Co	5.32 ± 0.24	5.41 ± 0.09
Cr	4.49 ± 0.38	4.08 ± 0.07
Cu	4.40 ± 0.11	4.55 ± 0.06
Fe	19.6 ± 0.60	19.6 ± 0.40
Mn	7.72 ± 0.44	7.80 ± 0.13
Ni	12.3 ± 0.71	12.5 ± 0.20
Pb	4.0 ± 0.60	3.93 ± 0.04
Ti	*	*

[*] No reference values provided for NIST SRM 1643e.

3.2.1. *Demonstration of accuracy*

To determine the accuracy of the proposed procedure with real samples, it was applied to fresh water (NIST SRM 1643e). Due to its high trace metal levels for most investigated elements the SRM was diluted prior to analysis. For this purpose 1 part SRM has been mixed with 4 parts of purified water. Furthermore, since the SRM is stabilized with nitric acid (0.8 mol L^{-1}), it was necessary to increase the concentration of the buffer solution to 3 mol L^{-1}. To overcome the influence of an enhanced buffer concentration, the concept of Matrix Matched calibration (MMC) has been applied for signal quantification. In case of analysis of natural samples MMC is also advantageous since it accounts for matrix effects altering the adsorption process, e.g. the presence of competitive ions which reduce the sorbent capacity or complexing agents such as dissolved organic compounds which hamper analyte retention on the nanoparticles.

All other analysis parameters were set according to Table 3. The RSDs ($n=4$) ranged from 2% to 5% for most elements. For trace metals with very low concentrations such as Cd and Pb increased RSDs up to 15% were observed. The determined concentrations as well as final sample concentrations of SRM are shown in Table 4. Although concentrations of coexisting ions such

Table 5
Average trace metal concentrations in drinking water samples collected at different sites in Vienna, Austria.

Element [$\mu g\ L^{-1}$]	Tower building 9th floor	Genius wing	Lehar wing	Vienna 7th	Vienna 20th	Langenzersdorf	Guntramsdorf
Al	24.2 ± 0.9	27.3 ± 1.5	48.4 ± 0.8	44.8 ± 0.9	32.1 ± 1.2	39.4 ± 1.5	36.2 ± 1.0
Be	0.21 ± 0.07	0.16 ± 0.01	0.18 ± 0.04	0.15 ± 0.01	0.17 ± 0.03	0.17 ± 0.03	0.17 ± 0.01
Cd	2.2 ± 0.6	2.4 ± 0.5	2.3 ± 0.6	1.4 ± 0.7	2.3 ± 0.4	1.9 ± 0.5	1.9 ± 0.6
Co	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
Cr	3.4 ± 0.8	3.4 ± 0.9	4.3 ± 0.9	2.2 ± 0.4	2.5 ± 0.8	3.9 ± 0.9	3.1 ± 0.3
Cu	15.0 ± 1.3	88.3[a] ± 5.7	31.0 ± 1.4	14.8 ± 1.3	71.3[a] ± 1.4	75.3[a] ± 4.1	23.3 ± 1.4
Fe	607.2[a] ± 7.9	358.7[a] ± 4.9	55.5[a] ± 6.5	36.1 ± 1.4	34.8 ± 5.1	80.0[a] ± 5.5	33.6 ± 3.7
Mn	18.8 ± 1.6	4.0 ± 0.6	2.7 ± 0.5	2.9 ± 0.4	2.0 ± 0.6	3.4 ± 0.5	1.8 ± 0.5
Ni	4.1 ± 1.6	10.5 ± 1.3	5.7 ± 2.1	3.8 ± 1.0	6.2 ± 1.7	8.0 ± 1.7	6.2 ± 1.2
Pb	29.7 ± 4.5	38.9 ± 3.4	43.8 ± 3.9	38.9 ± 5.9	41.3 ± 6.7	42.2 ± 6.3	45.7 ± 4.8
Ti	6.2 ± 0.2	6.0 ± 0.3	9.2 ± 0.4	8.0 ± 0.2	8.2 ± 0.2	9.0 ± 0.5	8.7 ± 0.6

[a] Tentative values only—concentrations outside calibrated range ($>50\ \mu g\ L^{-1}$).

as Ca, Mg, Na and K were in the range of several mg L^{-1}, and thus 56 (in case of Mg and Al) to approximately 4900 (in case of Ca and Cd) times higher than the investigated target analytes, excellent agreement was found for all investigated elements demonstrating that the proposed procedure is applicable for the analysis of natural samples containing dissolved organic carbon and inorganic ions such as SO_4^{2-}, Cl^-, NO_3^-, Na^+, K^+, Ca^{2+} and Mg^{2+}.

3.2.2. *Application*

The procedure was applied for analysis of drinking water samples which were collected in the vicinity of Vienna (Austria) as well as in buildings of the Vienna University of Technology (TU, Campus Getreidemarkt). Water samples were taken from water taps, each heeding the following sampling procedure: The water tap was opened and after a purge time of 2 min water was collected in a pre-cleaned 500 mL sterile bottle. The first content was discarded, before collecting the actual 500 mL as sample. Immediately after sample collection 0.25 mL nitric acid (conc.) was added to each sample as stabilizer and the bottle was closed until the start of sample pre-treatment.

For sample pre-treatment the conditions shown in Table 3 were applied. To comply for any matrix influences 20 mL of each sample were pooled and used as a joined basis solution for a matrix matched calibration performed with spike levels of 10, 20 and 40 $\mu g\ L^{-1}$ ($n=4$ replicates). Derived calibration functions showed a strong linear correlation between analyte concentration and emission signal for all investigated elements. Quantification of sample signals revealed trace metal concentrations ranging from less than approximately 0.2 to more than 600 $\mu g\ L^{-1}$. Values obtained for the individual sampling sites are compiled in Table 5.

In general the trace metal concentrations given in Table 5 were in the same range or below the values found in literature [33] or the Drinking Water Ordinance. When comparing the concentrations from the sample collecting sites, elements like Be, Cd, Cr and Ni have a resembling concentration level, whereas Al and Pb show a much profounder deviation from one another. However, greatest differences were observed for Cu, Fe and Mn, showing variations of more than one order of magnitude. The concentrations found for Co were below the LOD in all samples.

Deviations between the individual sites are assumed to originate from differences in the initial water quality as well as from the condition of the water supply system. Since all the tap water for the Vienna region is originating from the mountains Hoch-schwab, Rax and Schneeberg the trace element concentrations should be rather identical at all sites. Thus the diverging parameters result from differences in the water supply system—in particular the used pipe materials and the presence of surface deposits (rust, scale, oxide layers, etc.) have to be considered. Deviations in these two parameters are expected since the supply-pipe systems are from different employment stages (installation in different years or even decades). This is of special importance when comparing the results achieved for the buildings on the TU campus which were located in the same area but built in different periods. Looking at Fe and Mn on the one hand, the new built "Lehar wing" (erected in 2010) shows the lowest amounts of trace metals in the tap water samples. We assume these low values are owing to the new valves, pipes and accessories used in this building, whereas the high Fe concentrations in Genius wing and tower building result from the rather old installations. On the other hand all samples show almost equal concentrations for Cd, Cr, Ni, Pb and Ti, leading to the conclusion that the water contents of these four elements depend initially on the whole campus supply-system and local differences between the building are only of minor importance.

4. Conclusions

With dispersed particle extraction (DPE) a novel sample pretreatment method for multi trace element enrichment prior to analysis with ICP-OES has been introduced. The procedure was carefully optimized and the effects of particle introduction during slurry measurement have been thoroughly studied. It was demonstrated that the effects of particles introduced into the plasma are more than compensated by the enrichment capabilities. By using 14.4 mL of sample volume, treated with acetate buffer to pH 5.1 and the use of 5 mg of the self-synthesized ion-exchange particles an average enrichment factor of 10.4 could be achieved. Especially for samples with low matrix levels a further decrease of the detection limits is possible by increasing the applied initial sample volume.

Compared to conventional solid phase extraction this method includes all of SPEs advantages like high enrichment, high recovery, low cost and low consumption of solvents and shows distinct advantages for sorbent handling and memory effects by implementing the renewable surfaces approach. Furthermore the BI approach is surpassed by the direct particle introduction into the ICP-OES, which abdicates the elution of target analytes from the sorbent material prior to measurement. This feature of the developed procedure establishes access to sorbent materials with irreversible bonding mechanisms for sample pre-treatment, which, to our best knowledge, has not yet been implemented for a multi-element procedure. By utilizing this aspect much more selective bonding mechanisms can be introduced for extraction purposes from complex matrices. Furthermore the target analytes are bound stronger and with a higher affinity, affecting analytes in different dissolved stabilized states like metal complexes, which are only poor or not accessible with the current extraction mechanisms.

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