

Determination of metallic nanoparticles in soils by means spICP-MS after a microwave-assisted extraction treatment

Carlos Gómez-Pertusa^a, M. Carmen García-Poyo^b, Guillermo Grindlay^{a,*}, Ricardo Pedraza^b, M. Adela Yáñez^b, Luis Gras^a

^a University of Alicante, Department of Analytical Chemistry, Nutrition and Food Sciences, PO Box 99, 03080, Alicante, Spain

^b LABAQUA S.A.U, c/ Dracma, 16-18, Polígono industrial Las Atalayas, 03114, Alicante, Spain

ARTICLE INFO

Keywords:

Nanomaterials
Soils
Microwave extraction
Single particle
Inductively coupled plasma mass spectrometry

ABSTRACT

Current sample preparation strategies for nanomaterials (NMs) analysis in soils by means single particle inductively coupled plasma mass spectrometry have significant constraints in terms of accuracy, sample throughput and applicability (i.e., type of NMs and soils). In this work, strengths and weakness of microwave assisted extraction (MAE) for NMs characterization in soils were systematically investigated. To this end, different extractants were tested (ultrapure water; NaOH, NH₄OH, sodium citrate and tetrasodium pyrophosphate) and MAE operating conditions were optimized by means of design of experiments. Next, the developed method was applied to different type of metallic(oid) nanoparticles (Se-, Ag-, Pt- and AuNPs) and soils (alkaline, acid, sandy, clayey, SL36, loam ERMCC141; sludge amended ERM483). Results show that Pt- and AuNPs are preserved and quantitatively extracted from soils in 6 min (12 cycles of 30 s each) inside an 800 W oven by using 20 mL of 0.1 M NaOH solution. This methodology is applicable to soils showing a wide range of physicochemical properties except for clay rich samples. If clay soil fraction is significant (>15%), NMs are efficiently retained in the soil thus giving rise to poor recoveries (<10%). The analysis of labile NMs such as Se- and AgNPs is not feasible by means this approach since extraction conditions favors dissolution. Finally, when compared to current extraction methodologies (e.g., ultrasound, cloud point extraction, etc.), MAE affords better or equivalent accuracies and precision as well as higher sample throughput due to treatment speed and the possibility to work with several samples simultaneously.

1. Introduction

Nanomaterials (NMs) have attracted considerable attention in many fields due to their unique properties and wide range of applications [1, 2]. According to the Nanodatabase [3] and the Nanotechnology Products Database [4] there are more than 10,000 products containing NMs on the market and this figure is expected to increase in the years to come. Though the great potential and applicability of NMs, our current knowledge about NMs-associated hazards is still limited [5]. When NMs are released into the environment, they may eventually end up in soils through various pathways [6] and, once there, NMs may be accumulated but also being transform into other species affecting biota [7]. To properly understand all these phenomena, robust and accurate analytical methodologies for NMs determination in soils are required.

Single particle inductively coupled plasma mass spectrometry (spICP-MS) has emerged as a powerful analytical technique for NMs

characterization in complex media. This technique provides information on the composition, size distribution and concentration of NMs at ultra trace levels as well as on the ionic dissolved fraction [8–10]. Prior to spICP-MS determinations, an extraction treatment is mandatory to isolate the NMs from the soil. To this end, different strategies have been proposed such as: (i) liquid extraction at ambient temperature [11]; (ii) ultrasound assisted extraction procedures [12–15]; and (iii) cloud point extraction [16,17]. While all these methodologies have demonstrated that NMs determination in soils is feasible, we are far from having accurate and robust methodologies. In general, NMs recovery are not always quantitative [11,14], and there are a great variability on the data reported in the literature, even when using the same experimental procedure [12–14]. Thus, silver nanoparticles (AgNPs) recoveries ranging from 57% to 100% have been reported for ultrasound assisted extraction procedure with 2.5 mM tetrasodium pyrophosphate (TSPP) [12,13]. On the other hand, since there is currently not available

* Corresponding author.

E-mail address: guillermo.grindlay@ua.es (G. Grindlay).

<https://doi.org/10.1016/j.talanta.2024.125742>

Received 12 October 2023; Received in revised form 23 January 2024; Accepted 1 February 2024

Available online 9 February 2024

0039-9140/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

certified reference material in the market, method development relies on the use of non-commercial samples showing a very specific set of physicochemical characteristics that could affect the outcome of the experiments. In fact, most of the studies are performed with a single type of soil [12,14–17] and no information about soil characteristics is usually provided [16,17]. Similarly, a single type of NM (mostly Ag- and AuNPs) is usually covered, being unclear whether other type of NMs could be successfully determined using the same approach [11–13, 15–17]. Finally, most of the strategies proposed are time consuming thus affecting negatively sample throughput. For instance, CPE procedures are particularly cumbersome due to the high number of experimental steps and time required (>1 h) [16,17].

Microwave Assisted Extraction (MAE) is a well-established sample preparation technique in analytical chemistry for the analysis of both inorganic and organic species. It allows fast, controlled, and efficient sample heating which favors analyte extraction rates and increase sample throughput [18,19]. Our research group has recently demonstrated that MAE is highly beneficial for recovering NMs from air filters [20]. Metallic NMs (Pt- and AuNPs) are quantitatively extracted from the filter in 4 min inside an 800 W microwave oven by using 40 mL of a 2.0% w w⁻¹ NH₄OH solution. According to these findings, it could be highly advantageous to apply MAE for NMs analysis in soils. To the best of author's knowledge, no study has been carried out in this regard.

The aim of this work is to evaluate the strengths and weakness of MAE for NMs characterization in soils by means spICP-MS. To this end, both NPs (Se-, Ag-, Pt- and AuNPs) and soil samples (alkaline; acid; sandy; clayey; SL36, loam ERMCC141; sludge amended ERM483) covering different physicochemical characteristics were selected. First, extraction capabilities of different media (i.e., NaOH, NH₄OH, sodium citrate dihydrate, and TSPP) were studied. Next, MAE working conditions were optimized by means of design of experiments (DoE). Finally, it has been examined how MAE is affected by NPs and soils characteristics.

2. Materials and methods

2.1. Reagents

All solutions were prepared using ultrapure water from a Milli-Q-purification system (Millipore Inc, France).

Stock suspensions of different NMs were employed through this work: (i) 150 nm SeNPs with a concentration of 2.0·10¹⁰ mL⁻¹ (Glan-treo, Cork, Ireland); (ii) 60 nm AgNPs with a concentration of 1.9·10¹⁰ mL⁻¹ (NanoComposix, San Diego, USA); (iii) 70 nm PtNPs with a concentration of 1.2·10¹⁰ mL⁻¹ (NanoComposix); (iv) and 50, 100 and 150 nm AuNPs with a concentration of 3.5·10¹⁰, 3.9·10⁹ and 3.6·10⁹ mL⁻¹, respectively (Cytodiagnosics, Burlington, Canada).

Selenium, Ag, Pt and Au mono-elemental 1000 mg L⁻¹ standards (Sigma-Aldrich, Steiheim, Germany) were employed for calibration purposes with spICP-MS. Finally, NaOH, 28% w w⁻¹ NH₄OH solution, sodium citrate (Sigma-Aldrich) and tetrasodium pyrophosphate (Pan-reac, Barcelona, Spain) were employed for preparing extraction media.

2.2. Soils samples

Seven soil samples covering a broad range of matrix characteristics were investigated: (i) alkaline; (ii) acid; (iii) sandy; (iv) clayey; (v) SL36 (certified reference material manufactured from a proficiency Testing scheme following ISO17034 IELAB, Alicante, Spain) (vi) loam (ERMCC141, JRC, Belgium); and (vii) sludge amended (ERM483, JRC). The latter three samples were specifically selected following the recommendations made by S. A. Wise [21] to improve field metrology since the characteristics (e.g., homogeneity, stability, etc.) and availability of certified reference materials (CRM) allow to use them in future studies as a common material for benchmarking.

All the samples were dried overnight in an oven at 105 °C, sieved (63

µm) and stored in polyethylene tubes. Prior to this work, each soil was physicochemical characterized (i.e., pH, conductivity, organic matter, carbonates and texture) using different established protocols (See Appendix) [22–25]. Table 1 shows physicochemical characterization data for each soil sample. For all the CRMs, experimental data agreed with the information provide in the certificate. It is important to note that texture determination for CRMs was not feasible due to the limited amount of sample available. In the case of the ERM-CC141, indicative values included in the certificate of analysis were employed.

2.3. MAE extraction methodology

Microwave-assisted extraction of NMs from soil samples was performed in a similar way to that previously described for air filters [20]. First, soils were dried overnight at 60 °C. Next, the extractant media was added to 1 g of a given sample and heated inside of a domestic microwave oven (Bluesky BMG20M – 18) using 800 W, the highest power available. Extractions were performed with six samples per run with the same extractant. To minimize sample projections and liquid evaporation, samples were covered with a glass watch during the extraction process. Next, samples were allowed to cool at room temperature and diluted with Milli-Q water for a final volume of 40 mL. Finally, an aliquot of 10 mL of each sample were centrifuged 5 min at a 500 g to remove soil particles and avoid nebulizer blockage and 5 mL of the supernatant were analyzed by spICP-MS. In agreement with other authors [14,15], these operating conditions allow the analysis of NMs suspension without particle losses or aggregate formation. No differences on both particle number and particle size distributions were noticed for NMs standards with and without centrifugation (Table S1, Appendix).

According to previous works about NMs extraction methodologies [11,12,14–17,20,26], a total of 5 extractant media were selected: (i) ultrapure water; (ii) NaOH, (iii) NH₄OH; (iv) sodium citrate dihydrate; and (v) TSPP. Optimization of the MAE operating conditions was carried out by means of DoE using a circumscribed central composite design (CCD) and five levels per factor. Main variables (factors) investigated were: (i) extractant concentration (0–1 M); (ii) extractant volume (5–50 mL); and (iii) time (0–5 min).

2.4. Instrumentation

A triple-quadrupole based 8900 ICP-MS from Agilent Technologies (Santa Clara, USA) was used throughout this work. Operating conditions are shown in Table 2.

Single particle calibration was carried out using the frequency methodology [27] with NaOH matrix-matched standards. This calibration strategy was preferred over the particle size method since it allows a direct assessment of NMs transport efficiency thus minimizing bias on both particle number concentration and particle size distribution [28]. Five sigma criterion was employed to discriminate NP event signals from the background [29].

Prior to ICP-MS measurements, all the NPs were characterized by means of transmission electron microscopy (TEM) thus allowing to evaluate the accuracy of spICP-MS data. Experimental procedure is described elsewhere [20].

3. Results and discussion

This work evaluates, for the first time, the use of MAE for NMs determination in soils by means spICP-MS. To evaluate the potential benefits of using MAE for recovering NMs from soils, some preliminary experiments were carried out using PtNPs and the sandy soil sample. Platinum nanoparticles were preferred over the remaining NMs because they are highly stable and spICP-MS measurements are straightforward (i.e., no memory effects and spectral interferences, low background signal, etc.) [28] and sandy soil because, apart from texture, their characteristics are approximately an average of all the samples

Table 1Physicochemical characteristics of soil samples investigated. Data expressed as the mean value \pm s, n = 5.

	pH	Conductivity (μ S/cm)	Organic matter (%)	Carbonates (g CO ₃ /kg soil)	Clay/%	Loam/%	Sand/%
Alkalike	8.10 \pm 0.05	553 \pm 6	1.89 \pm 0.03	335 \pm 8	12.9 \pm 0.2	31.6 \pm 0.6	55.5 \pm 0.8
Clayey	8.33 \pm 0.02	1710 \pm 14	0.124 \pm 0.008	331 \pm 5	32.9 \pm 0.4	40.0 \pm 0.5	27.1 \pm 0.4
Acid	6.31 \pm 0.05	7460 \pm 120	3.17 \pm 0.05	1.4 \pm 0.2	3.28 \pm 0.05	19.6 \pm 0.4	77.1 \pm 1.2
Sandy	7.63 \pm 0.06	1140 \pm 30	1.39 \pm 0.02	81 \pm 4	2.88 \pm 0.08	1.80 \pm 0.06	95.3 \pm 1.1
SL 36	7.85 \pm 0.05	1280 \pm 20	2.47 \pm 0.04	7.5 \pm 1.1	–	–	–
ERM-CC141	5.93 \pm 0.04	1290 \pm 20	6.40 \pm 0.08	81 \pm 8	15.0 \pm 0.5 ^a	80.0 \pm 1.2 ^a	5.0 \pm 0.2 ^a
ERM-483	6.91 \pm 0.04	95 \pm 2	0.92 \pm 0.02	5.6 \pm 1.5	–	–	–

^a Indicative values of the certificate of analysis.**Table 2**

ICP-MS operating conditions.

	Single particle mode
Plasma forward power (W)	1550
Sampling depth (mm)	4 ^a ; 8 ^b
Argon flow rate (L min ⁻¹)	
Plasma	15
Auxiliary	0.9
Nebulizer (Q _g)	1.00
Torch i.d. (mm)	1.0
Sample introduction system	
Nebulizer	MicroMist® nebulizer
Spray chamber	Scott double pass
Sample uptake rate (Q _i) (μ L min ⁻¹)	300
Dwell time (ms)	0.1
Measuring time (s)	60
Nuclides	⁷⁸ Se; ¹⁰⁷ Ag; ¹⁹⁵ Pt; ¹⁹⁷ Au

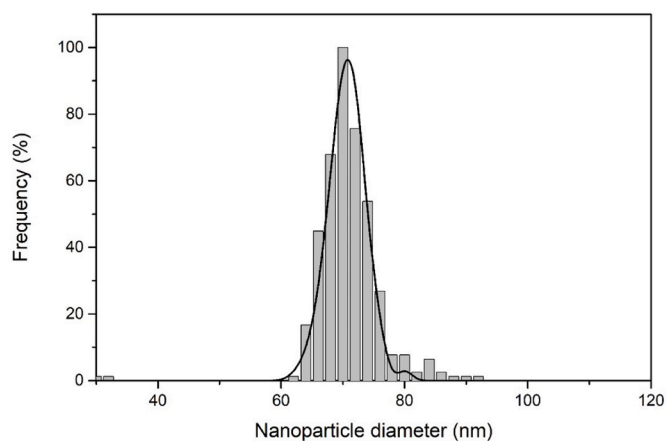
^a Se; ^b Ag, Pt and Au.

investigated. In addition, because its higher silica content, this sample is closer from a chemical point of view to the microquartz filter employed in our previous work [20] thus making results interpretation easier.

According to previous works in the literature [12–14], water and several basic extractants at a concentration of 0.1 M (i.e. NaOH, NH₄OH, sodium citrate dihydrate, and TSPP) were initially investigated. In fact, this type of extractants are particularly useful to improve soil dispersibility and, hence, NMs extraction [12–14]. To this end, 1 g of sandy soil was spiked with a known quantity of the stock 70 nm PtNPs suspension (1 mL of a 6·10⁵ NPs mL⁻¹ suspension), mixed vigorously for homogenization and dried overnight at 60 °C. Then soils were analyzed by means spICP-MS after a MAE treatment of 3 min with 40 mL of extractant. For the sake of comparison, the extraction treatment was also carried out without MW heating. Table 3 shows both PtNPs particle size and particle concentration recoveries for the different extraction treatments tested. Irrespective of the strategy selected, the mean diameter of the NPs recovered was equivalent to the value obtained by means TEM (69 \pm 2 nm) thus confirming that PtNPs remained mostly unaltered by the extraction treatments with and without MWs (Fig. 1). Though the high sodium content of the extractant solution, there was no sign of PtNPs agglomeration. On the other hand, it is clearly observed that the use of MW has a beneficial effect on NMs extraction. For instance, when using NaOH 0.1 M, PtNPs recovery improved 3.1-fold when using MAE

Table 3Average PtNPs size and particle recovery for sandy soil using different extractant solutions. Results are expressed as the mean value \pm s, n = 5. Extraction time 3 min; extractant volume 40 mL. Reference value obtained by TEM 69 \pm 2 nm.

Extractant	MW	Size/nm	Recovery/%
H ₂ O	No	69.0 \pm 1.5	3 \pm 3
NaOH 0.1 M	No	68.5 \pm 1.0	17 \pm 3
H ₂ O	Yes	67.5 \pm 1.2	9 \pm 3
NaOH 0.1 M	Yes	67.2 \pm 1.0	53 \pm 4
NH ₄ OH 0.1 M	Yes	69.0 \pm 1.8	27 \pm 4
Citrate 0.1 M	Yes	66.9 \pm 1.0	34 \pm 5
TSPP 0.1 M	Yes	65.0 \pm 1.8	45 \pm 4

**Fig. 1.** Platinum NPs size distribution for sandy soil after a MAE treatment with NaOH 0.1 M (grey bars). Extraction time: 3 min. Continuous black line represents TEM particle size distribution.

with regard the extraction procedure at ambient temperature. Among the extractants tested, none of them provide PtNPs quantitative recoveries (Table 3). The highest values were obtained with NaOH (53 \pm 4%) followed by TSPP (45 \pm 4%). For the remaining extractants, recoveries were always below 40%. In fact, when using water (with and without MAE), PtNPs recoveries were particularly low (<10%). According to these findings, NaOH was selected as the extraction media for further experiments. Finally, it is important to note that this study was repeated changing both the spiking procedure (NMs concentration, 1·10⁵–1·10⁷ NPs mL⁻¹, and suspension volume, 60 μ L–1mL) and drying time, 1–3 days) and similar results to those shown in Table 3 were observed.

3.1. Optimization of the extraction procedure

Microwave-assisted extraction conditions were optimized using a CCD model. After preliminary experiments, extractant concentration, volume and MW time were identified as the most significant variables controlling PtNPs extraction. Sample temperature was not considered as a relevant parameter for our experimental setup due to soil extracts start boiling after 30–40 s of MW heating. Each of the above-mentioned variables were investigated in five levels: (i) NaOH concentration (0, 0.01, 0.1, 0.5 and 1 M); (ii) extractant volume (5, 10, 25, 40 and 50 mL); and (iii) MW time (0, 2, 3, 4 and 5 min). A total of 16 experiments were performed in triplicate using the sandy soil spiked with PtNPs (Table S2, Appendix). According to General requirements for the competence of testing and calibration laboratories - ISO/IEC 17025:2017 standard, recoveries were considered quantitative within the range 80–120% [30].

To evaluate the significance of the above-mentioned variables on PtNP extraction, data were analyzed using ANOVA and the effects were summarized by means of the corresponding Pareto charts (Fig. 2). The ANOVA data analysis revealed the significance of considering not only

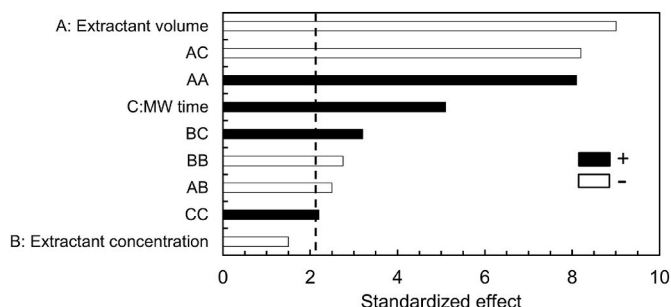


Fig. 2. Pareto chart obtained in the optimization study of the main variables affecting PtNPs extraction in sandy soil. Dotted vertical line correspond to 95% confidence level.

single variables effects but the interplay with them since PtNPs extraction is indeed affected by NaOH concentration, extractant volume and MW time. The quality of fit of the model equation was represented by the coefficient of determination (R^2 and adjusted- R^2). R^2 of 0.92 and adjusted- R^2 of 0.90 showed a good relationship between experimental data and fitted model, thus indicating the high potential of model in prediction of response. Table 4 shows the optimum experimental conditions derived from the CCD model for PtNP extraction. It can be observed that optimum conditions are those favouring sample heating, that is, low extractant volumes (5 mL) and high MW time (4 min) and NaOH concentration (0.5 M) (Fig. S1, Appendix). Under these conditions, PtNP extraction was re-evaluated, but recoveries were still not quantitative ($63 \pm 16\%$) and precision was significantly deteriorated. It must be considered that, because sample heating is so efficient, extractant solutions starts boiling giving rise to solution splashes thus affecting extraction accuracy and repeatability. Therefore, MAE procedure was modified for improving sample heating control. First, sample volume was increased up to 20 mL whereas extractant concentration was reduced to 0.1 M. Because these changes decrease MW heating efficiency and there is less energy per unit of mass available, extraction time was increased up to 6 min by using 12 cycles with a duration of 30 s of MW heating. Operating this way, solution splashes are minimized, and accurate and precise PtNPs recoveries (i.e., $95 \pm 4\%$) were obtained.

3.2. Influence of the NPs nature and size

Next, the influence of NMs characteristics on MAE extraction was evaluated. To this end, metallic NPs covering different chemical composition and size were selected (150 nm SeNPs, 60 nm AgNPs, and 50, 100 and 150 nm AuNPs). As it was done before with PtNPs, sandy soil was spiked with a known amount of each NMs and analyzed by spICP-MS after a MAE treatment using MW heating compromise conditions (Table 4). The mean particle size and particle recovery obtained for all the NMs tested is shown in Table 5. As it was previously observed for PtNPs and irrespective of NMs size, the mean diameter of the AuNPs was equivalent to the value obtained by means TEM and recoveries were mostly quantitative ($\approx 90\%$). However, when operating Ag- and SeNPs, significant differences were observed on both particle size and particle number with regard the reference values. Thus, when working with AgNPs, the mean size obtained was 22% lower than the value obtained by means TEM (Fig. 3), and particles recovery was just $75 \pm 4\%$. As

Table 4
Optimum and compromise conditions for metallic NPs analysis by means MAE.

Extraction parameters	Extraction conditions	
	Optimum	Compromise
Extractant volumen/mL	5	20
NaOH concentration/M	0.5	0.1
MW time/min	4	6 (0.5x12 cycles)

Table 5
Average NMs particle size and particle recovery for sandy soil under compromise extraction conditions. Results are expressed as the mean value \pm s, $n = 5$.

	Reference size/nm	Size/nm	Recovery/%
Pt	69 ± 2	68.1 ± 0.9	95 ± 4
Au	52 ± 6	48.5 ± 0.5	90 ± 3
Au	102 ± 8	93.9 ± 0.4	91 ± 7
Au	155 ± 12	145.3 ± 0.7	88 ± 5
Ag	60 ± 1.5	46.7 ± 0.5	75 ± 4
Se	154 ± 12	n.d.	1.4 ± 1.3

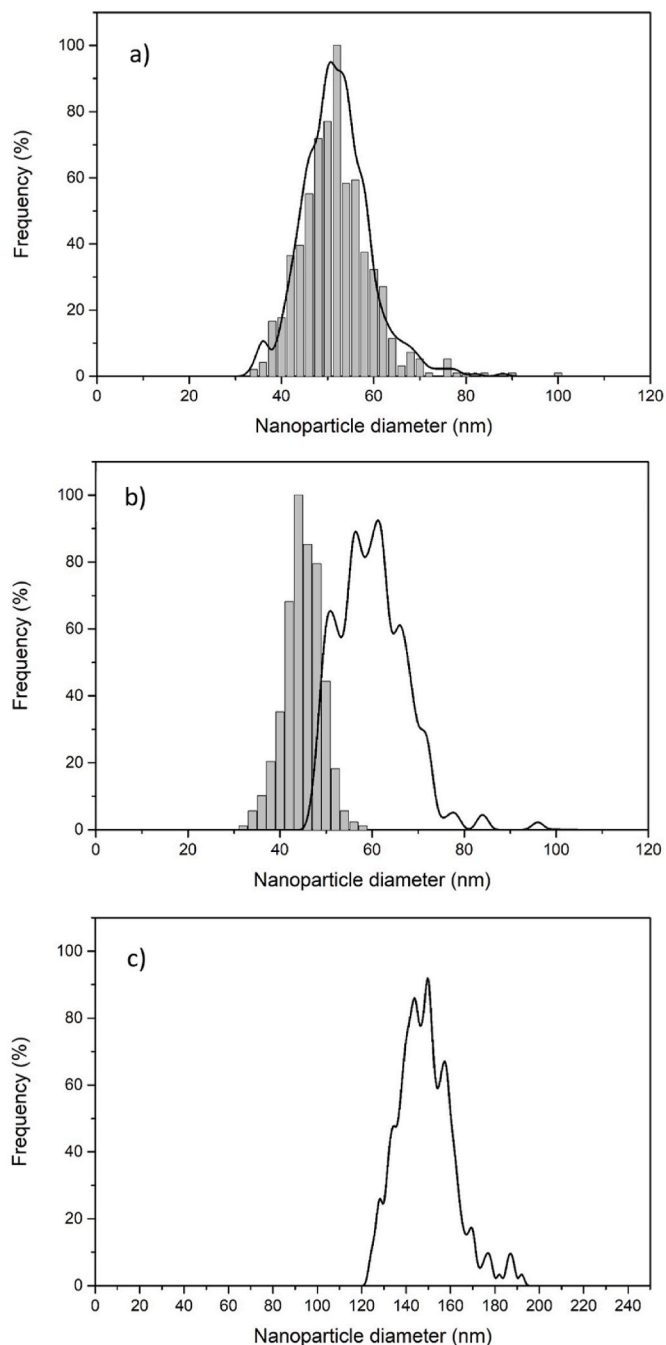


Fig. 3. Nanoparticle size distributions for (a) 50 nm AuNPs, (b) 60 nm AgNPs, and (c) 150 nm SeNPs in sandy soil using MAE compromise conditions. Continuous black line represents TEM particle size distribution.

regards SeNPs, neither particle size distribution or concentration could be determined since no signal pulse was detected. On this regard, it was observed that ICP-MS background signal for Ag (m/z 107) and Se (m/z 78) increased, respectively, about 1.4-fold and more than 4-fold, with regard a reference solution (i.e., pristine NMs suspension) (Fig. 4). These results fully indicate that Ag- and SeNPs are degraded thus hampering NMs characterization. On this regard, it should be noted that metallic Se is only stable under negative solution redox potential and, hence, it is prone to dissolution with and without MW heating. Similar findings have been reported by other authors operating conventional and ultrasound-extraction methodologies due to the high lability of these NMs [12,13]. Nevertheless, when working with these strategies, mean diameter bias are usually lower than the value observed for MAE (<10%), probably due to extraction treatment are less harsh. To avoid changes on particle size for both type of NMs, the use of a milder MW extraction process was explored (i.e., NaOH 0.01 M and 2 min). Using this strategy, bias on particle size distribution for AgNPs was only 10% but recoveries were reduced to $47 \pm 8\%$. No improvement on SeNPs characterization was noticed. From these results, it can be concluded that there is a trade-off to consider between the effectiveness of the extraction and NMs preservation. So, if the characterization of labile NMs is required, special care is required when selecting MAE operating conditions.

3.3. Influence of the soil characteristics

According to previous works in the literature, soil characteristics (i.e., organic matter content, pH, etc.) do have a significant effect on NMs extraction efficiency [11–17]. Consequently, seven soil samples covering different physicochemical properties have been tested to gain insight into the effect of soil characteristics on MAE. Among them, commercial reference soil samples (i.e., SL36, ERMCC141 and ERM483) have been included thus they can be used in future studies for

comparison purposes under a common framework. All the soils have been previously characterized (i.e., pH, conductivity, organic matter, carbonate and texture) by means different analytical procedures (Appendix). Physicochemical characterization details for each soil are shown in Table 1.

Because the low stability of Ag- and SeNPs, this study was just performed with Pt- and (50 & 150 nm) AuNPs. Irrespective of the soil considered, Pt- and AuNPs mean diameter was equivalent to the value obtained by means TEM (Table S3, Appendix). However, significant differences in NMs recovery were found among the soil investigated (Fig. 5). In the same way as with the sandy soil (Section 3.2), Pt- and AuNPs recoveries for acid and SL36 soils were quantitative (>80%). Recoveries for alkaline, ERM 483 and ERM CC141 samples were reasonably good since they were between 70% and 80%. Clayey soil, however, presented extremely low recoveries. For all the NMs tested, recoveries were below 10% with high uncertainties.

Based on experimental data gathered in Table 1 about soils characteristics, none of the parameters checked have apparently a significant influence on NMs extraction except for clay levels. It was observed that recoveries were mostly quantitative for those samples (sandy and acid soils) showing the lowest clay content (2–3%). If the clay levels increase, however, NMs recovery get worse. Thus, soils with clay levels of 15% (alkaline and loam ERM-CC141) corresponds to those samples showing NMs recoveries of 70–80%. Obviously, the clayey soil presented the highest clay fraction ($32.9 \pm 0.4\%$) and, hence, shown the lowest recoveries values. To further confirm the negative role of clays on NM extraction, a recovery assays was performed using both pure silica and pure clay (kaolin) in the same way as with soil samples. As expected, recoveries for pure silica were mostly quantitative (>90%) whereas they were significantly deteriorated for pure kaolin, being lower than 40% for both Pt- and AuNPs. These findings might be explained considering that the small pore size shown by clays allow an efficient retention of NMs making their release more difficult [31–34]. Nevertheless, the potential

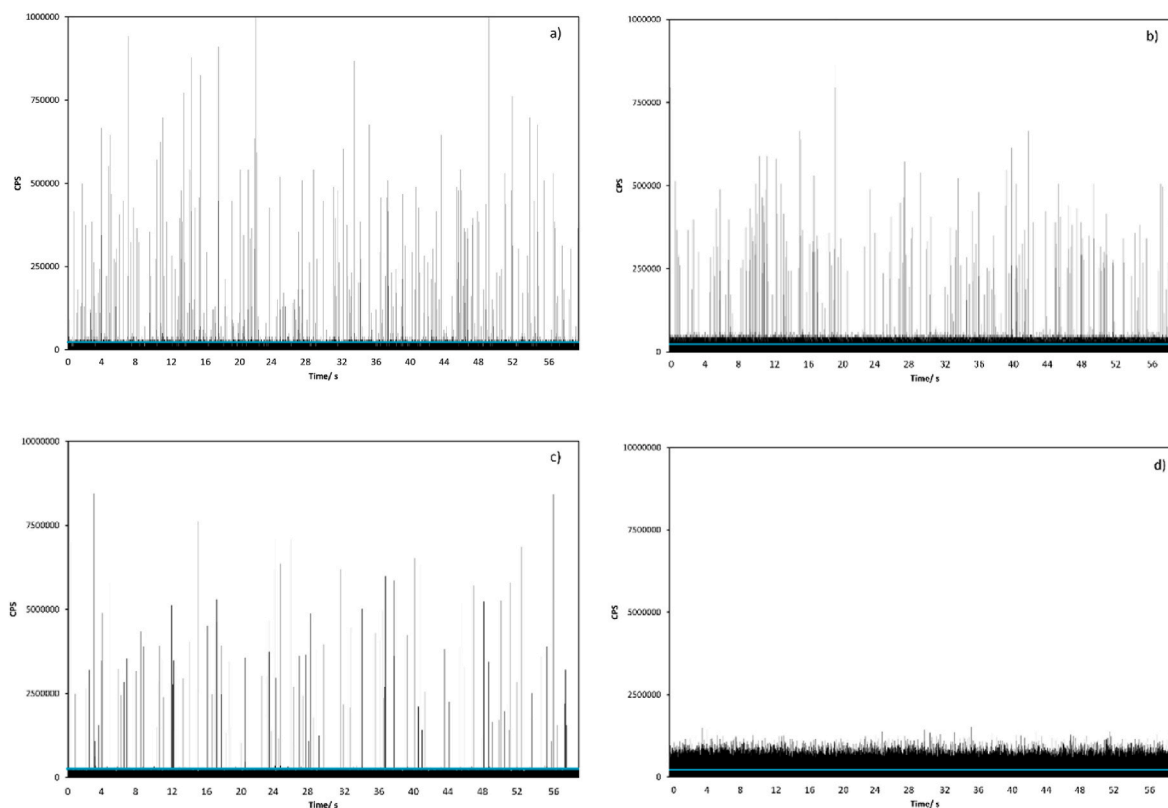


Fig. 4. Signal spectra of the a) 60 nm AgNPs reference solution ($1.7 \cdot 10^4 \text{ mL}^{-1}$), b) 60 nm AgNPs after extraction, c) 150 nm SeNPs reference ($1.2 \cdot 10^4 \text{ mL}^{-1}$) and d) 150 nm SeNPs after extraction. Blue line indicates particle baseline.

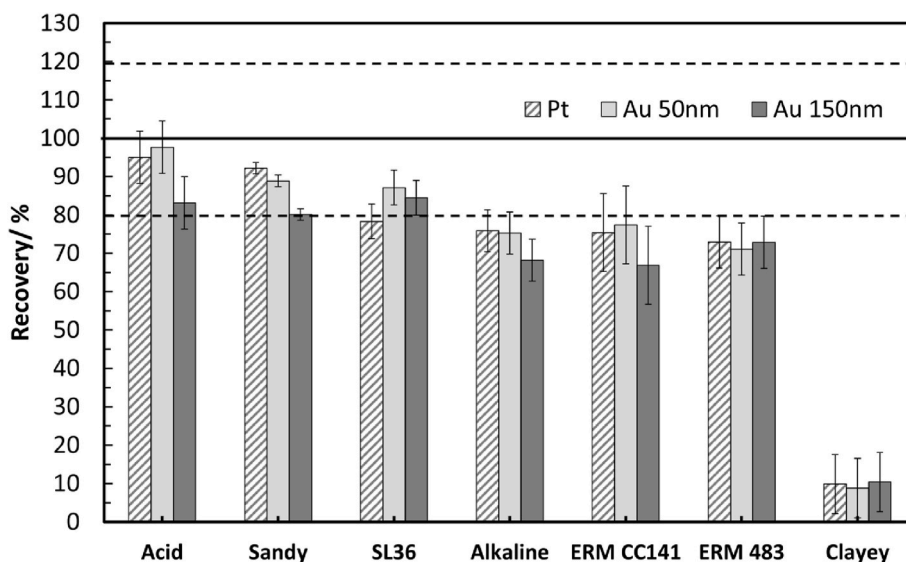


Fig. 5. Particle number recovery for Pt- and AuNPs in different soil samples after a MAE treatment using compromise conditions. Data expressed as the mean value \pm s, n = 5. Dashed lines limit the quantitative recovery interval.

influence of chemical-based phenomena (e.g., electric attraction) should also be considered [34,35]. *A priori*, considering clay retention capabilities, complete release of NMs requires the use of harsher extraction conditions which are far beyond the capabilities of the domestic MW oven employed in this work. To this end, commercial MW instruments could be highly beneficial since they allow better sample heating efficiencies as well as controlled extraction procedures.

3.4. Analytical figures of merit

Particle size (LOD_{Size}) and particle number (LOD_{Part}) limits of detection for Pt and AuNPs were calculated following the procedure proposed by Bolea et al. [29].

The former was estimated using the following equation.

$$LOD_{Size} = 10^4 \cdot \sqrt[3]{\frac{6 \cdot L \cdot t_{Dwell} \cdot Q_i \cdot \eta_n \cdot f_a}{\pi \cdot \rho_{NP} \cdot b_{Cal} \cdot 60}} \quad (3)$$

where L is the particle detection threshold (i.e., 5σ criterion) (counts); t_{Dwell} , dwell time (s); η_n , transport efficiency; Q_i , sample uptake rate (mL min^{-1}); f_a , fraction of analyte in the NP; ρ_{NP} , nanoparticle density (g mL^{-1}); and b_{Cal} , ICP-MS response for ion standard (counts mL ng^{-1}). As regards LOD_{Part} , it was calculated using the following equation:

$$LOD_{Part} = \frac{5 \cdot \sigma_{N,B} + 3}{\eta_n \cdot Q_i \cdot t_{Scan}}$$

where $\sigma_{N,B}$ is the standard deviation of the number of particles detected in at least 10 replicate measurements of the blank; and t_{Scan} , measuring time (min).

Irrespective of soil characteristics, LOD_{Size} and LOD_{Part} for PtNPs were, respectively, 17 nm and $5 \cdot 10^3$ particles per gram of soil. Similar values were obtained for AuNPs (i.e., 18 nm and $6 \cdot 10^3$ particles per gram of soil). LOD_{Size} were similar to those reported by other authors operating quadrupole-based ICP-MS instruments. It is difficult to compare LOD_{Part} with previous studies because this information is not usually provided. Nevertheless, they were equivalent to those obtained in water samples with this same sample introduction system [29].

Finally, analytical characteristics of the proposed method have been compared with those previously reported in the literature for other methodologies dealing with NMs extraction from soils (Table 6). Because most of the studies reported in the literature do not include a detailed soil characterization, special care is required to compare NMs recovery values. Nevertheless, it is safe to say that, when operating non-labile NMs, MAE provides higher recoveries than conventional extraction and it is on par with US-assisted procedures and CPE. For labile NMs

Table 6

Main characteristics of the proposed method and previous strategies described in the literature for NMs extraction from soils.

Extraction	NPs	Size/nm	Type of soil	Extractant	Extraction time/min	Recovery/%	Ref.
Conventional	AgNPs	60–100	Sandy Clayey	Mili-Q water	>3600	37–46	[11]
CPE	AgNPs	60–100	Unknown	Mili-Q water + 5% Triton X-114	>60	–	[16]
	AuNPs	60	Unknown	Mili-Q water + 5% Triton X-114 + NaCl; HNO ₃ ; CaCl ₂	>40	>80	[17]
US	AgNPs	40	Sandy loam	2.5 mM TSPP	>20	80	[12]
	AgNPs	60–100	Loam	2.5 mM TSPP	>45	73–105	[13]
			Sediment	2.5 mM TSPP		80–99	
	AgNPs	60–80	Sewage sludge	2.5 mM TSPP	>1000	57–69	[14]
	AuNPs						
MW	PtNPs	30	Road dust	Mili-Q water	<10	98	[15]
	PtNPs	50–150	Alkaline	NaOH 0.1 M	<10	72–78	This work
			Clayey			4–10	
			Acid			81–92	
			Sandy			83–95	
			Loam (ERM-CC141)			68–76	
			ERM-483			66–73	
			SL 36			75–87	

such as Se- and AgNPs, however, special care is required when selecting operating condition to avoid (partial or even total) dissolution issues. Conventional and US-assisted approaches seem more suitable for this type of analytes since they do not affect significantly NMs mean diameter. If there is one thing that MAE stands out of the most it is sample throughput. Using this methodology, two samples (three replicate each) can be simultaneously treated in 10 min. An equivalent treatment with US wands systems and/or CPE is significantly more tedious and time consuming. When operating US wands, each sample replicate should be treated independently. This means that, even in the best scenario, the analysis of 2 samples (3 replicates each) takes at least 1 h. This issue is even worst for CPE since this procedure requires a conventional extraction as the first step [16,17].

4. Conclusions

Results in this work demonstrate that, for the first time, MAE is a powerful sample preparation methodology for isolating metallic NMs from soil samples. When compared to current extraction strategies, MAE affords significant advantages in terms of simplicity, speed and sample throughput. Nevertheless, further research is still required considering that NMs recoveries are not satisfactory for clay-rich samples and labile NMs might be partially dissolved during MAE thus giving rise to biased data.

There is no doubt that extracting NMs from soils samples is particularly challenging since both NMs and soils characteristics should be simultaneously considered. *A priori*, it seems rather difficult developing a universal methodology for any possible scenario. This is particularly true for labile NMs which might be deteriorated if harsh treatments are employed for improving extraction efficiencies. To meet this challenge, a better knowledge of NMs chemistry and NM-soil interactions is mandatory and, hence, further research efforts are urgently required in this regard. As suggested by A.S. Wise [21], current soil CRMs could be particularly useful to establish a common comparison framework until NMs metrology is better developed and a proper soil CRM is developed for validation studies. From our point of view, MAE is well positioned to play a major role in this area since it could make feasible highly controlled and reproducible extraction treatments, particularly if commercial MW oven are specifically employed.

CRedit authorship contribution statement

Carlos Gómez-Pertusa: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **M. Carmen García-Poyo:** Writing – review & editing, Visualization, Supervision, Methodology, Formal analysis, Data curation. **Guillermo Grindlay:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Ricardo Pedraza:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **M. Adela Yáñez:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Luis Gras:** Writing – review & editing, Visualization, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors would like to thank the Vice-Presidency for Research of the University of Alicante for the financial support of this work (VIG-ROB-050) and the fellowship UAIND21-05C.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2024.125742>.

References

- [1] N. Baig, I. Kammakam, W. Falath, I. Kammakam, Nanomaterials: a review of synthesis methods, properties, recent progress, and challenges, Mater. Adv. 2 (2021) 1821–1871, <https://doi.org/10.1039/d0ma00807a>.
- [2] F. Piccinno, F. Gottschalk, S. Seeger, B. Nowack, Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world, J. Nano Res. 14 (2012) 1109, <https://doi.org/10.1007/s11051-012-1109-9>.
- [3] The nanodatabase, (n.d.). <https://nanodb.dk/> (accessed May 15, 2023).
- [4] Nanomaterials Database - Statnano, (n.d.). <https://statnano.com/nanomaterials> (accessed May 15, 2023).
- [5] B. Nowack, T.D. Bucheli, Occurrence, behavior and effects of nanoparticles in the environment, Environ. Pol. 150 (2007) 5–22, <https://doi.org/10.1016/j.envpol.2007.06.006>.
- [6] G. Cornelis, K. Hund-Rinke, T. Kuhlbusch, N. Van Den Brink, C. Nickel, Fate and Bioavailability of engineered nanoparticles in soils: a review, Crit. Rev. Environ. Sci. Technol. 44 (2014) 2720–2764, <https://doi.org/10.1080/10643389.2013.829767>.
- [7] A.R. Whitley, C. Levard, E. Oostveen, P.M. Bertsch, C.J. Matocha, F. Von Der Kammer, J.M. Unrine, Behavior of Ag nanoparticles in soil: effects of particle surface coating, aging and sewage sludge amendment, Environ. Pollut. 182 (2013) 141–149, <https://doi.org/10.1016/j.envpol.2013.06.027>.
- [8] F. Laborda, I. Abad-Álvoro, M.S. Jiménez, E. Bolea, Catching particles by atomic spectrometry: benefits and limitations of single particle - inductively coupled plasma mass spectrometry, Spectrochim. Acta Part B. At. Spectrosc. 199 (2023) 106570, <https://doi.org/10.1016/j.sab.2022.106570>.
- [9] E. Bolea, M.S. Jimenez, J. Perez-Arantezgui, J.C. Vidal, M. Bakir, K. Ben-Jeddou, A. C. Gimenez-Ingalaturre, D. Ojeda, C. Trujillo, F. Laborda, Analytical applications of single particle inductively coupled plasma mass spectrometry: a comprehensive and critical review, Anal. Methods 13 (2021) 2742–2795, <https://doi.org/10.1039/d1ay00761k>.
- [10] D. Mozhayeva, C. Engelhard, A critical review of single particle inductively coupled plasma mass spectrometry-A step towards an ideal method for nanomaterial characterization, J. Anal. At. Spectrom. 35 (2020) 1740–1783, <https://doi.org/10.1039/c9ja00206e>.
- [11] K.N.M. Mahdi, R.J.B. Peters, E. Klumpp, S. Bohme, M. van der Ploeg, C. Ritsema, V. Geissen, Silver nanoparticles in soil: Aqueous extraction combined with single-particle ICP-MS for detection and characterization, Environ. Nanotechnol. Monit. Manag. 7 (2017) 24–33, <https://doi.org/10.1016/j.enmm.2016.12.002>.
- [12] D.M. Schwertfeger, J.R. Velicogna, A.H. Jesmer, S. Saatcioglu, H. McShane, R. P. Scroggins, J.I. Princz, Extracting metallic nanoparticles from soils for quantitative analysis: method development using engineered silver nanoparticles and SP-ICP-MS, Anal. Chem. 89 (2017) 2505–2513, <https://doi.org/10.1021/acs.analchem.6b04668>.
- [13] L. Li, Q. Wang, Y. Yang, L. Luo, R. Ding, Z.G. Yang, H.P. Li, Extraction method development for quantitative detection of silver nanoparticles in environmental soils and Sediments by single particle inductively coupled plasma mass spectrometry, Anal. Chem. 91 (2019) 9442–9450, <https://doi.org/10.1021/acs.analchem.8b05575>.
- [14] G. Moreno-Martín, B. Gómez-Gómez, M.E. León-González, Y. Madrid, Characterization of AgNPs and AuNPs in sewage sludge by single particle inductively coupled plasma-mass spectrometry, Talanta 238 (2022) 123033, <https://doi.org/10.1016/j.talanta.2021.123033>.
- [15] A. Sánchez-Cachero, N.R. Fariñas, M. Jiménez-Moreno, R.C.R. Martín-Doimeadys, Quantitative analysis and characterization of PtNPs in road dust based on ultrasonic probe assisted extraction and single particle inductively coupled plasma mass spectrometry, Spectrochim. Acta Part B. At. Spectrosc. 203 (2023) 106665, <https://doi.org/10.1016/j.sab.2023.106665>.
- [16] L. Torrent, F. Laborda, E. Marguí, M. Hidalgo, M. Iglesias, Combination of cloud point extraction with single particle inductively coupled plasma mass spectrometry to characterize silver nanoparticles in soil leachates, Anal. Bioanal. Chem. 411 (2019) 5317–5329, <https://doi.org/10.1007/s00216-019-01914-y>.
- [17] H. El Hadri, V.A. Hackley, Investigation of cloud point extraction for the analysis of metallic nanoparticles in a soil matrix, Environ. Sci.: Nano 4 (2017) 105–116, <https://doi.org/10.1039/c6en00322b>.
- [18] S. Eskilsson Cecilia, E. Bjorklund, Analytical-scale microwave-assisted extraction, J. Chromatogr. A. 902 (2000) 227–250.
- [19] M. Llopart, C. Garcia-Jares, M. Celeiro, T. Dagnac, Extraction | microwave-assisted extraction, in: Encyclopedia of Analytical Science, Elsevier, 2019, pp. 67–77, <https://doi.org/10.1016/B978-0-12-409547-2.14442-7>.

- [20] D. Torregrosa, G. Grindlay, M. de la Guardia, L. Gras, J. Mora, Determination of metallic nanoparticles in air filters by means single particle inductively coupled plasma mass spectrometry, *Talanta* 252 (2023) 123918, <https://doi.org/10.1016/j.talanta.2022.123818>.
- [21] S.A. Wise, What if using certified reference materials (CRMs) was a requirement to publish in analytical/bioanalytical chemistry journals? *Anal. Bioanal. Chem.* 414 (2022) 7015–7022, <https://doi.org/10.1007/s00216-022-04163-8>.
- [22] R.H. Loeppert, C.T. Hallmark, M.M. Koshy, Routine procedure for rapid determination of soil carbonates 1, *Soil Sci. Soc. Am. J.* 48 (1984) 1030–1033.
- [23] M. Konert, J. Vandenberghe, Comparison of laser grain size analysis with pipette and sieve analysis: a solution for the underestimation of the clay fraction, *Sedimentology* 44 (1997) 523–535, <https://doi.org/10.1046/j.1365-3091.1997.d01-38.x>.
- [24] E.O. Mclean, Soil pH and lime requirement Chapter 12, in: *Methods of Soils Analysis, Part 2, Chemical and Microbiological Properties*, 1983, pp. 199–224.
- [25] J.D. Rhoades, Salinity: electrical conductivity and total dissolved solids chapter 14, in: *Methods of Soil Analysis. Part 3, Chemical Methods*, 1996, pp. 417–435.
- [26] F. Tou, Z. Niu, J. Fu, J. Wu, M. Liu, Y. Yang, Simple method for the extraction and determination of Ti-, Zn-, Ag-, and Au-containing nanoparticles in sediments using single-particle inductively coupled plasma mass spectrometry, *Environ. Sci. Technol.* 55 (2021) 10354–10364, <https://doi.org/10.1021/acs.est.1c00983>.
- [27] H.E. Pace, N.J. Rogers, C. Jarolimek, V.A. Coleman, C.P. Higgins, J.F. Ranville, Determining transport efficiency for the purpose of counting and sizing nanoparticles via single particle inductively coupled plasma mass spectrometry, *Anal. Chem.* 83 (2011) 9361–9369, <https://doi.org/10.1021/ac201952t>.
- [28] D. Torregrosa, G. Grindlay, L. Gras, J. Mora, Unraveling the role of aerosol transport on nanomaterial characterization by means single particle inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 28 (2023) 1874–1884, <https://doi.org/10.1039/D3JA00134B>.
- [29] F. Laborda, A.C. Gimenez-Ingalaturre, E. Bolea, J.R. Castillo, About detectability and limits of detection in single particle inductively coupled plasma mass spectrometry, *Spectrochim. Acta Part B. At. Spectrosc.* 169 (2020) 105883, <https://doi.org/10.1016/j.sab.2020.105883>.
- [30] Asociación Española de Normalización, *General Requirements for the Competence of Testing and Calibration Laboratories*, 2018. ISO/IEC 17025:2017, Spain.
- [31] J. Fang, X. Shan, B. Wen, J. ming Lin, G. Owens, Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns, *Environ. Pollut.* 157 (2009) 1101–1109, <https://doi.org/10.1016/j.envpol.2008.11.006>.
- [32] D. Kasel, S.A. Bradford, J. Šimůnek, T. Pütz, H. Vereecken, E. Klumpp, Limited transport of functionalized multi-walled carbon nanotubes in two natural soils, *Environ. Pollut.* 180 (2013) 152–158, <https://doi.org/10.1016/j.envpol.2013.05.031>.
- [33] J. Fang, X. Shan, B. Wen, R. Huang, Mobility of TX100 suspended multiwalled carbon nanotubes (MWCNTs) and the facilitated transport of phenanthrene in real soil columns, *Geoderma* 207–208 (2013) 1–7, <https://doi.org/10.1016/j.geoderma.2013.04.035>.
- [34] F. Reith, G. Cornelis, Effect of soil properties on gold- and platinum nanoparticle mobility, *Chem. Geol.* 466 (2017) 446–453, <https://doi.org/10.1016/j.chemgeo.2017.06.033>.
- [35] P.S. Tourinho, C.A.M. van Gestel, S. Lofts, C. Svendsen, A.M.V.M. Soares, S. Loureiro, Metal-based nanoparticles in soil: Fate, behavior, and effects on soil invertebrates, *Environ. Toxicol. Chem.* 31 (2012) 1679–1692, <https://doi.org/10.1002/etc.1880>.