



# Determination of metallic nanoparticles in air filters by means single particle inductively coupled plasma mass spectrometry

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## ABSTRACT

Single particle inductively coupled plasma mass spectrometry (spICP-MS) has been explored for the determination of metallic nanoparticles (NPs) in air. Different extraction strategies (i.e., direct immersion, hard cap espresso, ultrasound-assisted and microwave-assisted extraction) and extracting solvents (i.e., citric acid, trisodium citrate, potassium nitrate, sodium nitrate, thiourea, disodium pyrophosphate and ammonium hydroxide) were investigated for platinum and gold NPs recovery from glass and microquartz fiber filters with a nominal size cut-off of 300 nm. Results show that metallic NPs are preserved and quantitatively extracted from the filter in 4 min inside an 800 W microwave oven by using 40 mL of a 2.0% w w<sup>-1</sup> NH<sub>4</sub>OH solution. For the remaining extraction procedures, either incomplete recoveries or NPs degradation occur. As regards the influence of filter material, microquartz fiber affords better NPs capturing performance than glass fiber ones, enabling the quantification of NPs with diameters above 28 nm. This methodology has been successfully applied to determine PtNPs in filters from environmental monitoring stations and to gain insight into NPs transport through ICP-MS sample introduction system. Care should be taken during spICP-MS calibration since biased results might be obtained due to differences on NPs transport efficiency between standards and samples.

## 1. Introduction

Nanomaterials (NMs) are seen as one of the game changer technologies of this century because they offer unique physical, chemical, and biological properties for a broad range of industrial applications [1]. According to *Nanodatabase* repository [2], there are currently over 5,000 products in the market containing NMs, but this number is expected to significantly increase in the upcoming years. Our current knowledge about NMs impact on human health and the environment is still limited and further research efforts are required to properly understand their effects on human health as well as their fate and behavior in the environment [3]. On this regard, several authors have indicated the need to improve current analytical methods for assessing NMs exposure [3–5], particularly for air samples, since NMs are easily deposited through the respiratory system and translocated into the body (e.g., blood, urine, etc.).

Nanomaterials exhibit a wide range of physicochemical properties (e.g., shape, size, composition, etc.) and, hence, a plethora of techniques are usually required for their proper characterization such as electron microscopy, Z-potential, dynamic light scattering, X-ray diffraction,

among others [6,7]. Single particle inductively coupled plasma mass spectrometry (spICP-MS) has recently emerged as a powerful analytical tool for detecting, characterizing, and quantifying NMs in complex samples [8]. In this technique, a diluted NM suspension is directly introduced into the plasma and, for each NM atomized and ionized, a signal peak is obtained over a continuous base line. The intensity of the signal peak is related to the mass of the element present in the NM and, hence to its size if there is information available about its composition, shape, and density, whereas the baseline provides information about dissolved forms of the measured element. The frequency of the events, however, is related to the number concentration of particles in the suspension. In general, this technique has been employed for the characterization of different type of NMs (i.e., metals, metaloxides, polymers, etc.) in both liquids and solid samples. For a detailed description of current spICP-MS applications, readers are referred to recent reviewers by Mozhayeva et al. [9] and Bolea et al. [10]. In general, the number of works devoted to NMs characterization in gas phase has been scarcer and mostly focused on hyphenating well-established technique for aerosol physical characterization (e.g., scanning mobility particle sizer or differential mobility analyzer) with spICP-MS [11–15]. Thus, it is

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feasible to simultaneously obtain information about chemical composition, size distribution, and number concentration of ultrafine particulate matter present in the air. The lack of works in this area is particularly striking considering that conventional ICP-MS has been traditionally employed as the reference technique to determine the elemental content of airborne particulate matter [16,17]. To this end, aerosols are aspirated through a filter with the aid of a vacuum pump for a given period and the particulate matter collected is analyzed after an acid digestion treatment. From a practical point of view, it could be highly advantageous to adapt this methodology for the determination of NMs in air and evaluate potential occupational, and environmental hazards derived to the presence of this emerging pollutant. Moreover, such methodology could be highly beneficial for those areas requiring accurate information about the content and behavior of NMs in aerosol phase. For instance, it would allow measuring NMs transport rate through the sample introduction system for spICP-MS thus improving our understanding of technique fundamentals. This could eventually improve spICP-MS figures of merit by developing efficient sample introduction systems and robust methodologies for NMs characterization [9]. In fact, both sample introduction system efficiency and matrix effects of dissolved ions in ICP-based techniques has been thoroughly investigated by capturing the aerosol at the exit of the sample introduction system with the aid of filters [18–21].

In this study, we have developed a protocol for determining metallic nanoparticles (NPs) previously retained in air filters by means spICP-MS. Different extraction strategies (i.e., direct immersion, hard cap espresso, ultrasound-assisted and microwave-assisted extraction) and extracting solvents (e.g., trisodium citrate, ammonium hydroxide, potassium nitrate, etc.) were investigated for NPs recovery from air filters. Metallic NPs covering different composition and size (i.e., 70 nm PtNPs, and 50 and 150 nm AuNPs) were selected. The influence of filter material (i.e., glass fiber and microquartz fiber filters) on NPs capturing efficiency on aerosol phase was also investigated. This new methodology has been applied to determine PtNPs in filters from environmental monitoring stations as well as to gain insight into NPs transport through the sample introduction system in spICP-MS.

## 2. Materials and methods

### 2.1. Instrumentation

A triple-quadrupole based 8900 ICP-MS instrument (Agilent, Santa Clara, USA) was employed throughout this work. This instrument was operated using either conventional or single-particle mode. Table 1 summarizes operating conditions. Data acquisition and analysis were conducted via the single nanoparticle application module of the ICP-MS MassHunter software, version 4.5. Single particle calibration was carried out using the frequency methodology proposed by Pace et al. [22] A commercial NPs suspension of known concentration was employed to evaluate transport efficiency and metal dissolved standards were used for building a calibration curve to determine the mass of analyte per NP

**Table 1**  
ICP-MS operating conditions for the detection of dissolved ions and NPs.

	Conventional mode	Single particle mode
Plasma forward power (W)		1550
Argon flow rate (L min <sup>-1</sup> )		
Plasma		15
Auxiliary		0.9
Nebulizer (Q <sub>g</sub> )	1.05	1.00
Sample introduction system		
Nebulizer		MicroMist® nebulizer
Spray chamber		Scott double pass
Sample uptake rate (Q <sub>i</sub> ) (μL min <sup>-1</sup> )		300
Dwell time (ms)	10	0.1
Measuring time (s)	10	60
Nuclides		<sup>197</sup> Au; <sup>195</sup> Pt

and hence particle diameter.

### 2.2. Reagents and materials

All solutions were prepared using ultrapure water (Milli-Q water purification system, Millipore Inc, Paris, France). Platinum nanoparticle suspension (0.05 mg mL<sup>-1</sup> 70 nm) from nanoComposix (San Diego, USA) and AuNPs suspensions (0.05 mg mL<sup>-1</sup> 50 nm AuNPs and 0.012 mg mL<sup>-1</sup> 150 nm) from Cytodiagnostics (Burlington, Canada) were diluted to prepare working NPs suspensions. Citric acid, trisodium citrate, potassium nitrate, sodium nitrate, thiourea and disodium pyrophosphate from Panreac (Barcelona, Spain) as well as 28% w w<sup>-1</sup> ammonium hydroxide solution and 69% w w<sup>-1</sup> nitric acid from Sigma-Aldrich (Steinheim, Germany) were employed to prepare NPs extracting solutions. Glass fiber filters (47 mm diameter, 0.3 mm nominal pore size), from Sigma-Aldrich (Steinheim, Germany), and Munktell Microquartz-fiber filters (50 mm diameter, 0.3 mm nominal pore size), from Thermo-Fisher Scientific (Waltham, USA), were tested for capturing NPs in both, dry and wet aerosols. Finally, Pt and Au 1000 mg L<sup>-1</sup> mono-elemental stock solutions (Merck, Darmstadt, Germany) were employed for spICP-MS calibration.

### 2.3. Nanoparticle extraction methodologies

Four different methodologies were evaluated to extract NPs from filters: (i) direct immersion; (ii) hard cap espresso; (iii) ultrasound-assisted; and (iv) microwave-assisted extraction. Considering previous works about NPs extraction from solid samples and given the strong influence of the elution solvent on liquid-solid phase extraction procedures [23–25], several extraction media, as indicated before, were tested. In all cases, the optimization of experimental conditions was carried out by means Multivariate Experimental Design using a Central Composite + Star model. Variables investigated were extractant solution concentration in the range from 0 to 2% w w<sup>-1</sup> and extraction times up to 120 min.

The hard cap espresso extraction, based on a previous work of Armenta et al. [26], was carried out using a Nespresso Essenza Manual XN2003 Krups coffee machine for achieving short time high temperature and 19 bar pressure extracting conditions. Filters were folded and introduced into stainless steel reusable capsules with 2 g of Ottawa sand and NPs were extracted.

The ultrasound-assisted extraction was performed using an ultrasound water bath (50 W power) Selecta (Barcelona, Spain).

For microwave-assisted extraction, filters were immersed into the extractant solution and heated inside of a domestic microwave oven (Bluesky BMG20M – 18) using the highest power available of 800 W. To avoid sample projections and to minimize water loss by evaporation, samples were covered with a glass watch during the extraction process. A total of 6 samples can be simultaneously treated by means this approach.

For all the treatments, samples were let to cool at room temperature and sonicated 1 min prior to ICP-MS analysis.

### 2.4. Evaluation of NPs capturing efficiency by the filters

The classical experimental setup for measuring analyte transport efficiency in atomic spectrometry was employed to evaluate filters retention capabilities of metallic NPs and to gain insight into NPs transport through the sample introduction system (Fig. S1, Supplementary material) [19–21]. To this end, a 10<sup>7</sup> mL<sup>-1</sup> NPs suspension was nebulized during a given period (10–20 min) and tertiary aerosols were collected at the exit of the spray chamber. A vacuum pump was employed to force aerosol passing through the filter. Next, NPs were extracted from the filters with an appropriate extraction procedure, and the supernatant was measured by means ICP-MS. Unless otherwise stated, the nebulizer gas flow rate (Q<sub>g</sub>) was set at 1.0 L min<sup>-1</sup> (optimum

value for ICP-MS measurements) and the sample uptake rate ( $Q_1$ ) was fixed at  $100 \mu\text{L min}^{-1}$ . To gain insight into NPs transport through the sample introduction system, some additional experiments were carried out modifying  $Q_1$  ( $50 \mu\text{L min}^{-1}$ ) and temperature ( $120^\circ\text{C}$ ). For the latter, the spray chamber was heated up with the aid of a heating tape connected to a temperature controller and a thermostat.

## 2.5. Samples

The new extraction methodology was applied to determine metallic NPs in real samples. First, PtNPs content in filters from two different environmental monitoring stations in Valencian Community (Generalitat Valenciana; Conselleria de Agricultura, Desarrollo Rural, Emergencia Climática y Transición Ecológica) was studied. The samples from Valencia (location:  $39.47948825^\circ\text{N}$   $0.36955032^\circ\text{E}$ ; 800,000 inhabitants; filtered air volume  $707.774 \text{ m}^3$ ; reference 46250043) were representative of a high-polluted area whereas filters from Morella ( $40.63636436^\circ\text{N}$   $0.0929485^\circ\text{E}$ ; 2,400 inhabitants; filtered air volume  $712.248 \text{ m}^3$ ; reference 12080007) corresponded to a low-polluted area.

## 3. Results and discussion

This work explores, for the first time, the use of spICP-MS for measuring metallic NPs in air, after their retention on filters. It was investigated the recovery of metallic NPs from filters and then, the retention capabilities of different filters when operating aerosols containing NPs.

### 3.1. Nanoparticle extraction from filters

Microquartz filters were spiked with a known quantity of PtNPs ( $40 \mu\text{L}$  of a  $10^7 \text{ mL}^{-1}$  PtNPs suspension) and were allowed to stand overnight. Later, filters were soaked with  $40 \text{ mL}$  of different extractant solutions (i.e., citric acid, trisodium citrate, potassium nitrate, sodium nitrate, thiourea, disodium pyrophosphate and ammonium hydroxide) at  $1\% \text{ w w}^{-1}$  concentration and the extracts were analyzed by spICP-MS. As previously mentioned, spICP-MS calibration was performed using the frequency methodology proposed by Pace and, because potential matrix effects may appear in ICP-MS signal from the extraction solution [27, 28], matrix matched standards were employed. In order to ensure the integrity of nanoparticles during the extraction procedure, transmission electron microscopy (TEM) was used as a reference methodology. The sample preparation for TEM observations was based on the principles described by Vladár and Hodoroba [29]. Briefly, the nanoparticle liquid suspension was sonicated for  $30 \text{ s}$  and a single drop was directly deposited on the typical TEM copper/carbon membrane grids. The drop was air dried for  $10 \text{ min}$  and directly observed with the microscope. Given the low concentrations of extracting solvents employed, no rinsing of the suspensions was needed.

Except for thiourea and citric acid solutions, the mean diameter of the NPs released from the filters was equivalent to the value obtained by means TEM (Table S1). This diameter value was also consistent with that provided by NPs supplier and, hence, it was confirmed that NPs remained mostly unaltered by the extraction treatments. This conclusion was further confirmed by the lack of changes on the spectra baseline between NPs extracts and matrix standards. Nevertheless, irrespective of the extractant solutions employed, PtNPs concentration recoveries (determined only via spICP-MS) were not quantitative, and the reproducibility was low (Table S2). The highest recoveries were achieved for ammonium hydroxide ( $20.1 \pm 1.3\%$ ) and citrate solutions ( $13.9 \pm 0.5\%$ ), so these extractants were selected for further studies. For the remaining extractants, NPs recovery was below  $12\%$ .

To improve NPs extraction efficiency, experimental conditions were optimized via Experimental Design [30]. For both ammonium hydroxide and trisodium citrate, extractant solution concentration ( $0\text{--}2\% \text{ w w}^{-1}$ ) and extraction time ( $1\text{--}120 \text{ min}$ ) were investigated. Though extraction

volume usually exerts a strong influence on extraction efficiency for metal ions [29], no significant influence of this parameter on NPs extraction was noticed within the experimental range investigated ( $20\text{--}200 \text{ mL}$ ). Therefore, the extraction volume was fixed at  $40 \text{ mL}$ , thus allowing efficient filter soaking and direct analysis of NPs suspension without any further treatment (i.e., dilution). The optimal conditions found for the extractants under study (Table 2) were equivalent. Under optimal operating conditions, no significant improvement of NPs extraction efficiency was achieved, regardless the extractant employed. From these findings, it can be concluded that NPs are efficiently adsorbed on the surface of microquartz filters through electrostatic attraction, diffusion, etc. [31] and, hence, an enhanced efficiency extraction procedure is required to recover quantitatively the retained NPs. For this purpose, three additional strategies were evaluated: (i) hard cap espresso [26]; (ii) ultrasound-assisted; and (iii) microwave-assisted extraction. For all of them, experimental conditions were optimized by means Experimental Design in the same way as for the direct immersion treatment. Thus, ammonium hydroxide and citrate solutions up to  $2.0\% \text{ w w}^{-1}$  were tested. As regards the extraction time, there were no differences between the ultrasound-assisted extraction and direct immersion, since previous studies demonstrate that long sonication times for extraction (i.e.,  $>30 \text{ min}$ ) does not affect NPs integrity [25]. However, because some experimental constraints, the extraction time range tested for the hard cap espresso and the microwave-assisted extraction treatment was different. Time extraction and extraction volume are not independent variables for the hard cap espresso treatment and, hence, extraction times higher than  $50 \text{ s}$  ( $250 \text{ mL}$  of extractant) were not evaluated to avoid excessive NPs dilution. On the other hand, extraction times for the microwave-assisted treatment were limited to  $5 \text{ min}$  since otherwise NPs suspension is significantly evaporated and solution splashes might occur.

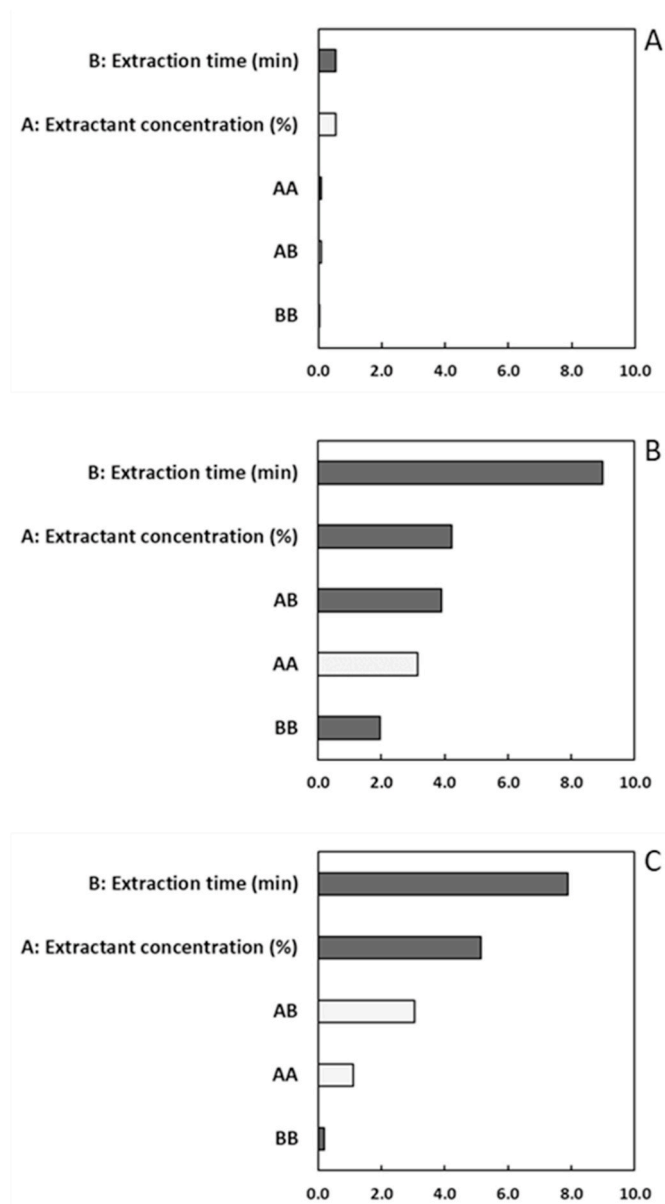
To evaluate the significance of both, extractant solution concentration and extraction time, on PtNPs recovery for each treatment, data were analyzed using ANOVA and the effects were summarized by means of the corresponding Pareto charts (Fig. 1). The ANOVA data analysis revealed that, irrespective of the extractant solution, NPs extraction efficiency for ultrasound-assisted and microwave-assisted extraction procedures improves with the extractant solution concentration and extraction time. For the hard cap espresso extraction, none of these parameters exerts a significant influence on NPs recovery, probably due to the limited contact time between the extraction solution and the microquartz filters ( $<50 \text{ s}$ ). Table 3 shows the best results obtained for NPs extraction by each treatment using trisodium citrate and ammonium hydroxide solutions. Differences among the extraction procedures depends on the extraction time but not on the extractant concentration.

As it can be seen in Table 3, the use of extra energy is required to enhance the recovery of PtNPs retained on microquartz fiber filters. It can be noticed that the extraction efficiency was increased on moving from hard cap espresso extraction to ultrasound-assisted and microwave-assisted extraction. In all cases, the use of ammonium hydroxide provided higher recoveries than the use of trisodium citrate. When using hard cap espresso extraction, the limited time of sample treatment affected the extraction efficiency and a maximum recovery of  $37 \pm 4\%$  was found. However, a filter sonication for  $50 \text{ min}$  provided an extraction efficiency higher than  $70\%$  and a 4-min treatment inside a

**Table 2**

Optimal experimental conditions for extracting NPs from microquartz filters using direct immersion, hard cap espresso, ultrasound- and microwave-assisted extraction treatments.

Variable	Immersion	Hard cap espresso	Ultrasound	Microwave
[Extracting agent] (% $\text{w w}^{-1}$ )	2.0	2.0	1.4	2.0
$t_{\text{Extraction}}$ (min)	120	0.7	50	4.0

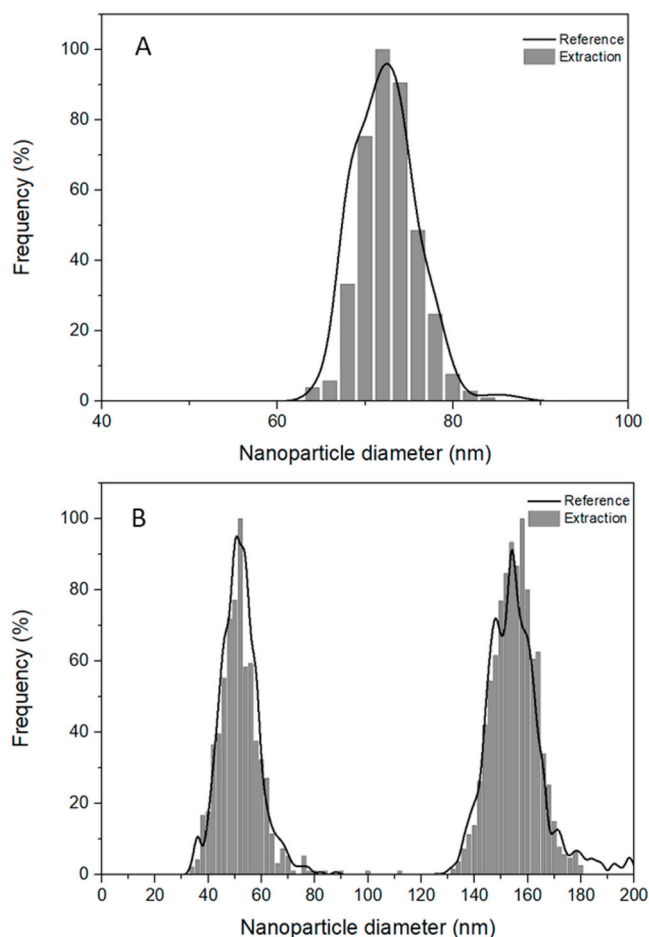


**Fig. 1.** Standardized Pareto charts and response surfaces for (A) hard cap espresso; (B) ultrasound-assisted and (C) microwave-assisted extractions. Extractant used:  $\text{NH}_4\text{OH}$ . Black bars = positive effect; grey bars = negative effect.

microwave oven permitted the quantitative recovery of PtNPs adsorbed on a microquartz filter. It must also be noticed that any of the assayed filter treatments affected the original structure nor the mean diameter of PtNPs, as can be observed on TEM images in Fig. S2 for the microwave-assisted extraction (similar findings were found for all the treatments

studied).

Because of the benefits of the microwave-assisted extraction treatment with ammonium hydroxide in terms of NPs recovery and sample throughput, this approach was further investigated using other type of metallic NPs and filters (Table S3). Essays made on AuNPs of 50 and 150 nm adsorbed on microquartz fiber filters provided average recoveries of  $99 \pm 3$  and  $109 \pm 4\%$  respectively, thus evidencing that the microwave-assisted extraction of NPs adsorbed on filters can be quantitatively achieved in few minutes independently on the nature and size of the studied particles. In addition, size distributions obtained for the different NPs under study (Fig. 2) demonstrate that the structure of the nanoparticles is not compromised during the microwave procedure. Similarly, it was observed that metallic NPs are also quantitatively recovered from glass fiber filters. Finally, it is worth to note that, *a priori*, this extraction procedure would allow the simultaneous determination of NPs and elements soluble in basic conditions (2.0% ammonium



**Fig. 2.** Particle size distributions obtained for (A) 70 nm PtNPs and (B) 50/150 nm AuNPs before (black line) and after (grey bars) a microwave-assisted extraction from microquartz filters.

**Table 3**

Influence of the extraction treatment on PtNPs recovery from microquartz filters and PtNPs size mean diameter. Data expressed as the mean value  $\pm$  s, n = 3 were obtained under optimal extraction conditions.

Method	Extractant	PtNPs mean diameter (nm)	$[\text{PtNPs}]_{\text{Spiked}} (10^7 \text{ mL}^{-1})$	$[\text{PtNPs}]_{\text{Recovered}} (10^7 \text{ mL}^{-1})$	Recovery (%)
Hard cap	Sodium citrate	$67.0 \pm 0.8$	1.4	$0.22 \pm 0.06$	$15 \pm 4$
	Ammonium hydroxide	$71 \pm 2$	1.4	$0.52 \pm 0.05$	$37 \pm 4$
Ultrasound	Sodium citrate	$64.4 \pm 0.2$	1.5	$1.05 \pm 0.03$	$69.6 \pm 0.9$
	Ammonium hydroxide	$72 \pm 4$	1.5	$1.26 \pm 0.07$	$84 \pm 2$
Microwave	Sodium citrate	$69.6 \pm 0.4$	1.3	$1.07 \pm 0.09$	$83 \pm 7$
	Ammonium hydroxide	$70.0 \pm 0.9$	1.5	$1.58 \pm 0.02$	$107 \pm 2$

hydroxide solution, pH: 11/12) such as alkalines.

### 3.2. Nanoparticle capturing efficiency by filters

For the accurate determination of metallic NPs in aerosols, it is critical to verify that they are quantitatively retained by the filter. In this work, microquartz and glass fiber filters with a nominal size cut-off of 300 nm were used and, hence, NPs could pass the filter and provide non-quantitative recoveries, thus underestimating their levels in real samples. To evaluate filter retention efficiency, a  $10^7 \text{ mL}^{-1}$  PtNPs suspension was nebulized, and the aerosol emerging the spray chamber was captured using two filter of each type in a row (Fig. S1). Operating this way, it is feasible to evaluate whether NPs can pass through the first filter.

Fig. 3 shows the particle number concentration found in the two filters installed on-line for microquartz and glass fiber filters in the setup of Fig. S1. As it can be observed, irrespective of the type of filter employed, the number of NPs are mostly retained by the first filter, being the quantity of NPs retained by the second filter as low as 1.2%, thus at the same level than the experimental error. However, the retention capacity of filters strongly depends on their composition. Thus, NPs retention efficiency for microquartz filters was 5 times higher than for the glass ones. Similar findings were also noticed for 50 and 150 nm AuNPs.

Interaction between (liquid and solid) aerosols and filters depend on the simultaneous occurrence of several mechanisms, namely: (i) interception; (ii) inertial collisions, (iii) diffusion; (iv) gravity attraction; and (v) electrostatic interactions [32]. To gain insight into the origin of NPs retention for microquartz and glass fiber filters, some additional experiments were performed. Pore network structure for both filters was investigated by means mercury porosimetry but no significant differences were observed. Based on these results, NPs retention capabilities for both filters are expected to be similar in terms of interception, inertial collisions, diffusion, and gravity attraction. However, the observed electrostatic interaction of the microquartz filters with plastic gloves could explain the improved NPs retention capability of these filters as compared with the glass fiber ones. On this regard, it is important to remark that metallic NPs surface [33] and aerosols generated by pneumatic nebulization show net electrical charge, thus potentially favouring this phenomenon [34,35]. To verify the importance of electrostatic charge, filters were soaked in isopropanol for 2 h and let dry overnight to modify these interactions [30] and, as it can be seen in Table 4, the retention capability of glass fiber filters was reduced in a 40/50% level, being maintained the efficiency of microquartz ones. Considering these

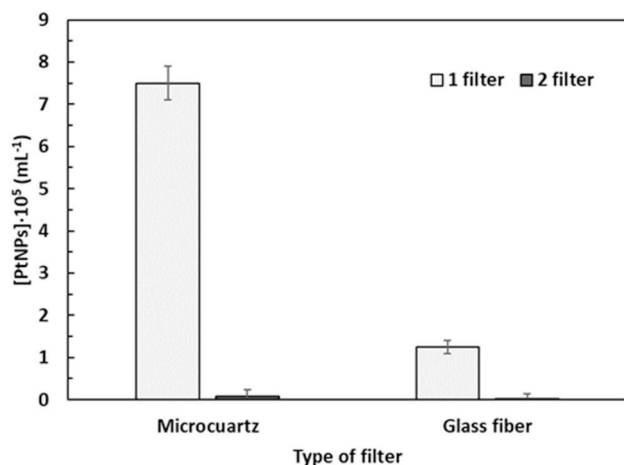


Fig. 3. Platinum NPs concentration number found on the set of two filters located at the exit of the spray chamber.  $[\text{PtNPs}]_{\text{Nebulized}} = 10^7 \text{ mL}^{-1}$ . Results are expressed as the mean value  $\pm$  s,  $n = 3$ . Nebulization time = 10 min.

Table 4

PtNPs concentration number found on a single filter system at the exit of the spray chamber.  $[\text{PtNPs}]_{\text{Nebulized}} = 3.0 \cdot 10^7 \text{ mL}^{-1}$  for both, untreated and electricity discharged filters. Discharge conditions: 2 h treatment with isopropanol, 22 h overnight air drying. Results are expressed as the mean value  $\pm$  s,  $n = 3$ .

Filter	[PtNPs] ( $10^4 \text{ mL}^{-1}$ )	
	Untreated	Isopropanol
Microquartz	$5.92 \pm 0.17$	$5.93 \pm 0.15$
Glass Fiber	$1.27 \pm 0.09$	$0.81 \pm 0.03$

findings, microquartz filters were selected for further studies.

Finally, no specific experiment was carried out for assessing the minimum particle size retained by the microquartz filter. Nevertheless, a roughly estimate can be drawn from NPs size distributions measured by spICP-MS. The size distribution for the 50 nm AuNPs suspension by means spICP-MS spans from 28 to 60 nm and, because there are no differences with regard TEM, it can be concluded that NPs above at least 28 nm can be determined by this approach.

### 3.3. Methodology implementation to real samples

Once it has been demonstrated that filters can be used for NPs characterization in aerosol phase by means spICP-MS, the methodology developed has been applied to determine PtNPs in filters from environmental monitoring stations as well as to gain insight into NPs transport through the sample introduction system for spICP-MS.

#### 3.3.1. Platinum nanoparticles determination in filters from environmental monitoring stations

Platinum nanoparticles are employed as a catalyst in combustion engines, and they can be potentially released to the environment [23]. Therefore, it has been investigated whether the new methodology developed allows determining them in the filters employed by the environmental monitoring stations, particularly considering that they are equivalent to those employed in this work. Filters from two monitoring regions in Valencian Community (Valencia and Morella) were selected for covering different matrix characteristics. Valencia monitoring station was in a high-polluted urban area whereas Morella was in a low-polluted one.

Method accuracy and precision were evaluated by means a recovery test due to the lack of a proper certified reference material for this type of application. Filters were spiked with 40  $\mu\text{L}$  of a  $1.15 \cdot 10^7 \text{ mL}^{-1}$  commercial 70 nm PtNPs suspension over their surface. Next, NPs were extracted according to the procedure developed in Section 3.1 and analyzed by means spICP-MS using 2% w  $\text{w}^{-1}$  ammonium hydroxide standards. Irrespective of filters origin, NPs recovery concentration and mean size diameter were significantly biased. The former parameter was overestimated (Valencia:  $151 \pm 12\%$ ; Morella:  $130 \pm 20\%$ ) but the latter was underestimated (Valencia:  $64.2 \pm 1.9 \text{ nm}$ ; Morella:  $66.4 \pm 0.8 \text{ nm}$ ). *A priori*, the lack of accuracy and precision on these parameters might be related to matrix effects by airborne particulate matter retained on the filters. Unlike those employed under laboratory conditions, filters from environmental monitoring stations were grey colored due to airborne particulate matter (Fig. S3). To verify this hypothesis, airborne particulate matter for both locations was analyzed by means ICP-MS after a microwave-assisted acid digestion treatment with aqua regia. Sample digests were made up to the sample volume employed for NPs extraction (i.e., 40 mL). As expected, airborne particulate matter digests contained significant levels of Na ( $0.6\text{--}10 \text{ mg L}^{-1}$ ); S ( $1\text{--}3 \text{ mg L}^{-1}$ ), Cl ( $9\text{--}33 \text{ mg L}^{-1}$ ) and K ( $0.1\text{--}0.3 \text{ mg L}^{-1}$ ). None of the samples showed significant levels of Pt ( $<0.02 \mu\text{g L}^{-1}$ ) neither in ionic nor particulate form. Unfortunately, no values for Pt levels have been reported for the air monitoring stations under study. However, previous works addressing airborne particulate matter analysis in urban areas reported concentrations of this element similar to those obtained in this work

[36]. Because easily-ionizable elements give rise to significant non-spectral interferences in plasma-based techniques (i.e., aerosol transport, plasma atomization/ionization conditions, etc.) [27,28], matrix-matched standard (salts + 2% w<sup>-1</sup> ammonium hydroxide) were prepared to analyze PtNPs extracts. In this case, PtNPs recoveries were quantitative (Valencia: 98 ± 2%; Morella: 98 ± 2%) and the mean size diameter determination was accurate (Valencia: 69.0 ± 0.2 nm; Morella: 69.0 ± 1.0 nm). Particle size (LOD<sub>Size</sub>) and particle number concentration (LOD<sub>Conc</sub>) limits of detection were calculated as described elsewhere [8], giving values of 18 nm and 180 particles mL<sup>-1</sup>, respectively. In this work, LOD<sub>Conc</sub> could also be determined referred to the volume of air aspirated by the environmental monitoring stations (i.e., c. a. 710 m<sup>3</sup> for both stations), thus giving a value of 10 particles m<sup>-3</sup>.

### 3.3.2. Fundamental study about NPs transport through the sample introduction system

For spICP-MS calibration, certified reference or commercially available NPs are widely employed for determining analyte transport efficiency ( $\eta$ ), defined as the ratio of the analyte amount introduced into the plasma to the amount of analyte aspirated, and then calculate NPs size distribution and concentration for unknown samples [22]. According to this scheme, it is critical that NPs in both standards and unknown samples behave similarly otherwise biased results could be obtained. Witzler et al. [37] have reported a 20% bias in the size determination of AgNPs when employing 50 nm AuNPs as the calibration standard. Similar findings were also noticed by other authors [38–42].

So far, the origin of the above-mentioned findings is unclear, and it could be related to changes on aerosol transport through the sample introduction system and/or plasma [43]. To gain insight into this phenomenon, it is mandatory to assess both factors independently, but current methodologies for assessing NPs transport through the sample introduction system (e.g., waste collection method, particle frequency method, etc.) are not particularly suitable this purpose. The proposed method, however, allows measuring NPs transport directly in aerosol phase and, hence, it has been applied to evaluate  $\eta$  for 70 nm PtNPs and 50/150 nm AuNPs under different experimental conditions. The experimental setup for measuring  $\eta$  was analogous to that previously outlined for checking filters retention capabilities (Section 3.2).

Fig. 4 shows the influence of the sample uptake rate on  $\eta$  at different temperatures. It can be observed that  $\eta$  depends on both, NPs characteristics and experimental conditions. Irrespective of the NP selected,  $\eta$  improves when decreasing  $Q_I$  as well as when heating the sample introduction system. These results are totally expected considering that aerosol generation and transport is favored [19]. For most of the experimental conditions tested, 70 nm PtNPs showed the highest  $\eta$  values followed by 50 and 150 nm AuNPs. For instance, when operating at 50  $\mu\text{L min}^{-1}$  and 25 °C,  $\eta$  for 70 nm PtNPs values were, respectively, 1.3 and 1.5-fold higher than for 50/150 nm AuNPs. Interestingly, differences on  $\eta$  between PtNPs and AuNPs diminished when decreasing  $Q_I$  as well as increasing temperature. In fact, differences on  $\eta$  are mostly mitigated at 50  $\mu\text{L min}^{-1}$  and 120 °C. These results suggest that the lack of accuracy in previous works might be indeed related to differences on NPs  $\eta$  between standards and samples.

A possible explanation of the previous fact could be related to the differences in Z-potential (i.e., charge that develops at the interface between a solid surface and its liquid medium) between PtNPs and AuNPs suspensions. Zeta potential for 70 nm PtNPs is  $-21.8 \pm 0.5$  mV whereas for 50 nm and 150 nm AuNPs is  $-47.6 \pm 0.3$  and  $-48.6 \pm 0.5$  mV (Table S1), respectively. As it has been previously mentioned, aerosols generated have a net electrical charge on their surface and there is a critical diameter below which a charged droplet breaks down giving rise to other progeny with lower diameters (Coulomb effect) [34]. Given the differences on the Z-potential, this phenomenon is expected to affect PtNPs and AuNPs transport through the sample introduction system differently. According to our data, the former NPs might travel to the

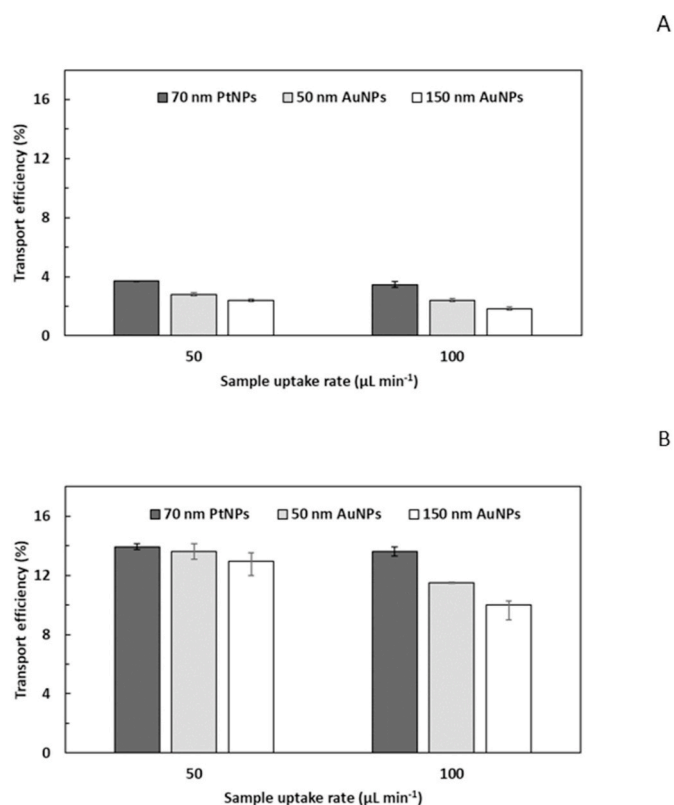


Fig. 4. Influence of the sample uptake rate on NPs transport efficiency at (A) 25 °C and (B) 120 °C. Experimental conditions:  $Q_g$  1.0 L min<sup>-1</sup>; [NPs] = 10<sup>7</sup> mL<sup>-1</sup>. Nebulization time = 10 min at  $Q_I$  = 100  $\mu\text{L min}^{-1}$ , 20 min at  $Q_I$  = 50  $\mu\text{L min}^{-1}$ . Results are expressed as mean value  $\pm$  s, n = 3.

plasma on the finest aerosol droplet fraction thus giving rise to higher  $\eta$ . This hypothesis is experimentally supported considering that differences on  $\eta$  among NPs decreased when aerosol evaporation is favored by operating low  $Q_I$  and high temperatures. These results are in line with previous findings for dissolved ion solutions where matrix effects on aerosol transport decrease when aerosol transport is enhanced [27]. From these findings, care should be taken during spICP-MS calibration since biased results (i.e., size distribution and concentration) might be obtained when NPs present in the sample do not behave as those in the standards.

## 4. Conclusions

This work demonstrates the feasibility of monitoring metallic NPs in aerosols by using microquartz filters and spICP-MS. The quantitative extraction of NPs collected in the filter is easily carried out with a 2% w<sup>-1</sup> ammonium hydroxide solution and a microwave-assisted treatment for 4 min at a maximum power of 800 W. Nanoparticle size distribution is preserved during the whole process thus ensuring the accuracy of the analysis. According to our data, metallic NPs above 28 nm are efficiently collected by microquartz filters with a nominal size cut-off of 300 nm. Nevertheless, it is expected that smaller NPs could be retained by modifying filter characteristics.

This novel methodology shows a great potential since it not only allows environmental monitoring of NPs in air but to gain insight into about NPs transport through the sample introduction system in atomic spectrometry. On this regard, because it allows measuring NPs transport efficiency directly, it could be employed for direct calibration of spICP-MS.

## Credit author statement

D.T, G.G. and M.G. contributed to the study conception and design. L.G, D.T, J.M. and G.G, validation; D.T, G.G, L.G. and M.G, data analysis; and D.T, G.G. and J.M. wrote the main manuscript text. All authors reviewed the manuscript.

## 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.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2022.123818>.

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