

Article

Assessment of Emerging Particulate Contaminants in Industrial Wastewater Using Advanced ICP-MS Techniques

Portia Madzivha ^{1,2,*}, Andile Mkhohlakali ^{1,*}, Mokgehele Refiloe Letsoalo ¹, James Tshilongo ^{1,2} and Heidi Richards ²

¹ Analytical Chemistry Division, Mintek, Private Bag X3015, Randburg, Johannesburg 2125, South Africa

² School of Chemistry, University of Witwatersrand, Private Bag 3, Johannesburg 2050, South Africa

* Correspondence: portiamad@mintek.co.za (P.M.); andilem@mintek.co.za (A.M.)

Abstract

The increasing use of nanomaterials in modern industries and consumer products has led to the release of various contaminants into wastewater streams and the surrounding environment. However, nanoparticle detection and characterisation in wastewater remain analytically challenging due to the presence of dissolved metals, suspended solids, natural colloids, and heterogeneous particulate matter. In this study, we demonstrate an integrated analytical workflow combining single-particle inductively coupled plasma mass spectrometry (SP-ICP-MS) with transmission electron microscopy (TEM) and ImageJ version 1.54g image analysis for the comprehensive characterisation of engineered nanoparticles (ENPs) in industrial wastewater. In contrast to earlier research on well-defined manufactured nanoparticles in controlled laboratory suspensions, this work uses complementary analytical techniques to analyse real industrial wastewater, allowing for quantitative elemental analysis, particle sizing, and morphological confirmation in South Africa. Additionally, a supporting bibliometric analysis serves as supporting evidence to identify research trends and knowledge gaps, revealing limited application of integrated analytical workflows to complex industrial wastewater matrices. Analytical conditions were optimised according to the recommendations of previous publications, with a dwell period of 3 μ s to limit particle coincidence and enable reliable single-particle detection. The combined approach was effectively applied to characterise silver (AgENPs) and gold (AuENPs) nanoparticles with median particle sizes of 14 nm and 8 nm, respectively. The particle number concentrations ranged from 3.00×10^7 to 3.60×10^8 particles L^{-1} for AgENPs and 3.80×10^8 particles L^{-1} for AuENPs. Comparing dissolved metal concentrations with particle mass concentrations gave some insight into the partitioning of metals between the dissolved and nanoparticulate fractions. Moreover, bibliometric analysis has shown that despite the exponential growth of research on SP-ICP-MS, very few studies have simultaneously employed analytical techniques to describe nanoparticles in complicated industrial wastewater matrices. These results show the utility of integrating complementary analytical approaches for the reliable characterisation of particulate pollutants in environmentally relevant samples and promote improved environmental monitoring and risk assessment of manufactured nanoparticles.



Academic Editor: Claudia Belviso

Received: 11 June 2026

Revised: 11 July 2026

Accepted: 13 July 2026

Published: 16 July 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and

conditions of the [Creative Commons](#)

[Attribution \(CC BY\)](#) license.

Keywords: industrial wastewater; single-particle ICP-MS; engineered nanoparticles; nanoparticle characterisation; environmental monitoring

1. Introduction

The increasing complexity of industrial activity has led to the introduction of various contaminants, notably engineered nanoparticles (ENPs), into aquatic systems through industrial effluents and wastewater streams [1,2]. ENPs are widely used in healthcare, energy, food, construction, and consumer products owing to their unique physicochemical properties, including their high surface area-to-volume ratio, enhanced catalytic activity, and size-dependent optical properties such as surface plasmon resonance in gold nanoparticles [3–6]. Additionally, the surface reactivity that allows them to bind or absorb more effectively is due to their wide surface, making them excellent for applications such as medication administration and photocatalysis. Consequently, growing concerns have emerged regarding the unintended release of ENPs into the environment, particularly through industrial effluent streams [5,6].

Accurate detection and characterisation of ENPs in environmental systems continue to present significant analytical challenges owing to the heterogeneous nature of these systems. Industrial wastewater contains dissolved metals, suspended solids, natural colloids, and heterogeneous particulate matter that may interfere with nanoparticle detection and quantification. Single-particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is now known as a powerful analytical tool for determining particle size, particle number concentration, and dissolved metal concentrations in aqueous samples [7–9]. Consequently, complementary analytical techniques are required to validate particle size, morphology, and concentration measurements and improve confidence in nanoparticle characterisation [8].

In order to provide the scientific background of this work, a bibliometric analysis was conducted to assess research trends and identify knowledge gaps concerning the application of SP-ICP-MS for nanoparticle characterisation. The analysis showed a significant increase in research related to SP-ICP-MS in the last decade, but a relatively low application of integrated analytical approaches for real industrial wastewater matrices. The majority of the published studies have focused on well-characterised ENPs in laboratory-prepared suspensions or simple aqueous systems, whereas a relatively limited number of studies have been conducted on nanoparticles in complex industrial wastewater [10–12].

Based on this identified research gap, in this study, we demonstrate an integrated analytical workflow combining SP-ICP-MS with TEM and ImageJ image analysis for the comprehensive characterisation of ENPs in industrial wastewater. The complementary application of these established analytical techniques enables quantitative determination of particle size distributions, particle number concentrations, and ionic metal concentrations in environmentally relevant samples. The bibliometric analysis serves as supporting evidence to identify research trends and motivate the experimental investigation rather than as a primary objective of the study.

Overview of Research Activity in SP-ICP-MS

The methodology consisted of multiple stages: identifying research, evaluating its relevance to our objectives, collecting data, and employing data analysis methods. Figure 1 provides a summary of our methodology. Using the Scopus Database, the data collection was carried out, and publications were extracted depending on the relevancy of the various searches. In addition, the data acquired was further characterised by year, document type, publication by country, and authors [11,13].

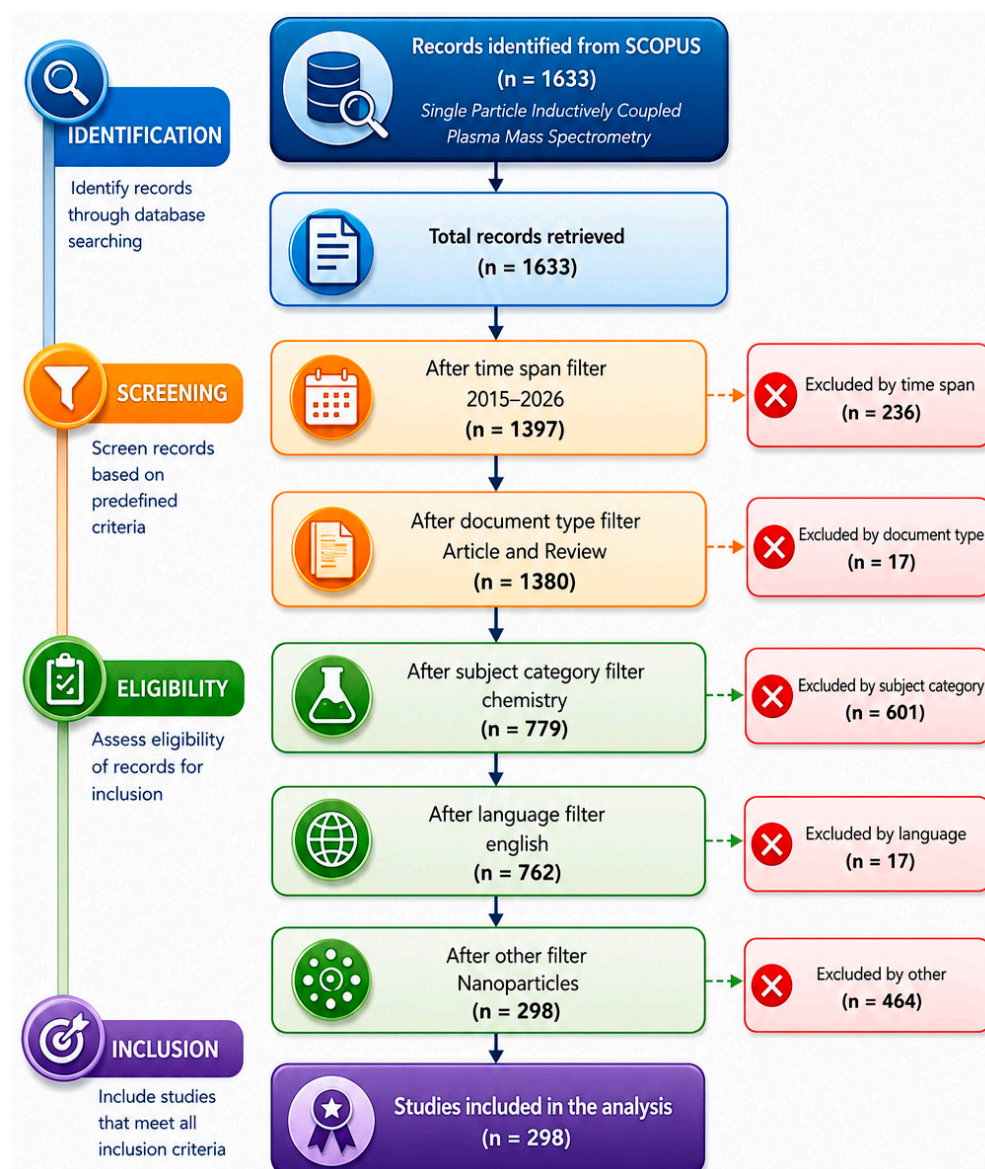


Figure 1. Flow diagram based on PRISMA guidelines outlining the research framework for single-particle ICP-MS (SP-ICP-MS) characterisation. Records were screened using predefined inclusion criteria, including publication year (2015–2026), document type, subject category, language, and nanoparticle relevance. Red boxes indicate records excluded at each screening stage. Colours and icons are used only to visually distinguish the four PRISMA phases (Identification, Screening, Eligibility, and Inclusion) and do not represent additional methodological categories.

Bibliometric analysis was performed to provide a comprehensive overview of the development and progression of SP-ICP-MS, highlighting its origins, methodological advancements, and expanding applications across various scientific disciplines [13]. Using publication patterns and citation networks, the study underscores the maturation of SP-ICP-MS, tracing its journey from a niche analytical technique to a broadly adopted approach for nanoparticle characterisation across diverse scientific fields [14].

The literature on SP-ICP-MS has indeed experienced significant growth over the past decade, reflecting its increasing recognition and application in scientific research [15,16]. This rise is evidenced by the expanding number of publications, advancements in instrumentation, and the broadening scope of applications, particularly in environmental analysis (Figure 2). The apparent reduction in publications in 2023–2025 may be due to the incomplete database indexing of recent years. In addition, the results of bibliometric analysis

are influenced by the search method that was used and the database coverage that was utilised [17]. Importantly, such a dip highlights the need to focus on addressing outstanding issues and finding new applications, ensuring that SP-ICP-MS remains a valuable tool in nanoparticle research [18].

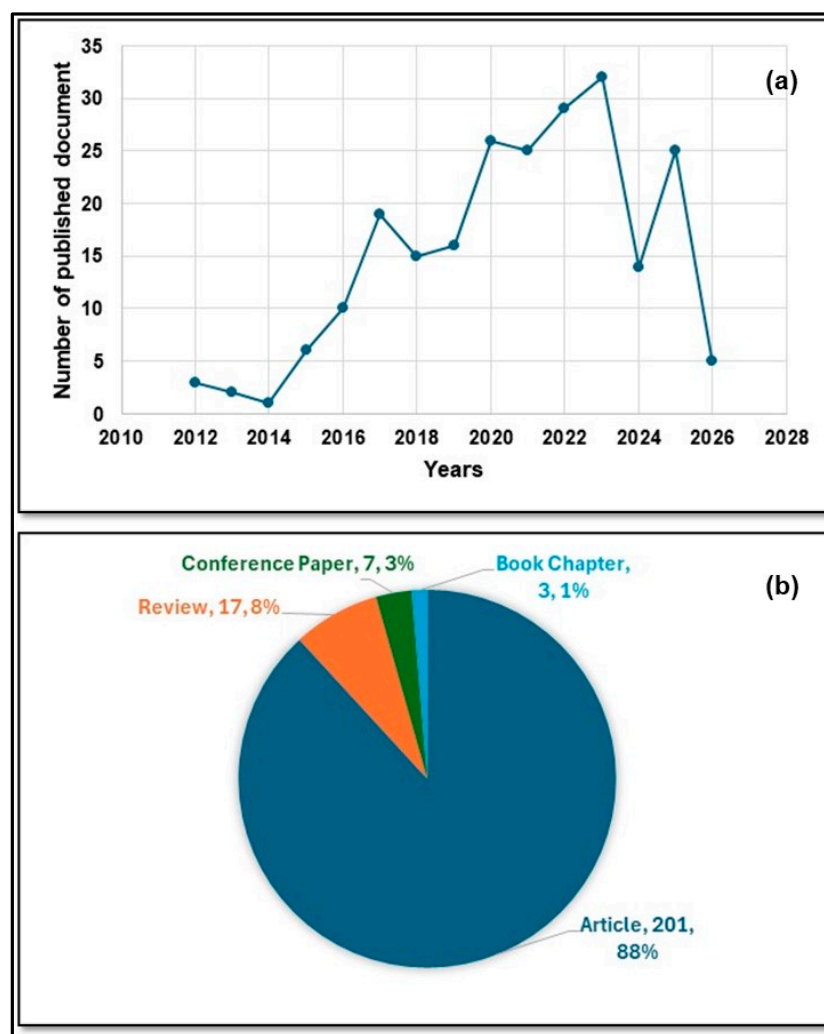


Figure 2. Bibliometric overview of published literature showing (a) the number of published documents by each year from 2012 to January 2026; (b) the distribution of document types, showing the relative proportions of journal articles, conference papers, reviews, articles, and book chapters.

Figure 3a presents the word-cloud visualisation of the most frequently occurring keywords in the titles and abstracts on nanoparticle measurement [19]. In this visualisation, the relative size of each word corresponds directly to its frequency of occurrence, providing a clear and intuitive summary of dominant research themes [20,21]. Larger words such as “mass spectrometry,” “metal nanoparticle,” “particle size,” “single particle,” “chemistry,” and “article” stand out prominently, reflecting their central role in the discourse and their repeated citation across the literature. The results emphasise the advancement of SP-ICP-MS, which is a powerful tool for characterising nanoparticles.

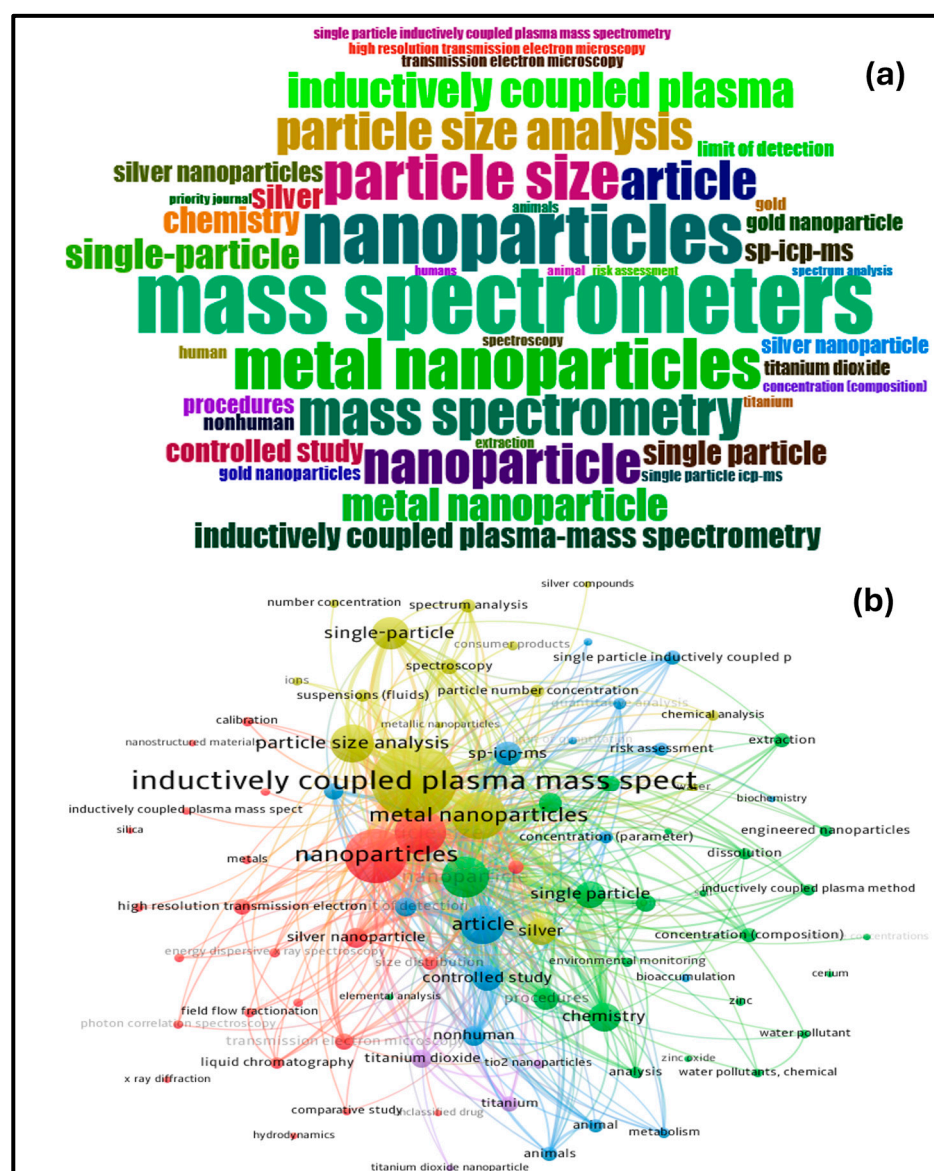


Figure 3. Bibliometric overview of published literature showing (a) the word cloud of keywords and (b) the co-occurrence network for nanoparticle quantification.

The co-occurrence network map in Figure 3b reveals four distinct clusters: (i) red, attributed to nanoparticles; (ii) green, assigned to single-particle mass spectrometry; (iii) blue, linked to articles and controlled studies; (iv) yellow, associated with metal nanoparticles. SP-ICP-MS research is organised into theme clusters, with methodological development and application domains being interconnected. Importantly, the node sizes in the visualisation are proportional to the frequency of keyword occurrence in the literature. Larger nodes, such as “inductively coupled plasma mass spectrometry,” “nanoparticles,” “single particle,” and “chemistry,” dominate the map, indicating their importance and high citation frequency in the subject. Medium-sized nodes, such as “particle size analysis,” “field flow fractionation,” and “liquid chromatography,” suggest specialised but recurring themes, while smaller nodes, such as “bioaccumulation,” “titanium,” and “water pollutant,” might represent a developing field.

This distribution demonstrates how nanoparticles and metal nanoparticles are closely related to analytical methods like SP-ICP-MS, indicating methodological and application overlap. Large nodes emphasise the maturity of key principles, whereas smaller, peripheral nodes indicate potential research frontiers in environmental nanotechnology and biomed-

ical applications. The map suggests that SP-ICP-MS is becoming an important global method for monitoring nanoparticles, combining analytical chemistry with environmental and toxicological investigations.

2. Experimental Section (Materials and Methods)

2.1. Materials and Chemicals

The single-particle method was validated using certified reference materials (RMs) from the NIST, specifically the gold nanoparticle (AuNPs) NIST reference materials (RM) 8011 (nominal 10 nm diameter; National Institute of Standards and Technology, Gaithersburg, MD, USA). Gold nanoparticles (20 nm diameter, OD 1, suspension in citrate buffer; Sigma-Aldrich, St. Louis, MO, USA) and silver nanoparticles (60 nm particle size, 0.02 mg/mL in aqueous buffer containing sodium citrate as a stabiliser; Sigma-Aldrich, St. Louis, MO, USA) were used as reference nanoparticle suspensions. Millipore water obtained from Sigma-Aldrich, Burlington, MA, USA, was used for all aqueous preparations. Nitric acid (65% *w/w*) and hydrochloric acid (37% *w/w*) were purchased from Sigma-Aldrich South Africa, Modderfontein, Johannesburg, South Africa, and were used to prepare dilute samples and standards to obtain high precision. Gold, silver, and multi-element ionic calibration standards prepared in a 5% nitric acid (HNO₃) matrix were obtained from LGC Standards (Kyalami, Johannesburg, South Africa) and Inorganic Ventures (Christiansburg, VA, USA) and were used for instrument calibration and quality control.

2.2. Sample Collection and Preparation

The wastewater samples were collected from a South African mining and mineral processing company where silver- and gold-based ENPs are routinely used for analytical, sensing, and environmental applications. Therefore, AgENPs and AuENPs were identified as the most relevant target nanoparticles for this study. Wastewater samples were collected as grab samples in polyethene bottles. Sampling was conducted at four-month intervals. Wastewater samples were collected in pre-cleaned polyethene bottles, stored at 4 °C, and analysed within 24 h of collection to minimise alterations in nanoparticle characteristics. Samples were prepared by acidifying with 2% HNO₃ and diluting the wastewater 10-fold to ensure that particle events accounted for less than 10% of the total reading. All sample dilutions were carried out on the day of analysis to minimise sample degradation and maintain particle integrity. Additionally, gold and silver ionic solutions were diluted to 1 µg/L to calibrate the analytical system's sensitivity for each element.

2.3. Instrumentation and Operating Conditions

An Agilent 7800 ICP-MS (Agilent Technologies Inc., Santa Clara, CA, USA) was employed to perform measurements of both nanomaterials and conventional elemental analyses. The operating parameters applied during the analyses are summarised in Table 1. To ensure sample integrity and prevent cross-contamination between successive measurements, a rinse solution containing 2% nitric acid was used between analyses to effectively remove residual material from the sample introduction system. Analytical measurements were performed using the Single-Element/Isotope Analysis mode of the Agilent ICP-MS Mass-Hunter software (version D.01.01, SI 637). Elemental data were obtained by the use of time-resolved analysis (TRA) software, and the dwell duration for each point was 3 µs, as a result of the optimisation strategy reported by Yang et al. [22].

Table 1. The operating conditions for the Agilent 7800 ICP-MS instrument.

Category	Parameter	Operating Condition
ICP-MS system configuration	Instrument	Agilent 7800 ICP-MS
	Nebuliser	Standard Micro Mist concentric nebuliser
	Spray chamber	Double-pass quartz spray chamber
ICP-MS operating conditions	Carrier gas flow rate	1.05 L min ^{−1}
	RF power	1550 W
	Sample uptake rate	0.346 mL min ^{−1}
	Spray chamber temperature	20 °C
	Monitored isotope	¹⁹⁷ Au or ¹⁰⁷ Ag
Single-particle (TRA) operating conditions	Transport efficiency	2–5%
	Acquisition time	60 s
	Dwell time	3 µs

2.4. Transport Efficiency Determination

An RM, NIST-8011 with 10 nm Au NPs and the particle frequency method were used to measure transport efficiency. The sample suspensions were diluted to allow for single-particle detection, and the dwell time was kept the same for all analyses to make sure the data were consistent and particles could be reliably distinguished. Transport efficiency was assessed using the particle frequency method and applied for the calculation of particle size and particle number concentration. Particle number concentration was calculated based on the frequency of detected particle events, sample flow rate, acquisition time, dilution factor, and transport efficiency [22].

2.5. Data Processing

Time-resolved data were analysed using Agilent 7800 ICP-MS Musshunter workstation software (v4.6; Agilent Technologies Inc., Santa Clara, CA, USA), for distinguishing particle events from dissolved background signals through an auto-calculated threshold based on mean background intensity and standard deviation. Particle mass was derived from signal intensity, factoring in instrument sensitivity and transport efficiency, while particle diameters were calculated under the assumptions of spherical geometry and bulk metal density [23].

The software automatically calculated particle number concentrations and size distributions by converting signal intensities into equivalent spherical diameters. This conversion assumed complete ionisation of the particles, spherical geometry, and known material densities (10.49 g/cm³ for Ag and 19.3 g/cm³ for Au) [24]. The background equivalent diameter (BED), representing the theoretically smallest detectable particle size, was also calculated automatically by the instrument software [25]. This value reflects the influence of the baseline signal on detection limits and was used to define the minimum particle size reliably distinguished from the dissolved background. Number concentrations were expressed in particles per litre, and size distributions were reported as median diameters. Dissolved and particulate fractions were differentiated by comparing continuous background signals with discrete particle events. All calculations followed the manufacturer's protocols, ensuring consistency with the published SP-ICP-MS methodology [26].

3. Method Optimisation and Performance Evaluation

Instrumental Optimisation and Method

A dwell time of 3 µs was selected for all SP-ICP-MS measurements, following the optimisation strategy reported by Yang et al. (2016), which demonstrated reduced particle

coincidence at short dwell times [22]. This dwell time was suitable for the nanoparticle concentrations examined in this study and was determined based on Poisson statistical principles regarding random particle arrival at the plasma. Mass calibration curves were produced by measuring ionic standard solutions. To guarantee the consistency and repeatability of the results of the RM recovery, each and every analysis was carried out in duplicate. The BED is the smallest theoretical particle size that can be detected in the background signal. It comes from changing the baseline noise level into a particle diameter that is the same [27]. Therefore, the BED directly reflects the influence of background signal intensity on the lower detection limit of single-particle mode. All datasets were exported in CSV format.

The SP-ICP-MS method was assessed in terms of detection limits, transport efficiency, accuracy, and precision. The Agilent 7800 ICP-MS software's single-particle analysis module automatically determined the size and particle number concentration detection limits based on the calibration data, transport efficiency, and optimised instrument parameters determined during method optimisation [28]. The detection thresholds were established based on the background signal, statistical discrimination of particle events, and element density according to established SP-ICP-MS principles [28]. The minimum detectable particle size BED was automatically calculated by the Agilent 7800 SP-ICP-MS software [29]. Depending on the matrix composition and background signal strength, the usual detection limits for AgENPs are approximately 14–20 nm, and for AuENPs, they are around 10–15 nm, according to the literature findings [18,30]. Our instrument-calculated values were within the reported range for AuENPs, confirming consistency with published benchmarks. However, for AgENPs, we managed to detect 10 nm, which suggests that the Agilent was sensitive towards AgENPs.

4. Results and Discussion

4.1. Analysis of Reference Materials and Nanoparticle Standards

The histogram of signal distribution shows a clear difference between the dissolved background signal and nanoparticle-derived events. Most of the signal intensities were concentrated at low CPS values, corresponding to the dissolved metal fraction and instrumental background [29,30]. In contrast, discrete high-intensity events extending to approximately 2×10^9 CPS were observed, confirming the presence of nanoparticulate species, as shown in Figure 4.

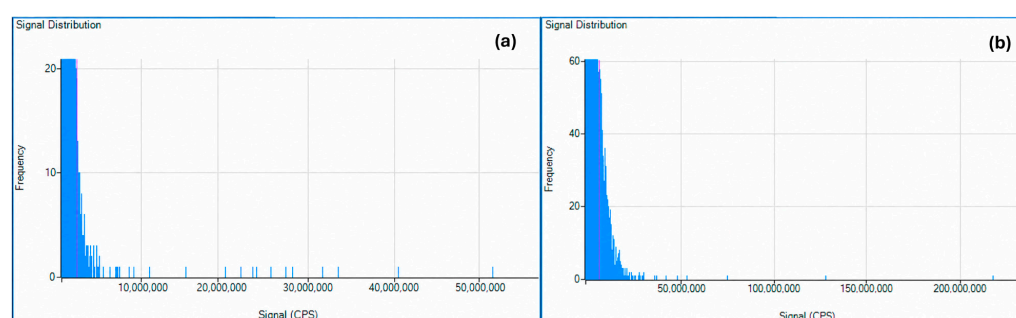


Figure 4. Signal scan obtained by SP-ICP-MS for (a) commercially purchased gold reference material (Au RM) and (b) 20 nm gold nanoparticles.

The time-resolved cps signal profile displays a series of discrete peaks above the continuous baseline. These peaks correspond to individual Au nanoparticle events detected in the 10 nm gold reference material (RM), while the baseline represents dissolved gold ions or background noise shown on the left side of Figure 5. The presence of numerous sharp peaks indicates that particulate gold is present in the solutions, not only in dissolved

form [15,31,32]. The median particle size is 10 nm, and it is displayed on the right side of the picture. The results indicate a prevalence of smaller nanoparticles, aligning with manufacturer specifications, proving that our approach is fully functional.

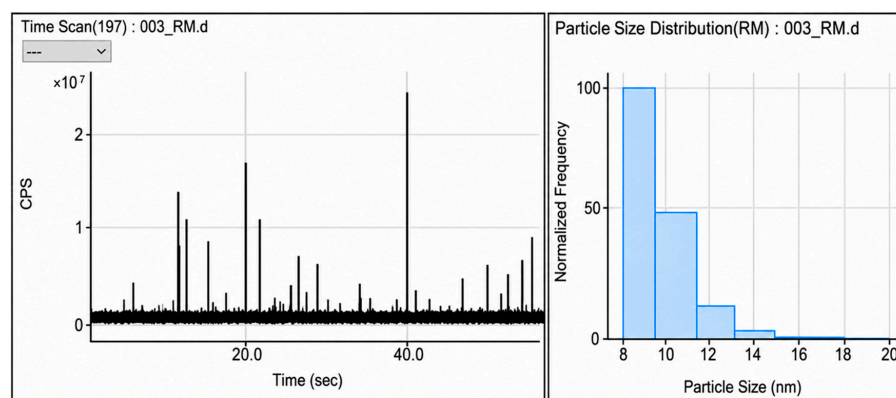


Figure 5. Time-resolved signal profile and particle size distribution of 10 nm gold RM.

The results for 20 nm Au nanoparticle analysis are shown in Figure 6, revealing that the time-resolved cps signal profile displays a series of discrete peaks above the continuous baseline. Additionally, the peaks also indicate that Au nanoparticle events were detected in the industrial contaminated wastewater sample, while the baseline represents dissolved gold ions or background noise [16]. The presence of numerous sharp peaks indicates that particulate gold is present, and the median particle sizes of 8–14 nm align with the manufacturer’s specifications.

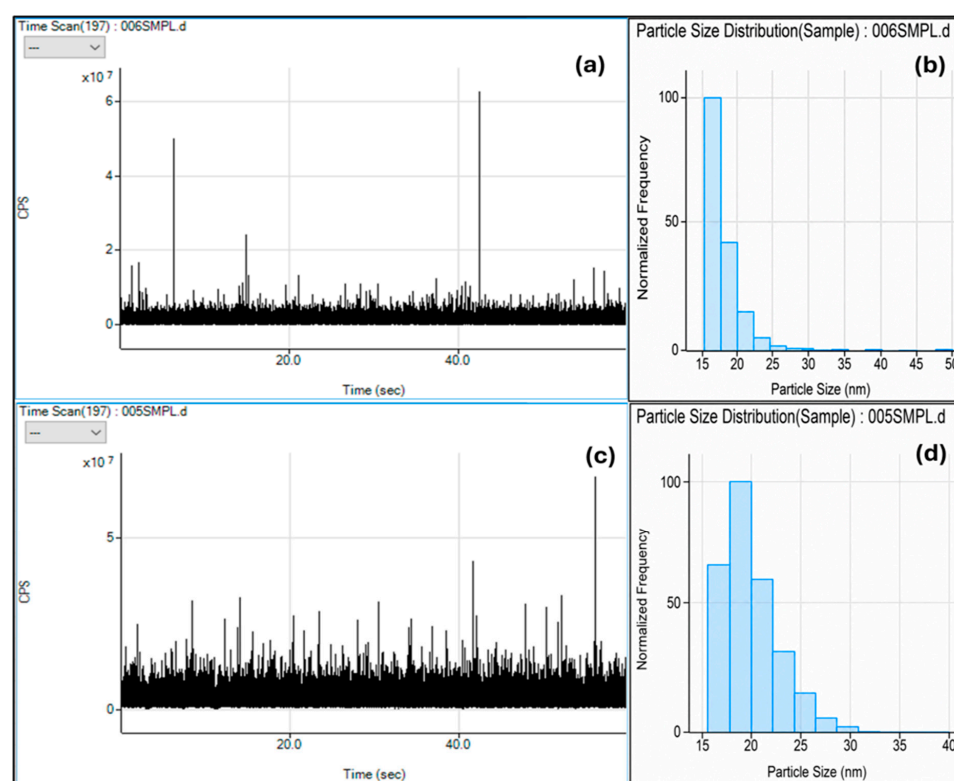


Figure 6. Time-resolved intensity profiles and particle size distributions of two commercially purchased 20 nm gold samples: (a,b) sample 1 and (c,d) sample 2.

4.2. Dissolved Metal Concentrations in Wastewater

Both the dissolved concentrations of silver and gold were determined by ICP-MS; their results are tabulated in Table 2. Total Ag concentrations were measured at $631.3 \mu\text{g L}^{-1}$ and $628.2 \mu\text{g L}^{-1}$ for the Ag-containing wastewater. The total Au concentrations resulted in $49.54 \mu\text{g L}^{-1}$ and $49.52 \mu\text{g L}^{-1}$ for the Au-containing wastewater, confirming the presence of Au in the contaminated wastewater. The presence of silver and gold in the investigated water is consistent with the industrial use of these elements. Their occurrence is likely associated with process effluents and equipment washing during manufacturing and research activities involving silver- and gold-based materials [33–35].

Table 2. Silver (Ag) and gold (Au) concentrations in industrial wastewater samples measured by ICP-MS.

	Gold (Au)-Containing Wastewater Concentrations $\mu\text{g L}^{-1}$	Silver (Ag)-Containing Wastewater Concentrations $\mu\text{g L}^{-1}$
S1	49.54	631.3
S2	49.52	628.2

While TEM and SP-ICP-MS focus on particle-level characterisation, bulk elemental composition was evaluated using X-ray fluorescence (XRF, XEPOS) to understand the overall chemical composition affecting nanoparticle behaviour. XRF scans identified major and trace elements in the wastewater samples, including matrix components that may influence transport efficiency and particle stability [32]. This compositional overview offered context for interpreting the nanoparticle data, as shown in Figure 7a,b. For AuENPs, the XRF scan results indicate a major concentration of sodium (Na) at 14,500 ppm and a low concentration of silver (Ag) at 12 ppm. For AgENPs containing wastewater, the major concentration of silica (Si) is 3474 ppm, and the calcium (Ca) and chloride (Cl) are both at low concentrations of 68 ppm.

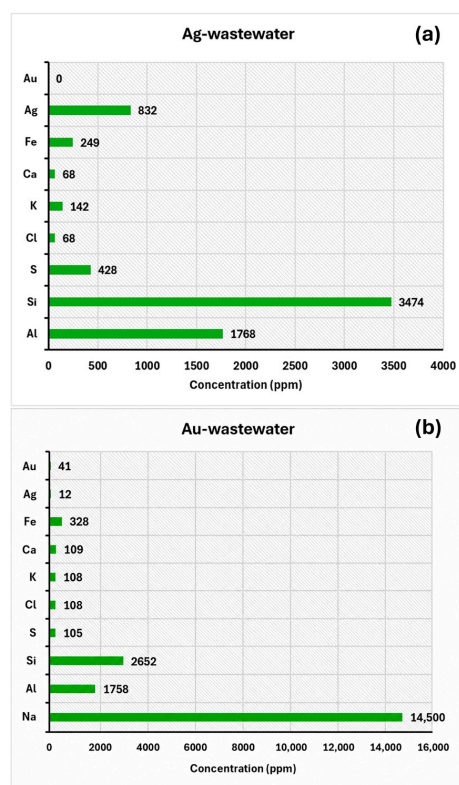


Figure 7. (a) Semi-quantitative results of silver-containing wastewater and (b) gold-containing wastewater using the X-ray fluorescence (XRF, XEPOS).

4.3. Nanoparticle Detection of Time-Resolved Signal and Particle Size

The time-resolved cps signal profile shows a series of separate peaks above the steady baseline. These peaks represent individual AgENP events found in the Ag-containing wastewater sample, while the baseline shows dissolved silver ions or background noise, as shown in Figure 8a,c, indicating that particulate silver predominates over dissolved silver in the wastewater, as indicated by the numerous sharp peaks. The particle size of AgENPs in the Ag-containing wastewater is shown in Figure 8b,d. The median size is 14 nm. The size distribution is between 10 and 20 nm. Additionally, the size distribution is right-skewed, meaning that most values are low or moderate, with fewer extremely high values.

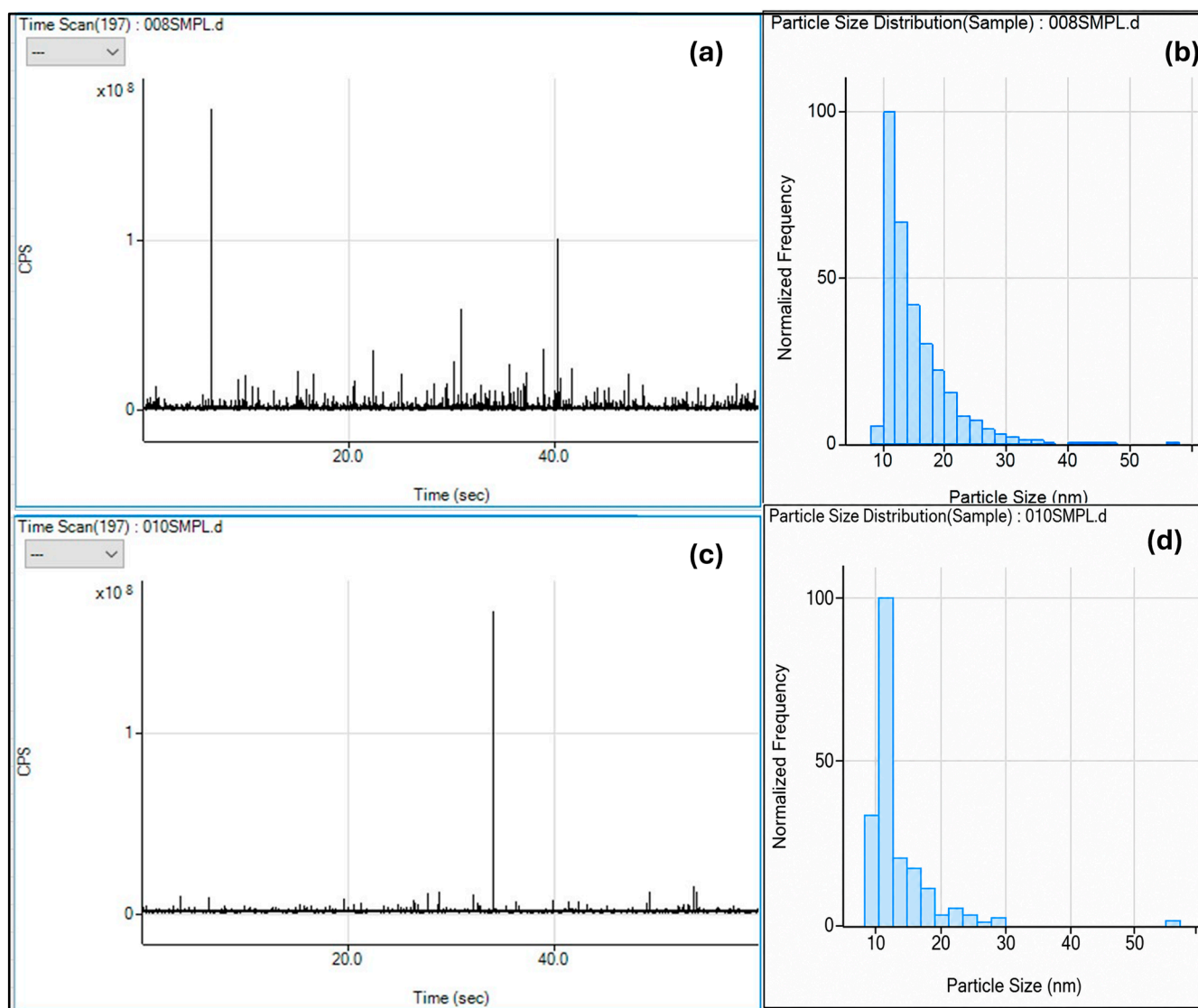


Figure 8. Time-resolved intensity profiles and particle size distributions of silver-containing wastewater are shown in panels (a,b) and (c,d), respectively.

The time-resolved intensity results of AuENPs are shown in Figure 9a,c and resemble those observed for silver. Numerous sharp peaks indicate that the Au-contaminated wastewater contains predominantly particulate gold rather than dissolved gold. The particle size of AuENPs in the wastewater is shown in Figure 9b,d. The median size is 8 nm. The size distributions are between 5 and 15 nm. Additionally, the size distribution is right-skewed, meaning that most values are low, with fewer extremely high values.

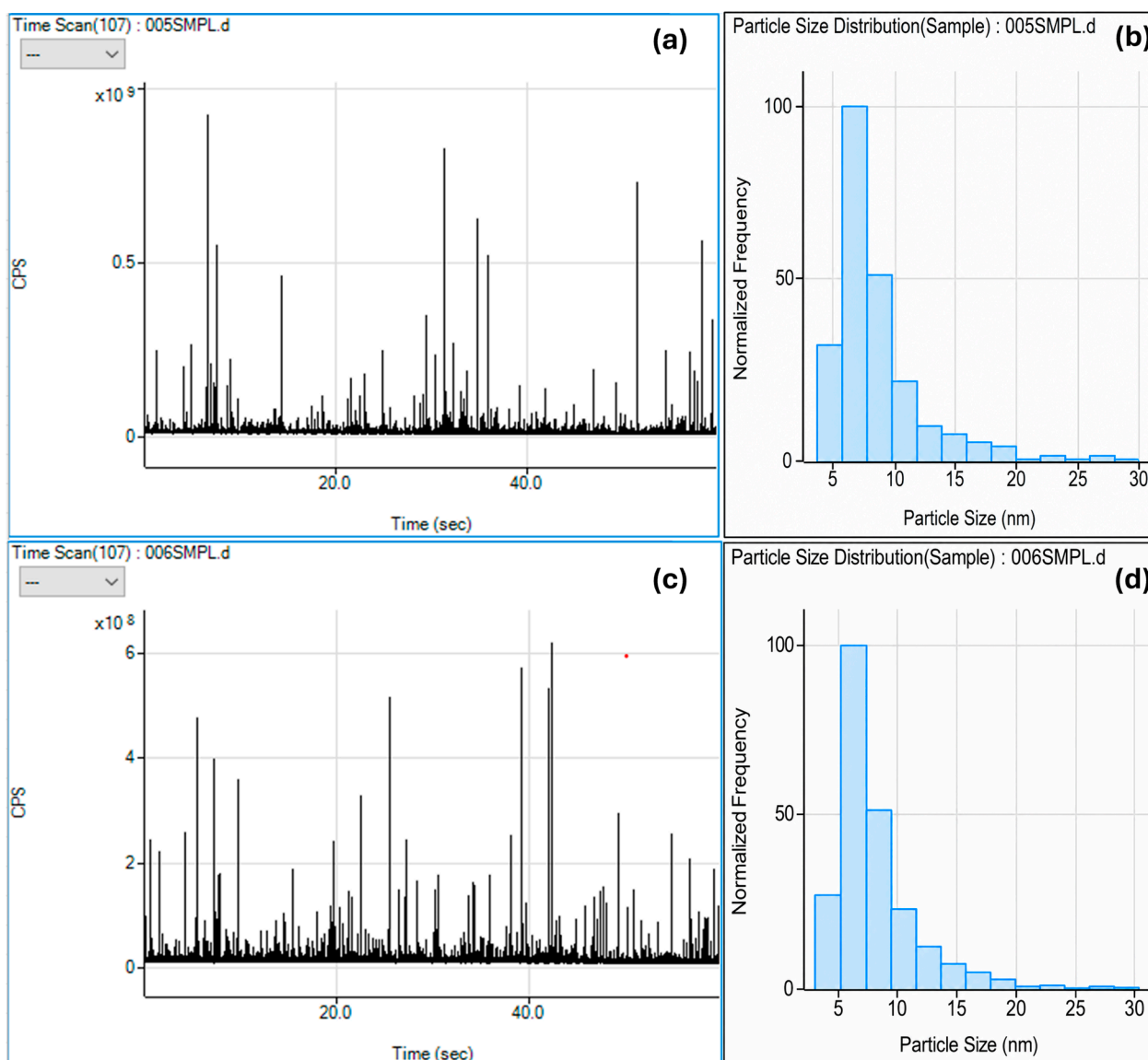


Figure 9. Time-resolved intensity profiles and particle size distributions of gold-containing wastewater are shown in panels (a,b) and (c,d), respectively.

4.4. Particle Number Concentrations and TEM Results

The particle number concentration analysis by SP-ICP-MS clearly shows the presence of AgENPs and AuENPs with different particle number concentrations shown in Table 3. These values are not only quantitatively significant but also qualitatively important, as they confirm that a substantial fraction of the gold exists in nanoparticulate form rather than solely as dissolved ionic species. The high number of particle events observed in Table 3 illustrates the high sensitivity of SP-ICP-MS, demonstrating its ability to discriminate between particulate and ionic forms, a feature that is important for precise nanoparticle characterisation. These findings demonstrate the effectiveness of SP-ICP-MS for detecting and characterising ENPs in complex environmental matrices. The technique provides direct evidence of nanoparticle occurrence while simultaneously determining particle size distributions, particle number concentrations, and dissolved metal fractions.

Table 3. The particle number concentration of both silver (Ag) and gold (Au) ENPs in industrial wastewater samples determined by SP-ICP-MS.

Number	Gold-Containing Wastewater Concentrations (Particles L ⁻¹)	Silver-Containing Wastewater Concentrations (Particles L ⁻¹)
S1	9.80×10^7	1.40×10^9
S2	9.40×10^7	1.30×10^9

4.5. TEM Characterisation Images

Figure 10a,b shows TEM images of AgENPs present in industrial wastewater. They are spherical in shape; some nanoparticles form chain-like aggregates. These observations confirm the morphology assumed in SP-ICP-MS calculations. Figure 10c,d shows TEM micrographs of AuENPs present in industrial wastewater. The images show spherical nanoparticles that are evenly distributed throughout the sample, with a range of particle sizes visible. This morphological evidence supports the particle size distributions obtained by SP-ICP-MS, while also providing direct visualisation of nanoparticle dispersion and uniformity. The presence of size variation highlights the heterogeneity of nanoparticles in complex wastewater matrices, a crucial factor in understanding their behaviour and potential environmental impacts.

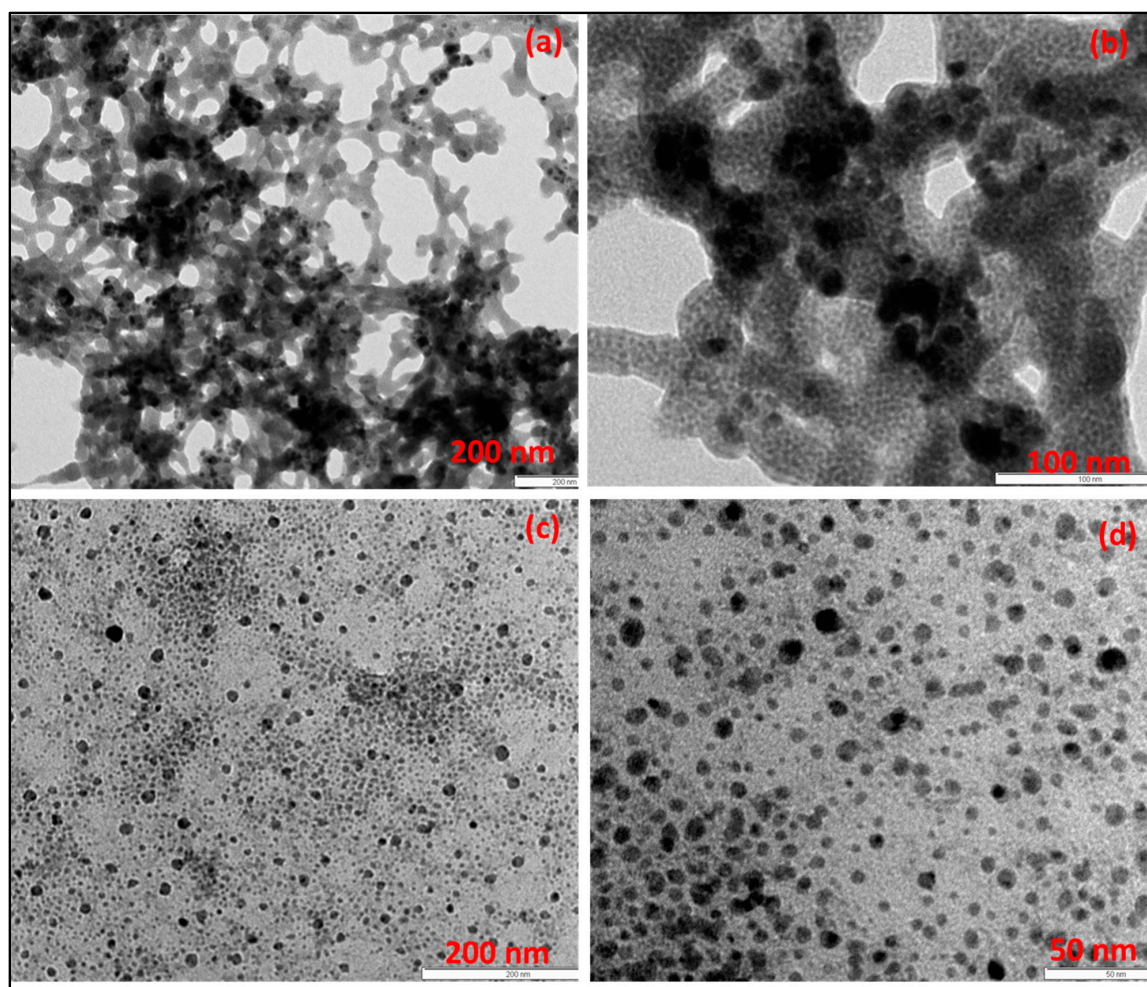


Figure 10. TEM images for both wastewaters of silver nanoparticles (AgENPs) (a,b) and gold nanoparticles (AuENPs) (c,d).

The size distributions of ENPs were determined using the SP-ICP-MS technique. To validate these results, TEM images of the ENPs were analysed with ImageJ software, where the particle sizes were measured according to the calibrated scale provided in the images, and its results are shown in Figure 11; ImageJ analysis of the TEM micrographs revealed narrow particle size distributions, with median particle diameters of 14 nm for AgENPs and 9 nm for AuENPs. These values were in close agreement with the particle sizes determined by SP-ICP-MS (14 nm for AgENPs and 8 nm for AuENPs), with differences of ≤ 1 nm between the two techniques. This close agreement provides independent validation of the SP-ICP-MS measurements. Minor discrepancies are expected because TEM directly measures the physical particle diameter, whereas SP-ICP-MS estimates the equivalent spherical diameter based on the elemental mass of each particle, assuming spherical geometry and a known particle density [36,37].

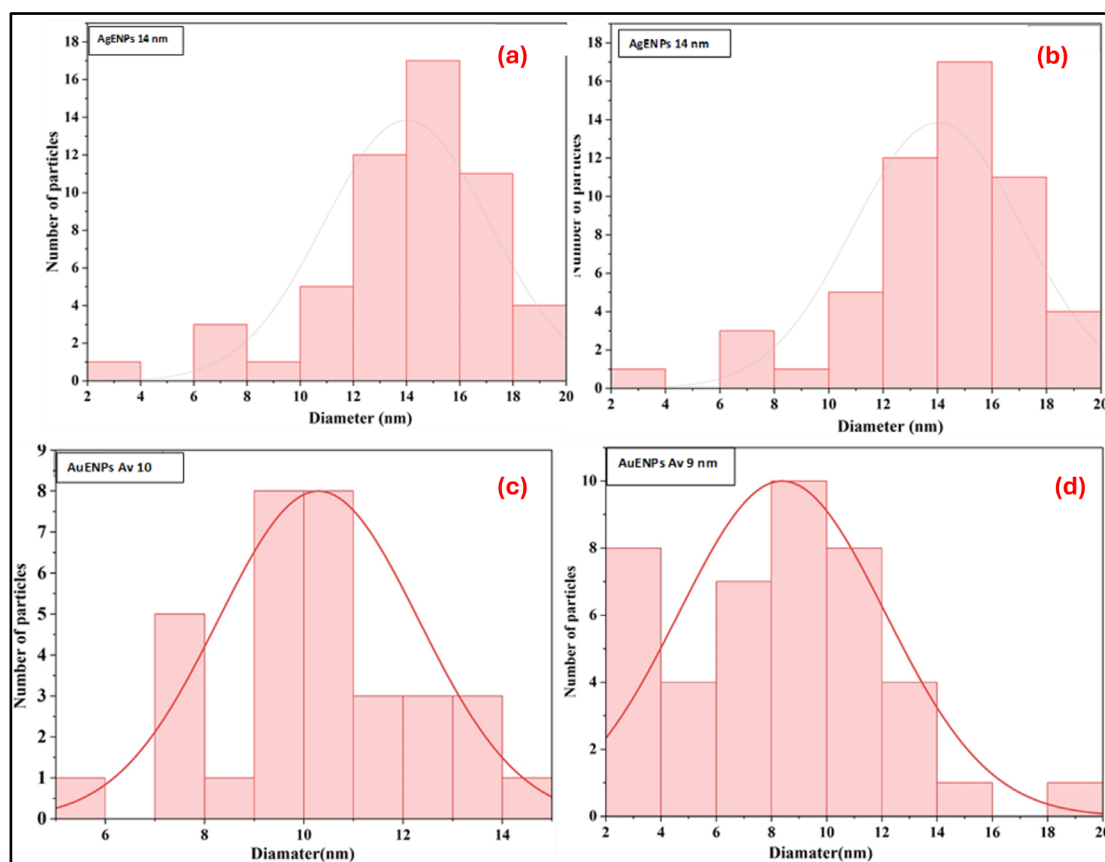


Figure 11. Size distributions of silver nanoparticles (AgENPs) (a,b) and gold nanoparticles (AuENPs) (c,d) obtained from ImageJ and Origin for both categorised wastewaters.

Table 4 compares the particle sizes and concentrations of AgENPs and AuENPs obtained in the present study with those reported in previous investigations. The AgENP particle sizes measured in this study were comparable to those reported by study 2 and study 3, whereas the AuENP particle sizes were smaller compared to the other studies. Differences in particle size distributions and concentrations among studies are expected due to variations in industrial processes, wastewater composition, nanoparticle sources, sampling strategies, and analytical methodologies. The dissolved metal concentrations also varied between studies, with high concentrations in the present study, reflecting differences in wastewater characteristics and treatment processes. The overall consistency of the present results with the published literature confirms the reliability of the integrated

SP-ICP-MS and TEM approach for the characterisation of ENPs in complex industrial wastewater matrices.

Table 4. Comparison of silver (Ag) and gold (Au) ENP characteristics reported in previous studies and the present study.

Study	Matrix	AgENPs Size (nm)	AuENPs Size (nm)	Dissolved Ag [$\mu\text{g/L}$]	Dissolved Au [$\mu\text{g/L}$]
Yuan Yang et al., 2016 [22]	Natural water	20	19	-	-
Yuxiong Huang et al., 2021 [25]	Wastewater	17.7	47	0.09	-
Gajec et al., 2020 [27]	Sewage	16.2–33.3	-	0.0402–5.112	-
Mavro Lučić et al. [37]	Sewage sludge	21.8	19.6	3.21	0.003
This study	Industrial wastewater	14–15	8–10	631.3	49.54

5. Conclusions

The increasing use of ENMs in industrial applications highlights the need for reliable analytical methods to monitor their occurrence in complex environmental matrices. In this study, an integrated analytical approach combining ICP-MS, single-particle ICP-MS (SP-ICP-MS), and transmission electron microscopy (TEM) with ImageJ image analysis was successfully applied to characterise silver and gold nanoparticles in industrial wastewater. The complementary use of these techniques enabled the determination of dissolved metal concentrations, particle size distributions, and particle number concentrations, thereby providing a comprehensive assessment of ENMs in a complex wastewater matrix.

The results showed that the dissolved gold was approximately $49.54 \mu\text{g L}^{-1}$ in the Au-containing wastewater, whereas SP-ICP-MS revealed the presence of AuENPs ranging from 5 to 15 nm, with a median size of 9 nm. The dissolved silver concentration was approximately $631.3 \mu\text{g L}^{-1}$. The median particle size of the silver nanoparticles was 14 nm, with a size distribution ranging from 5 to 20 nm. The particle size distributions were validated by TEM, demonstrating a strong correlation between the values recorded by ImageJ and SP-ICP-MS, thereby providing independent confirmation of the analytical results. Furthermore, the measured particle sizes and concentrations were found to be in agreement with published studies on similar wastewater matrices, thereby confirming the reliability of the integrated analytical approach.

The supporting bibliometric study showed a growing interest in the use of SP-ICP-MS for the characterisation of nanoparticles while highlighting the limited number of studies that have applied integrated analytical techniques to characterise engineered nanoparticles in real industrial wastewater matrices. This identified knowledge gap provided the motivation for the present study. Overall, this study reveals that the combined use of ICP-MS, SP-ICP-MS and TEM offers a solid basis for the characterisation of manufactured nanoparticles in industrial wastewater and contributes to improving environmental monitoring of emerging particulate pollutants. Future work should apply this approach to other environmentally relevant nanoparticles such as titanium dioxide, zinc oxide, and platinum-based nanoparticles and study their transformation and fate during wastewater treatment and their occurrence across different industrial sectors in order to inform environmental risk assessment and the development of standardised monitoring protocols.

Author Contributions: Conceptualisation, P.M.; Methodology, P.M. and A.M.; Formal analysis, A.M. and M.R.L.; Investigation, M.R.L.; Resources, J.T.; Data curation, A.M., J.T. and H.R.; Writing—original draft, P.M., A.M. and M.R.L.; Writing—review and editing, P.M., A.M. and H.R.; Supervision, M.R.L., J.T. and H.R.; Funding acquisition, J.T. and H.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Mintek grant number ASR-002625.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors Portia Madzivha, Andile Mkhohlakali, Refiloe Letsoalo and James Tshilongo were employed by the company Mintek. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Singh, S.; Prasad, S.M.; Bashri, G. Fate and toxicity of nanoparticles in aquatic systems. *Acta Geochim.* **2023**, *42*, 63–76.
2. Hochella, M.F.; Mogk, D.W.; Ranville, J.; Allen, I.C.; Luther, G.W.; Marr, L.C.; McGrail, B.P.; Murayama, M.; Qafoku, N.P.; Rosso, K.M.; et al. Natural, incidental, and engineered nanomaterials and their impacts on the Earth system. *Science* **2019**, *363*, eaau8299. [[CrossRef](#)] [[PubMed](#)]
3. Altammar, K.A. A review on nanoparticles: Characteristics, synthesis, applications, and challenges. *Front. Microbiol.* **2023**, *14*, 1155622. [[CrossRef](#)] [[PubMed](#)]
4. Madzivha, P.; May, B.M.; Jijana, A.; Hlatshwayo, L.; Graham, S.M.; Tshilongo, J.; Richards, H. Quantitative analysis of silver and gold nanomaterials in industrial wastewater. *Mater. Today Proc.* **2023**. [[CrossRef](#)]
5. Kumah, E.A.; Fopa, R.D.; Harati, S.; Boadu, P.; Zohoori, F.V.; Pak, T. Human and environmental impacts of nanoparticles: A scoping review of the current literature. *BMC Public Health* **2023**, *23*, 1059. [[CrossRef](#)] [[PubMed](#)]
6. Shakeel, M.; Ahmed, S. The nexus of nanotechnology and industrial effluents: A comprehensive review of promising nanomaterials employed for treatment. *Int. J. Environ. Sci. Technol.* **2025**, *22*, 17299–17326. [[CrossRef](#)]
7. Loula, M.; Kaňa, A.; Koplík, R.; Hanuš, J.; Mestek, O.; Loula, M.; Kaňa, A.; Koplík, R.; Hanuš, J. Analysis of Silver Nanoparticles Using Single-Particle Inductively Coupled Plasma–Mass Spectrometry (ICP-MS): Parameters Affecting the Quality of Results Analysis of Silver Nanoparticles Using Single-Particle Parameters Affecting the Quality of Result. *Anal. Lett.* **2019**, *52*, 288–307. [[CrossRef](#)]
8. Laborda, F.; Alvaro, I.A.; Jim, M.S.; Bolea, E. Catching particles by atomic spectrometry: Benefits and limitations of single particle-inductively coupled plasma mass spectrometry. *Spectrochim. Acta Part B At. Spectrosc.* **2023**, *199*, 106570. [[CrossRef](#)]
9. Heilgeist, S.; Sekine, R.; Clases, D.; Sahin, O.; Stewart, R.A. Invisible? Assessing the Fate of Sunscreen-Derived Titanium Dioxide Nanoparticles in Swimming Pool Water Using Single Particle and Laser Ablation Inductively Coupled Plasma Mass Spectrometry. *ACS ES&T Water* **2023**, *3*, 1192–1200. [[CrossRef](#)]
10. Meng, Z.; Zheng, L.; Fang, H.; Yang, P.; Wang, B.; Li, L.; Wang, M. Single Particle Inductively Coupled Plasma Time-of-Flight Mass Spectrometry—A Powerful Tool for the Analysis of Nanoparticles in the Environment. *Processes* **2023**, *11*, 1237. [[CrossRef](#)]
11. Passas, I. Bibliometric Analysis: The Main Steps. *Encyclopedia* **2024**, *4*, 1014–1025. [[CrossRef](#)]
12. Hassan, W.; Duarte, A.E. Bibliometric analysis: A few suggestions. *Curr. Probl. Cardiol.* **2024**, *49*, 102640. [[CrossRef](#)] [[PubMed](#)]
13. İri, R.; Ünal, E. Bibliometric Analysis Bibliometric Analysis of Research (1980–2023). *Ahi Evran Üniv. Sos. Bilim. Enstitüsü Derg.* **2024**, *10*, 386–403. [[CrossRef](#)]
14. Flores, K.; Turley, R.S.; Valdes, C.; Ye, Y.; Cantu, J.; Hernandez-Viezcas, J.A.; Parsons, J.G.; Gardea-Torresdey, J.L. Environmental applications and recent innovations in single particle inductively coupled plasma mass spectrometry (SP-ICP-MS). *Appl. Spectrosc. Rev.* **2021**, *56*, 1–26. [[CrossRef](#)]
15. Mozhayeva, D.; Engelhard, C. A critical review of single particle inductively coupled plasma mass spectrometry—A step towards an ideal method for nanomaterial characterization. *J. Anal. At. Spectrom.* **2020**, *35*, 1740–1783. [[CrossRef](#)]
16. Bustos, A.R.M.; Winchester, M.R. Single-particle-ICP-MS advances. *Anal. Bioanal. Chem.* **2016**, *408*, 5051–5052. [[CrossRef](#)] [[PubMed](#)]
17. Davison, C.; Beste, D.; Bailey, M.; Felipe, M. Expanding the boundaries of atomic spectroscopy at the single-cell level: Critical review of SP-ICP-MS, LIBS and LA-ICP-MS advances for the elemental analysis of tissues and single cells. *Anal. Bioanal. Chem.* **2023**, *415*, 6931–6950. [[CrossRef](#)] [[PubMed](#)]

18. dos Santos, L.M.G.; Barata-Silva, C.; Neto, S.A.V.; Bazilio, F.S.; da Silva, A.L.O.; Jacob, S.C.; Moreira, J.C. Development of the methodology for the detection and quantification of zinc oxide nanoparticles and dissolved zinc by single-particle inductively coupled plasma mass spectrometry. *J. Nanoparticle Res.* **2024**, *26*, 233. [[CrossRef](#)]
19. Goodman, A.J.; Benner, B.F.; Montañó, M.D. Out of the lab and into the environment: The evolution of single particle ICP-MS over the past decade. *Environ. Sci. Nano* **2025**, *12*, 1789–1800. [[CrossRef](#)]
20. Tshilongo, J.; Lee, J.B.; Kim, J.S.; Mkhohlakali, A.; Ntsasa, N.; Letsoalo, M.R.; Toona, M.P.; Mabowa, M.H. Hydrogen isotope analysis: Experimental approach and research trends analysis. *Talanta* **2026**, *298*, 128881. [[CrossRef](#)] [[PubMed](#)]
21. Lohmann, S.; Lange, S.; Ertl, T. Word Cloud Explorer: Text Analytics based on Word Clouds. In *Proceedings of the 2014 47th Hawaii International Conference on System Sciences*; IEEE: Waikoloa, HI, USA, 2014. [[CrossRef](#)]
22. Yang, Y.; Long, C.L.; Li, H.P.; Wang, Q.; Yang, Z.G. Analysis of silver and gold nanoparticles in environmental water using single particle-inductively coupled plasma-mass spectrometry. *Sci. Total Environ.* **2016**, *563–564*, 996–1007. [[CrossRef](#)] [[PubMed](#)]
23. Bolea, E.; Laborda, F. Spectrochimica Acta Part B: Atomic Spectroscopy Single particle inductively coupled plasma mass spectrometry metrology: Revisiting the transport efficiency paradigm. *Spectrochim. Acta Part B At. Spectrosc.* **2024**, *216*, 106941. [[CrossRef](#)]
24. Du, A.M.; Eiden, G.C.; Hoegg, E.D.; Sumner, R.I.; Cell, T.; Wood, L.S. Temporal analysis of ion arrival for particle quantification. *J. Anal. At. Spectrom.* **2021**, *36*, 133–141. [[CrossRef](#)]
25. Huang, Y.; Keller, A.A.; Cervantes-Avilés, P.; Nelson, J. Fast Multielement Quantification of Nanoparticles in Wastewater and Sludge Using Single-Particle ICP-MS. *ACS Environ. Sci. Technol. Water* **2021**, *1*, 205–213. [[CrossRef](#)]
26. Woods, G.; Wilbur, S. Analysis of 10 nm Gold Nanoparticles using the Agilent 7800 ICP-MS. *Agilent* **2018**, 8012. Available online: https://www.agilent.com/cs/library/applications/5991-8827EN_10nm_au_np_application.pdf (accessed on 29 May 2026).
27. Gajec, M.; Kukulska-Zajac, E.; Król, A. Determination of silver nanoparticles in liquid environmental samples. *Appl. Ecol. Environ. Res.* **2020**, *18*, 5775–5788. [[CrossRef](#)]
28. Zhang, J.; Cui, Y.; Zhou, T.; Wang, J.; Zhu, Z.; Liu, F.; Xiao, G.; Yu, J.; Wang, X.; Huang, B.; et al. Development of Certified Reference Materials of Trace Elements in Gold Solution (GBW02797–GBW02800). *Accredit. Qual. Assur.* **2023**, *28*, 299–310. [[CrossRef](#)]
29. Bolea, E.; Jimenez, M.S.; Perez-Arantegui, J.; Vidal, J.C.; Bakir, M.; Ben-Jeddou, K.; Gimenez-Ingalaturre, A.C.; Ojeda, D.; Trujillo, C.; Laborda, F. Analytical applications of single particle inductively coupled plasma mass spectrometry: A comprehensive and critical review. *Anal. Methods* **2021**, *13*, 2742–2795. [[CrossRef](#)] [[PubMed](#)]
30. Chang, Y.J.; Shih, Y.H.; Su, C.H.; Ho, H.C. Comparison of three analytical methods to measure the size of silver nanoparticles in real environmental water and wastewater samples. *J. Hazard. Mater.* **2017**, *322*, 95–104. [[CrossRef](#)] [[PubMed](#)]
31. Fern, G. Single particle ICP-MS: A tool for the characterization of gold nanoparticles in nanotheranostics applications. *J. Anal. At. Spectrom.* **2024**, *39*, 2508–2513. [[CrossRef](#)]
32. Stanberry, J.S.; Andrews, H.B.; Thompson, C.V.; Ticknor, B.W.; Manard, B.T. Microextraction-Single Particle-Inductively Coupled Plasma-Mass Spectrometry for the Direct Analysis of Nanoparticles on Surfaces. *Anal. Chem.* **2025**, *97*, 1688–1694. [[CrossRef](#)] [[PubMed](#)]
33. Hendricks, N.; Olatunji, O.; Ofori, I.; Gumbi, B.P. Occurrence, fate, and impact of engineered metal/carbonaceous nanomaterials in the environment, detection, and quantitation methods. *Int. J. Environ. Sci. Technol.* **2023**, *20*, 12937–12954. [[CrossRef](#)]
34. Lead, J.R.; Batley, G.E.; Alvarez, P.J.J.; Croteau, M.N.; Handy, R.D.; McLaughlin, M.J.; Judy, J.D.; Schirmer, K. Nanomaterials in the environment: Behavior, fate, bioavailability, and effects—An updated review. *Environ. Toxicol. Chem.* **2018**, *37*, 2029–2063. [[CrossRef](#)] [[PubMed](#)]
35. Carter, S.; Fisher, A.; Gibson, B.; Marshall, J.; Russell, B.; Whiteside, I. Atomic spectrometry update: Review of advances in the analysis of metals, chemicals and materials. *J. Anal. At. Spectrom.* **2017**, *32*, 2068–2117. [[CrossRef](#)]
36. Montoro Bustos, A.R.; Purushotham, K.P.; Possolo, A.; Farkas, N.; Vladár, A.E.; Murphy, K.E.; Winchester, M.R. Validation of Single Particle ICP-MS for Routine Measurements of Nanoparticle Size and Number Size Distribution. *Anal. Chem.* **2018**, *90*, 14376–14386. [[CrossRef](#)] [[PubMed](#)]
37. Lučić, M.; Ščančar, R.M.; Ščančar, J.; Fiket, Ž.; Arah, B.; Vidmar, J. Optimized extraction, quantification and characterization of seven environmentally relevant metallic nanoparticles in sewage sludge: Occurrence, composition and environmental risk assessment. *J. Hazard. Mater.* **2025**, *497*, 139734. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.