Short Communication

Analysis of gold nanoparticles in a hydrocarbon solvent by single particle-inductively coupled plasma mass spectrometry (spICP-MS) and TEM

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Abstract

Single-particle inductively coupled plasma mass spectrometry (spICP-MS) is used increasingly to characterize element-containing nanoparticles (NPs) in various samples, providing data on the number, concentration, size of particles, as well as the dissolved element concentration. Because there are currently only three examples of spICP-MS analysis of NPs in hydrocarbons in the literature. There is a clear need for hydrocarbon-based NP reference materials (RMs), available for analysts to develop and validate new methods. Here, an analysis of spICP-MS data is presented for two custom-developed gold NP RMs in toluene. The particle size data obtained by spICP-MS is compared with the total particle diameter obtained by transmission electron microscopy (TEM) and shows the excellent agreement among both techniques.

Graphical abstract

Keywords Au nanoparticle · Hydrocarbon · spICP-MS · TEM

1 Introduction

Nanoparticles (NPs) have attracted extensive attention in various fields of chemistry, physics, material science, medicine, and photonics, due to their unique physical and chemical properties. They are considered spherical-like

material with a large surface-to-volume ratio, among other properties [1]. Particularly gold nanoparticles, they have been used in different fields such as biomedical [2, 3], drug delivery [4], virus detection [5], catalysis [6–8], among others.

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Once NPs are synthesized and fabricated, they need to be characterized. Standard characterization techniques used in many facilities, upon availability, are; atomic force microscopy (AFM), dynamic light scattering (DLS), scanning electron microscopy (SEM), FTIR spectroscopy, UV–visible spectroscopy (UV–VIS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

spICP-MS has been recognized as a powerful tool for the characterization of NPs matrices. The initial concept was introduced to determine colloidal particles in water, and it opened the door for further applications [9]. The basic assumption is that each recorded pulse registered at the mass spectrometer represents a single NP. Then with that information, two valuable pieces of data can be easily accessed. First, the pulses' frequency correlates to the number of concentrations of NPs. Second, the intensity of each pulse is proportional to the mass of the element [10, 11]. Both are deemed necessary for advanced NP characterization.

To determine the particle size of NPs by spICP-MS, the nebulization efficiency needs to be calculated. It is defined as the number of particles detected divided by the number of particles known to be present in a reference solution [12]. This value is required to calculate both the particle number concentration (number of particles per ml) and then convert the measured particle signals to NP mass and size. It will then provide data on the number, concentration, size of particles, and then provide data on the number, concentration, size of particles, and the dissolved element concentration. Detailed information about the principle of this technique can be found elsewhere [13]. To obtain particle size information and concentration, a calibration with a known NP standard or reference material (RM) of the same chemical composition (if it is available) is required. In the absence of the standard, a dissolved analyte target is used to determine the analyte's mass per NP, and the diameter is calculated [14].

Particularly for gold nanoparticles, two aqueous reference materials (RM 8012 and RM 8013) were evaluated using spICP-MS capabilities to measure the mean size and size distribution in suspensions of varying AuNP size and surface charge comparison with HR-SEM [15]. The results showed that comparable results for the mean AuNP size could be obtained using both techniques; spICP-MS results differed by < 3% from the HR-SEM values and exhibited relative precisions of 0.5%.

Applications of this technique have grown considerably in the last fifteen years. A very recent review shows that the emphasis has been on the aqueous rather than organic/hydrocarbon media [16]. Our group has been focusing on the applications of spICP-MS to characterize NPs in petroleum feedstocks, those that contain one or more hydrocarbon classes (e.g., linear, branched, or cyclic

alkanes and aromatics). In this sense, only three examples of spICP-MS analysis use for NPs in hydrocarbons are reported in the literature [17–19]. So far, no available RM for gold determination in hydrocarbon media is available.

This study aimed to use spICP-MS to measure hydrocarbon solvent compatible gold nanospheres in two custom-developed reference materials (RMs) and compare TEM results. Stable NP RMs are fundamental for method development capable of accurately quantifying NPs, accessing particle number, concentration, and size of particles and the dissolved element concentration in a hydrocarbon matrix.

2 Materials and methods

2.1 Reagents

Trace metal grade purity chemicals and reagents were used in this study without further purification. The reagents included *o*-xylene (Fisher Scientific, Fair Lawn, NJ, USA), S-21 standard (1 mg kg^{-1} , Conostan, Quebec, Canada), sulfur-free gold (1000 mg kg^{-1}) in hydrocarbon oil (LGC Standards, VHG Labs, Inc Manchester, NH, USA) and 40 nm and 100 nm gold nanospheres (polystyrene coated) RMs in toluene (nanoComposix, Inc. San Diego, Ca, USA).

2.2 Synthesis of nanoparticle RMs

Polystyrene-coated gold nanospheres with nominal diameters of 40 nm and 100 nm were developed by nanoComposix (San Diego, CA, USA). The NP surface was functionalized with a 50 kDa thiol-terminated polystyrene ligand (Polymer Source, Montreal, Canada) to render the particles compatible with non-polar solvents modification of literature methods [20]. This was performed through the slow addition of the aqueous NP dispersion into a ligand solution in tetrahydrofuran. The particles were purified from excess ligand through three cycles consisting of flocculation of the particles with methanol, pelleting of the NPs, and removal of the supernatant following centrifugation, re-dispersing the particles into neat toluene or another compatible solvent. The particles were characterized by TEM and UV–visible spectroscopy, and ICP-MS determined the gold mass concentration.

2.3 TEM of polystyrene gold NP RM

Samples for TEM imaging are prepared by drying a small volume (2 μL) of a colloidal dispersion of nanoparticles onto a copper mesh grid coated with a thin carbon support film (Ted Pella, Inc.). Typically, the solvent is evaporated under vacuum; once dry, the samples are imaged

using a JEOL 1010 TEM (Tokyo, Japan), operating at an accelerating 100 kV voltage. The electron density and The NP core size, and the size distribution of the polystyrene-coated NPs were measured by direct sample imaging of more than 200 particles.

2.4 spICP-MS method

A 7900 ICP-MS (Agilent Technologies, Inc., Santa Clara, CA, USA) fitted with an Octopole Reaction System (ORS⁴) collision reaction cell (CRC) was used. The instrument was equipped with platinum sampling and skimmer cones, a standard glass concentric nebulizer, a quartz spray chamber, and a small internal diameter (1.0 mm) quartz torch. 10% of oxygen gas (100%, not balanced with Ar) was added as the optional gas to the sample gas flow to prevent carbon in *o*-xylene from depositing on the cones. Samples were introduced directly into the ICP-MS via the standard peristaltic pump and tubing (i.d. 0.89 mm). Analyses were performed in time-resolved analysis (TRA) mode using an integration time (dwell time) of 100 μ s per point with no settling time between measurements. The spICP-MS method setup, data collection, and analysis were conducted via a method wizard within the Single Nanoparticle Application Module of the ICP-MS MassHunter software, version 4.5 (Agilent Technologies, USA). The instrumental settings used for spICP-MS analysis are summarized in Table 1.

To determine the particle size of NPs by spICP-MS, the nebulization efficiency was calculated. This value is required to calculate both the particle number concentration (number of particles per ml) and convert the measured particle signals to NP mass, therefore, size [12]. The 100 nm gold NP standard, surface-functionalized with polystyrene (nanoComposix), was used as the RM, and gold in hydrocarbon oil (LGC Standards) was used as dissolved standard. The dissolved standard was diluted to 10 ng g⁻¹ in *o*-xylene. The 100 nm gold NP standard was sonicated for approximately 30 s and cut between in *o*-xylene. ICP-MS analyzed both solutions, and the spICP-MS software automatically calculated the nebulization efficiency. The nebulization efficiency (using the “calculated by size” option in the software) was found to be approximately 0.05 (5%). The sensitivity of ionic gold diluted in *o*-xylene was 12,500 cps/ppb, on average.

Table 1 Optimized spICP-MS settings used for Au NP analysis

Parameter	Value
RF power (W)	1550
Carrier gas flow rate (l min ⁻¹)	0.45
Sampling depth (mm)	8
Spray chamber temp (°C)	− 2
Option gas (%)	10
(O ₂ 100%)	Or (0.1 L/min)
Dilution gas (l min ⁻¹)	0.1
Helium CRC cell gas (ml min ⁻¹)	2
Dwell time (ms)	0.1
Monitored mass for Au	197

Table 2 Particle information of gold NP RMs provided by the manufacturer

	Gold nanospheres	
	Nominal diameter 40 nm	Nominal diameter 100 nm
Total particle diameter (TEM)	42 ± 4 nm	103 ± 13 nm
Coefficient of variation	9.2%	12.4%
Particle surface	Polystyrene	Polystyrene
Solvent	Toluene	Toluene
Mass concentration (Au)	0.158 mg ml ⁻¹	0.296 mg ml ⁻¹

3 Results and discussion

Physical and measured information for the two gold NP RMs (with nominal diameters of 40 nm and 100 nm) is given in Table 2. Before analysis using spICP-MS, both RMs were sonicated and diluted in *o*-xylene approximately 1,00,000–1,50,000 times. The 100 nm standard was identified as an “RM” in the software. Both the 100 nm and the 40 nm RMs were run as an unknown sample. The spICP-MS results shown in Table 3 for the median, mode, and mean particle sizes for both RMs were within ± 10% of the expected sizes obtained by TEM (Table 2).

3.1 Particle size distribution and signal distribution

Figures 1 and 2 show the TRA time scan, particle size distribution, and signal distribution for the two gold NP RMs in *o*-xylene. Both figures were run multiple times (n = 3) over multiple days (n = 3). The statistics are showing one

Table 3 spICP-MS results for the two RMs containing Au NPs at 43 nm and 103 nm run as unknown samples

Sample name	Median size (nm)	Most frequent size (nm)	Mean size (nm)
Nanocom_Au_42nm	44.1	46.0	44.2
Nanocom_Au_42nm	43.9	46.0	44.0
Nanocom_Au_42nm	44.2	46.0	44.4
Nanocom_Au_42nm	44.0	44.0	44.2
Average	44.1	45.5	44.2
SD	0.1	1.0	0.2
Nanocom_Au_103nm	99.8	116.0	101.5
Nanocom_Au_103nm	101.3	88.0	102.6
Nanocom_Au_103nm	102.5	118.0	103.0
Nanocom_Au_103nm	102.5	96.0	103.1
Average	101.5	104.5	102.6
SD	1.3	14.8	0.7

representative analysis. The figures show that the signals generated from the Au NPs were separated from the background signals. The mean measured particle size for each standard was around 44 nm and 102 nm, respectively, consistent with the TEM diameters of 42 ± 4 nm and 103 ± 13 nm (Fig. 3). In both cases, the RMs were diluted, allowing sp-ICP-MS would measure between 900 and 1400 particles per TRA measurement.

In Fig. 2, the signal distribution for the 103 nm Au NP synthesized RM diluted in *o*-xylene obtained using spICP-MS yielded a bimodal distribution near 300 kcps and approximately 700 kcps. This was consistent with every replicate for three days of running the same sample. The presence of bimodal distribution has been honored by others, using a different synthetic approach. For example, Majerič et al. noticed the same behavior, using Ultrasonic spray pyrolysis (USP) protocol. The authors noticed that Gas-To-Particle (GTP) mechanisms obtain smaller nanoparticles. In comparison, Droplet-To-Particle (DTP) synthesis mechanisms obtain larger nanoparticles in spray pyrolysis [21].

The proposed that a combination of both mechanisms most probably causes bimodal particle size distribution. The author determined that depending on the experimental conditions, the DTP mechanism is favored, and in some conditions, smaller particle sizes were produced and connected to the GTP mechanism. This bimodal distribution could also be observed in the TEM data in Fig. 3. However, it is not as pronounced due to the histogram's bin size being much more extensive in TEM data versus the spICP-MS data.

We noticed that most of the particles were found to the smaller size, and after averaging all sizes, the values obtained by sp-ICP-MS are within those obtained by TEM. That provides confidence in the accuracy of the size determination using this technique.

The results obtained in this work demonstrate the suitability of using these RM's in toluene as standards for NP's characterization in hydrocarbon solution. Our results indicate that it can be safely be used to determine transport efficiency for any analyte by using a given Au NP (i.e., 60 nm, 100 nm) and soluble Au standard to characterized NPs of many elements. This same approach *in aqueous solutions* was demonstrated by characterizing more than 20 elements, using 100 nm of Au NP and ionic Au standard [22].

These standards were used to validate an engineered iron oxide (Fe_3O_4) nanoparticles reference material (RM) for the determination of Fe NP in petroleum hydrocarbon media. The sp-ICP-MS was calibrated using these two gold synthesized standards after diluting in *o*-xylene ($100,000 \times$ to $150,000 \times$). The 100 nm Au NP determined the nebulization efficiency required to obtain particle size and concentration. In contrast, the 40 nm Au NP was used as a quality control check standard for particle size. For the iron oxide engineered nanoparticles (Fe_3O_4), TEM results gave a (63 ± 6 nm) value for the Fe_3O_4 core diameter, while spICP-MS gave 61.1 ± 4.5 nm ($n = 36$). These results demonstrate excellent agreement among methods. [19]

4 Conclusion

The characterization of NPs in hydrocarbon matrices using spICP-MS is less well-developed than the detection of NPs in aqueous sample matrices. To facilitate more research

Fig. 1 The time scan (top) shows 1425 particles measured, particle size distribution (bottom right), and signal distribution (bottom left) for the 42 nm Au NP synthesized RM diluted in *o*-xylene obtained using spICP-MS

Fig. 2 The time scan (top) shows 960 particles measured, particle size distribution (bottom right), and signal distribution (bottom left) for the 103 nm Au NP synthesized RM diluted in *o*-xylene obtained using spICP-MS

Fig. 3 TEM data for 42 ± 4 nm (top) and 103 ± 13 nm (bottom) Au NP synthesized RMs in toluene

in this emerging field, two custom gold NP synthesized RMs in toluene. Following simple dilution in *o*-xylene, the RMs were measured as unknown samples using spICP-MS. The mean measured particle size for each synthesized RM was within $\pm 10\%$ of the particle diameters determined by TEM (42 ± 4 nm and 103 ± 13 nm), confirming the spICP-MS method.

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Author contributions The manuscript was written through the contributions of all authors. JN and LP designed and conducted the studies, developed methods, and analyzed data. AS prepared and characterized the Au nanoparticle materials. JN, LP, AS, and FL-L wrote the paper together. FL-L contributed to data analysis and final editing. All authors read and approved the final manuscript.

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Data availability The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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