Application Note
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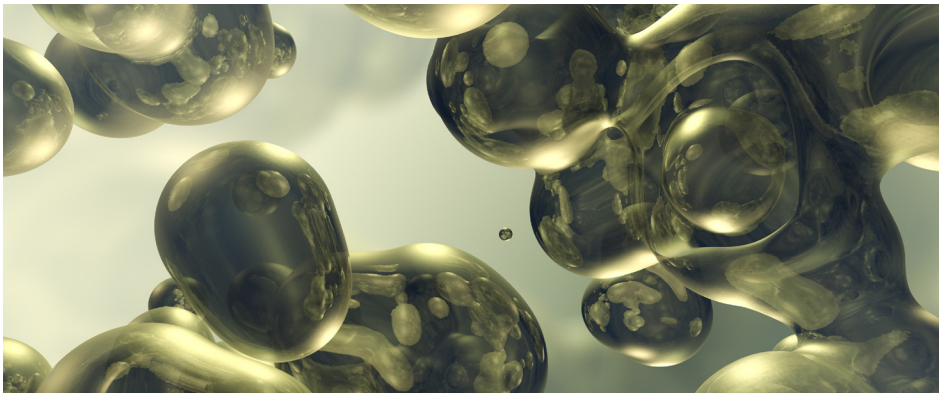
Characterization of Iron Nanoparticles in Hydrocarbon Matrices by Single Particle (sp)ICP-MS

Evaluation of Agilent 7900 spICP-MS method using solvent-compatible nanoparticle reference materials



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Introduction

Inorganic impurities—including nanoparticles (NPs)—can be problematic during the processes associated with petrochemical refining (*1*). Iron-containing compounds, including iron particles, can lead to corrosion of refinery equipment, adversely affecting the petroleum value chain (*2*).

In the semiconductor industry, Fe NPs can be even more problematic, leading to cone defects on the surface of wafers, which cause short circuits and device failure (*3*). Therefore, analysts in these industries must have access to reliable techniques that can determine the dissolved metals and NP content of hydrocarbon matrices.

Single particle inductively coupled plasma mass spectrometry (spICP-MS) is increasingly used to study NPs. However, most studies published so far have focused on NPs in aqueous sample matrices, with relatively few reports on organic matrices (*4*). To help analysts achieve good quality data for the analysis of NPs in hydrocarbon matrices, solvent compatible reference nanomaterials (RMs) are needed to validate new methods. Due to a lack of suitable RMs, the authors worked with nanoComposix Inc (San Diego, CA USA) to develop new NP RMs that are stable in organic solvents. Two polystyrene-coated gold (Au) NP RMs in toluene, and an alkylsilane-modified, silica-shelled iron oxide (Fe_3O_4) NP RM in *o*-xylene were synthesized (*5, 6*). Both spICP-MS and transmission electron microscopy (TEM) were integral to developing and characterizing the NP standard materials.

In spICP-MS analysis, the ICP-MS acquires data using a fast time resolved analysis (TRA) acquisition mode. This fast acquisition mode allows the ICP-MS to measure the signal generated by each NP as it passes through the plasma. The high sensitivity and low background noise of Agilent ICP-MS instruments enable the signals generated from individual NPs to be distinguished from the background. The intensity of the NP signal peak is proportional to the size of the particle and the concentration (mass fraction) of the analyte element within the particle. And the frequency of the individual NP signals is directly proportional to the number of NPs in the sample. These measurements allow dedicated NP software to fully characterize NPs, from a single ICP-MS measurement. spICP-MS provides data on particle number, concentration, size, and the dissolved element concentration, while imaging methods, such as TEM, are useful for detection, shape, and size determinations. Unlike spICP-MS, TEM data is not quantitative or element specific.

In this study, the spICP-MS acquisition mode of the Agilent 7900 ICP-MS was used with TEM to characterize the synthesized Au and Fe NP RMs from nanoComposix. Single Nanoparticle Application Module of Agilent ICP-MS MassHunter software was used to simplify method setup, acquisition, calibration, and data reporting. spICP-MS was also used to measure the natural Fe NP content of NIST crude oil standard reference material (SRM) and a NIST residual fuel oil SRM.

Experimental

Element standards: determination of elemental response factor

Standards were prepared for Au using sulfur-free gold (1000 mg/kg) in hydrocarbon oil (LGC Standards, VHG Labs, Inc. Manchester, NH, USA) and for Fe using S-21 (1 mg/kg, Conostan, Quebec, Canada). The standards were diluted in *o*-xylene (Fisher Scientific, Fair Lawn, NJ, USA) to a concentration of 10 ng/g for Au and Fe. The standards were used to measure the elemental response factor. For the Single Nanoparticle Application Module software to convert the raw NP signal to particle size, the elemental response factor must be determined by ICP-MS. The sensitivity of soluble Au and Fe in the respective standards was around 12,500 cps/ng/g for Au and about 5000 cps/ng/g for Fe based on runs carried out over several days.

NP reference materials: determination of nebulization efficiency

Gold nanospheres with nominal diameters of 40 and 100 nm were developed and supplied by nanoComposix. To prepare Au nanospheres that were compatible with nonpolar solvents, the NP surface was functionalized with a 50 kDa thiol-terminated polystyrene ligand (Polymer Source, Montreal, Canada). The particles were characterized by TEM and UV–visible spectroscopy, and ICP-MS was used to determine the gold mass concentration (*6*).

The gold nanosphere RM in toluene with a nominal particle size of 100 nm was used to measure the nebulization efficiency of the 7900 ICP-MS. The Au NP standard was sonicated for 5–10 seconds and diluted in *o*-xylene to approximately 2 ng/g. The nebulization efficiency is the ratio of the amount of sample transported to the ICP, divided by the amount of sample introduced through the nebulizer. 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 and therefore size (*8*). The nebulization efficiency (using the "calculated by size" option in the ICP-MS MassHunter software) was found to be approximately 0.05 (5%).

Iron oxide nanoparticle clusters with a 60–70 nm diameter, coated with uniform silica shells, and dispersed in *o*-xylene were also synthesized at nanoComposix. So that the NPs dispersed in nonpolar solvents, the surface was modified using n-octadecylsilane.

Samples and sample preparation

NIST 2717a sulfur in residual fuel oil and NIST 8505 vanadium in crude oil SRMs (Gaithersburg, MD, USA) were used as samples. The samples were diluted 1:10 in *o*-xylene.

Instrumentation

A 7900 ICP-MS was used for all measurements. The instrument was equipped with the standard glass concentric nebulizer, quartz spray chamber, a quartz torch with a small internal diameter (1.0 mm) injector, and platinum sampling and skimmer cones. Oxygen was added to the carrier gas flow to prevent carbon from the organic matrix depositing on the cones. Samples were introduced directly into the ICP-MS via the peristaltic pump and solvent-resistant tubing (i.d. 0.89 mm). To remove the ArO polyatomic ion interference on ^{56}Fe by kinetic energy discrimination (KED), the ORS^4 collision/reaction cell of the 7900 was used in helium collision mode (*7*). If H_2 cell gas (optional) is used, a better MDL for Fe can be obtained, as H_2 eliminates ArO even more effectively than He. The fast TRA mode of the 7900 ICP-MS allows single element acquisition at a sampling rate of 100 µs (10,000 measurements per second). No settling time is needed between measurements.

Analyses were performed using the Single Nanoparticle Application Module of the Agilent ICP-MS MassHunter software. ICP-MS MassHunter guides the user through the entire setup process and automatically provides or calculates the required method parameters such as elemental response factor and nebulization efficiency. Instrument operating parameters are given in Table 1.

Table 1. Optimized Agilent 7900 ICP-MS parameters used for spICP-MS analysis of Fe_3O_4 NPs in NIST crude oil and residual fuel SRMs.

Parameter	Value
RF Power (W)	1550
Nebulizer Gas (L/min)	0.45
Sampling Depth (mm)	8
Spray Chamber Temp (°C)	–2
Option Gas: O_2	10% or 0.1 L/min
Dilution Gas (L/min)	0.1
Helium Cell Gas (mL/min)	3.7
Dwell Time (ms)	0.1
Monitored Mass for Fe (*m/z*)	56

Results and discussion

NP reference material analysis

The Au NP RM in toluene containing 40 nm sized particles was measured using the 7900 spICP-MS method. The Au RM was sonicated and diluted in *o*-xylene. The measured particle sizes were within ±10% of the expected values (Table 2), confirming the accuracy of the method for the characterization of Au NPs in a hydrocarbon matrix.

Table 2. Particle size results for two nanoComposix Au NP RMs analyzed by spICP-MS, n=4.

Sample (Nominal Size)	TEM Result* (nm)	Median Size (nm)	Most Frequent Size (nm)	Mean Size (nm)
Au (40 nm)	42	44.1 ± 0.1	45.5 ± 1.0	44.2 ± 0.2
Au (100 nm)	103	101.5 ± 1.3	104.5 ± 14.8	102.6 ± 0.7

**Value provided by nanoComposix*

The Fe_3O_4 core diameter of the synthesized silica shell NPs was determined to be 63 ± 6 nm by TEM and 61.1 ± 4.5 nm (n = 36) by spICP-MS, demonstrating good agreement between the methods (*6*). Figure 1 shows a 60 s TRA scan at *m/z* 56 of the silica shelled Fe_3O_4 NP RM that had been diluted in *o*-xylene and sonicated before analysis. The Single Nanoparticle Application software reported a total of 1050 particles for the 60 s TRA scan. The signals generated from the Fe NPs were clearly separated from the background signals, as shown by the zoomed in section of the time scan. The Single Nanoparticle Application Module software automatically set the particle threshold at 55.5 nm, as indicated by the red line in the signal distribution plot. More information on the method development and stability of the solutions can be found elsewhere (*6*).

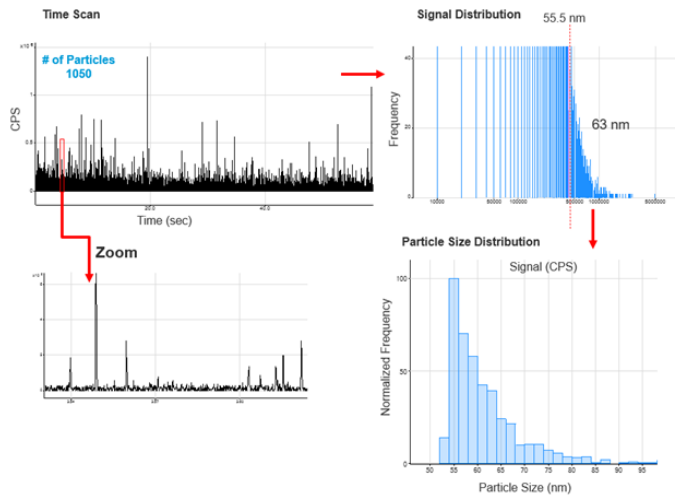

Figure 1. TRA scan of silica-shelled Fe_3O_4 NPs (top left), with a zoomed in region (bottom left). Signal distribution (top right), leading to the corresponding particle size distribution histogram (bottom right).

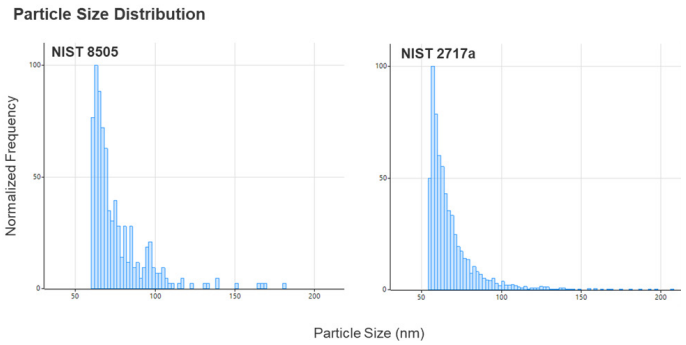

Figure 2. spICP-MS particle size distribution results for NIST 8505 crude oil (left) and NIST 2717a residual fuel (right). Number of Fe particles in crude oil SRM: 1416; median size: 69 nm; most frequent size: 64 nm; mean size: 77 nm. Number of Fe particles in residual fuel SRM: 1260; median size: 63 nm; most frequent size: 58 nm; mean size: 68 nm.

Analysis of Fe NPs in petrochemical SRMs

To test the spICP-MS method for the characterization of Fe NPs in a more complex petroleum matrix than *o*-xylene, NIST 8505 crude oil and NIST 2717a residual fuel oil SRMs were analyzed. The certified concentration for Fe in the 2717a SRM ranges from 21.73 to 28.16 mg/kg depending on the sample preparation method and detection technique (*9*). While there is no reported value for Fe in the 8505 SRM, it has often been analyzed by the authors as a quality control sample for an ICP-OES test method following direct dilution. The concentration is below 20 mg/kg. Based on the total Fe concentrations, the SRMs were diluted between 40,000 and 50,000 times with *o*-xylene before analysis by spICP-MS.

Figure 2 shows the spICP-MS results. The mean particle size in the crude oil SRM was 77 nm, which was within the range of 30 to 92 nm measured by TEM. The mean particle size in the residual fuel oil SRM was 68 nm, which was also within the range of 11 to 263 nm measured by TEM.

Conclusion

Hydrocarbon-stable NP reference material and standard materials are critical to the advancement of single particle ICP-MS methods for the characterization of NPs in organic matrices. RMs are important for method validation and proficiency testing of petroleum products, as well as for many other applications.

The Agilent 7900 ICP-MS operating in spICP-MS mode was used as a complimentary technique to TEM to characterize two Au NP RMs in toluene and an Fe_3O_4 NP RM in *o*-xylene. Method development was simplified using the single particle application software module of ICP-MS MassHunter. There was good agreement between the spICP-MS and TEM results for the particle sizes of the Au and Fe_3O_4 NP RMs, providing confidence in the method and materials. The spICP-MS method was also successful in determining the size of naturally occurring Fe NPs in crude oil and residual fuel SRMs, within the range of the TEM data.

The study has shown that spICP-MS methodology can be applied to the measurement of NPs in complex hydrocarbon-based matrices of interest in petroleum refining, semiconductor, and other industries.

References

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Ordering information

Agilent 7900 ICP-MS

- Instrument mainframe and ICP-MS MassHunter workstation (G8403AA)
- Option gas line for O_2 addition (G5720A)
- Advanced Acquisition software (#102 or G5713A)

Consumables list

- Quartz torch with 1.0 mm i.d. injector (G3280-80081)
- Organic solvent sample introduction kit (G3280-60580)
- Easy-Fit Peristaltic pump tubing, 0.76 mm i.d. Solvaflex (5005-0026)
- Pt sampling cone (G3280-67036)
- Pt skimmer cone for x-lens (G8400-67201)

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