

ICP - Mass Spectrometry

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Iron Nanoparticles by SP-ICP-MS: Overcoming Spectral Interferences Using Universal Cell Technology

Introduction

With the increasing interest in nanoparticles, various ways of detecting and measuring them are being used. One of the most

promising techniques for analyzing metallic nanoparticles is inductively coupled plasma mass spectrometry (ICP-MS) run in single particle mode (SP-ICP-MS). Due to its sensitivity, flexibility, and analysis speed, ICP-MS is an ideal technique to detect and measure nanoparticles since it can determine a number of nanoparticle characteristics: inorganic composition, concentration, size, size distribution, and agglomeration.

One of the challenges with ICP-MS is overcoming interferences which can compromise results. However, this has not been an issue with most SP-ICP-MS work done to date since very few matrix-based interferences exist, and most of the nanoparticles examined thus far do not suffer from common spectral interferences. For example, gold and silver nanoparticles have many industrial applications and neither suffers from common interferences. Also, most nanoparticles are present in simple matrices which will not produce interferences.

As the field of nanotechnology is expanding, the analytical requirements are increasing, particularly, the need to measure nanoparticles containing elements which have common interferences, such as titanium, iron or silicon. As an example, zero-valent iron (ZVI) nanoparticles are being widely used in environmental remediation projects since they have specific chemical properties and a considerable surface area, making them more effective than their larger counterparts. Because of their unique properties, ZVI nanoparticles have the potential to dechlorinate organic solvents, transform fertilizer run-off to less harmful compounds, detoxify pesticides, and immobilize metals. However, in order to monitor the ZVI particles, iron must be detected, which can pose a challenge for ICP-MS because of the presence of plasma-based interferences, most notably ArO^+ which occurs at the same mass (56) as the most abundant iron isotope ($^{56}\text{Fe}^+$ is 91.72% abundant). The most effective way to remove this interference on iron is with Reaction mode ICP-MS, using ammonia as a reaction gas.

To date, most published SP-ICP-MS work has focused on nanoparticles which do not have interferences, so Reaction mode SP-ICP-MS has not been employed extensively. This work will focus on demonstrating the ability of NexION's Universal Cell Technology to measure nanoparticles in Reaction mode SP-ICP-MS.

Experimental

All analyses were performed on a NexION[®] SP-ICP-MS (PerkinElmer Inc., Shelton, CT USA); the operating conditions are given in Table 1. Gold and iron nanoparticles were analyzed and prepared by diluting standards in deionized water. Gold was measured at mass 197 and iron at mass 56.

Results and Discussion

Since gold nanoparticles have been well characterized, these were first run in Standard mode to establish baseline performance. To evaluate the effect of adding a reaction gas to the ICP-MS during SP-ICP-MS analysis, the same solution was then run in Reaction mode. This is possible since gold does not react with ammonia. Figure 1 shows the SP-ICP-MS traces of 100 nm gold particles run in both Standard and Reaction modes. Note that both traces look similar, strongly indicating that Reaction mode does not alter the ability to measure nanoparticles. This is confirmed when the actual number of gold particles detected in both modes is compared, as shown in Table 2. This data indicates that a similar number of particles are counted in both modes, showing that the use of Reaction mode is not biasing the measurement of particle events.

Table 1: NexION SP-ICP-MS Conditions.

Parameter	Condition
Nebulizer	Glass Concentric
Sample Uptake Rate	250 $\mu\text{L}/\text{min}$
Spray Chamber	Glass Cyclonic
RF Power	1600 W
Dwell Time	100 μs
Total Analysis Time	60 s
Reaction Gas	NH_3 at 0.3 mL/min
RPq	0.45

Table 2: Number of 100 nm Au Particles Detected in Standard and Reaction Modes.

Replicate	Standard Mode	Reaction Mode
1	825	858
2	805	848
3	841	905
Average	824	870
RSD	2%	3%

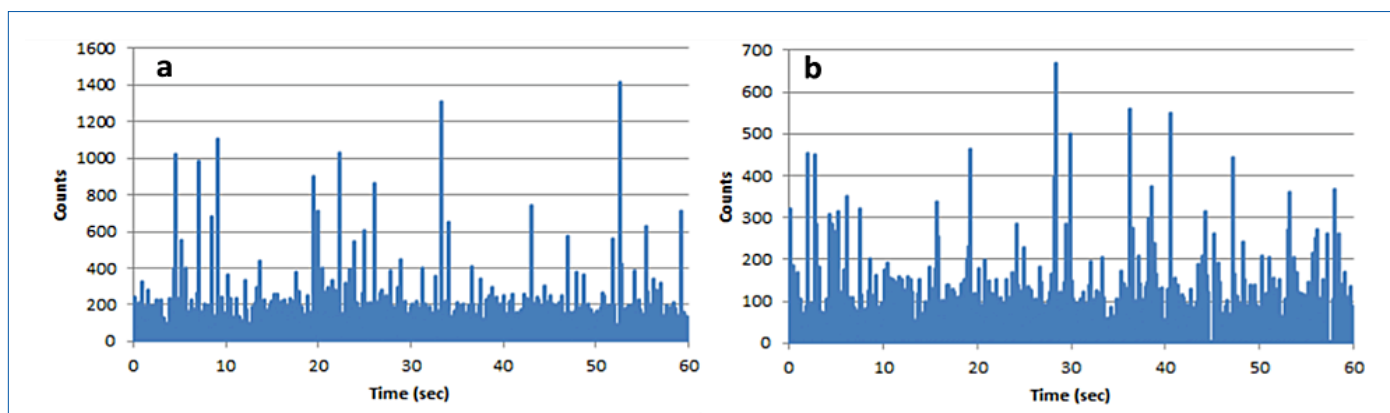


Figure 1: SP-ICP-MS traces of 100 nm gold particles in both Reaction (a) and Standard (b) modes.

Due to the significant background that masks the iron nanoparticle events at $^{56}\text{Fe}^+$, the same experiment cannot be completed for iron.

Next, a solution of 60 nm iron (III) oxide (Fe_2O_3) nanoparticles was measured in Reaction mode; the results are shown in Figure 2. The similarity of this trace compared to the gold traces in Figure 1a indicates that iron nanoparticles are being

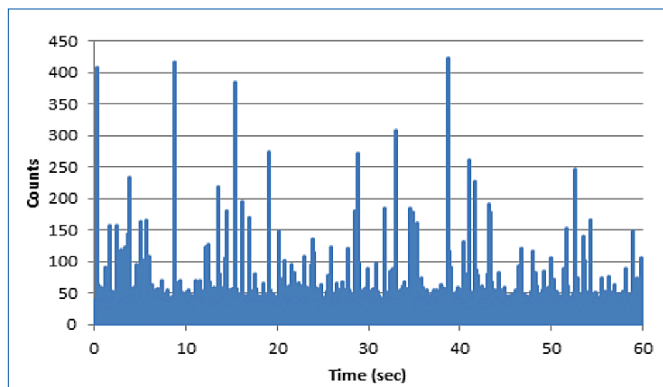


Figure 2: SP-ICP-MS trace of 60 nm iron oxide particles in Reaction mode.

seen in Reaction mode. Although Collision mode is also capable of removing interferences, it cannot adequately remove the ArO^+ interference on $^{56}\text{Fe}^+$ without significantly reducing instrument sensitivity, meaning that nanoparticle-size detection limit will be reduced. Using any of the less-abundant iron isotopes in Collision mode is possible, but their low abundance means that the iron nanoparticles would not be seen. Therefore, using ammonia in Reaction mode and measuring iron at mass 56 is the best way to accurately measure iron nanoparticles due to the large signal-to-background ratio.

Conclusion

This work demonstrates the ability of the NexION SP-ICP-MS to measure iron nanoparticles in Reaction mode. Because iron suffers from plasma-based interferences, the use of Reaction mode is necessary to detect iron nanoparticles and provides significant benefits over Collision mode. This work can be extended to other metal nanoparticles which suffer from interferences, such as titanium, chromium, zinc, or silicon.

Though detection limits, background equivalent concentrations and sensitivities may vary, the method presented in this work (e.g. isotope selection, gas choice, sample introduction materials and properties etc.) is transferable to any PerkinElmer NexION ICP-MS system which can match the cell gas and analyzer quadrupole requirements.