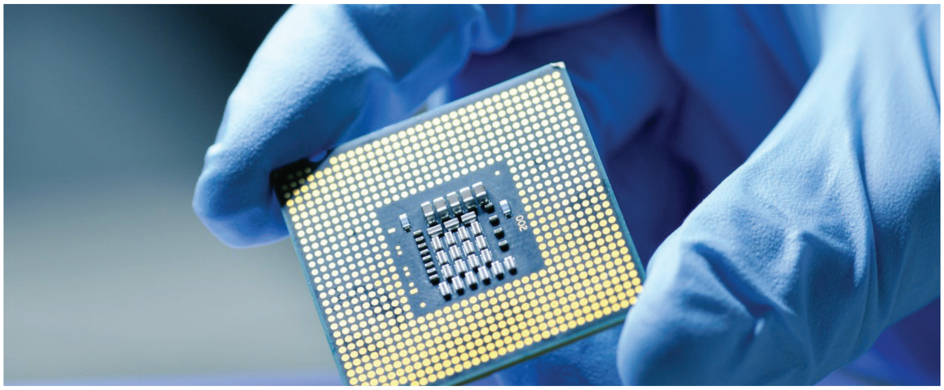
Application Note
Semiconductor

Multielement Nanoparticle Analysis of Semiconductor Process Chemicals Using spICP-QQQ

Characterization of Ag, Fe_3O_4, Al_2O_3, Au, and SiO_2 NPs in TMAH in a single analytical run



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Introduction

Technologies such as smartphones, cloud computing, the Internet of Things (IoT), and development of autonomous vehicles continue to drive demand for semiconductor products. To meet the requirements for higher integrated circuit (IC) performance and improved device yield, contamination must be controlled in the wafer substrate and on the surface of the device during fabrication. Given the nanometer scale of device features, there is a critical need to monitor metallic nanoparticles (NPs), as well as dissolved metals. Analysis of NPs present in bulk chemicals, silicon wafers, and cleaning bath solutions is important. If a particle is present between two metal lines, it may cause electrical shorting to occur, and surface defects can affect the growth of new layers on the silicon wafer. To fully investigate the cause/source of any particle contamination, multi-element analysis of NPs is necessary. ICP-MS is used increasingly to measure nanoparticles directly in sample solutions, using single particle inductively coupled plasma mass spectrometry (spICP-MS). With growing interest in characterizing NPs in various semiconductor samples, the technique is currently being evaluated within the industry.

The Single Nanoparticle Analysis software module available for ICP-MS MassHunter provides the method setup, analysis, and data interpretation tools for single particle ICP-MS analysis. spICP-MS has been used for a range of studies, from the analysis of gold NPs in simple matrices to TiO_2 NPs in complex samples (*1–4*). To facilitate multiple element NP analysis, Agilent has developed Rapid Multi-Element Nanoparticle Analysis software. The software can collect data sequentially for up to 16 elements in a single sample analysis, using optimum conditions for the measurement of each individual element (*5*, *6*). This function saves time and reduces the risk of sample contamination compared to conventional spICP-MS analysis, as data for multiple elements can be obtained with only one visit to the sample vial.

In this study, multiple element NPs including Ag, Fe_3O_4, Al_2O_3, Au, and SiO_2 were measured in semiconductor grade tetra methyl ammonium hydroxide (TMAH). TMAH is widely used as a basic solvent in the development of photoresist in the photolithography processing of ICs. Since TMAH comes into direct contact with the wafer surface, avoiding contamination of the chemical is critical. The Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) was used for the analysis because of its high sensitivity, low background, and effective interference removal capability.

Experimental

Sample reagents and NP standards

A 60 nm silver NP (Sigma Aldrich, P/N 730815) reference material (RM) was used to measure the nebulization efficiency, which is required for the calculation of particle size and particle concentration. The value was calculated using RM size and the sensitivity of an ionic Ag solution (Kanto Chemical, Japan).

Solutions containing 30 nm iron oxide (Fe_3O_4) NPs (Sigma Aldrich, P/N 747408), 30~60 nm aluminum oxide (Al_2O_3) NPs (Sigma Aldrich, P/N 642991), 200 nm silica (SiO_2) NPs (nanoComposix, P/N SISI200), and 60 nm gold NPs (NIST 8013) were used as NP standards. The sample comprised 25 wt% TMAH diluted to 1 wt % (25 times dilution) with de-ionized water (Organo, Japan).

Sample preparation

To verify the method for the measurement of multiple element NPs, the Ag RM and four NP standards were dispersed in 1 wt % TMAH using the preparation procedure shown in Figure 1. To prepare the intermediate solutions, 1% TMAH was used as the diluent for Al_2O_3 NPs, while DIW was used for the other NPs. Better dispersion was obtained for Al_2O_3 NPs using TMAH as the diluent.

Instrumentation

An Agilent 8900 ICP-QQQ (Semiconductor configuration) was used for all measurements. The sample introduction system comprised a quartz torch with a 1.5 mm i.d. injector, quartz spray chamber, a PFA concentric nebulizer, and platinum-tipped interface cones. The samples were self-aspirated using an Agilent I-AS integrated autosampler.

The 8900 ICP-QQQ was operated in MS/MS mode for all measurements, with Q1 and Q2 acting as unit mass filters. Q1 selects which elements enter the ORS^4 collision/reaction cell (CRC), allowing controlled reaction chemistry to take place in the cell when a reactive cell gas such as hydrogen (H_2) or ammonia (NH_3) is used. The 8900 can also operate in helium (He) collision mode, which is effective for the elimination of many common polyatomic ions using kinetic energy discrimination (KED).

NPs containing ^{28}Si, ^{197}Au, ^{27}Al, ^{56}Fe, or ^{107}Ag were measured in fast Time Resolved Analysis (fast TRA) mode. Fast TRA allows single element acquisition at a sampling rate of 100 µs (10,000 measurements per second) with no settling time between measurements (*7*). All elements were measured on-mass in MS/MS mode, with Q1 and Q2 set to the same mass. H_2 cell gas was used to eliminate any on-mass polyatomic interferences on ^{28}Si, such as $^{12}C^{16}O$ and $^{14}N_2$. NH_3

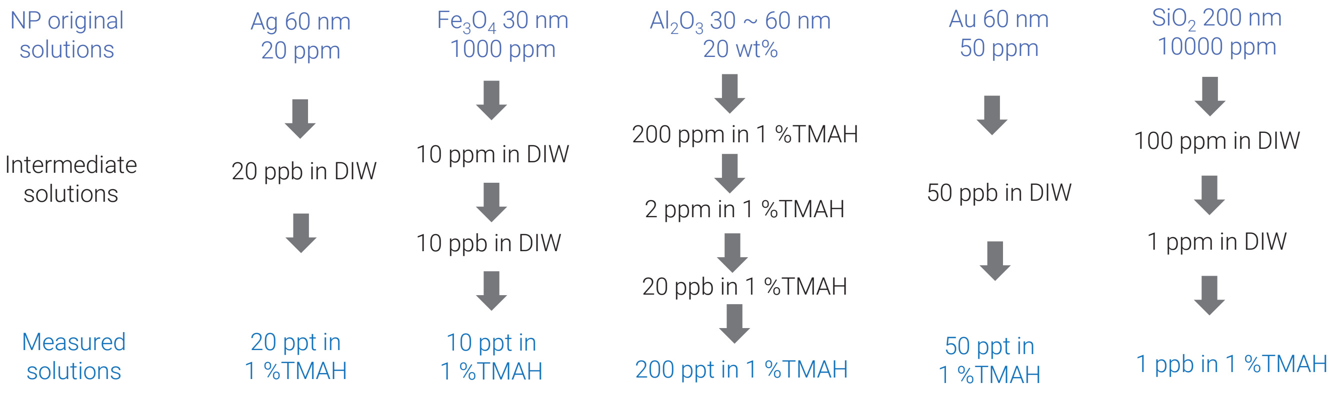

Figure 1. Sample preparation procedure.

mode was used to control the ArO and C_2O_2 interference on Fe at *m/z* 56 and the C_2H_3 and CNH interferences on Al at *m/z* 27. NH_3 was also used to eliminate any of potential interferences from the carbon matrix on Ag at *m/z* 107. Au is less susceptible to polyatomic interference so can be measured using He or no gas mode. During the analysis, ICP-MS MassHunter changes between each tune step sequentially, ensuring that optimum conditions are used for the measurement of each element.

Multiple element NP data acquisition and analysis were performed using the Rapid Multi-Element Nanoparticle Analysis mode of the Single Nanoparticle Application Module of ICP-MS MassHunter. In Rapid Multi-Element Nanoparticle Analysis mode, multi-element data is collected sequentially from a single sample acquisition, with the multi-element data being combined into a single data file. This approach saves time, as only one sample uptake and rinse time is required for all analytes. Data quality is likely to be improved, as the risk of sample contamination using a single analysis-approach is significantly reduced compared to performing multiple, separate analyses.

The operating conditions of the Agilent 8900 ICP-QQQ are detailed in Table 1.

Table 1. ICP-MS operating conditions.

Parameter	Value		
	H_2 mode	He mode	NH_3 mode
RF power (W)	1200		
Sampling depth (mm)	12		
Nebulizer gas (L/min)	0.70		
Makeup gas (L/min)	0.20		
Sample uptake rate (mL/min)	0.216 (self aspiration)		
Spray chamber temp. (°C)	2		
Extraction lens 1 (V)	−100		
Extraction lens 2 (V)	−10		
Octopole bias (V)	−18	−8	−8
Axial acceleration (V)	1	1	1.5
Energy discrimination (V)	3	3	−10
H_2 cell gas flow rate (mL/min)	6	0	0
He cell gas flow rate (mL/min)	0	2	1
NH_3* cell gas flow rate (mL/min)	0	0	3.0 (30 % of full scale)
Dwell time (µs)	100		
Masses monitored *(m/z)*	Si (Q1:28, Q2:28)	Au (Q1:197, Q2:197)	Al (Q1:27, Q2:27) Fe (Q1:56, Q2:56) Ag (Q1:107, Q2:107)
Data acquisition time (s/element)	30		

** 10% NH_3 balanced with 90% He*

Results and discussion

Nebulization efficiency measurement

To convert the signals measured using spICP-MS to the particle content of the original sample, it is necessary to calculate the nebulization efficiency. The nebulization efficiency is the ratio of the amount of analyte entering the plasma to the amount of analyte delivered to the nebulizer. Here, the nebulization efficiency was calculated by measuring a reference material (Ag NP) of known particle size. A 60 nm Ag NP RM dispersed in 1% TMAH and an ionic Ag solution (in 1% TMAH base) were measured. The Single Nanoparticle software automatically calculated the nebulization efficiency as 0.081 (8.1%). The signal distribution and the size distribution graphs of Ag NPs in 1% TMAH are shown in Figure 2.

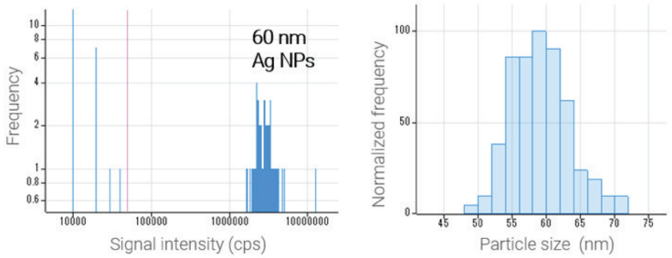

Figure 2. Signal distribution (left) and size distribution (right) of Ag NPs in 1% TMAH solution.

Analysis of various kinds of NPs in TMAH

Blank TMAH and TMAH solution spiked with Fe_3O_4, Al_2O_3, Au, or SiO_2 NPs were measured using the multi-element spICP-MS method. The time resolved signal, signal distribution, and size distribution for Fe_3O_4, Al_2O_3, Au, and SiO_2 NPs are shown in Figure 3.

The Rapid Multi-Element Nanoparticle Analysis software enabled multiple element NP data to be quickly collected. Less than six minutes were required for the measurement of all elements, which equates to a saving of 7 minutes compared to separate, single sample analyses. The time-saving per sample can be calculated using the following equation, which means that more time can be saved if more elements are measured.

Time saving per sample = (number of measured elements -1) × (sample uptake time + rinse time)

The improved Single Nanoparticle Application Module software automatically sets the signal baseline in the TRA data, which is shown in light blue in the time charts in Figure 3. The improved software also sets the particle threshold, which

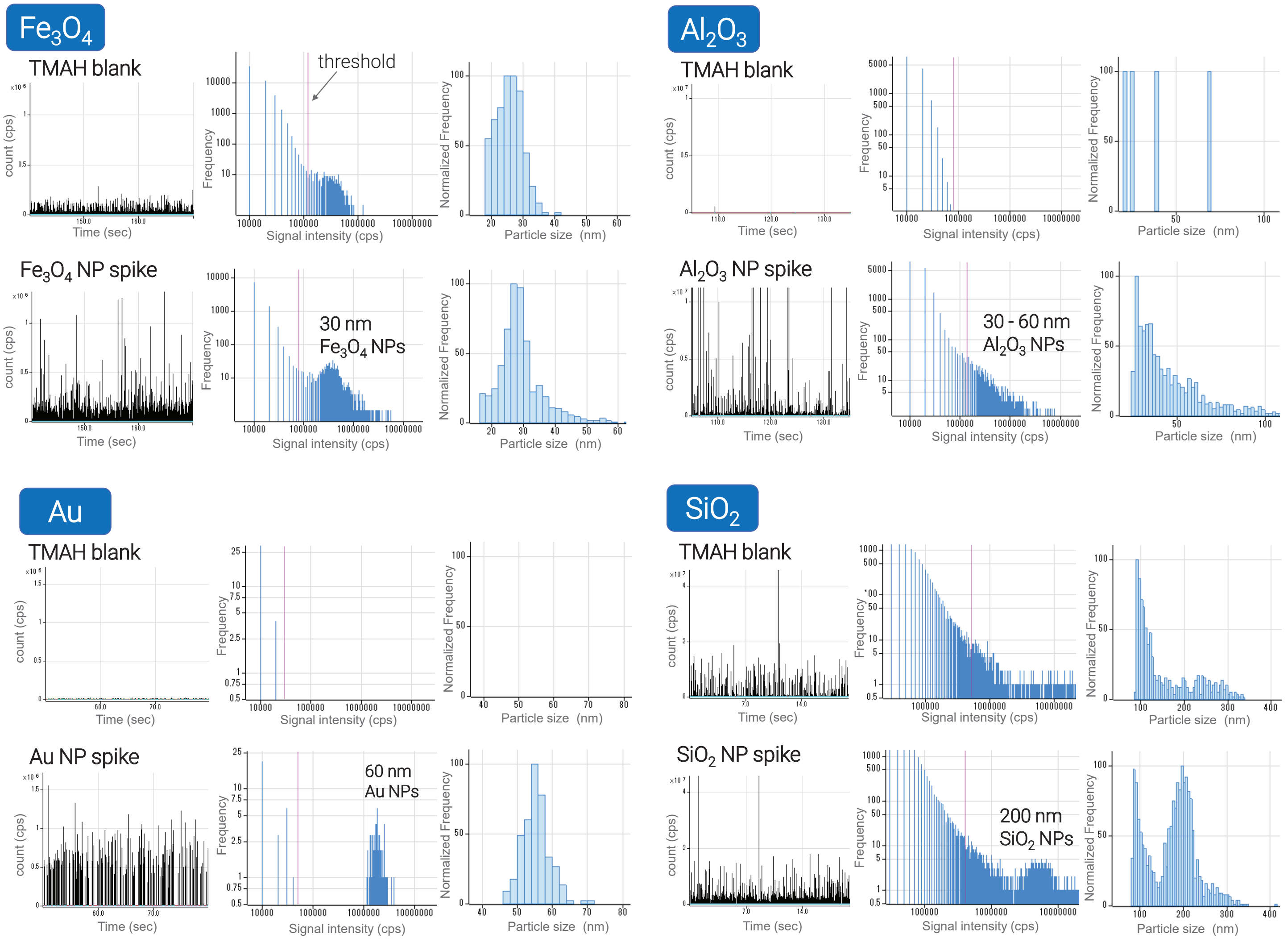

Figure 3. Time resolved signal, signal distribution, and size distribution graphs for Fe_3O_4, Al_2O_3, Au, and SiO_2 NPs. The upper graphs for each NP show the results from 1% TMAH without NP spike; the lower graphs show the results with NP spike.

separates particle-generated signals from the background or ionic signals. The particle threshold is shown by the vertical red/pink line in the signal distribution graphs in Figure 3.

The measured size and size distribution data for all four spiked NP samples agreed with the expected results (Figure 3). The results for Fe_3O_4 and SiO_2 NPs show that both NPs were present in the blank TMAH solution analyzed in this study, although not all TMAH solutions are likely to contain NPs.

Figure 4 summarizes the size data for multiple element NPs in 1% TMAH. The blue histograms show NPs present in the unspiked (original) TMAH solution. The green histograms show NPs present in the spiked TMAH solution. The results show that all five NPs were detected separately, even in the mixed NP TMAH solution. Using the multiple element spICP-MS method, small particles (e.g. 30 nm Fe_3O_4) can be clearly measured with good accuracy even in the presence of larger particles (e.g. 200 nm SiO_2).

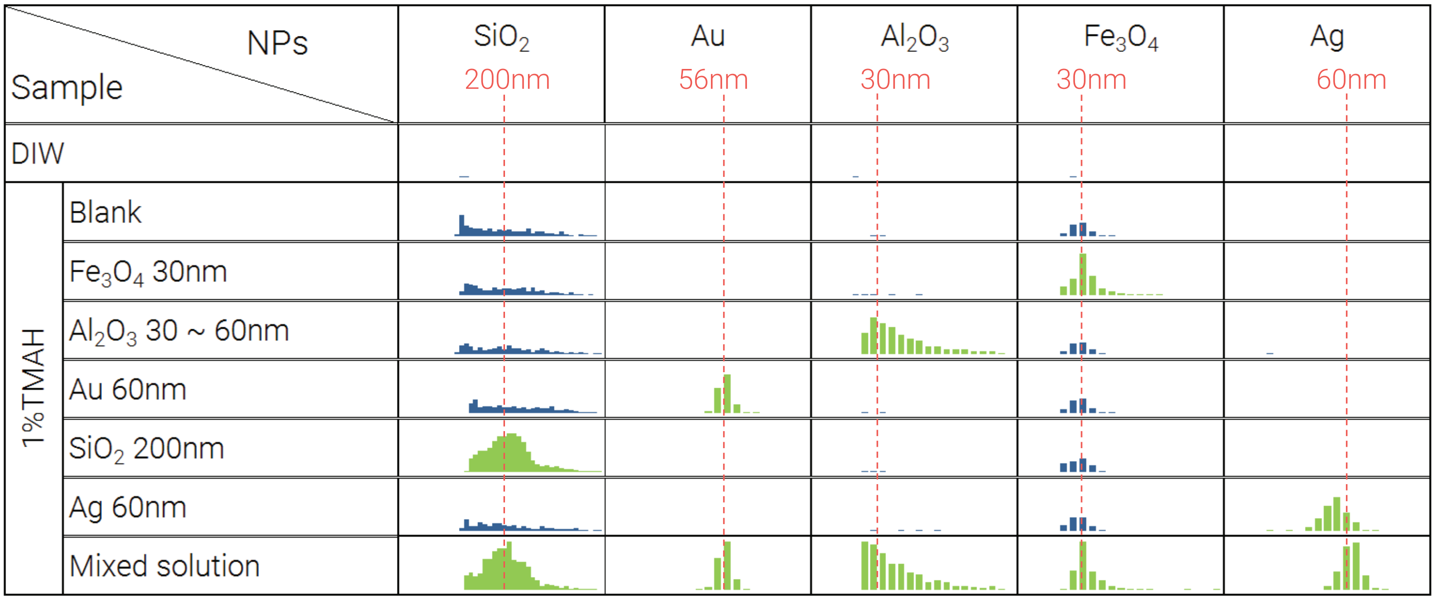

Figure 4. Size distribution overview for multiple element NPs in 1% TMAH. The results for the unspiked TMAH solution are shown in blue and the spiked TMAH solution results are shown in green.

Long-term stability test

Figure 5 shows the stability of particle concentration and particle size for five NPs in 1% TMAH over 10 hours. For Ag NPs, both the particle concentration and the size decreased over time, suggesting that Ag NPs are easily dissolved in 1% TMAH solution. For Fe_3O_4 NPs, the size was constant, but the particle concentration decreased over time. Rather than being dissolved in TMAH, Fe_3O_4 NPs are likely to settle or be adsorbed onto the surface of the sample container. Al_2O_3 and SiO_2 NPs were stable in terms of particle concentration and size over 10 hours. The size profile of the Au NPs remained constant over 10 hours, while the particle concentration remained broadly stable over 10 hours after a slight change during the first three hours.

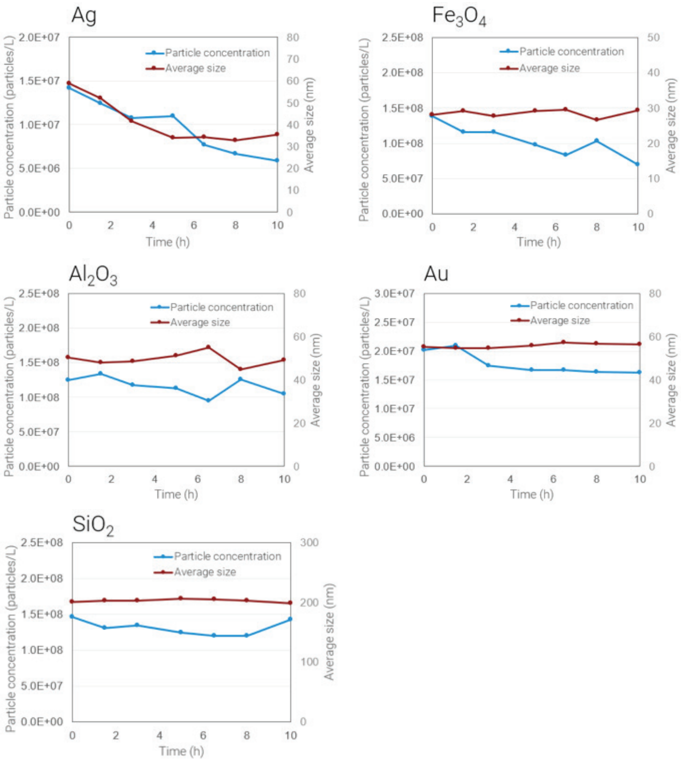

Figure 5. Long-term stability of NP solutions of Ag, Fe_3O_4, Al_2O_3, Au, and SiO_2. The blue line shows the particle concentration and the red line shows the average particle size.

Conclusion

Multiple element nanoparticles were determined and characterized in 1% TMAH using the Agilent 8900 ICP-QQQ operating in multi-element spICP-MS mode. The MS/MS method delivered the low background, high sensitivity, and interference control necessary for the analysis of multiple element NPs in semiconductor grade chemicals.

Using specially developed Rapid Multi-Element Nanoparticle Analysis software, multi-element data for Ag, Al_2O_3, Fe_3O_4, Au, and SiO_2 NPs were collected from a single sample acquisition and combined into a single table of results. The table provides comprehensive information about the nanoparticles containing each of the measured elements. The results showed that small particles such as 30 nm Fe_3O_4 NPs could be measured in solutions containing larger particles, such as 200 nm SiO_2 NPs. The particle size and particle concentration of Al_2O_3 and SiO_2 NPs were stable in 1% TMAH solution over 10 hours, while the particle concentration of Fe_3O_4 and Ag NPs decreased over time. The results suggest that Fe_3O_4 and Ag NPs in TMAH solutions should be measured as soon as they are prepared. While the particle size of Fe_3O_4 NPs remained stable in 1% TMAH, the variation in the concentration of NPs over time requires further investigation.

The study showed that samples containing nanoparticles composed of different and/or multiple elements can be determined quickly and accurately using spICP-MS. Compared to acquiring data separately for each NP, the Rapid Multi-Element Nanoparticle Analysis software simplifies the analytical method and shortens the sample run times by seven minutes. If more elements are measured, more time can be saved.

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