vitesse

Vitesse Note **NT08**

Influence of spectra accumulation speeds on multi elemental nanoparticle detection

Keywords:

- Sub millisecond speeds for saved spectra
- Precise particle identification
- High particle number concentrations
- Accurate nanoparticle data

Introduction

The analysis of small particles down to nanometer sizes has been a challenging undertaking over the past decades. With many tons of nanoparticles currently being produced and released into the environment annually and the abundance of nanoparticles from natural sources, the accurate identification and detection of particles is crucial. Whilst multiple techniques can be used for this purpose, single particle (SP)-ICP-MS has been an important one due to the sensitive detection, fast examination of large numbers of particles and low amount of sample preparation needed.

In recent years there have been improvements made to decrease the size detection limit of SP-ICP-MS methods by improving the sensitivity of the instruments. Furthermore, decreasing the acquisition times has improved the particle identification, especially in presence of ionic background signals in the samples. This has led to a reduced need for sample dilution and therefore quicker analyses and better statistics. All SP-ICP-MS on quadrupole or magnetic sector instruments to date has been using only one element as the transient signal from a particle is too short to reliably measure any more elements. The recent introduction of time-of-flight ICP-MS has made the detection of multiple elements in a single particle possible, and the Nu Vitesse combines the multielement capability of TOF with the sub-millisecond spectra accumulation times necessary for the best quality nanoparticle data. The detection of multiple elements has been shown to be valuable in the differentiation of man made and natural nanoparticles as well as the differentiation of particles based on composition. [1]

Herein the influence of the time taken to save each spectrum to disk, or dwell time as it is called in quadrupole and magnetic sector ICP-MS, whilst looking at single elemental nanoparticles will be discussed and then examined in detail through the multi element detection capabilities of the Vitesse.

Importance of fast dwell times in SP-ICP-MS

The capabilities of the Vitesse allow for a full mass spectrum acquisition of ~26 µs. After live spectral treatment using the acquisition hardware, the data can be stored to disk as accumulated spectra continuously at ~80 µs per spectrum. Since individual nanoparticle events introduced to the plasma only last a couple of milliseconds at most, fast dwell times of under 100 µs are required to acquire multiple datapoints in order to characterise a nanoparticle event. If the chosen dwell time is too long, individual nanoparticles can coincide in one dwell time leading to incorrect data as proven previously on quadrupole and magnetic sector ICP-MS. [2,3]

Figure 1 shows the transient signal acquired using a solution containing pure silver and pure gold nanoparticles. The raw data is shown in Figure 1a, acquired at 0.08 ms per spectrum. Figures 1B and 1C show the same data with spectra summed to 1 and 2 ms respectively. While the fast acquisition allows for an easy identification of the various pure nanoparticles, an identification in the millisecond-sampled data is impossible. For example, the particles at 4, 4.8 and 5.5 ms can easily be seen as 3 individual particles. When measured at 1 ms (B), 2 particles might be differentiated, one mostly gold nanoparticle and one mostly silver nanoparticle. When measuring at a dwell time of 2 ms only one particle is observed containing both silver and gold with a similar number of counts of each element.

In both millisecond dwell time cases incorrect data is obtained. The only way to reduce these issues would be to dilute the sample to reduce the particle number concentration. This would reduce the chance of coinciding events but would also require much longer sample measurement times to detect enough particles to obtain statistically robust data. Furthermore, reducing the amount of sample preparation is always desirable.

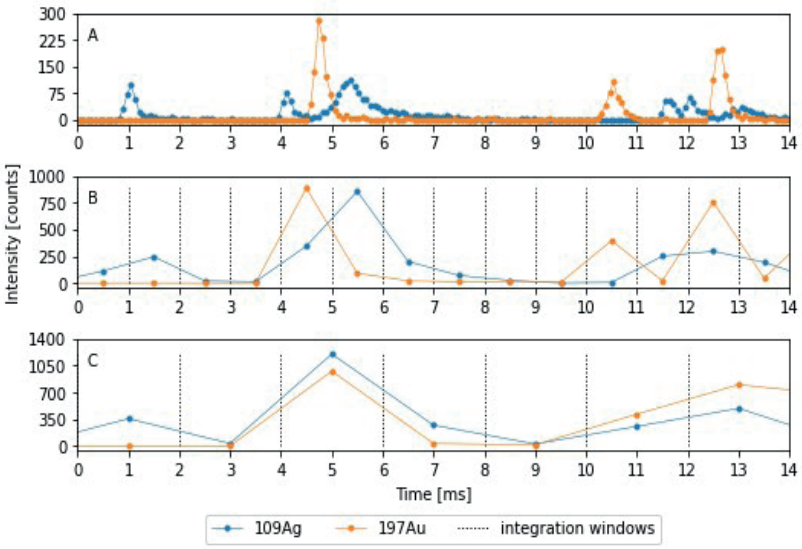

Figure 1: Transient signals of pure silver and pure gold nanoparticles introduced into the ICP-MS. The raw data acquired at 0.08 ms per spectrum is shown in A. B and C show the same data summed to 1 and 2 ms respectively.

High throughput analysis

Due to the nature of nanoparticles, they can be highly diverse and varying in composition and size. Therefore, it is crucial to collect data for a large number of individual particles with which statistically robust results can be obtained. Hence, the analysis time required is dependent on the number concentration of nanoparticles in the sample solution and the ability to differentiate as many particles as possible in the shortest time. As shown in the previous section, particles can only be differentiated effectively if fast dwell times are used.

For all measurements discussed below, a mixture of pure gold and pure silver nanoparticles with a size of 100 nm was used. This solution was diluted to various number concentrations to observe the effects on the detection of particles and varying dwell times. When increasing the particle number concentration in the solution there should be a proportionate increase in the detected particles and therefore a linear relationship should be expected until all individual particles cannot be differentiated anymore. Data for all samples were acquired for 1 minute and their transient signals were recorded at 0.08, 1 and 2 ms.

The number of particles detected at various particle number concentrations for both silver and gold nanoparticles at 0.08, 1 and 2 millisecond spectra accumulation times are shown in Figure 2. The above-mentioned near-linear relationship can only be seen for the fastest dwell times. For slower dwell times of 1 and 2 milliseconds the number of detected particles very quickly drops due to the amount of coinciding events in one dwell time period. The extrapolated particles per second are calculated based on the lowest concentration of nanoparticles since this solution is most likely to give the lowest number of coinciding particles. This value along with the relative concentration of the solution results in the extrapolated particles per second.

At a concentration of 50 particles per second a difference in the number of detected gold particles can already be observed for the longest dwell time while the number of particles detected at 0.08 and 1 ms is still very similar. At a slightly higher particle concentration a large difference can already be seen in these two spectra accumulation times. Therefore 50 particles per second seems to be the highest reliably measurable number concentration at 1 ms dwell times while the limit at 2 ms dwell times is lower still. At 0.08 ms dwell times a good linear relationship can be observed up to over 200 particles per second after which there is a slight drop in the number of detected particles compared to the behaviour at longer dwell times. This allows for the same number of particles to be analysed in a fraction of the time when using fast spectral accumulation rates.

vitesse

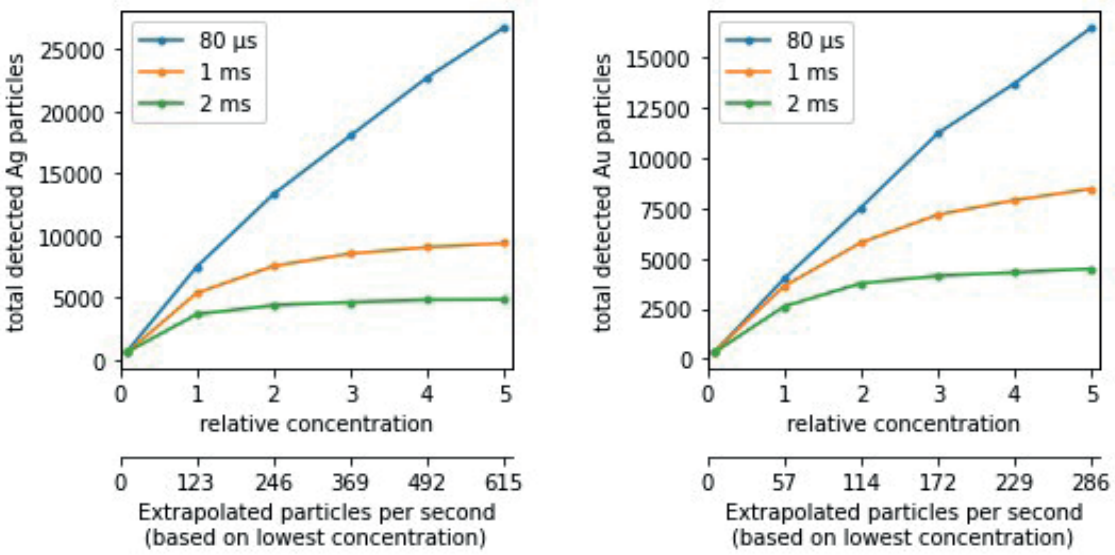

Figure 2: Total number of detected particles at varying number concentrations and acquisitions times. The left shows the detected silver particles while the right shows gold particles. The extrapolated particles per second are calculated using the relative concentration and the particles detected in the lowest concentration solution.

Accurate mono-elemental nanoparticle results

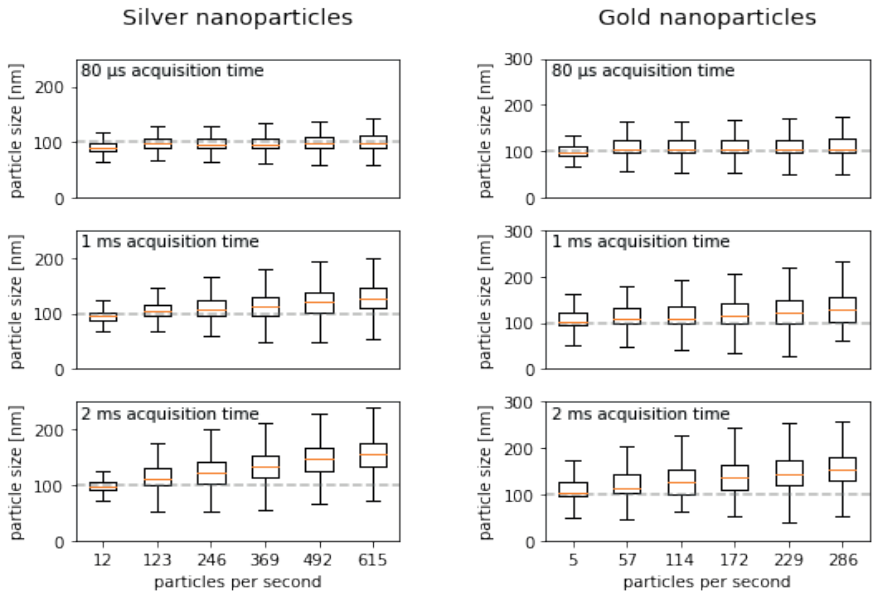

Figure 3: Boxplots showing the detected particle sizes for 100 nm gold and silver nanoparticles at varying concentrations and spectral accumulation times. The results for silver nanoparticles are shown in the left while gold nanoparticle results are shown on the right.

Two important measures obtained through nanoparticle analysis are the size and distribution of sizes in a nanoparticle population. Both can be represented as boxplots in which both the mean and standard deviation are shown for the entire population of particle events. As shown in the last section, fast dwell times are essential to differentiate individual particles and examine solutions with high particle number concentrations. Additionally, the mean size and distributions of these nanoparticle solutions at various dwell times were examined. The results can be seen in Figure 3. For both gold and silver when using a 0.08 ms dwell time, the examined 100 nm nanoparticles are measured as the same sizes across all number concentration ranges. At longer dwell times the detected size and standard deviation of the measured size for the particles gets larger. This is due to the measurement of multiple nanoparticles within one spectral accumulation time leading to artificially larger detected signals. If the number of particles measured per second is not monitored when using millisecond dwell times, the resulting data can be incorrect for size, distribution and number concentration.

vitesse

Accurate mulit-elemental nanoparticle results

When measuring only one isotope, particle coincidences can only be estimated by observing the increase in detected particle size. The only way to reliably examine particle overlaps is to look at multiple elements. Since the examined solutions contained only pure silver and pure gold nanoparticles, no events should be found that contain both elements and therefore only particle coincidences will result in events which contain both elements. These results at various dwell times can be seen in Figure 4. For this figure par cles are considered to be coinciding if the detected counts of the minor elements are at least 10% as high as for the major element.

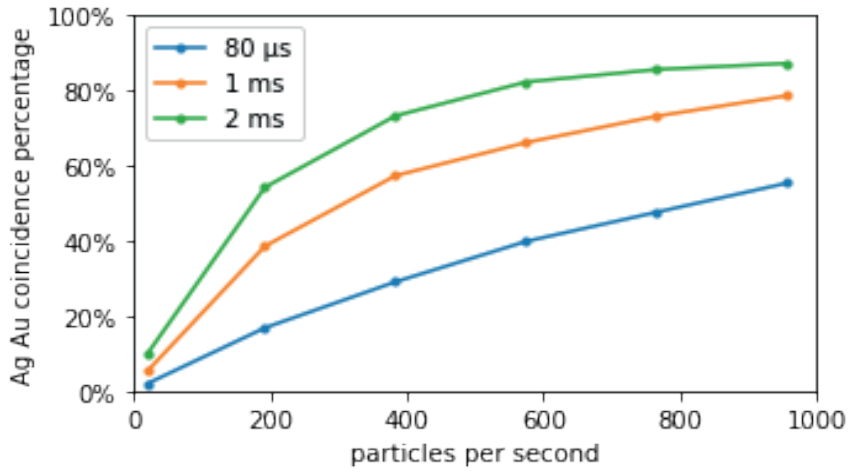

Figure 4: Percentage of particles which contain both silver and gold at various spectra accumulation times.

Even at low particle number concentrations the number of multi-element particles detected at 2 ms dwell times is already about 10% whereas at fast dwell times almost all detected particles are pure silver or gold. Moving to higher particle number concentrations shows a fast increase in the percentage of coinciding particles showing that the multi-elemental detection is significantly more reliable when using fast dwell times. Even at these fast dwell times the number of detected particles should be in the low hundreds of particles per second to maintain robust measurements.

Conclusion

Using SP-ICP-MS, the detection of metal and metalloid containing nanoparticles is possible, but for accurate and fast results the spectra accumulation times of individual data points must be faster than the particle event and optimally less than 0.1 ms. When using these fast dwell times, accurate data can be obtained even at high particle number concentrations reducing the total analysis time required to obtain meaningful data and the amount of sample preparation required. Using a time-of-flight ICP-MS, the composition of individual nanoparticles can be observed. Especially when examining multiple elements, fast dwell times become even more important to obtain accurate data since millisecond dwell times can lead to otherwise individual particle signals being detected at the same time giving false particle compositions as well as incorrect sizes which can lead to incorrect interpretation of the data.

(1) Azimzada et al.: Environ. Sci. Technol. 2021, 55, 14, 9836–9844
(2) Strenge and Engelhard: J. Anal. At. Spectrom., 2016, 31, 135-144
(3) Shaw and Donard: J. Anal. At. Spectrom., 2016,31, 1234-1242