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Nanoparticle Analysis Using Attom ES With 10^5 Hz Acquisition Rates

- **Nanoparticle analysis**
- **Dwell time between 10 Qs and 100 Qs**
- **Flexible peak location and integration**
- **Powerful data reduction capability Introduction**

The ICP-MS technique has promised to be a powerful analytical tool for the measurement of nanoparticles but has generally been found to be on the very edge of performance limitations for many applications. Aspirating an aerosol of nanoparticles creates transient signals of 100-400 µs in length which means that the commonly used millisecond data acquisition times for ICP-MS are not adequate. This has led some researchers to developing their own faster data acquisition hardware[(1)] but this not possible for most users.

Once data has been acquired, there are difficulties in reducing the data to manageable peak integrations. If the nanoparticles are not diluted sufficiently, it is possible to see two or more particle signals overlap. This means that any peak integration method which cannot readily distinguish nearby peaks will lead to errors or the sample will need to be diluted further and rerun.

An unfortunate outcome of using shorter dwell times is the reduced dynamic range that ICP-MS users have reported from their instrumentation (1, 2). With a 10 µs dwell, a single count is the equivalent of 100,000 cps when the upper ceiling of most ICP-MS is $5e^6$ cps, this limits the range to little more than one decade allowing for a minimum detectable peak being a few counts. As the diameter of a nanoparticle is related to the cube root of the mass or volume this means that the size dynamic range of current ICP-MS for nanoparticles is possibly only ~3-4.

Extending the range of both size and concentration would open up greater possibilities for the researcher in the field of nanoparticle analysis.

Data Acquisition

AttoM is able to acquire single ion data with dwell times as low as 10 µs continuously with no interruptions in the stream of data. The ability to daisy chain multiple methods together makes automation of collecting data with different conditions very easy. This can be modified to also run different analysis methods for different samples as required.

This makes collecting data for samples much simpler as a group of methods can be used that cover the full range of possible optimisations needed without having to pre-screen each sample and then decide which method to use. The data can then be imported into Nu Quant for further processing as a complete batch.

Data Reduction

Raw data files for single ion measurements can contain up to a million points and processing these to get integrated counts for each particle requires careful manipulation. A typical nanoparticle signal lasts a few hundred microseconds and when measuring at <100 µs dwell times, normal background signals for a blank equate to only one or two counts in the time that one particle might be measured (1 count in 500 µs equates to 2000 cps).

It would be possible now to set a fixed time window for a nanoparticle, starting with an initial count and then summing all counts after that for a fixed period. This is an effective method as long as particles are separated by a fixed time and all particles were of an expected width. This traditional method also requires the user to either generate a histogram for the particles or add a trigger value to discard all signals less than a certain value. Nu Quant uses a more sophisticated peak search and integration

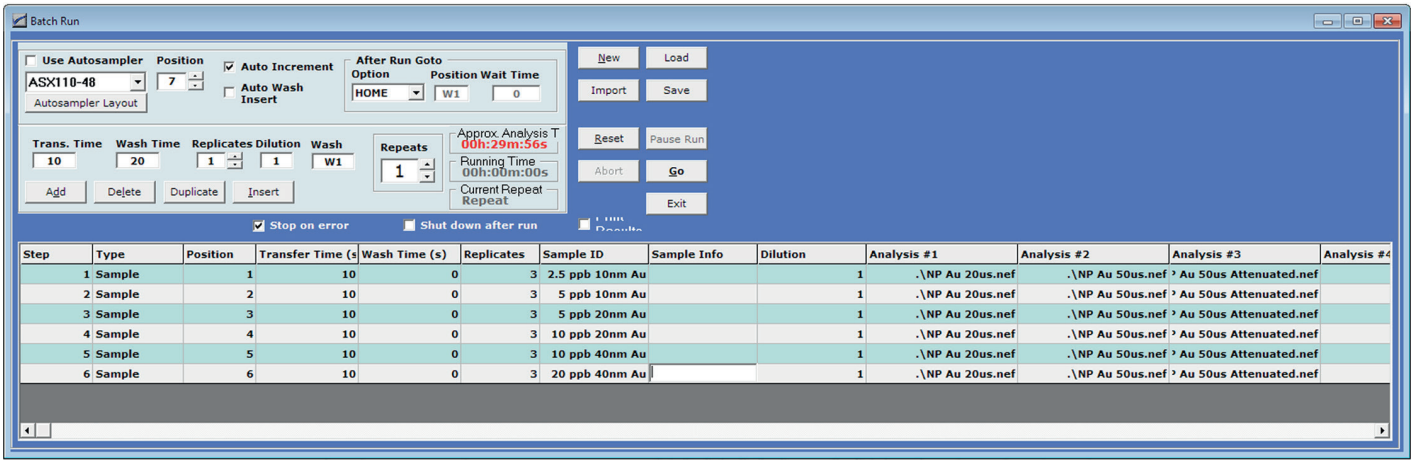

Figure 1: Showing the ability to acquire multiple methods linked together for each sample.

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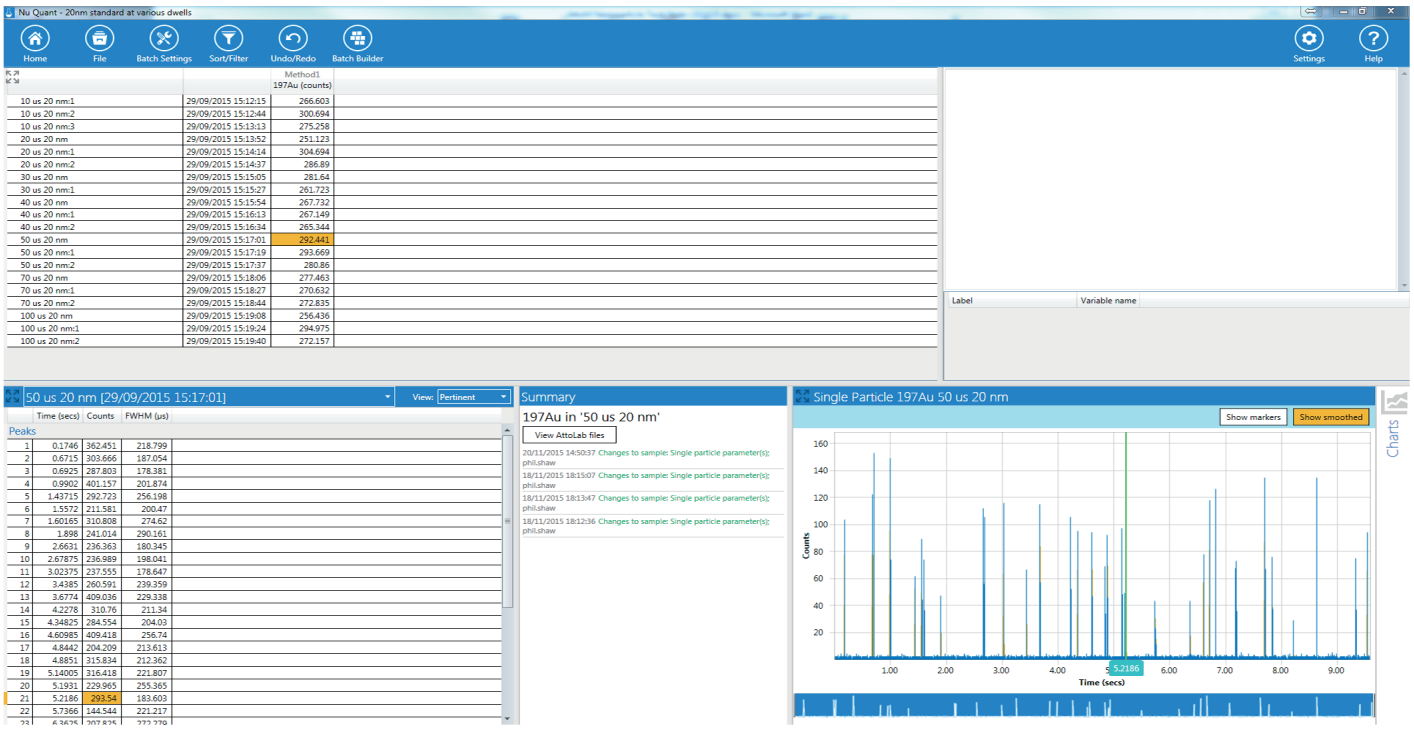

Figure 2: Showing how data can be acquired for multiple methods and multiple replicates automatically with batch acquisition. In this case, 7 different dwell times in triplicate during one sample introduction in approximately 7 minutes.

method which initially smooths the data and then looks for peak maxima and minima with criteria that allow different peak sizes, peak widths, partially merged peaks and continuous background signals to be distinguished easily.

Using a fixed window to integrate particle data does not easily manage a wide distribution of particle sizes (larger particles produce wider peaks) or variations in widths due to how the particle is broken down and ionised differently in different parts of the injector[2]. Nu Quant has the flexibility to manage a wide range of sizes and widths with the smooth and search method, the peak width for each peak is reported as the full width half maximum (FWHM) for each peak to aid peak evaluation.

To allow for wider peaks, traditional methods would set wider integration windows leading to higher dilutions being used to avoid particle signal coincidence. The Nu Quant peak search routine can even calculate when particle events are partially merged and report them separately. Nu Quant allows the user to choose a dwell time that gives the optimum signal to background without compromising the accuracy of the integrated signal for a given particle size.

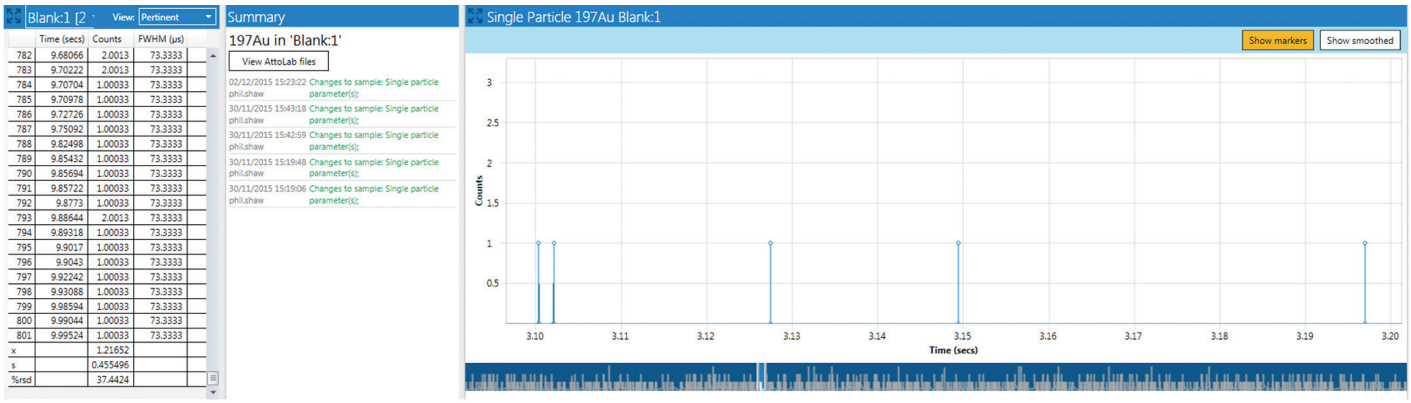

Figure 3: Typical data for a blank measured for gold at 20 µs dwell, 800 count events in 10 seconds at an average of 1.22 counts each equates to 97 cps.

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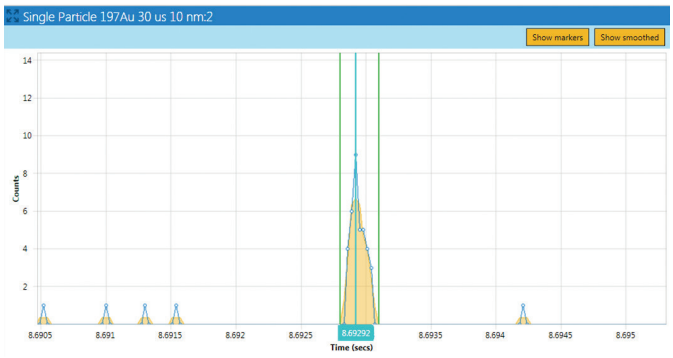

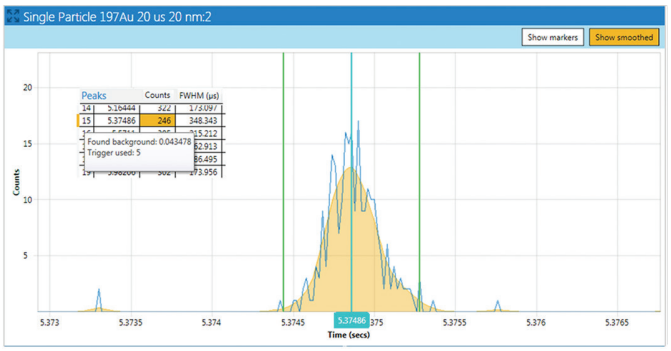

Figure 4: Shows how a 240 µs wide 10 nm Au particle peak acquired at 30 µs dwell is smoothed and easily distinguished from the background.

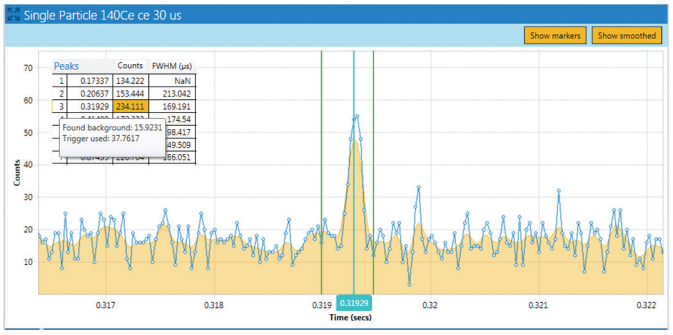

Figure 5: Shows how a CeO_2 particle (~20 µm) can be integrated with background correction using the smoothing technique. The ionic background of 15.9 counts in 30 µs equates to >500k cps.

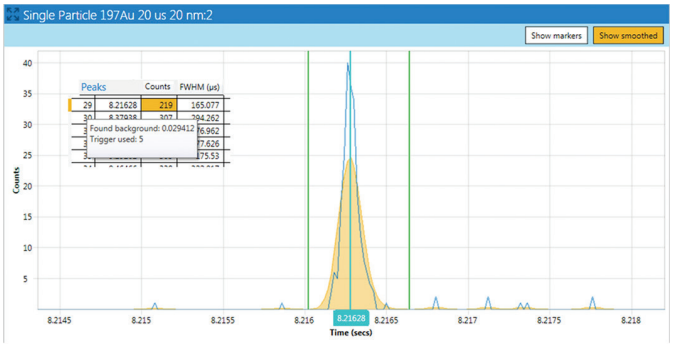

Figure 5a & 5b: Show two particles from the same 20 nm standard which produce similar integrated counts but have very different peak widths. Nu Quant deals with both situations using the some parameters.

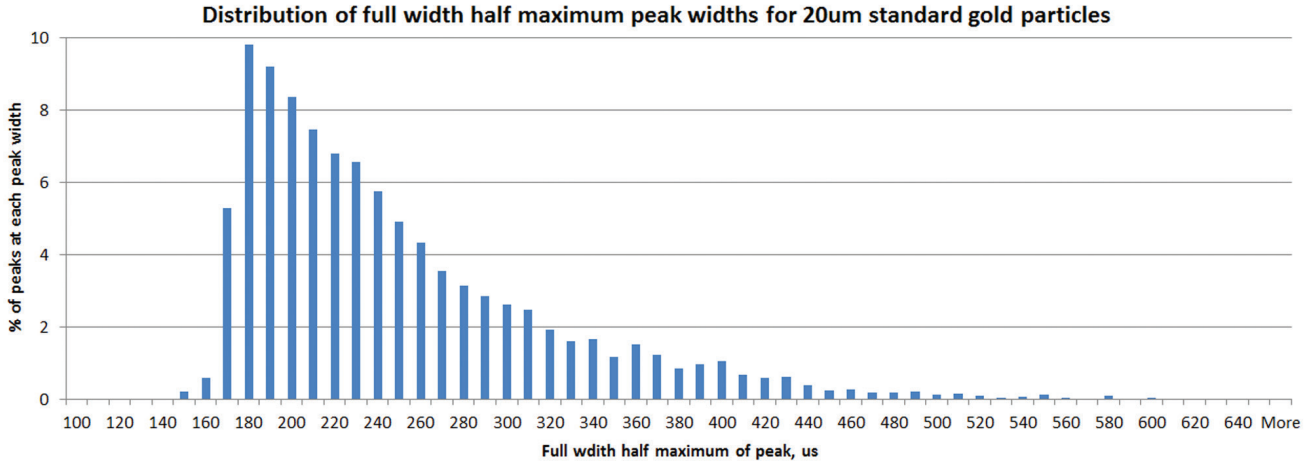

Figure 6: Creating a histogram of particle peak widths for the same 20 nm standard shows the importance of having a peak integration routine that accommodates a wide range of peak shapes.

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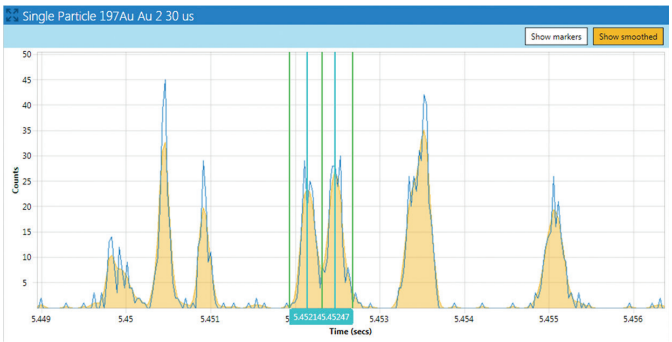

Figure 7: Showing the integration of two separate particles where the signal for the peaks is partially merged

Once the peaks have been integrated, Nu Quant can use the inbuilt Nu Instrument Calculations Editor (NICE) to calculate a range of information including particle size, particle mass and concentration. NICE Scripts and user guides are available from the Nu Instruments' Applications Team to calculate nanoparticle parameters and ionic content, using either known particle standards or counting efficiency calculations or a combination of both. These scripts can be used as provided or modified for specific requirements either by the user or with assistance from a Nu Instruments applications scientist. All raw data, processed peaks and NICE results can be exported as CSV files for use in other software packages.

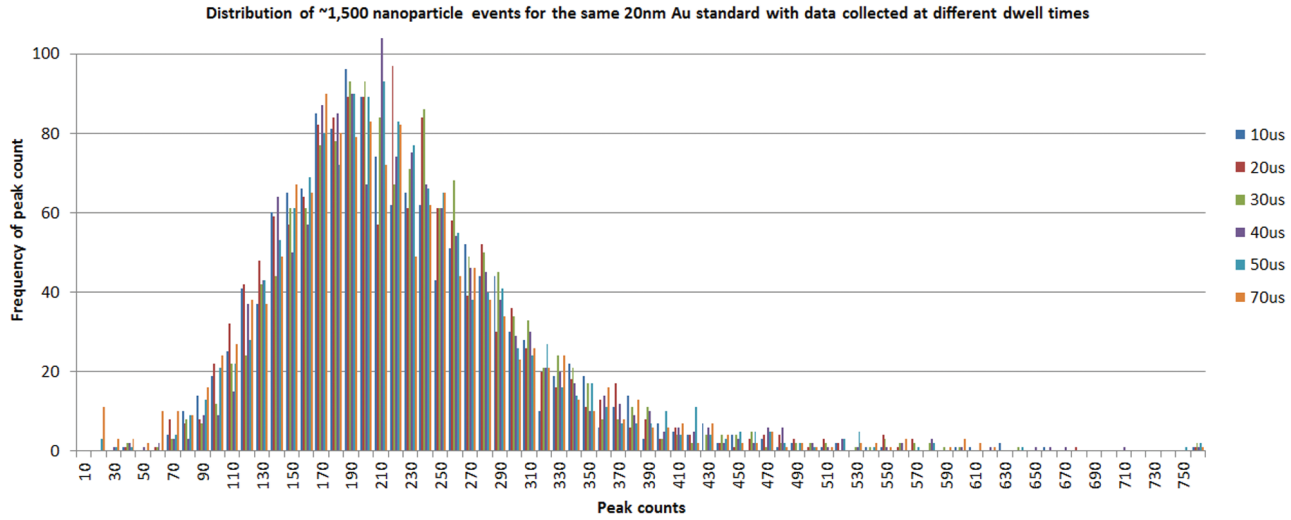

Figure 8: Shows that the particle count distribution is the some for all dwell times from 10 to 70 µs using the Nu Quant peak smooth and search routine.

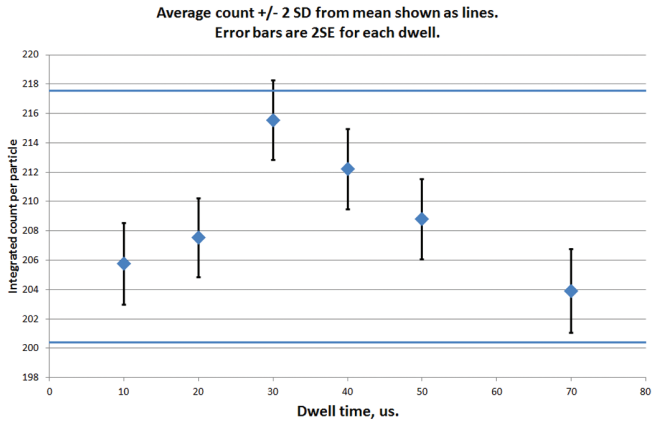

Figure 9: Shows that the variation in mean integrated counts for the same 20 nm standard with different dwell times varies by <±2.5%.

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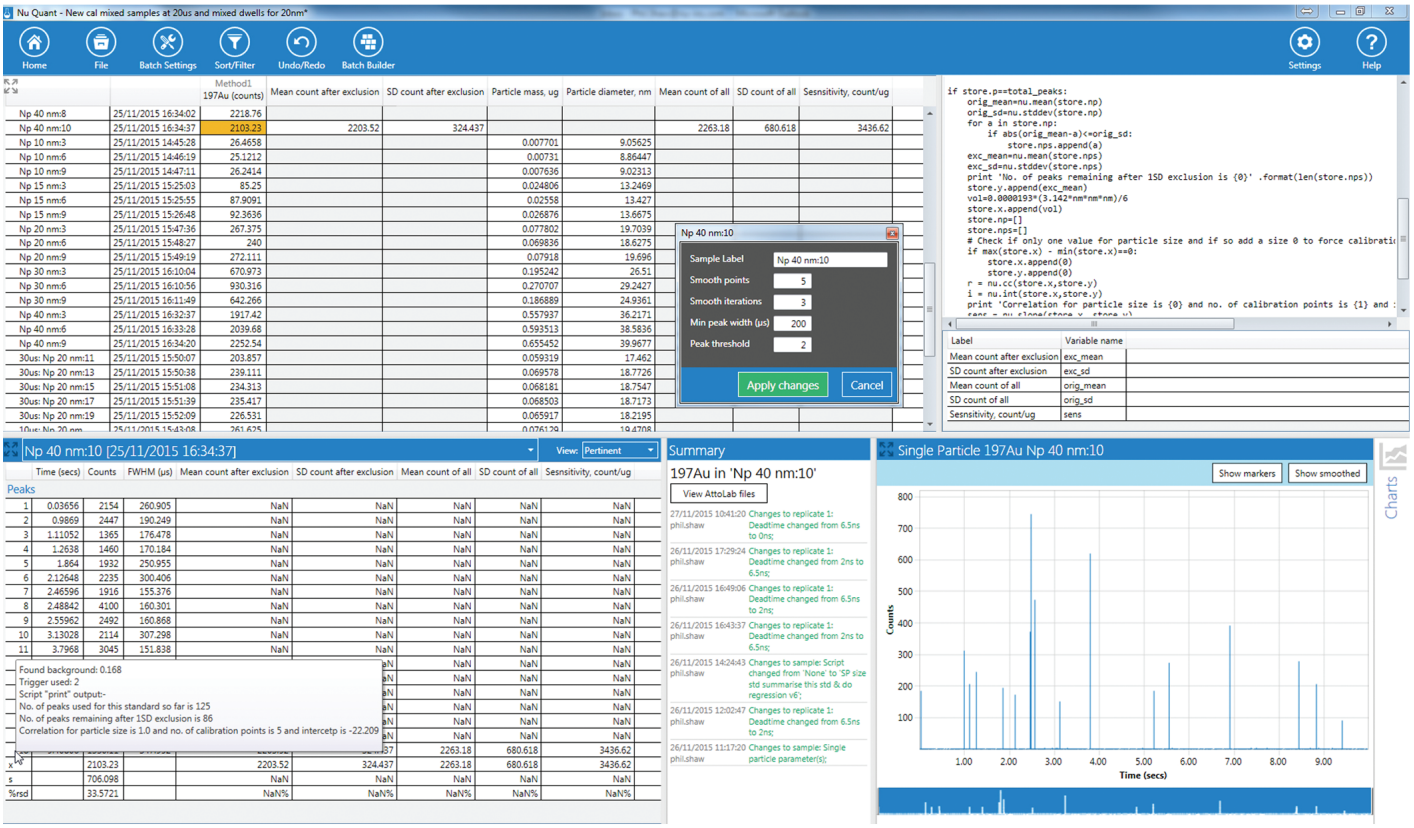

Figure 10: A screenshot of Nu Quant showing a NICE calculation of a 5 standard calibration (10, 15, 20, 30 and 40 nm Au particle standards) with a calculation of multiple samples for particle diameter and particle mass. The inset dialog box shows the sample variable parameters for the smooth and search peak integration routine.

Summary

Nu AttoM ES is proven to be a powerful and flexible ICP-MS for nano-particle analysis. Capable of fast data acquisition up to 105Hz and the ability to combine methods to improve both signal to background and dynamic range for a variety of samples.

Nu Quant easily and accurately integrates nanoparticle peak data for wide range of sizes and shapes without compromise. The inbuilt NICE scripts are flexible and powerful allowing the calculation of final results for a batch of samples quickly and simply.

References

[1] Strenge and Engelhard: DO!: 10.1039/c5ja00177c
[2] Olesik and Gray: I. Anal. At. Spectrom., 2012, 27, 1143-1155