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Vitesse Note **NT01**

Multi-element analysis of individual nanoparticles using Vitesse

- **Multi-element nanoparticle analysis**
- **Uninterrupted data collection at 25Qs to 100Qs per spectra**
- **Flexible peak location and integration**
- **Powerful data reduction capability**

Introduction

ICP-MS has proven to be a powerful analytical tool for the measurement of nanoparticles using the Single Particle mode. The ability to take ion count measurements faster than the duration of the signal from an individual nanoparticle is accepted as giving the highest quality of data in terms of particle size detection limits, discrimination of particles from ionic backgrounds, increased measurable particle concentration limits and particle size distribution accuracy[1-3]. Whilst useful information is obtained from the Single Particle ICP-MS technique when measuring one element with a sequential ICP-MS, the ability to measure multiple elements in individual nanoparticles offers more information than just additional distributions of particle mass or assumed size for a range of elements[4]. Being able to measure the coincidence of elements in particles gives important guidance to the origin of particles. For example, deciding if a particle is man-made or natural based on the purity of the main element within the particle or determining whether a particle found in a natural sample is from one mineral or another based on the mole fractions of elements in the particle. When looking at mixtures of particles the ability to determine if the mixture is of different homogeneous particles or whether the composition of the particles is inhomogeneous can only be determined by simultaneously measuring elements in many individual particles.

Data acquisition considerations

The only technique capable of capturing spectra for a wide range of elements with sub-millisecond data acquisition rates is Time of Flight mass spectrometry (TOF). A TOF can acquire a near full mass spectrum in under 30 µs but the amount of data collected can overwhelm the ability of a PC to process the spectra into counts per second values for individual isotopes unless many spectra are summed before calculating isotope counts. This has traditionally meant that TOF instruments either reported multi-element data every 1-3 ms or collected short bursts of data for a few tens of milliseconds at 30-50 µs per spectra. Neither of these methods is satisfactory for nanoparticle analysis as there is either a loss of data quality for peak detection and ionic background discrimination or a severely reduced duty cycle making it difficult to collect statistically significant numbers of particles in a reasonable timeframe.

The Vitesse uses a novel data acquisition and peak processing method where ion signals are acquired at between 5 and 30 µs per spectra but then the data is transferred directly to the Graphics Processing Unit (GPU) installed on the same PC bus as the data acquisition card. The acquired data can be transferred at 6 GB persecond which is considerably faster than it is possible to write data to a hard drive. The GPU then can process the TOF data in real time to produce integrated counts per second for each isotope measured. Using this technique, it is possible to write integrated isotope count data to a Solid State Hard Drive (SSD) as it is acquired.

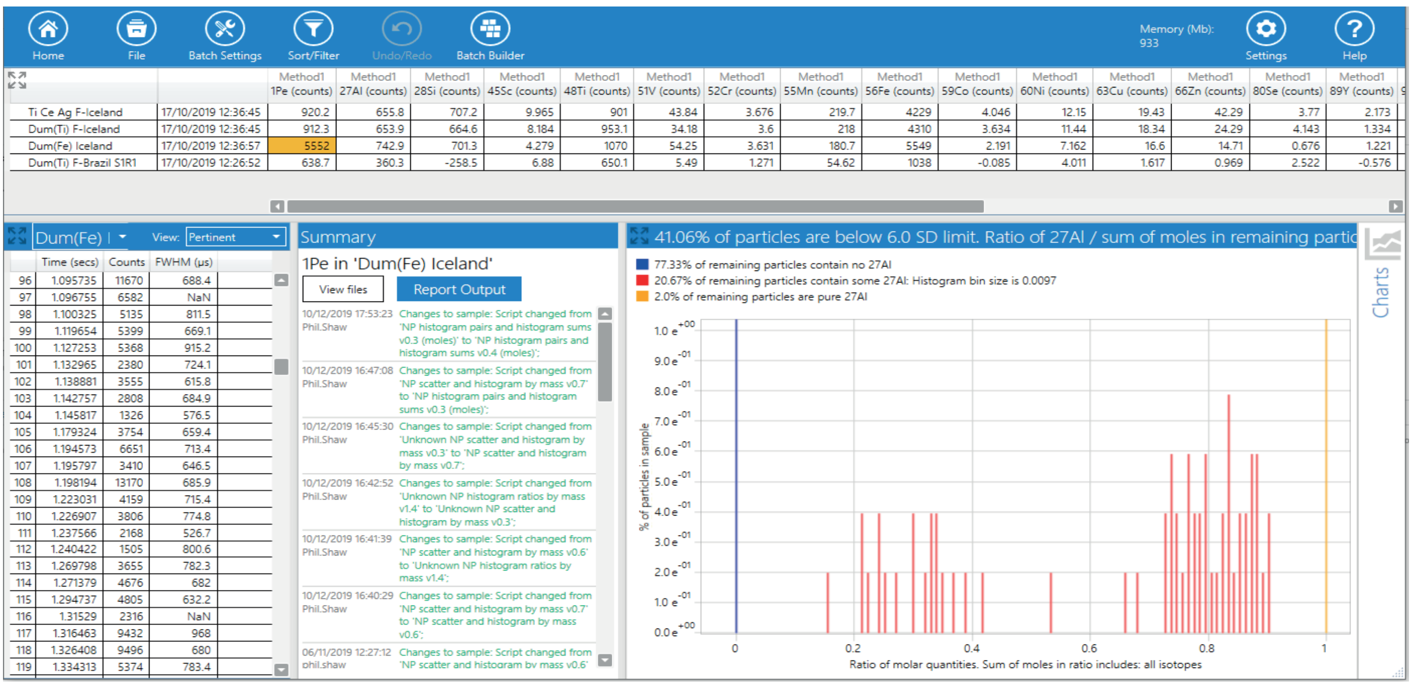
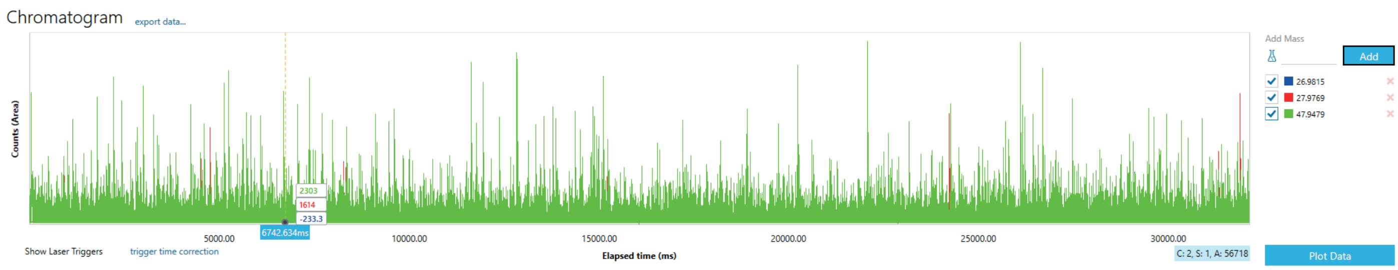
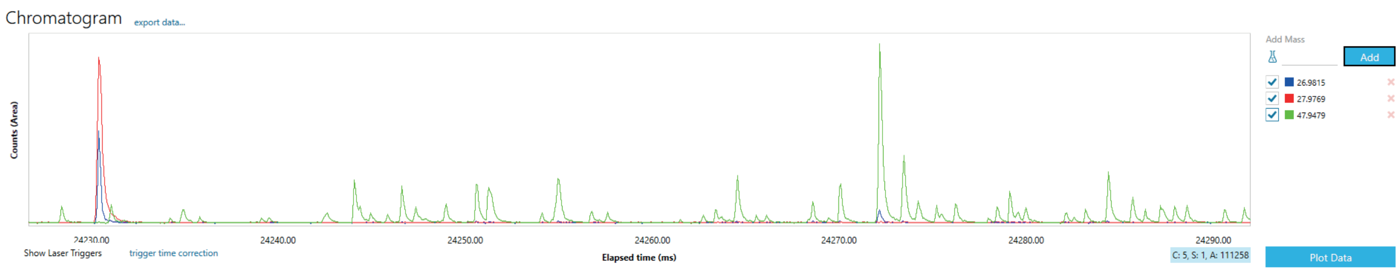


Figure 1: Data processing software: Nu Quant Vitesse

The data can be viewed as a chromatogram and sections zoomed into to qualitatively look at peak shape quality and where elements are coincidental in the same particle peak.





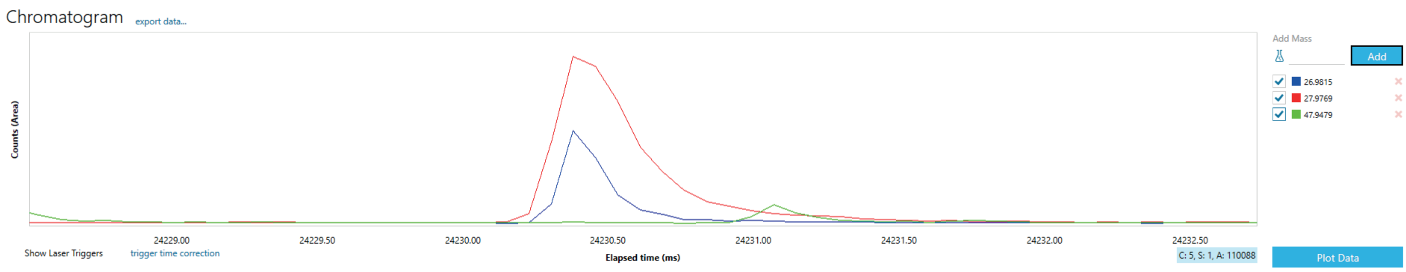


Figure 2: A diluted paint sample; 33 seconds of data acquired at 75 µs per spectrum (3 summed 25 µs spectra). First showing all data, then zoomed into a region believed to show some association between the Ti, Al and Si signals, then a zoom to 5 ms of data showing a large Al/Si particle which has a signal within a millisecond of a Ti particle but can obviously be seen as not part of the same particle.

Data reduction

Looking for associations in hundreds and even thousands of particle events would take many hours of investigation and deriving statistically relevant numerical associations would take even longer. To ease the burden, the data acquired on Vitesse can be opened and manipulated using the Nu Quant software developed for nanoparticle analysis on the Attom high resolution ICP-MS[3].

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After a qualitative evaluation of the sample it is possible to define which isotopes are the dominant ones for nanoparticles and then searches are made in Nu Quant for peaks of these target isotopes. The start and end points found for each particle signal are then used to integrate the signals for all isotopes measured in the mass spectra, i.e. sum the counts for each isotope in spectra collected between Time(start of particle) and Time(end of particle). Any data during the time of acquisition where particles have not been identified is treated as ionic background and is similarly integrated for all isotopes. The ionic backgrounds for each isotope are subtracted from each correlating isotope's peak integration and then these peak integrations and ionic backgrounds are accessible as variables to the Nu Instruments Calculations Editor (NICE) scripts for further data reduction.

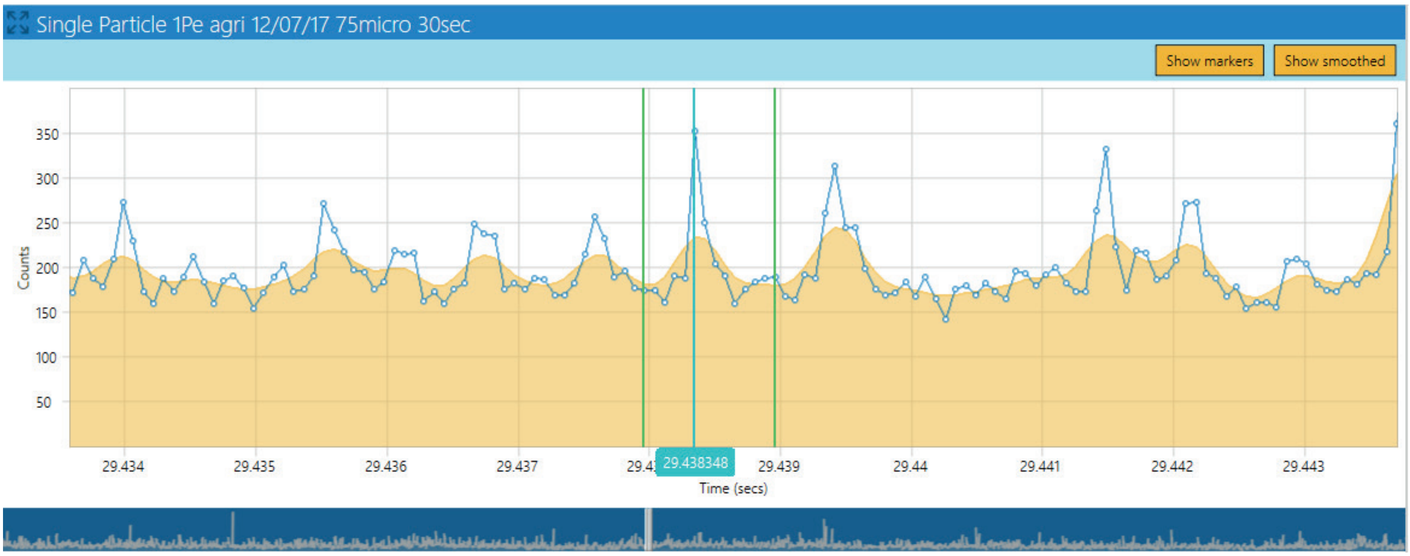

Figure 3: Example of Nu Quant being used to peak search for nanoparticles in a water sample using a combination of signals for Al, Si, Ti, Fe and Ce. The green lines indicate the found start and end points for that particle in amongst other particles and on top of the ionic background.

The scripts available in Nu Quant Vitesse allow multi-element calibrations and reporting of particle data in various ways.

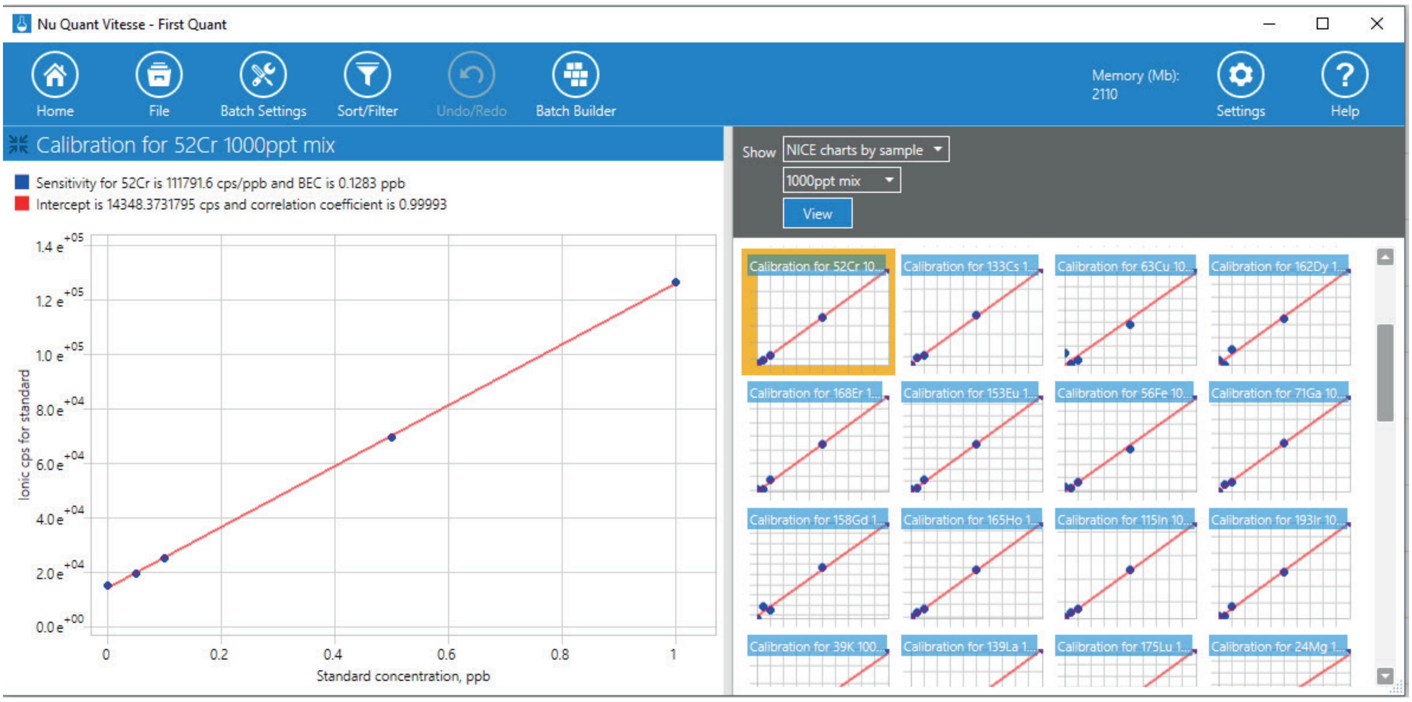

Figure 4: Shows multi-element calibration for ionic standards.

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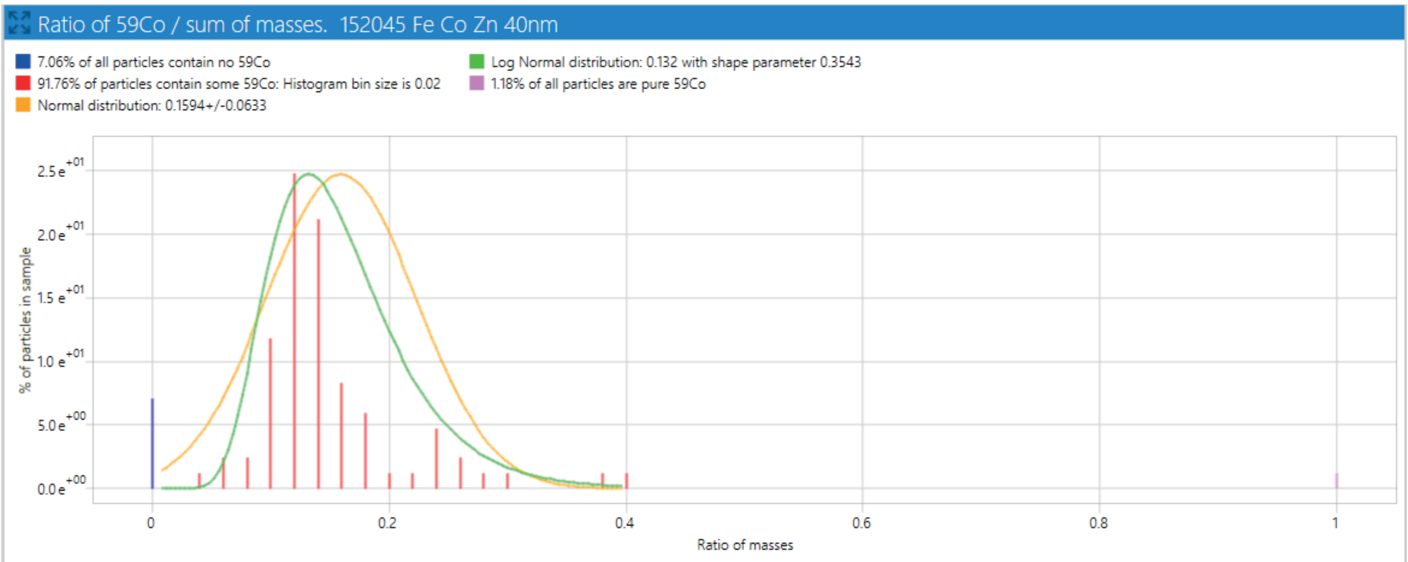
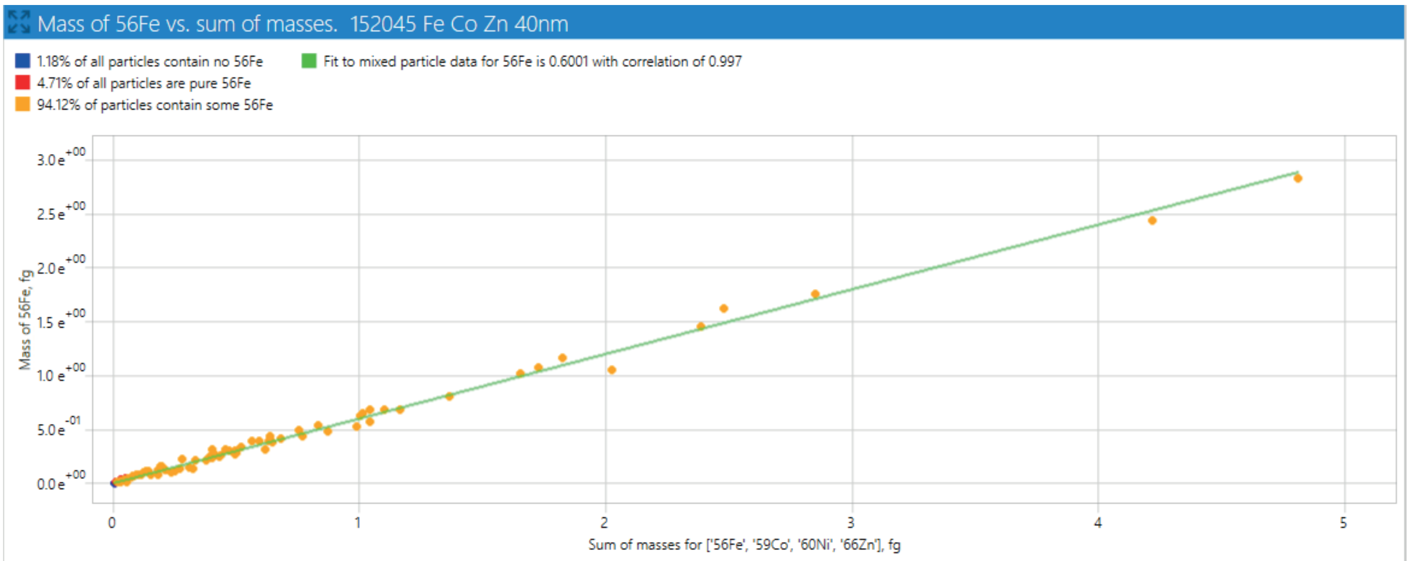
By knowing the calibrated multi-element sensitivities and the sample transport rate determined with a known size of nanoparticle, the mass of each element in each individual particle is calculated. By collecting composition data for many particles, it is then possible to have the scripts calculate and display histograms and scatter plots based on simple element to element ratios, elements ratioed to a group of elements or elements to the total of all measured elements. The histograms and scatter plots can also be shown for molar ratios by using a script which also divides each measured mass by the atomic weight of the isotope being used.

In some samples, the particles of interest may only represent a fraction of the total number of particles present in the sample and Nu Quant is able to count the number of particles containing only the element of interest, the number that contain some of the element of interest or those that have none of the element present. To ensure that noise does not contribute to the calculations, the scripts also allow a standard deviation test to the be applied. The standard deviation of the ionic background signal for an element in the sample is used along with the full width half maximum measured for the particle peak to calculate a noise floor for each element in each particle so only signals above the noise floor are reported. The script reports the percentage of the total found particles that are above the noise floor for all of the elements included in any ratio calculation.





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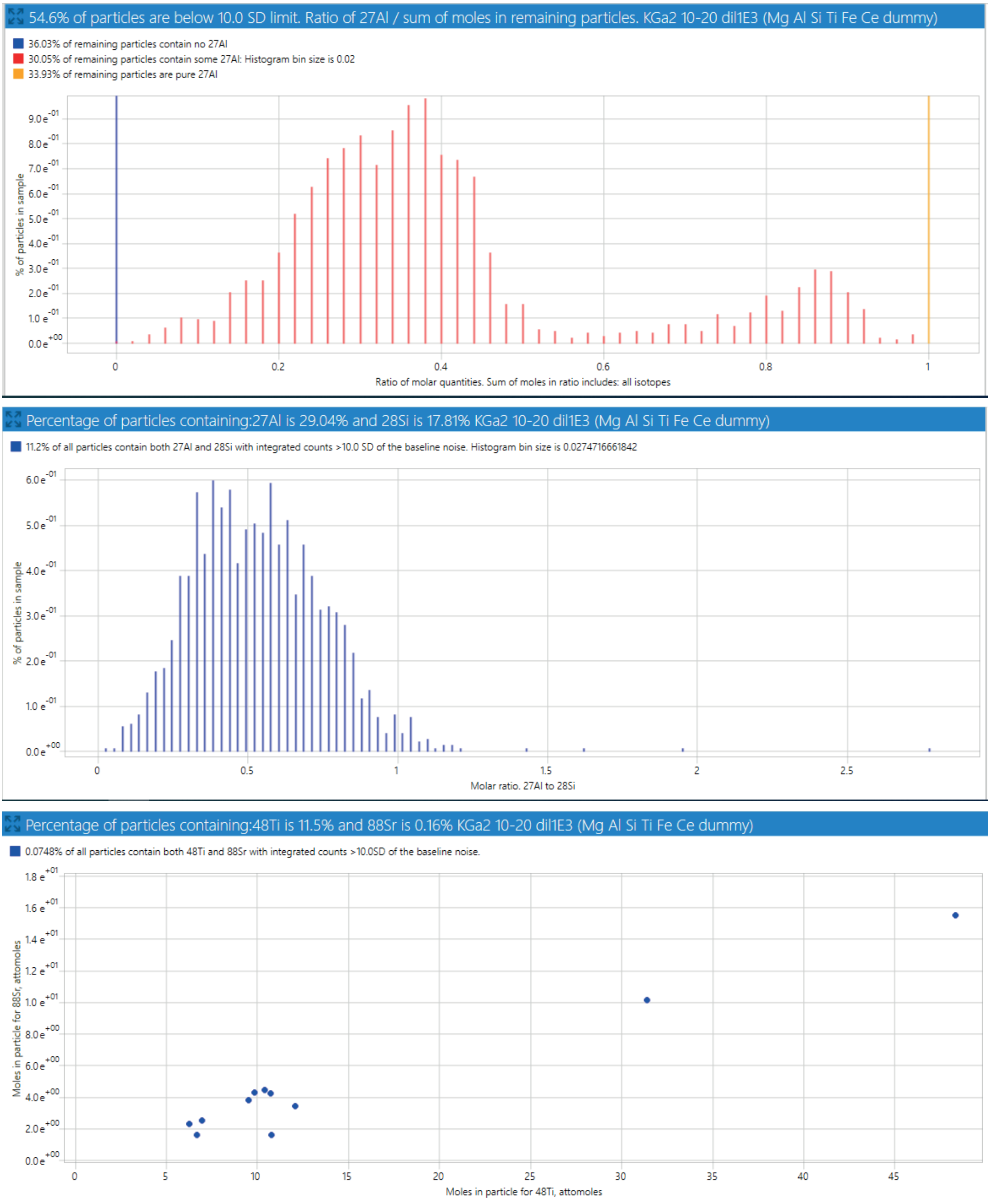

Figure 5: Examples of the types of information available from the NICE scripts.

All of the data for elements in each nanoparticle and any calculated associations are reported in a CSV text file that directly opens into a spreadsheet to allow manipulation by third party software as required.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	Sample name	152045 Fe Co Zn 40nm															
2	Sample time	09/10/2019 15:24															
3	Sample transport rate	0.020652549															
4																	
5	Time	FWHM (us)	27Al	140Ce	59Co	56Fe	139La	60Ni	141Pr	48Ti	66Zn	90Zr		56Fe / SUM	59Co / SUM	60Ni / SUM	66Zn / SUM
6	Background counts		1.26594	1.171608	1.136292075	1.613193946	1.062616	0.970007886	0.872355098	1.213408491	1.046166022	1.008398					
7	Background SD		0.520188	0.469283	0.464484162	0.635111025	0.447059	0.436063529	0.409720588	0.476849558	0.447613888	0.444276					
8	Background cps		12411.18	11486.35	11140.11838	15815.62692	10417.81	9509.881238	8552.500959	11896.16167	10256.52963	9886.259					
9	Background SD cps		5099.882	4600.812	4553.766289	6226.578673	4382.932	4275.132637	4016.868513	4674.995667	4388.371454	4355.645					
10	cps/ppb		1997.557	61878.94	42208.56016	42568.67627	71906.82	9152.759614	57457.15877	22609.72143	5268.732025	32044.34					
11	Unit		fg	fg	fg (in Sum)	fg (in Sum)	fg	fg (in Sum)	fg	fg	fg (in Sum)	fg					
12																	
13	0.074664	1000	0	0	0.069992819	0.309151332	0	0	0	0	0.116266889	0		0.624029962	0.141282315	0	0.234687723
14	0.075888	1243.395108	0.208435	0	0.134046608	0.479002577	0	0	0	0	0.255933166	0		0.551222446	0.154256997	0	0.294520557
15	0.263568	1243.395108	0	0	0.012433273	0.019090649	0	0	0	0	0	0		0.605592434	0.394407566	0	0
16	0.265098	898.5571492	0	0	0.014457151	0.069359455	0	0	0.004060841	0	0	0		0.827514475	0.172485525	0	0
17	0.38964	861.0742071	0	0	0.01330098	0.038730468	0	0	0	0.014637423	0	0		0.744366522	0.255633478	0	0
18	0.419832	850.3531284	0	0	0.067301296	0.249353204	0	0	0	0	0.11433765	0		0.578556254	0.156154344	0	0.265289402
19	0.421158	1137.283801	0.273105	0	0.062697556	0.263985783	0	0	0	0	0.109874928	0		0.604697708	0.143617841	0	0.251684451
20	0.423504	998.1326789	0	0	0.018504907	0.079657615	0	0	0	0	0.055902083	0		0.517040332	0.120111347	0	0.36284832
21	0.424932	908.5953802	0	0	0.082937105	0.319605148	0.004576	0	0	0	0	0		0.793966709	0.206033291	0	0
22	0.797334	897.3937182	0	0	0.01192226	0.035004857	0	0	0	0	0	0		0.745940921	0.254059079	0	0
23	0.870264	970.9503561	0	0	0.00858558	0.025695204	0	0	0	0	0	0		0.749551238	0.250448762	0	0
24	0.871692	887.9096914	0	0	0.071594086	0.37863881	0	0	0	0.012092048	0.195025472	0		0.586801859	0.110954138	0	0.302244002
25	0.940032	871.9928226	0	0	0.043325712	0.529289573	0	0	0	0	0.416164779	0.007637		0.535295555	0.04381734	0	0.420887105
26	0.941358	993.1867314	0	0	0.154530421	1.049251303	0	0	0	0	0.820208132	0		0.518407392	0.076349405	0	0.405243203
27	1.065594	800.0768649	0	0.003861	0.005516419	0.017337678	0	0	0	0	0	0		0.758624495	0.241375505	0	0
28	1.273266	861.0342569	0.164989	0	0.016325939	0.10486766	0	0	0	0	0	0.008194		0.865290418	0.134709582	0	0
29	1.43208	818.5440138	0	0	0.012389072	0.083662532	0	0	0	0	0	0		0.871016501	0.128983499	0	0
30	1.433508	917.739278	0	0	0.029114365	0.164839633	0	0	0	0	0	0		0.849890359	0.150109641	0	0
31	1.494912	855.8017847	0	0	0.010142646	0.049623619	0	0	0	0	0	0		0.8302948	0.1697052	0	0
32	1.606704	876.9505803	0	0	0	0.021717919	0.004576	0.031566849	0	0	0	0		0.407582128	0	0.592417872	0
33	1.610886	917.4930323	0	0	0	0.032894751	0	0	0	0	0	0		1	0	0	0
34	1.612314	934.5518769	0	0	0.121547417	0.654895391	0	0	0	0	0.23561015	0		0.647095971	0.120099859	0	0.232804171
35	1.628532	846.4707893	0	0.004576	0.049709067	0.272498965	0	0	0	0	0.171868401	0		0.551532004	0.100610076	0	0.347857921
36	1.663416	867.8206748	0	0	0.082958821	0.422554736	0.003984	0	0	0	0.173135142	0		0.622641341	0.122241185	0	0.255117475

Figure 6: Typical CSV text output from NICE.

Summary

Nu Vitesse is proven to be a powerful and flexible ICP-MS for nanoparticle analysis. Capable of uninterrupted data acquisition at 25-100 µs per spectra for several minutes, it is possible to collect complete elemental data for large numbers of particles.

The use of Nu Quant gives the flexibility to search for particles in a sample based on different criteria and then report associations between elements in simple and sophisticated ways. Nu Quant easily and accurately integrates nanoparticle peak data for a 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: J. Anal. At. Spectrom., 2016, 31, 135-144
2. Olesik and Gray: J. Anal. At. Spectrom., 2012, 27, 1143–1155
3. Shaw and Donard: J. Anal. At. Spectrom., 2016,31, 1234-1242
4. Naasz et al: J. Anal. At. Spectrom., 2018,33, 835-845