

Rapid sizing of quantum dots and nanoparticles

Keywords: *Hydrodynamic radius, diffusion coefficient, sizing, Taylor dispersion analysis, non-organic, quantum dots, quality control, gold nanoparticles*

Summary

Quantum dots are typically fluorescent nanoparticles of high quantum efficiency (see Figure 1). They can be custom synthesized for a wide variety of applications ranging from medical imaging to next generation LCD displays.

Paraytec have developed a new approach to determining the hydrodynamic radius of species in solution. This application note is a proof of principle study to demonstrate the use of the ActiPix HT Nano-Sizing System for determination of hydrodynamic radii of quantum dot and gold nanoparticle samples provided by the Physics Department at the University of Leeds. Excellent correlation was obtained between experimental and expected values with typical analysis times of less than 10 minutes. This approach is a significantly faster and more cost efficient approach compared to transmission electron microscopy (TEM) which typically takes several hours to perform this analysis. In addition, conventional particle measuring techniques cannot effectively measure down to sub 20 nanometre sizes.

Instrumentation and Materials

ActiPix HT Nano-Sizing System (beta)	(P/N NSS200)
ActiPix cartridge for sizing application	(P/N C102SIZE200)
254 nm wavelength filter	(P/N UVFILT254)
100 cm 75 x 200 μm fused silica capillary	(Polymicro Technologies)
Quantum Dots	(Dept of Physics, University of Leeds)
HPLC grade water	(Fisher Scientific)



Figure 1: Example of fluorescing quantum dots

Summary of Paraytec's Approach

Paraytec are developing a system for rapid determination of protein radii known as the ActiPix HT Nano-Sizing System (Figure 2). This technology is being applied to determine its applicability for rapid quality control of quantum dots. A detailed application note summarizing this technique¹ can be downloaded from Paraytec's website. For the purposes of this application note, a brief summary of the technique is given below.

The ActiPix HT Nano-Sizing System is a high precision nano-sizing system consisting of a precision nano-injector, autosampler and detector. Samples are typically stored in the autosampler prior to injection of a few nanolitres of each each sample into a fused capillary of outer diameter typically 200 to 360 μm .

A plug of the sample, typically 20-100 nL, is injected at the capillary inlet of a specially designed sizing cartridge (see Figure 3 below) and driven by application of external pressure along the capillary.

UV absorption of the sample is recorded in the first and the second detection window using the ActiPix D100 detector. Whilst the area of the peak is the same, the widths of both peaks are different: the signal from the second window has a greater width and lower amplitude due to Taylor dispersion.

The peaks are fitted with an appropriate peak fitting function using software supplied with the system. The area under the peak corresponds to the amount of the sample injected. The standard deviations are used to calculate the hydrodynamic radius of the sample.



Figure 2: ActiPix HT Nano-Sizing System

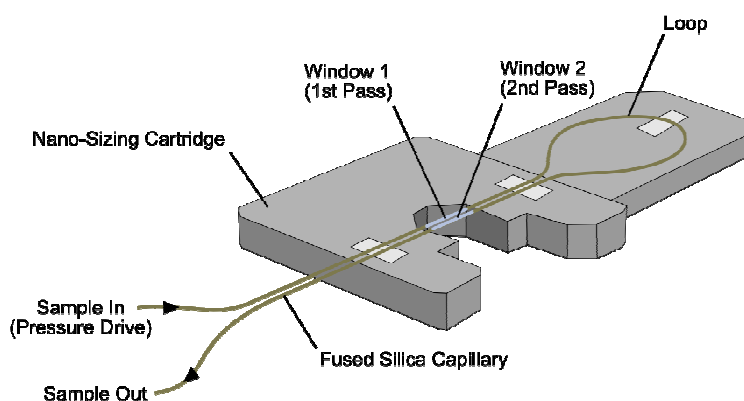


Figure 3: ActiPix Nano-Sizing Cartridge

Theory behind Taylor Dispersion Analysis

Band broadening due to Taylor dispersion has been well characterized in previous literature.^{1,2} In this method, the absorbance versus time data is processed to obtain the peak centre times at the first and second window, t_1 and t_2 respectively, and the corresponding standard deviations, τ_1 and τ_2 .

These values are used to calculate the hydrodynamic radius, R_h , using Equation 1

$$R_h = \frac{4k_B T (\tau_2^2 - \tau_1^2)}{\pi \eta r^2 (t_2 - t_1)} \quad (1)$$

where k_B is the Boltzmann constant, T the absolute temperature, η the viscosity of the solution, and r the capillary radius. For dilute solutions used in these experiments, the viscosity of the solution may be assumed to be that of water at that temperature. Further details concerning Equation 1 and data analysis are given in the Technical Note TN001 - Hydrodynamic radius using Taylor dispersion.

The ActiPix D100 software automatically locates the peaks and uses Equation 1 to calculate the hydrodynamic radius of the sample as seen in Figure 4.

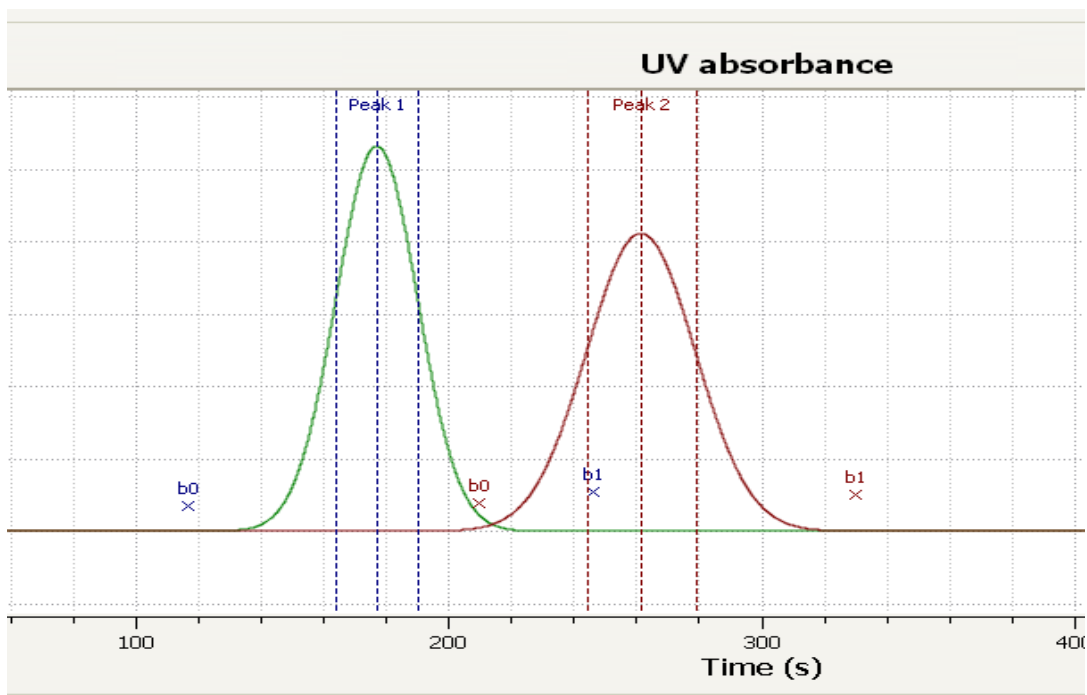


Figure 4. Example of a single Gaussian fitted peak using Paraytec software

Experimental Procedure

The quantum dot samples were made by the Molecular & Nanoscale Physics Group at Leeds University and supplied in glass vials labelled '3nm q dot', '5nm q dot' and '? nanoparticle'. The name refers to the predicted diameter of the sample, the 3rd radius was unknown to Paraytec. The samples were stored at 4°C and were allowed to reach room temperature prior to analysis.

The samples were transferred to a 300 µL glass vial and loaded onto an automated beta version of the ActiPix HT Nano-Sizing System.

A summary of the experimental conditions is given below:

System used: ActiPix HT Nano-Sizing System
 Capillary dimensions: Length 110 cm / detector window 1: 40 cm / detector window 2: 60 cm
 Programmed flow rate: 3.85 mm s⁻¹
 Volume of sample injected (programmable): 50 nL
 Detector wavelength: 254 nm
 Sampling Rate: 20 Hz
 Data filter: 0.0 s

Results

5 repeats of a caffeine standard and all samples were run. Representative data from the caffeine standard and the 3 samples are shown in Figure 5a to 5d.

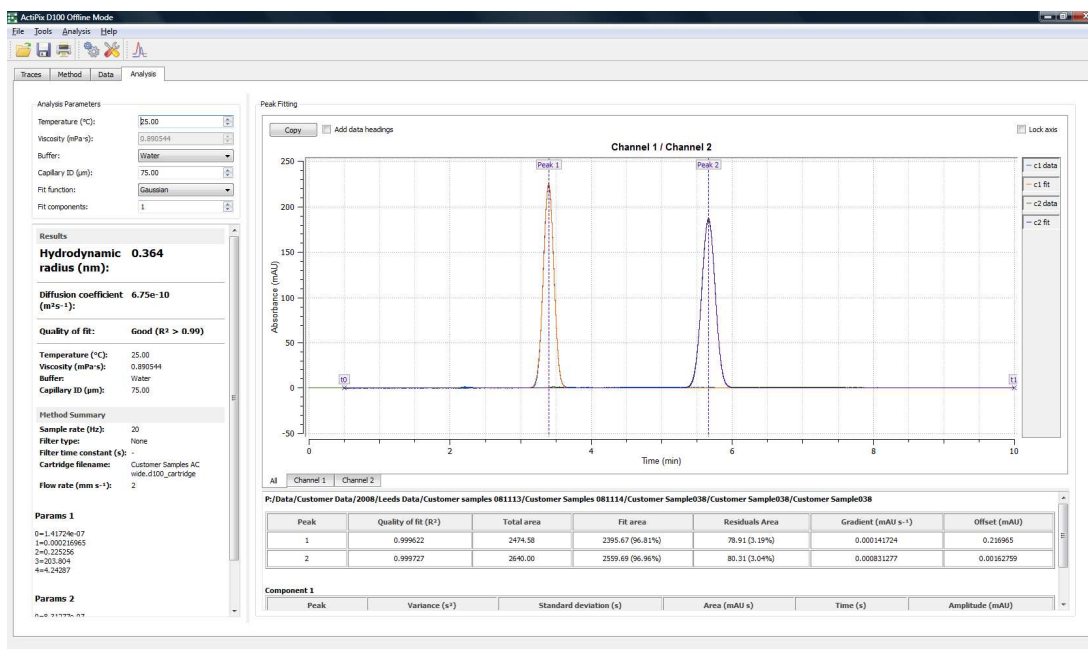
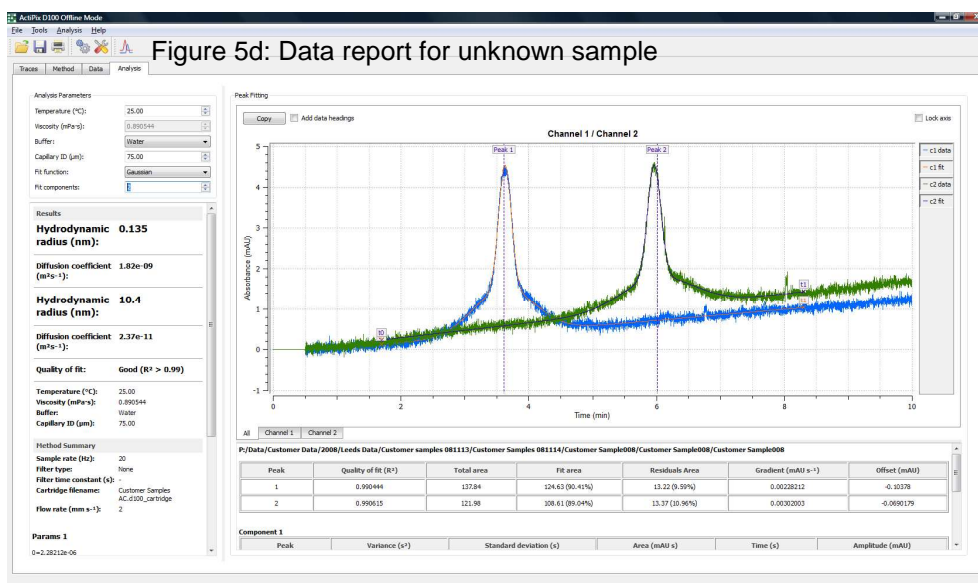
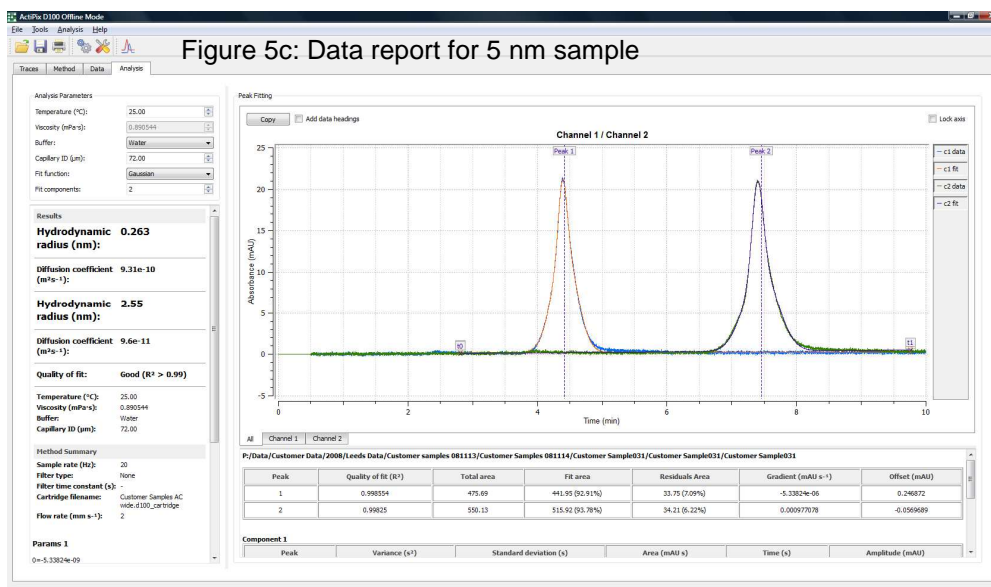
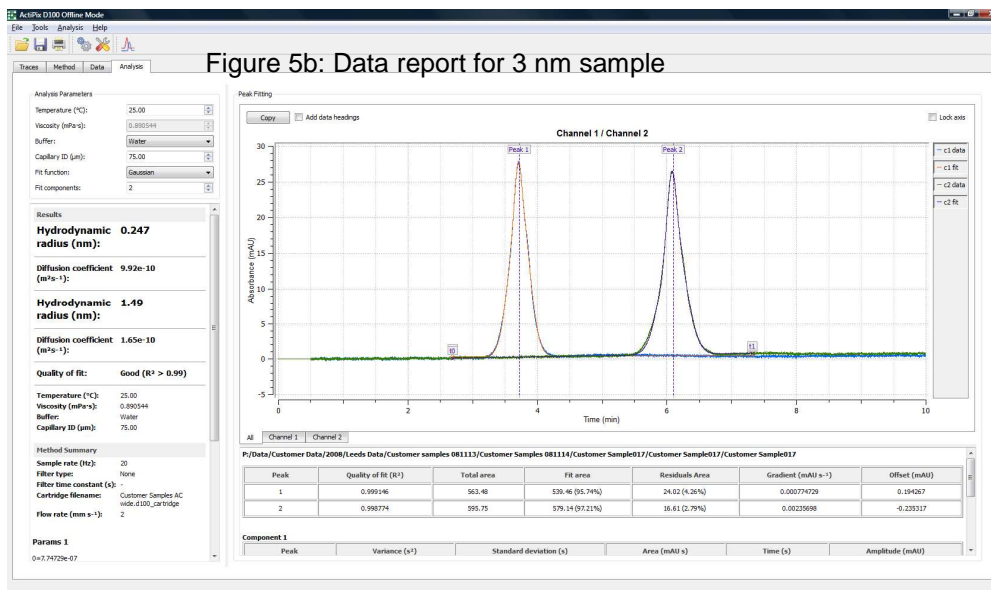


Figure 5a: Data report for caffeine standard



Summary of Results

Run Number	Sample Type	Hydrodynamic Radius (nm)
1	Caffeine	0.36
2	Caffeine	0.38
3	Caffeine	0.37
4	Caffeine	0.37
5	Caffeine	0.37
Average		0.37
SD		0.01
RSD		1.81%

Run Number	Sample Type	Hydrodynamic Radius (nm)
6	5nm q dot	2.43
7	5nm q dot	2.55
8	5nm q dot	2.53
9	5nm q dot	2.60
10	5nm q dot	2.67
Average		2.56
SD		0.09
RSD		3.47%

Run Number	Sample Type	Hydrodynamic Radius (nm)
11	3nm q dot	1.49
12	3nm q dot	1.42
13	3nm q dot	1.30
14	3nm q dot	1.38
15	3nm q dot	1.41
Average		1.40
SD		0.07
RSD		4.92%

Run Number	Sample Type	Hydrodynamic Radius (nm)
16	? Nanoparticle	10.84
17	? Nanoparticle	14.05
18	? Nanoparticle	8.29
19	? Nanoparticle	10.35
20	? Nanoparticle	11.47
Average		11.00
SD		2.08
RSD		18.91%

Table 1. Sizing data for all samples and caffeine standard

Conclusions

Excellent correlation was obtained between expected and actual data for the rapid determination of the quantum dot samples provided. The average radius of the unknown nanoparticle was found to be 11.0 nm, corresponding to a diameter of 22.0 nm. The actual diameter of this gold nanoparticle was 21.7 nm.³ The good agreement between observed and actual values demonstrates the promise of this technique for sizing unknown nanoparticles. Typical analysis time was less than 10 minutes per injection demonstrating the superior speed compared to existing techniques which take typically a few hours to perform the analysis.

For all nanoparticle samples, the peaks were well fitted by two overlapping Gaussian peaks.^{4,5} The radius of the larger component is that of the nanoparticle; the peak of radius <0.3 nm most likely corresponds to a small molecule component used to prepare the samples.

This proof of principle study demonstrates application of Paraytec's approach to the rapid size determination of quantum dots and nanoparticles of radii less than 20 nm which until now has not been achieved by other techniques.

References

1. Paraytec Technical Note TN001 - Hydrodynamic radius using Taylor dispersion.
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