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## Publishable Executive Summary

Different methods of analysis were applied to the Turbidity Spectrometry (TUS) data obtained for the 3 types of particle suspensions under study; 1) polymer dispersions, 2) silica and 3) ceramic NPs in electrolyte suspensions in order to determine the particle size in the suspension.

For case study 1) two methods were used to analyse the data and obtain the particle size, Method 1 (the W method) and Method 2 (the ST method). These particle sizes were compared to the reference sizes obtained by the standard dynamic light scattering (DLS) method. Analysis of polymer dispersions using Method 1 indicated that, the lower the wavelength used in the calculation, the closer the particle size was to the value obtained by the DLS method. Very good agreement was observed between the particle size obtained by using Method 2 and that obtained by the DLS method.

For case study 2) Methods 1 and 2 cannot be applied, as the SiO<sub>2</sub> NPs form fractal aggregates rather than spherical particles. For this case a model was developed to relate the turbidity measured by the TUS device to the particle size measured by DLS. The model provided accurate predictions of the particle size, based on the turbidity.

For case study 3) Methods 1 and 2 cannot be applied for the same reasons as for case study 2). Nor is it possible to develop a model to correlate the turbidity and the particle size, as this would require the concentration of the suspension to be known accurately. This is not the case in the industrial electroplating processes of case study 3). Instead, it is proposed to implement a function in the TUS software where, when the rate of change of turbidity or the absolute value of turbidity reaches a pre-defined threshold, the user is informed.

## Introduction

This deliverable summarises the Turbidity Spectrometry (TUS) results obtained in the laboratory and RTO scale pilot tests. It compares the results obtained by TUS to those obtained by standard particle characterisation techniques such as Dynamic Light Scattering (DLS), NTA, OF2i and evaluates the validity of the data models used for TUS data. Results for the 3 types of nanoparticle (NP) solutions previously chosen are included:

Subtask	Case Study	RTO	Industrial Partner
4.2.1	Polymer dispersion	UPV	DSM
4.2.2	Silica	UP	EVONIK
4.2.3	Ceramic NPs in electrolyte suspensions	MUG	CNANO

## Case Study 1: Polymer dispersion

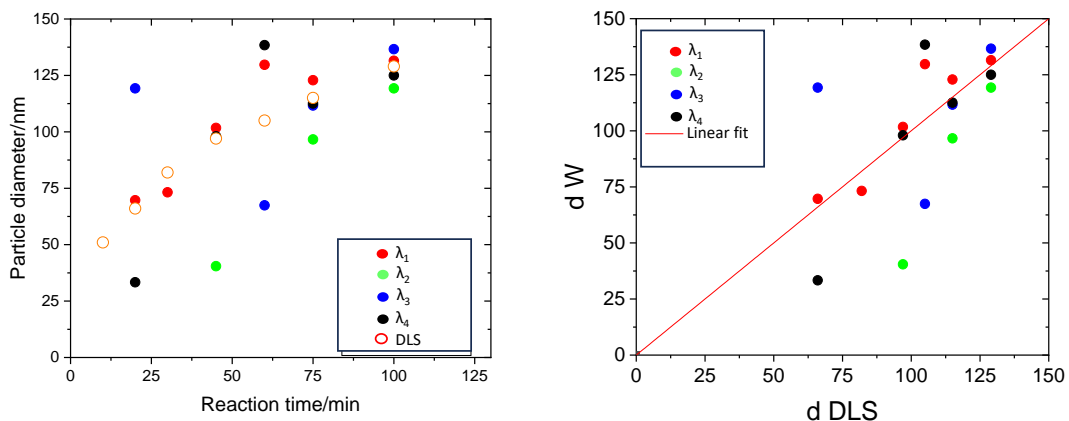
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### A) RESULTS FOR POLYACRYLATE LATEX SYNTHESIS

Waterborne polyacrylate dispersions were synthesized by semibatch emulsion polymerization. The polyacrylate latexes were analysed by TUS and DLS after dilution. The TUS measurements were analysed by two different approaches: Method 1 (the W method) and Method 2 (the ST method), as previously described in D4.2.

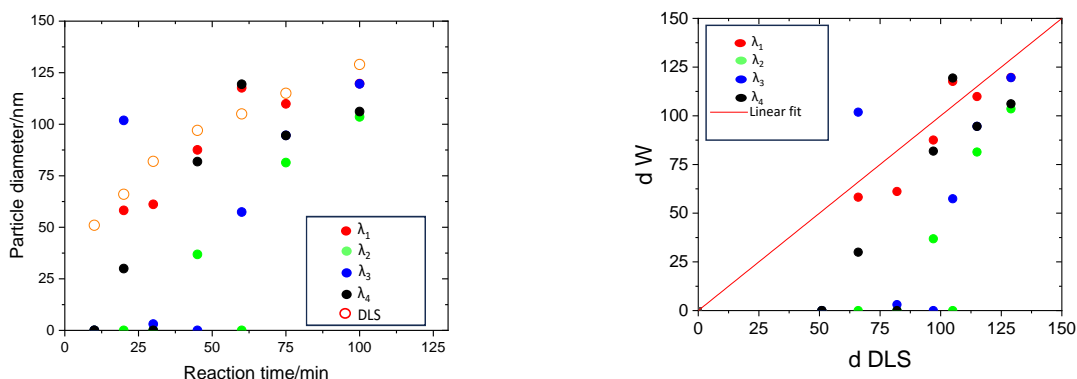
#### A.1) Method 1 (the W method)

Figure 1 presents the particle size results obtained from TUS, using the theoretical calibration curve for monodisperse samples.  $W$  calculated experimentally at different  $\lambda_0$  were used to derive the particle size from the TUS measurement. It was seen that the lower the  $\lambda_0$  used to calculate the  $W$ , the better the matching between the particle size values obtained by TUS and DLS.



**Figure 1. Particle size derived from the W method, using the theoretical calibration curve for monodisperse polyacrylate system. Comparison to reference DLS measurement (number average particle size).**

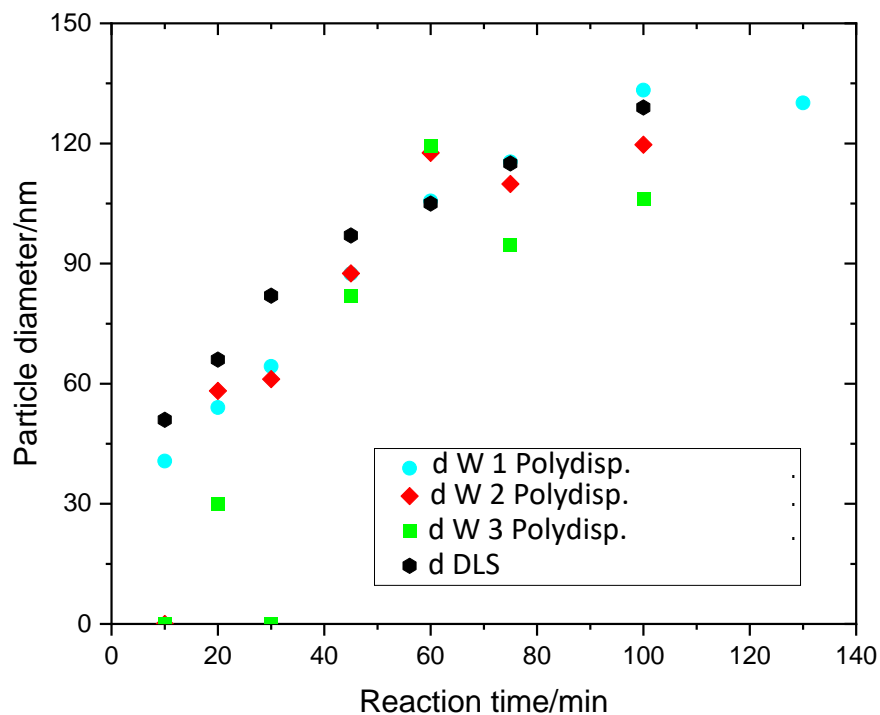
Figure 2 presents the particle size results obtained by using the W theoretical calibration curve obtained for polydisperse system with 20 % of standard deviation.



**Figure 2. Particle size derived from the W method, using the theoretical calibration curve for polydisperse polyacrylate system (SD 20%). Comparison to reference DLS measurement (number average particle size).**

As well as when using the monodisperse model, when the polydisperse model was used, the particle size results obtained from TUS approached more the DLS particle size values, the lower the wavelength used to calculate W.

Moreover, Figure 3 presents the particle size obtained when the experimental W was obtained using the complete linear range of the log (turbidity) vs log (wavelength), i.e. in the wavelength range W1 . Furthermore, this data was compared to the data obtained with the limiting wavelength cases, W1, shown in the previous Figure 2.

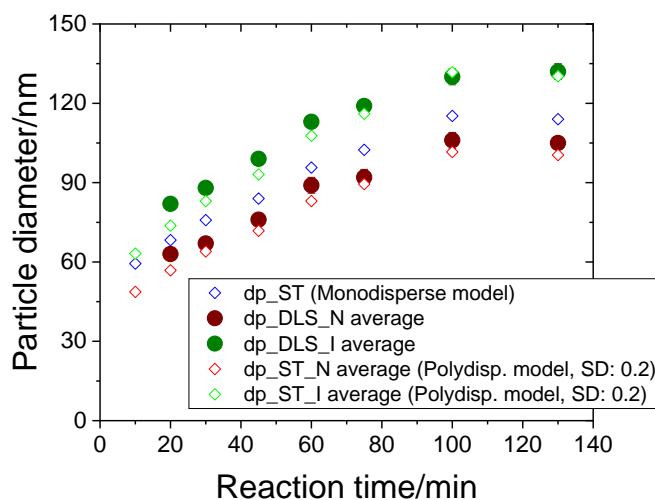


**Figure 3. Particle size derived from the W method, using the theoretical calibration curve for polydisperse polyacrylate system (SD 20%), using the W1 range to retrieve the experimental W. Comparison to reference DLS measurement (number average particle size).**

It seems that the wider the analysed wavelength range (being this always in the linear part of the log log spectra), the closer the data obtained by TUS to off-line analysis techniques.

#### A.2) Method 2 (the ST method)

The particle size results obtained from the ST method at a wavelength near to the start of wavelength range W1, and their comparison to DLS values are presented in Figure 4. Both monodisperse and polydisperse (SD=20%) theoretical models of ST have been used to retrieve the particle size from TUS measurements.



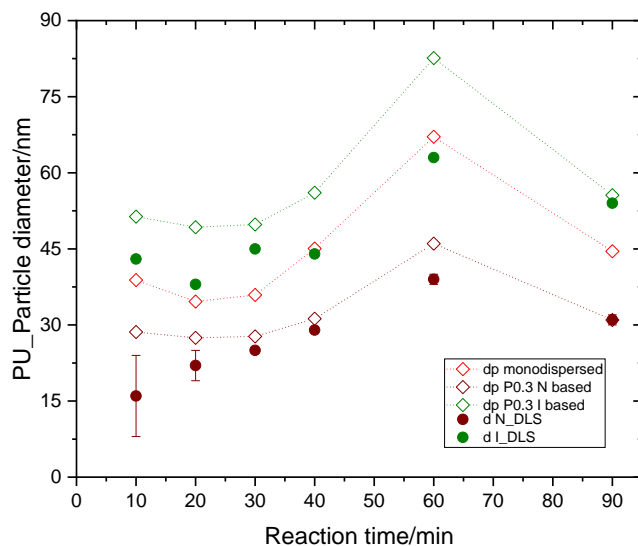
**Figure 4. Particle size derived from the ST method, using the theoretical calibration curve for monodisperse and polydisperse polyacrylate system (SD 20%). Comparison to reference DLS measurement (number and intensity average particle size).**

The data obtained from the ST models for the polydisperse samples with 20 % of SD, fit really well with DLS number and intensity average data.

## B) MONITORING OF POLYURETHANE LATEX SYNTHESIS

Waterborne polyurethane dispersions were produced by the prepolymer dispersion method. Due to the small particle size of the polyurethane latexes obtained by the process supplied by DSM, Method 1 (W method) could not be applied to monitor the particle sizes by TUS. Instead Method 2 (ST) analysis was directly applied to this case. The samples withdrawn from the reactor during the process were diluted and measured by TUS. The results obtained with the ST theoretical curves for the polyurethane case and the DLS reference measurements are shown in Figure 5.





**Figure 5. Particle size derived from the ST method, using the theoretical calibration curve for monodisperse and polydisperse polyurethane system (SD 30%). Comparison to reference DLS measurement (number and intensity average particle size).**

As it is shown in Figure 5, the results obtained by ST method follow the same trend as the DLS results. In fact, the number-average sizes obtained by the polydisperse ST model fit well to DLS number-average particle sizes. In the case of the Intensity average particles obtained by TUS, they are slightly larger than the results obtained by DLS. In this case, the results obtained from the monodisperse ST model approach the intensity-average particle size obtained by DLS.

In any case, it has to be mentioned that the samples withdrawn from the polyurethane dispersion case are not fully stable and tend to aggregate with time. Therefore, this system seems a good candidate to implement in-line or on-line measurement techniques for the particle size.

## Case Study 2: Silica Case Study

*Author: J. Bolton/IRIS*

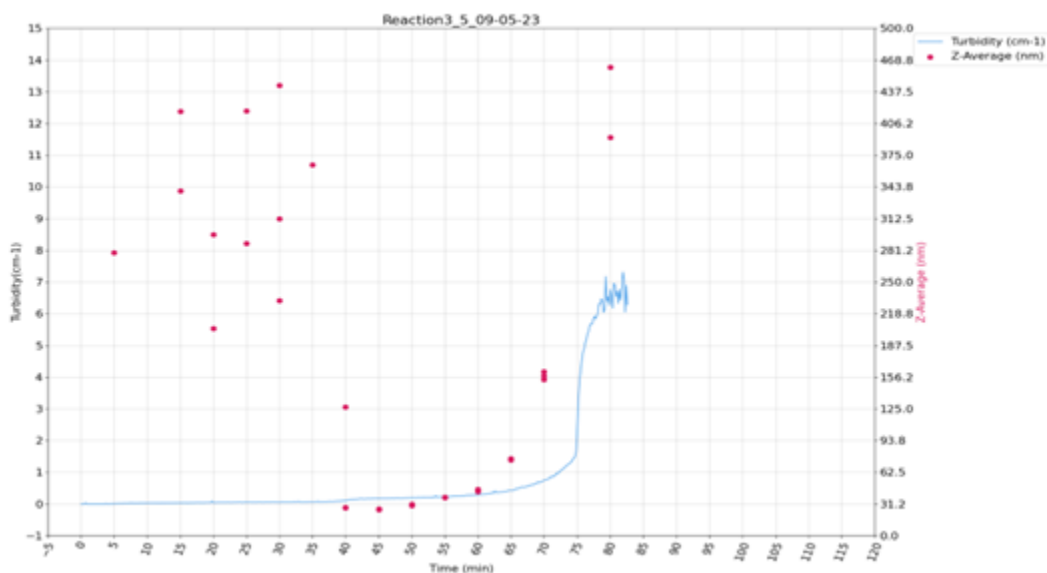
There were some delays to this task due to the following problems.

The TUS sensor was delivered by Iris to UP in May 2021. There was an initial mismatch between the volume of UP's reactor and the size of the TUS device which meant that it was not possible to perform TUS experiments. UP thus made an adaptor to allow the TUS sensor to be used with their 6L reactor. However in July 2022 the reactor broke. A new reactor arrived in Sept 2022. Iris TUS device was installed and tested at UP in Sept 2022 but 2 problems were found. Hot, dilute sulphuric acid in the reaction attacked the TUS device and it corroded. Also the TUS device was too short for the reactor so the liquid level did not reach the optical gap in the device until several minutes after the start of the reaction.

To solve these problems Iris made a new TUS device of corrosion resistant stainless steel and made an adaptor for the TUS device to allow height adjustment inside the reactor. Experimental trials were carried out with the new device and adaptor.

Syntheses of SiO<sub>2</sub> NPs in UP's 6L reactor were performed. During the synthesis the turbidity of the NP suspension was measured continuously using Iris's TUS device. Samples were taken from the reactor at regular intervals to be measured in the DLS apparatus and obtain the reference particle size.

It was possible to obtain turbidity measurements with the TUS device from a few minutes into the reaction i.e. the time at which primary NPs started to form due to the chemical reaction until the gelation point i.e. the point at which a large portion of all the precipitated material forms 1 big agglomerated mass, the gel. When the reaction gelation point was reached, the suspension was very turbid and the light transmission through the TUS device fell to zero. At this point the TUS device could no longer measure the suspension. The results are presented in Fig. 6.



**Figure 6. Graph of turbidity (blue line) measured by TUS device and particle size (red dots) measured by DLS during synthesis of SiO<sub>2</sub> NPs**

Both TUS and DLS techniques are based on the scattering of light by particles. In the 1st 30 mins of the synthesis reaction the NPs are too small to scatter sufficient light. As a consequence, the DLS measurements are not valid. However from 35 mins onwards reliable TUS and DLS measurements are obtained. At 80 mins the previously mentioned gelation point is reached and the suspension is too turbid to continue with TUS measurements. The graph shows that as the particle size increases, so does the turbidity of the suspension. This is consistent with the Mie theory of light scattering by particles. These results demonstrate the ability of the TUS device to continuously measure the turbidity of a suspension of SiO<sub>2</sub> NPs, whilst the NPs are synthesized and grow in size, for a large portion of the chemical reaction. In this way the inline continuous TUS measurements could be used to monitor the progress of the synthesis reaction.

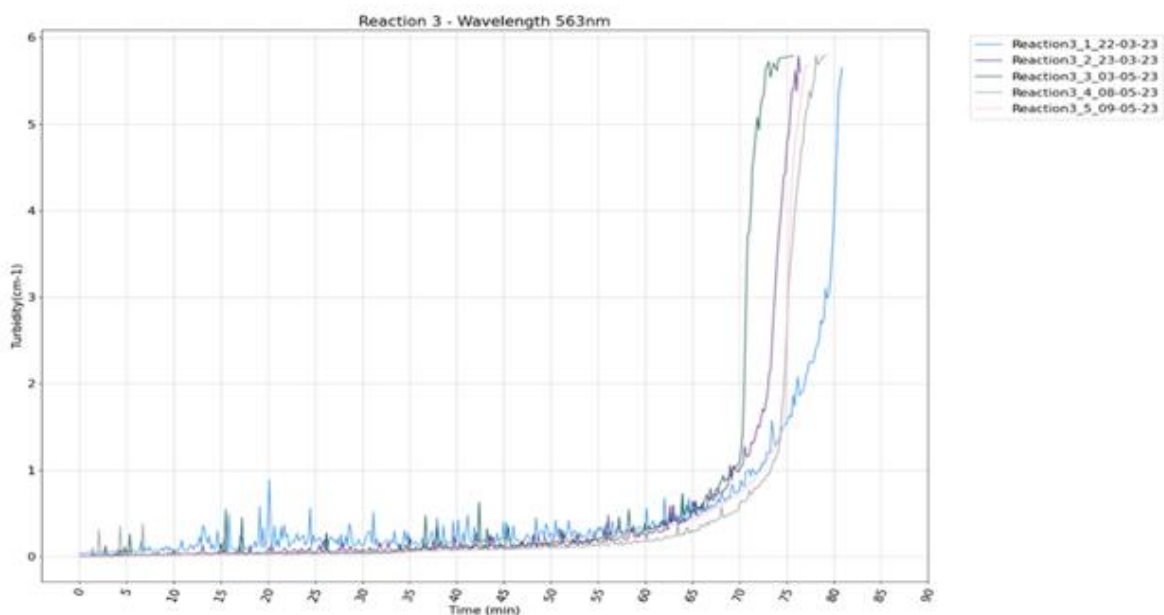


Figure 7. Graph of turbidity measured by TUS device during 5 syntheses of SiO<sub>2</sub> NPs

Figure 7 shows the turbidity measured for 5 runs of the SiO<sub>2</sub> synthesis reaction. There is some difference in the time needed for the reaction to reach the same state. This was possibly due to an issue with the pH sensor in runs 3, 4 and 5. In general, though, the turbidity curves have similar values and regions of behaviour. These results demonstrate the ability of the TUS device to obtain repeatable, reproducible measurements for SiO<sub>2</sub> NP synthesis reactions.

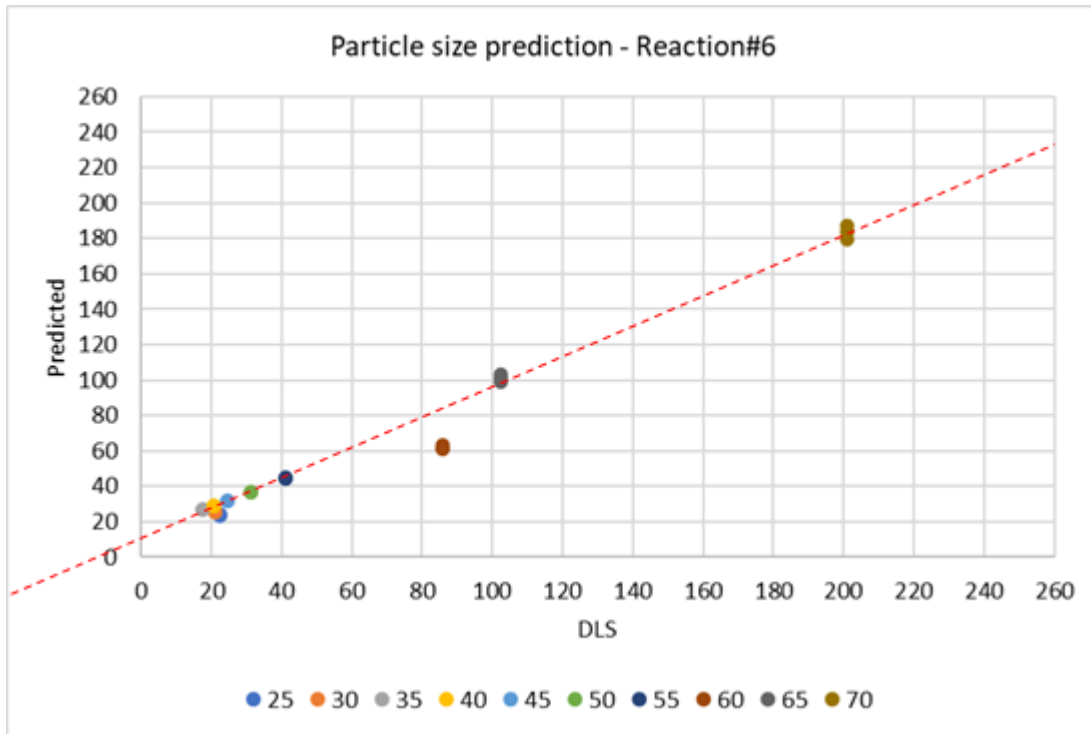


Figure 8. Particle size predicted from turbidity measurements (y axis) versus particle size measured by DLS (x axis)

The model’s predictions are accurate with most points lying on or very close to the straight line. The predicted particle size for the measured size of 87 nm is an outlier. Fig 8 thus demonstrates the ability of the model to estimate the particle size, based on the turbidity measurement by the TUS device.

### Case Study 3: Ceramic NPs in electrolyte suspensions

Author: J. Bolton/IRIS

SiC NPs in electrolyte suspensions of Ni-P with a dispersant of SDS were prepared and measurements using the TUS sensor were taken. The SiC NPs have a tendency to form aggregates and so ultrasound (US) was applied in order to control the particle size. In the tests at MUG 2 problems were found. NPs stuck to the glass windows of the TUS device. Also the high concentration of suspensions led to very low light transmission through the TUS device and so an inability to measure the turbidity. A change was made to the TUS device to increase the speed of flow of NPs through gap. This reduced the number of NPs sticking to the windows. The new device was tested at CNano. A lower concentration of SiC NPs was used to allow sufficient light transmission. The effect of ultrasound (US) on the NP size and the turbidity of the suspension was investigated. The results are presented in Fig. 9.

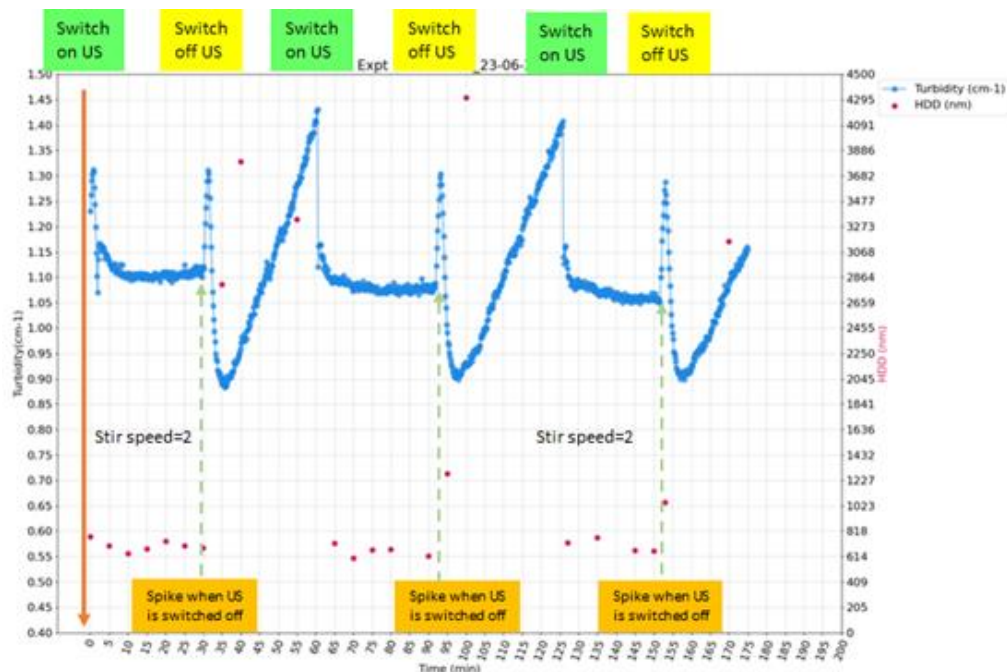


Figure 9. Graph of turbidity (blue line) measured by TUS device and particle size (red dots) measured by DLS whilst US was switched on and off for suspension of SiC NPs

When the US is on the turbidity and particle size remain constant as the US prevents particle aggregates from forming. When the US is off there is a sharp rise and then fall in turbidity after which the turbidity increases as the NPs form particle aggregates and the particle size increases. This behaviour is repeatable over 3 hours. It demonstrates the ability of the TUS device to take continuous measurements in SiC NP suspensions in which US is applied at various times.

Neither Method 1 nor Method 2, applied to case study 1), can be applied to this case study as the NPs are not spherical and are highly polydispersed. A different analysis technique that could be used is to develop a model to correlate the TUS turbidity data to the particle size found by the DLS reference method. However, such a model requires the concentration of the suspension i.e. the number of NPs per unit volume to be known accurately. In CNano's industrial electroplating processes, though, the concentration is not known accurately. The TUS software cannot therefore correlate the turbidity with the particle size using a model. Instead, Iris proposes to develop a function where, when the rate of change of turbidity or the absolute value of turbidity reaches a pre-defined threshold, the user is informed.

## Conclusions

For Case Study 1) the TUS system developed (apparatus, experimental configuration and protocol and data analysis model) provides accurate values for the particle size and is a good candidate to implement in-line or on-line measurement techniques for polymer dispersions.



For Case Study 2) the TUS system developed is able to measure the turbidity and provide accurate values for the particle size for syntheses of SiO<sub>2</sub> NPs in 6L reactors from a few minutes into the reaction, at which point the primary SiO<sub>2</sub> NPs start to form due to the chemical reaction, until the gelation point. In WP6 inline measurements will be taken with the TUS system in the larger reactors of the industrial partner.

For Case Study 3) the TUS system developed is able to measure the turbidity of the SiC NP suspension whilst ultrasound (US) is applied in 2L beakers. It is not possible to obtain the particle size from the turbidity as the concentration of the suspension is not known accurately enough. However, knowledge of the rate of change of the turbidity is enough to inform the user of the evolution in particle size. In WP6 inline measurements will be taken with the TUS system connected to the larger 40 L containers used by the industrial partner for electroplating.