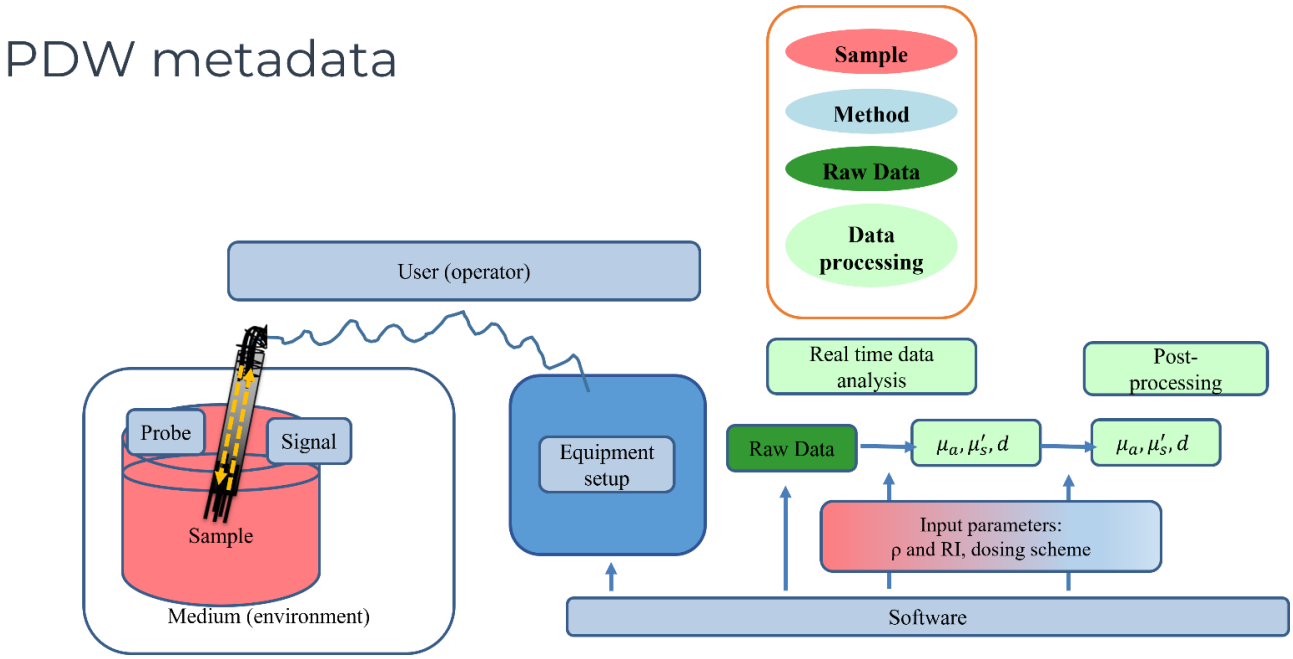
Characterisation data and description of a characterisation experiment for Photon Density Wave (PDW) spectroscopy used in NanoPAT

Overview of the characterisation

1	**Sample**	Photon Density Wave (PDW) spectroscopy can be deployed for dilution-free inline or online analysis of highly concentrated dispersed materials with particles or droplets in the size range of nano- to micrometers. In NanoPAT, PDW spectroscopy was optimised for the real time characterization of polymer, silica and zeolite (nano)particles production at lab- and pilot-plant scale.
2	**Chain of methods**	*Machine prep 1* - The probe is fully immersed into the sample, ideally in the middle of the vessel, with maximum distance to all sample boundaries.
		Machine prep 2 – The PDW spectrometer, computer and PDW software are turned on
		Method 1 - Selection of all input parameters and adequate laser wavelengths.
		Measurement - Acquire reduced scattering coefficient, absorption coefficient and, if needed, particle diameter until measurement is stopped (continuous operation). Measurement raw data is also acquired and stored.
		Machine prep 3 – Switch off the PDW software, the PDW spectrometer and computer.
		Machine prep 4 – Remove the probe from the sample and clean and store it appropriately.
3	**Data publication**	Measurement and analysis files may be stored and made public if deemed relevant and not compromising intellectual property rights of NanoPAT partners.
4	**Access conditions**	To define with the data owner e.g. when generated for a case study, the process owner (i.e. industry) is the dataset owner who defines data accessibility conditions.
5	**Workflow of the characterisation**	Raw data and processed data are acquired by following the chain of methods described in point 2 (above). It is then possible to filter the optical coefficients and diameter distribution data obtained by plotting them as function of time for the different wavelengths selected and identify nanomaterial production process relevant information.

NanoPAT project has received funding from the European Union's HORIZON 2020 research and innovation programme under **grant agreement n°862583**.

Workflow picture



NanoPAT project has received funding from the European Union's HORIZON 2020 research and innovation programme under **grant agreement n°862583**.

CHADA

1. SAMPLE		
1.1	**USER**	PDW spectroscopy provides an easy-to-use approach. The device is only used by specifically trained staff in research and development institutions and within the given technical specifications. Installation Qualification, Operational Qualification and Performance Qualification documents are available to verify that the equipment is correctly installed, operates according to requirements and performs safely. The installation and setup of the device must be conducted by or under the supervision of the manufacturer. User Manual including technical specifications is available.
1.2	**Process under investigation**	Nano-production processes e.g. nucleation, gelation, polymerization, and particle stability studies.
1.3	**Characterization environment**	Sensor is adapted to plant requirements when possible. Turn-key solution. Environmental considerations for sampling point: -stirred or flowing systems -compatible with high temperature -compatible with acidic environments
1.4	**Sampling process**	No sampling needed. Probe is placed directly in the reaction vessel (inline) or in the recirculation/ transfer loop (online). Offline characterisation of sample also possible with a min volume of approx. 0.5 L.
1.5	**Sample**	Materials of interest in suspension with a min volume of approx. 0.5 L and needs to exhibit min turbidity ($\mu_s' > 0.05$ mm^{-1}).
1.6	**Sample material properties**	Various (nano)particle compositions and sizes can be analysed by PDW depending on their scattering properties and refractive index of the medium. However, PDW spectroscopy requires that multiple light scattering occurs in the sample, i.e. min turbidity (reduced scattering coefficient $\mu_s' > 0.05$ mm^{-1}) is needed for accurate determination of optical coefficients of particles that are assumed to be spherical. Typically, PDW can characterise liquid suspensions or emulsions with a content of particles or droplets in between 0.1% to more than 50% and with a size between 50 nm to 500 µm depending on their refractive properties. In case of low scattering properties, the performance of a PDW spectroscopy measurement can be improved by applying shorter laser wavelengths at which light scattering is more pronounced.
1.7	**Sample preparation**	Inline/online measurement made without the need for any calibration or sample pre-treatment. Min sample volume of approx. 0.5 L, no max sample volume.
1.8	**Material**	PDW spectroscopy independently assesses the size distribution of particles from their absorption & scattering properties, allowing the indirect identification of key nano-production processes e.g. nucleation, gelation, polymerization and particle stability studies. Prerequisite is that the liquid materials exhibit min turbidity during their processing. It is compatible with various (nano)particle compositions (tested so far in pilot plant production of silica, zeolite, and polymeric nanoparticles in NanoPAT).

NanoPAT project has received funding from the European Union's HORIZON 2020 research and innovation programme under grant agreement n°862583.

1. SAMPLE		
1.9	**Hazard**	Intrinsically electronics-free safe, fibre-optics only probe with low optical light intensities for installations in critical environments (ATEX). Risk of puncture injury with fibre-optical probe, danger of uncontrolled exposure to optical radiation when probe cord gets damaged. Danger from lack of ventilation of spectrometer and measurement computer. Danger due to the electricity of the computer. Maintenance and repairs of the device can only be conducted by appropriately qualified staff.

2. METHOD/Experiment		
2.1	**Sample/probe physics of interaction**	PDW spectroscopy is a fibre-optical process analytical technology (PAT). Detection of the absorbance and scattering properties of a dispersion of particles interacting with different laser light wavelengths. Typical probe materials: stainless steel, glass, PTFE. Customer specific development possible.
2.2	**Volume of interaction**	0.25 L
2.3	**Equipment setup**	Laser wavelengths from approx. 450 to 980 nm, modulation frequencies from 10 MHz to 1 GHz, temporal resolution approx. 2 min^{-1}. Currently available probe dimensions: diameter 19 and 25 mm, length freely scalable
2.4	**Calibration**	PDW spectroscopy works calibration-free.
2.6	**Detector**	Inside the spectrometer
2.7	**Signal**	Photon density wave properties (amplitude, phase, wavelength). PDW spectroscopy uses intensity modulated laser sources throughout the visible and near infrared spectral range with modulation frequencies from 10 MHz well beyond 1 GHz to generate Photon Density Waves in strongly light scattering materials. Detection of amplitude and phase in dependence on modulation frequency and source-detector fiber distance allows for the precise determination of fundamental optical properties of the material under investigation, namely the absorption and reduced scattering coefficients (unit mm^{-1}).
2.8	**Time lapse (Measurement time)**	Time-resolution of approx. 2 min^{-1} and continuous operation possible inline (i.e., directly inside the reaction vessel without previous sampling or dilution) or online (i.e. if analysis required at recirculation/transfer loop system).
2.9	**Testing Input parameters (Measurement parameters)**	Required information for absolute particle size analysis: Refractive index of the continuous and disperse phase and volume fraction of the disperse phase.

NanoPAT project has received funding from the European Union's HORIZON 2020 research and innovation programme under grant agreement n°862583.

3. RAW DATA		
3.1	**Raw Data**	Time, emitter-detector fibre distance, intensity and phase
3.2	**Unit**	[dd:MM:yyyy hh:mm:ss], [mm], [dB], [°]
3.3	**Data acquisition rate**	approx. 30 min^{-1}

4. DATA PROCESSING		
4.1	**Level of expertise**	Little expertise: Person can read out particle sizes directly and plot particle size distributions from results. But Domain expertise required to interpret the particle stability profiles in terms of nano-production processes (e.g. gelation, nucleation).
4.2	**Data normalisation**	Not needed
4.3	**Data Processing reproducibility**	No limitations observed so far
4.4	**Data filtering processes**	High variability of the results obtained with a particular wavelength may lead to its exclusion for size particle characterization for the material and reaction process conditions under investigation.
4.5	**Data analysis procedures**	PDW spectroscopy allows for the independent, absolute quantification of the absorption and scattering properties of disperses materials, i.e., the absorption and reduced scattering coefficients, respectively, at a given measurement wavelength. Several laser wavelengths can be applied. The absorption coefficient contains information about the chemical composition and/or the temperature of the material. The reduced scattering coefficient is related to the number and size of the dispersed particles. The size of the dispersed particles can be retrieved from the reduced scattering coefficient by Mie theory and theories for dependent light scattering. The reduced scattering coefficient μ_s' is the inverse of the transport mean free path. The latter is the average distance a wave travels before its direction of propagation is randomised and depends on the particle diameter d and the particle volume fraction ϕ. To calculate particle sizes from the μ_s' measured by PDW spectroscopy, the refractive index of the sample n should be known. It can be calculated from the refractive index of the medium n_m and the particles n_p, and the particle volume fraction ϕ according to the Newton equation. It should be noted that particles are considered spherical.
4.6	**Main processed signals**	Changes to a sinusoidal wave wrt. amplitude and phase caused by light matter interaction
4.7	**Data processing through calibrations**	PDW works calibration-free.
4.8	**Properties (elaborated data)**	Absorption and reduced scattering coefficient per measurement wavelength as well as particle sizes distribution (average and standard deviation) plotted as function of time to identify nanomaterial production process relevant information.
4.9	**Quality of the data**	Standard Deviation of diameter as function of time is used to evaluate whether results obtained from a certain wavelength should be excluded.

NanoPAT project has received funding from the European Union's HORIZON 2020 research and innovation programme under grant agreement n°862583.

4. DATA PROCESSING		
		Robustness of the data may be evaluated with offline size characterisation techniques (such as DLS) for a sub-sample of the reaction suspensions.
4.10	**Data management**	Measurement and analysis files are stored automatically on the spectrometer control laptop. Further data management is left to the discretion of the data owners.

NanoPAT project has received funding from the European Union's HORIZON 2020 research and innovation programme under **grant agreement n°862583**.