Nuclear magnetic resonance (NMR) spectroscopy analysis for specific surface area determination

Date
30.05.2016

Version
1.0 English

Contents

1 Scope

This Standard Operating Procedure (SOP) describes the experimental procedure and settings of the nuclear magnetic resonance (NMR) spectroscopy analysis for the detection of the specific surface area of nanomaterials (NM) in aqueous suspension.

Note: The SOP is specific for the use of NMR instrument from Xigo nanotoolsTM.

2 Basics

Within the increased use of nanomaterials (NM) in the last years also the efforts to detect the specific surface area of NM increased. The specific surface area determines the contact area of the NM with other surfaces / substances in the environment. NM show a larger specific surface area compared to their microscale pendants, with the consequence that it has been suggested that NM are more "reactive". Thus, it is not surprising that the specific surface area is suggested to be a relevant dose metric e. g. in nanotoxicology. The surface area has been defined by ISO (2012) as "the quantity of accessible surface of a sample when exposed to either gaseous or liquid adsorbate phase." The specific surface area is defined as the surface area of a material divided by its mass or its volume. In this SOP the specific surface area per mass is used (m^2/g) and its determination using the Nuclear Magnetic Resonance (NMR) Spectroscopy is described. Briefly, this method detects the differences of adsorbed and free H-nuclear relaxation time after elicitation by magnetism. The ratio between the two signals (dependent on the area of the adsorbing surface) is used to calculate the specific surface area. Before the NMR analysis the NM were brought into suspension by using the nanOxiMet Dispersion protocol_sonication_cuphorn_1.1

2.1 Background: NMR for Surface Area Measurement

As previously mentioned, the NMR technique detects the differences of shorter relaxation time of bounded liquid at particle surfaces compared to unbound liquid (assumption all bound molecules have the same relaxation time). Based on the knowledge of the unbound relaxation time and further parameters, the specific surface area (S) can be calculated using the following equations:

$$Rav = \psi_p \, S \, L \, \rho_b \, (R_s - R_b) + R_b \qquad \text{(Equation 1)}$$

Rav = Average spin relaxation rate constant
ψ_p = Particle volume to solvent volume ratio
S = Total Surface Area per unit weight
L = Thickness of liquid surface layer
ρ_b = Bulk density of particles
R_s = Relaxation rate constant of bound solvent
R_b = Relaxation rate constant of bulk solvent

where,

$$K_a = L \, \rho_p \, (R_s - R_b) \text{ (specific surface constant)} \qquad \text{(Equation 2)}$$

the equation can be reduced to:

$R_{av} = K_a S \psi_p + R_b$ (Equation 3)

Finally the equation for surface area (S) is:

$S = R_{sp} R_b / K_a \psi_p$ (Equation 4)

where,
$R_{sp} = R_{av} / R_b - 1$ (Equation 5)

The K_a value depends on the interaction of particle and the dispersion liquid, so K_a is material and liquid specific and has to be estimated individually. For the determination of K_a at least one single value of the surface area (or size ↔ calculation of the surface area) must be known (e.g. via DLS, centrifugal sedimentation, microscopy). Hence the specific surface area determination is semi-quantitative.

Note: For the K_a calculations please refer to the provider's manual.

3 Materials & Instruments

3.1 Materials

The following materials and chemicals are required:

- Particle suspension for investigation
- Deionised water (DI)
- NMR tubes
- Cleaning wipes
- Pipette
- Ethanol (for hydrophobic materials; for dispersion a mixture of DI with Ethanol 0.5 vol% is used)

3.2 Instruments

The following instruments are required:

- Nuclear magnetic resonance (NMR) spectrometer (Xigo nanotools^{TM})
- Vortexer (≥ 2800 rpm)

Note: Mainly the settings for the NMR instrument, but not the detailed usage and maintenance of the instruments will be described in this SOP. For Usage and maintenance please refer to the manual.

4 Experimental procedure

The device has to be switched on / warm up for at least 24 hours before starting an experiment. Before measurements the resonant frequency Hz, pulse lengths (set at 90° = 6.78 µs, 180° = 13.55 µs,) pre-amp tuning value (220) and R(x) gain of 10 dB has to be entered or measured respectively. Therefore, a copper sulphate ($CuSO_4$) calibration standard solution (Xigo Nanotools, USA) is used at the beginning of the analysis. After this the T2 value of DI water was measured and relaxivity times from 2200 – 2500 ms were obtained and set as the bulk relaxation value for the analysis. The surface area was estimated using the "Area by T2 CPMG" sequence in the AreaQuant software. The specific surface relaxivity (K_a) and particle to liquid volume ratio is measured according to the provider's handbook suggestions via concentration row measurements and the AreaQuant software. At least three different concentrations of 1.5 - 20 w% have to be measured. For measurement details see following section 4.3.

4.1 Preparation and measurement

- The NM suspension (after suspended via Dispersion protocol nanOxiMet_cuphorn_1.1) is transferred (at least 2 mL) in a NMR tube via pipette
- The tube is placed in the NMR and the NMR T2 signal is measured for the following settings

4.2 NMR settings

- Resonant frequency (Hz) has to be determined via $CuSO_4$ calibration standard daily; pulse lengths were set at 90° = 6.78 µs, 180° = 13.55 µs; pre-amp tuning value = 220 and R(x) gain = 10 dB. Number of scans per experiment = 3, Number of experiments = 3.

4.3 NMR Measurements

For a detailed measurement procedure and software usage please refer to the manual. Just briefly due to the equation 4 following parameters have to be determined, respectively entered in the software prior measurement:

- Particle volume to solvent volume ratio (by entering the density of the particle and the density of the bulk solvent in the Particle system calculator)
- Specific surface relaxivity (to be determined via concentration row or using providers information/list)
- Relaxation rate constant of bulk solvent (to be determined prior first surface area measurement)

4.4 Quantification

- Quantification is carried out as given by the instrument software as specific surface area (m^2/g). An analysis protocol is saved parallel.

Note: Please refer to the instrument manual.

5 Safety precautions

For all working steps protective clothing, safety goggles and gloves have to be worn.

6 Waste disposal

NMR tubes filled with NM suspension have to be collected and disposed off separately.

7 Literature

ISO, ISO/TR 13014:2012: Nanotechnologies -- Guidance on physico-chemical characterization of engineered nanoscale materials for toxicologic assessment, 2012.

Title: NMR spectroscopy analysis for specific surface area determination

This SOP is valid from: 30.05.2016

This SOP replaces the SOP from: Primary version

Responsible for the implementation of this SOP: Measurement personal

Previous changes: Primary version (1.0)

Distribution: Management
Head of department
Measurement personal
Quality management

Signature, Date

Author: _____,_____
Dr. rer. nat. B. Hellack

Reviewed: _____,_____
Dr. rer. nat. C. Nickel