Static and Dynamic Testing for Determining Dissolution Rates of Metal Nanoparticles

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Background and aim

Metal nanoparticles may have adverse effects towards environment due to formation of dissolved species. (Li et al. (2011) Environ. Sci. Technol. 45, 1977-1983).

For environmental assessment the determination of the rate describing the release of dissolved species constitutes a crucial factor and is often required by the European Chemicals Agency (ECHA) for metal nanoparticles.

OECD GD 318 represents the approach for testing and calculation of dissolution rate for metal nanoparticles but test conditions can be varied to a greater extent (e.g. test medium, loading, sampling times). (OECD (2020) No 318; ENV/JM/MONO, 9; 2020).

Aim: Implementation and testing setups for static and dynamic test and determination of dissolution rates for chosen metal nanoparticles.
Choosing reasonable test conditions based on OECD GD 29.
(OECD (2001) No. 29; ENV/JM/MONO, 9; 2001).

Static batch test

Orbital shaking device

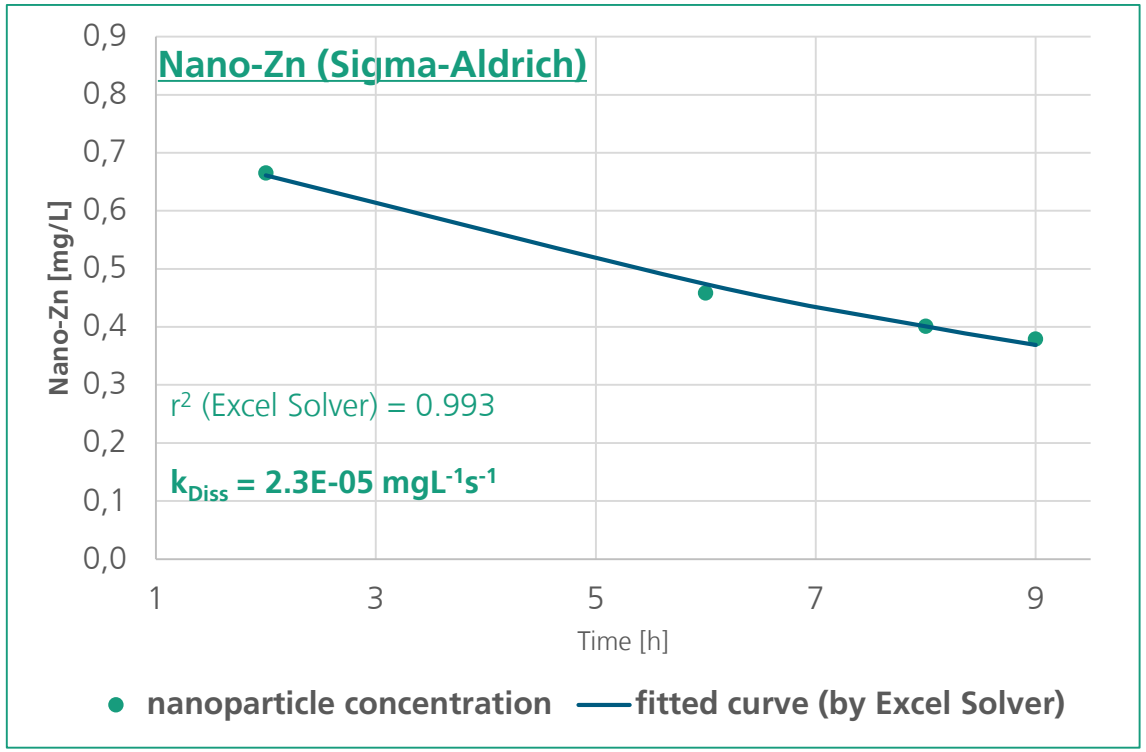
Centrifugal ultra-filtration tube

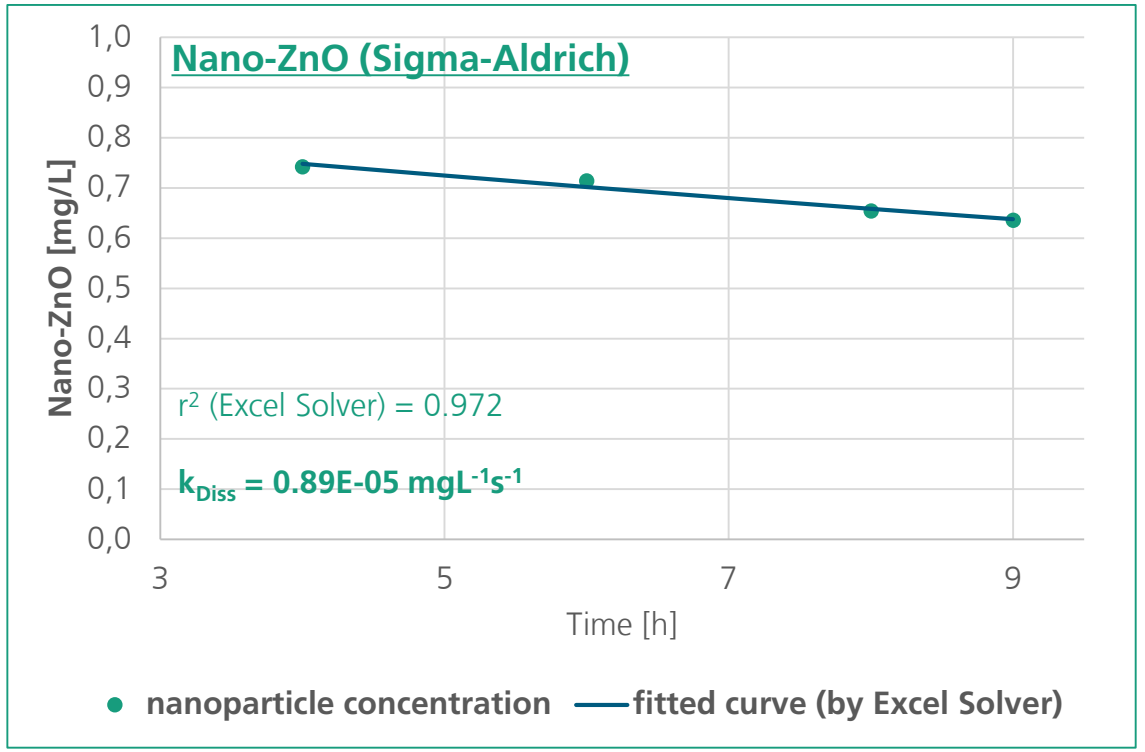
- Transformation/dissolution test setup and medium according to OECD GD29 and ISO 6341.
- Loading 1 mg/L test item and blanks in triplicate according to OECD GD 29.
- Sampling until solubility equilibrium has been established (OECD GD 29: Two last sampling points do not differ by more than 15%).
- Centrifugal ultra-filtration for separation of nanoparticles and dissolved species.
- Quantification by ICP-OES or ICP-MS.

Calculation of dissolution rate

- Dissolution rate describes the dissolution of metal nanoparticles in time (decrease in time)
- $\frac{d}{dt}m(t) = -k_{diss} \cdot m(t) \longrightarrow m(t) = m(0) \cdot exp(-kt)$
- Equation with two unknown [m(0) and k]
- Solving by EXCEL Solver to find the best fit for measured concentrations over time

Dissolution rates of chosen nano-Zn, ZnO, TiO_2 (batch test in OECD GD29 medium)





k_{Diss} (ZnO): 0.22E-05 $mgL^{-1}s^{-1}$ **Michaelis et al. (2017). Environ. Sci. Technol. 51, 4297-4305**;

=> most probably different material, however k_{Diss} is in a similar range in UHQ.

- **Nano TiO_2 (NM-105K)**: Measured dissolved concentrations below LOQ (LOQ_{Ti} = 130 ngL^{-1}).

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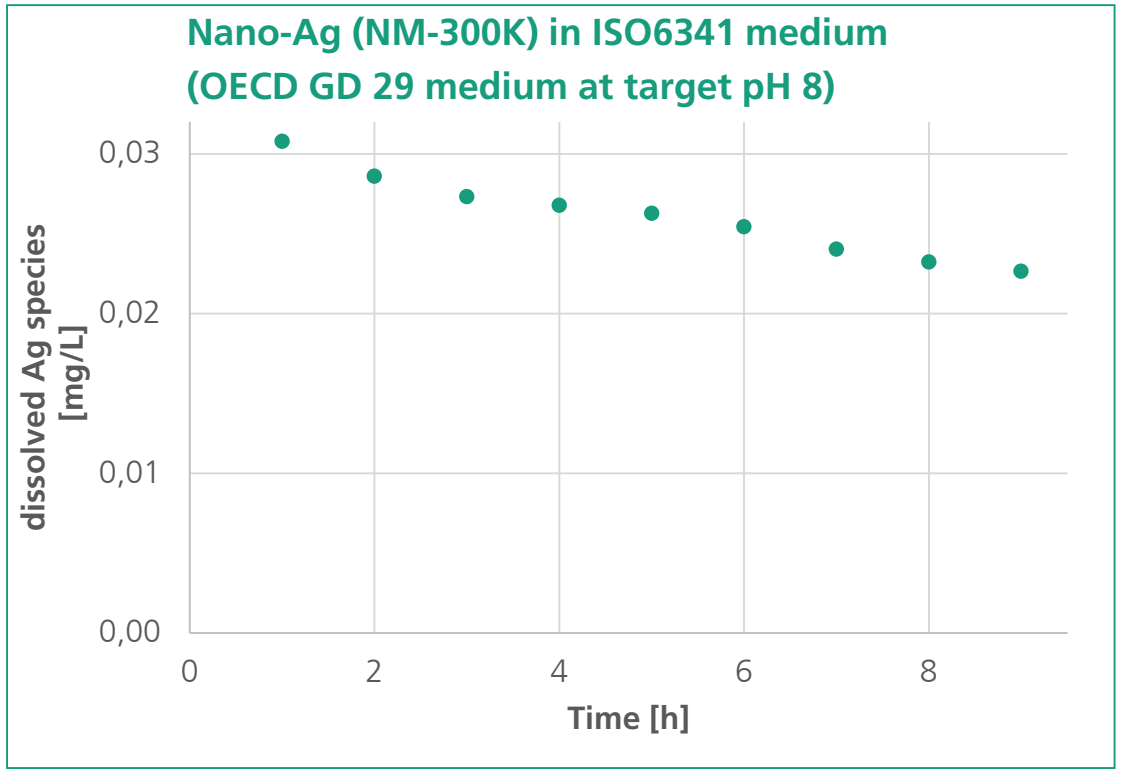
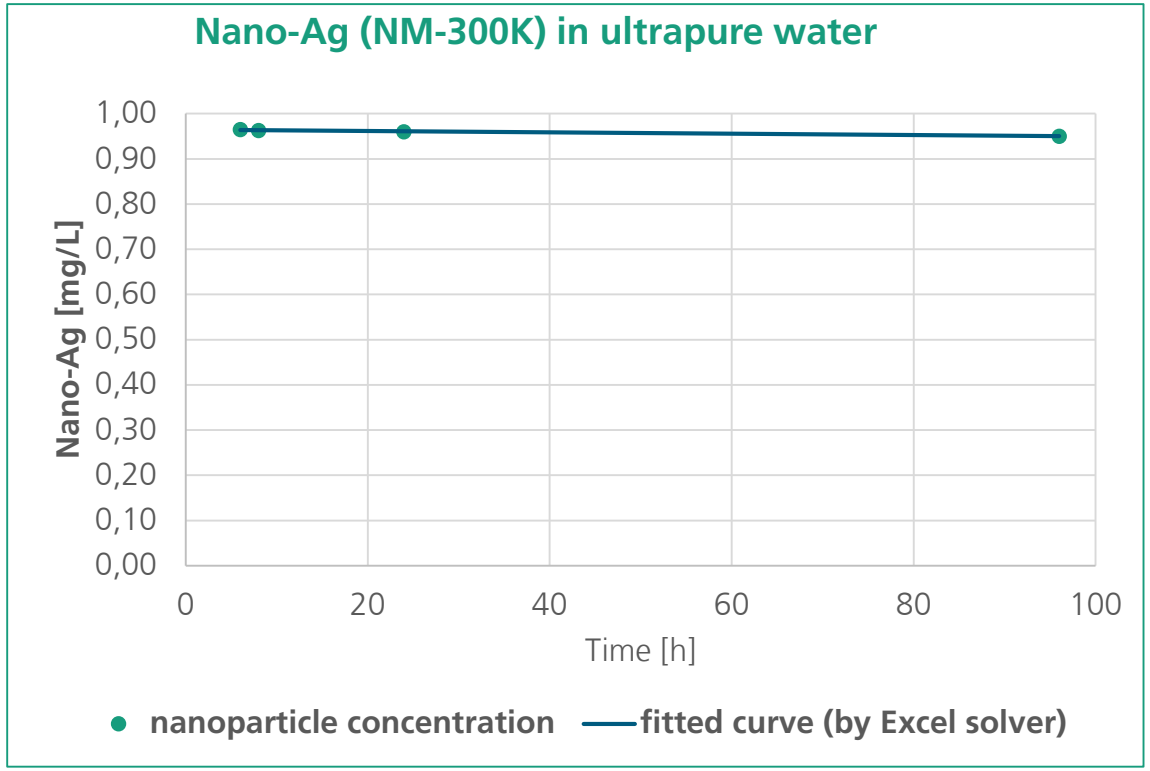
Dissolution rate of chosen nano-Ag (NM-300K) in batch test





- Decreasing trend in concentration [left plot]; reaction with medium is assumed.
- Checking possible reaction with medium by testing in ultrapure water, but solubility equilibrium seems to be established more or less instantly [right plot].

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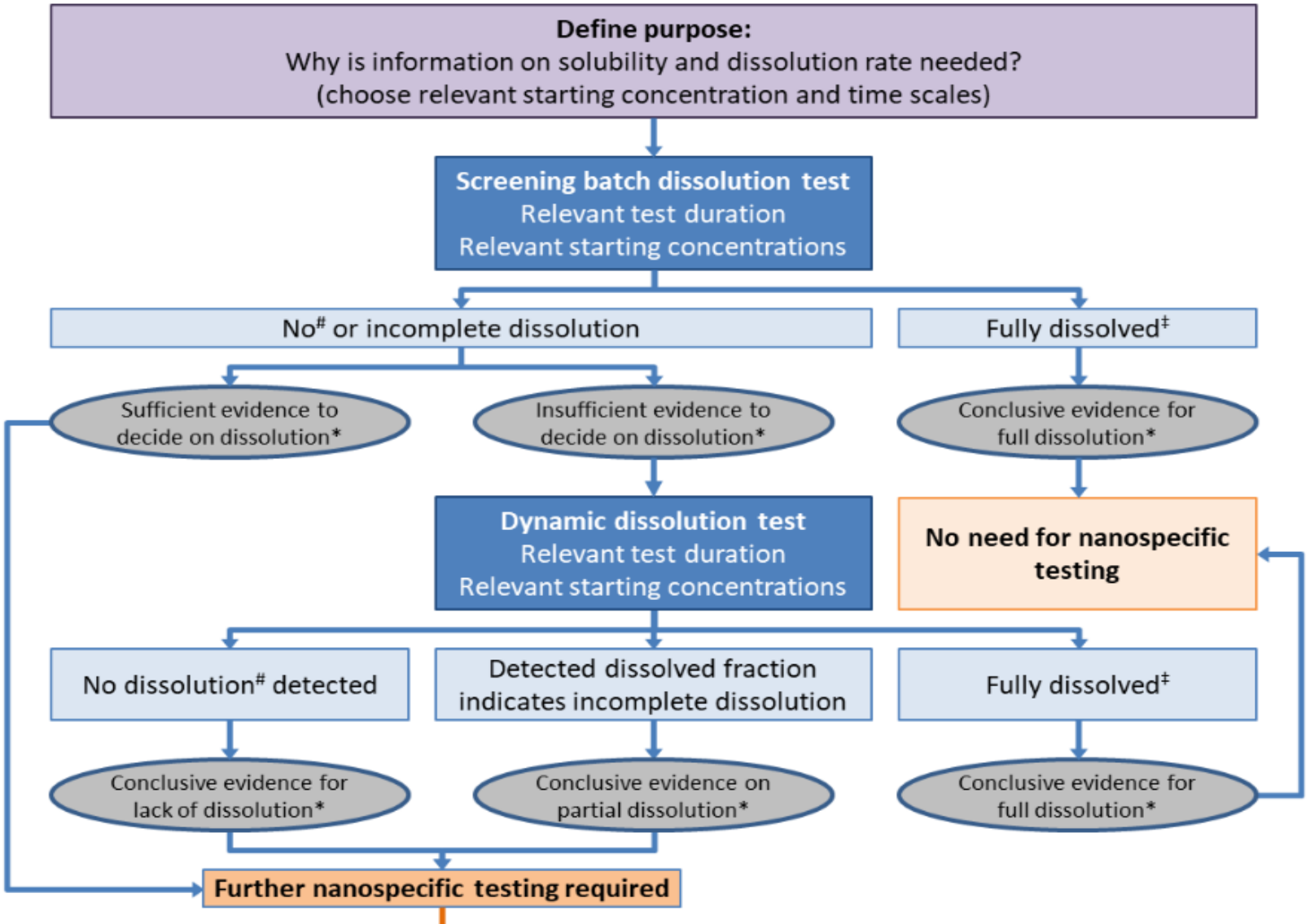
Decision tree from OECD GD 318



- Insufficient evidence to decide on dissolution in case of nano-Ag (NM-300K).
- **Dynamic test is required.**

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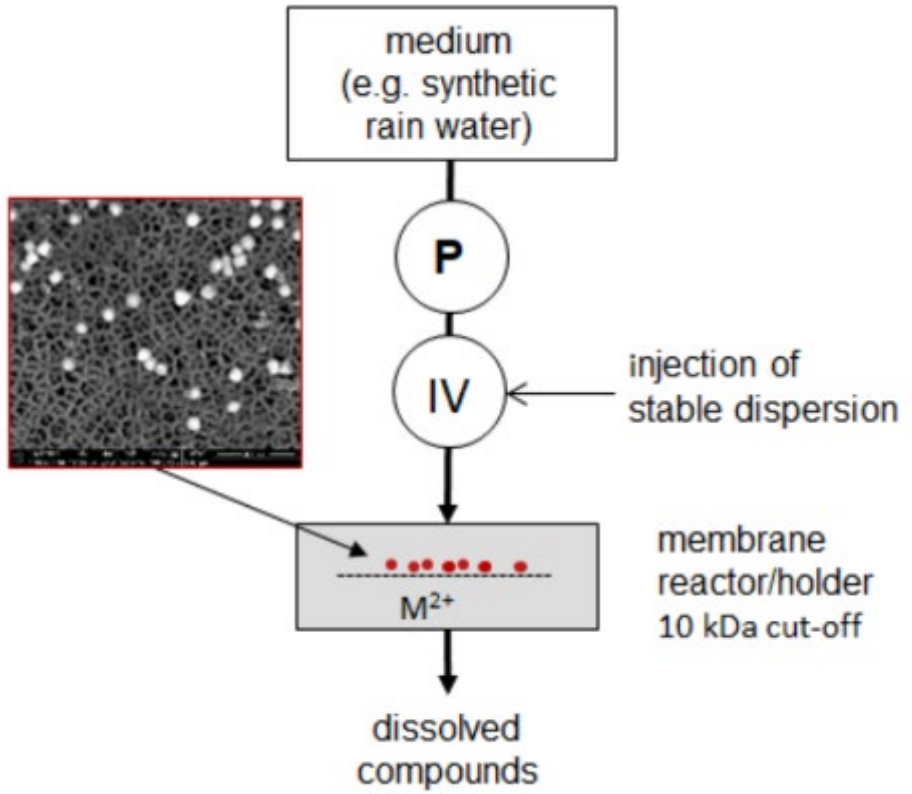
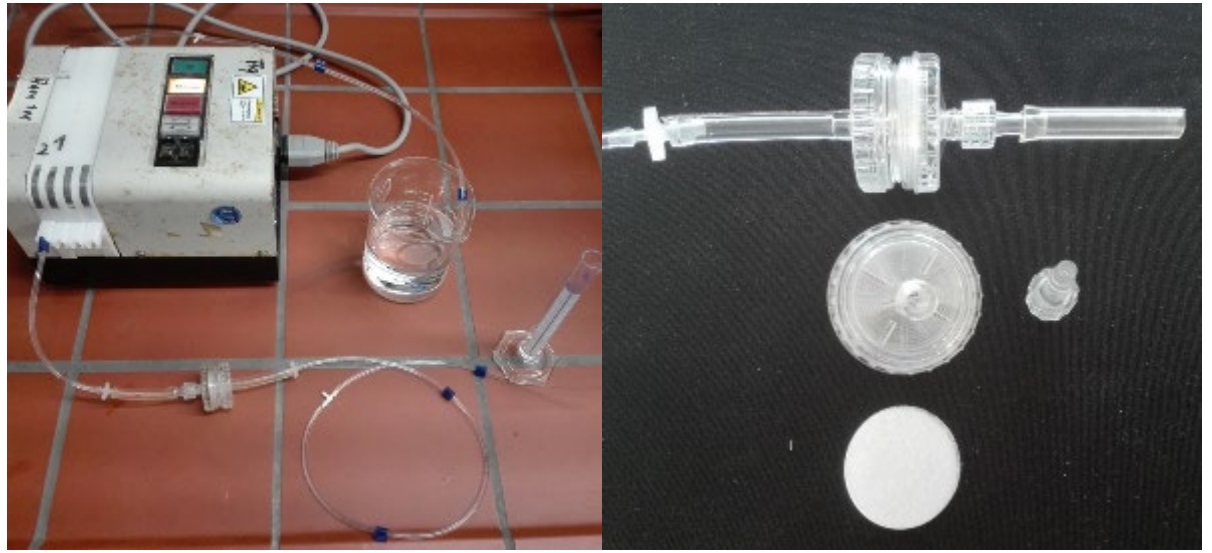
Dynamic test

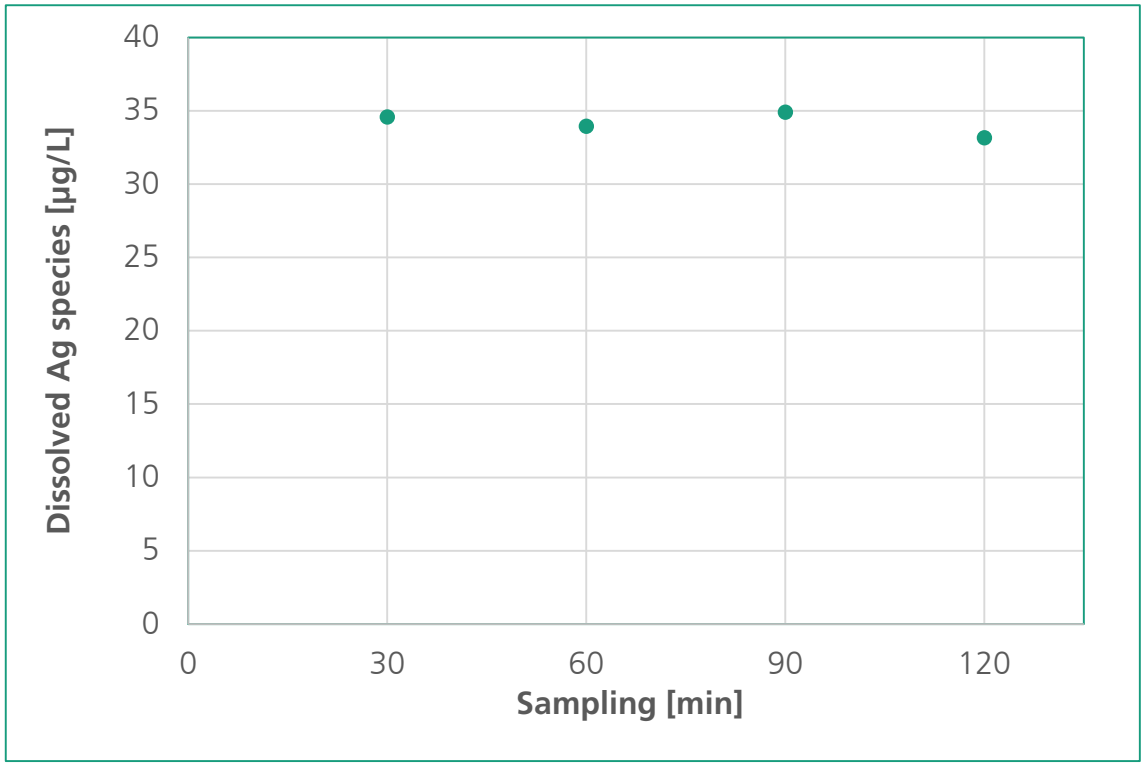


Scheme from OECD GD 318 suggesting possible test setup



Approach for test setup at Fraunhofer IME

Dissolution rate of nano-Ag (NM-300K) in dynamic test in ISO 6341 medium



- Constant concentration of dissolved Ag species.
- Flow rate, collected volume, time and mean concentration are known:

→ k_{Diss} = 1.9E-05 $mgL^{-1}s^{-1}$

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Summary

- Batch tests for determining of dissolution rates for selected metal nanoparticles were established according to OECD GD 318 (based on OECD GD 29).
- For nano-Ag (NM-300K) it turned out that batch testing resulted in insufficient evidence to decide on dissolution and dynamic testing is required.
- Implementation of a possible flow through test setup for dynamic testing.
- Execution of dynamic test for nano-Ag.

Outlook

- Investigation of influence of further environmental relevant media on dissolution rate.
- Investigation of influence of flow rates (dynamic test) on dissolution rate.
- Normalization of dissolution rate to either the mass or the surface area of investigated nanomaterial.
- Determination of further parameters for normalization (OECD GD 318) and applying respective equation for normalization.

Thank you for your attention