

Stability of silver nanoparticles in aqueous suspensions

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■ Nanoparticles

- sized between **1 and 100 nm**
- physical properties are different from both the ion/dissolved and the bulk material form (melting point, optical and catalytic activity)

■ Increasing application of **manufactured or Engineered Nanoparticles (ENP)**

- in industry (catalysis, food production, surface treatment),
- in medicine (pharmaceuticals),
- and in daily life (personal care products)

■ **Consequence:** ENP will find their way into **environmental systems.**

■ **Environmental behavior** of ENP

- interactions with water constituents, e.g. calcium and natural organic matter (NOM)
- alteration of pristine ENP (e.g. coating with NOM, aggregation)
- effects on stability, mobility, interactions with trace pollutants, toxicity

- **Focus:** behavior of **silver nanoparticles (n-Ag)** in aqueous solutions
- **Synthesis of n-Ag** by chemical reduction of AgNO_3 in the liquid phase
- **Stability of n-Ag suspensions**
- **Interactions** between n-Ag and calcium, sodium and NOM
- **Analytical methods** to characterize the stability and the interactions of n-Ag with water constituents:
 - **UV/vis spectroscopy:** detection of n-Ag
 - **Dynamic Light Scattering (DLS):** hydrodynamic radius
 - **Laser Doppler Electrophoresis (LDE):** zeta potential
 - **Asymmetric Flow Field-Flow Fractionation (AF⁴)** coupled with UV detection and inductively coupled plasma mass spectrometry (ICP/MS): particle size, chemical composition
 - benefits and limitations of the methods, challenges for further developments

■ Widely used

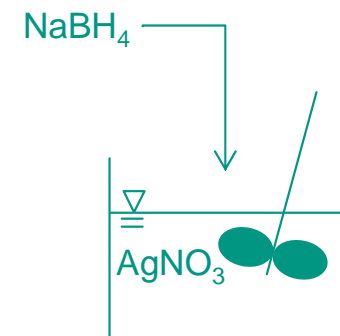
- as catalyst (oxidation of ethylene to ethylene oxide),
- as nanoelectronic device, or
- in treatment of textiles (antimicrobial properties) [Benn und Westerhoff 2008, ES&T, 42, 4133-4139].

■ Environmental impact (Switzerland):

Approx. **5 t/a** of n-Ag are released into the environment due to textiles (10 %), cosmetics (25 %), paint (35 %) and other (30 %) products [Müller and Nowack 2008, ES&T, 42, 4447-4453]

Preparation of n-Ag

- chemical reduction of AgNO_3 with NaBH_4 (in liquid phase):
$$2 \text{AgNO}_3 + 2 \text{NaBH}_4 + 6 \text{H}_2\text{O} \rightarrow 2 \text{Ag} + 2 \text{B(OH)}_3 + 2 \text{NaNO}_3 + 7 \text{H}_2$$
- theoretical molar ratio $R_{\text{theor}} = c(\text{reducing agent})/c(\text{AgNO}_3)$ (here: 1:1)
- Teflon bottles were used for preparation (stability problems in glass bottles)
- after systematic variation of reaction conditions (stirring time, R_{exp}):
 - $c_0(\text{AgNO}_3) = 0,2 \text{ mmol/L}$, $c_0(\text{NaBH}_4) = 1 \text{ mmol/L}$ ($R_{\text{exp}} = 5$)
 - stirring time of the solution $t_{\text{stirr}} = 24 \text{ h}$
 - liquid phases:
 - MilliQ water (MQ)
 - Brown Water (Lake Hohloh, Black Forest/Germany; HO26), $\rho(\text{DOC}) = 21 \text{ mg/L}$
 - Mixtures of MQ and HO26



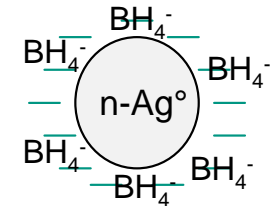
Basic characterization of the resulting suspensions

■ n-Ag in MilliQ water (MQ):

- **stable suspensions**, $\text{pH} \approx 8,3$
- **DLS**: hydrodynamic radius $r_H \approx 2,4 \text{ nm}$
- **LDE**: zeta-potential $\approx -40 \text{ mV}$ (layer of BH_4^- which surrounds the n-Ag [Song et al., 2009, Kor J Chem Eng, 26, 153-155])

■ Addition of Brown Water (HO26):

- similar pH value and negative zeta-potential
- increasing hydrodynamic radius with increasing DOC concentration:
 - **HO26:MQ = 1:1** ($\rho(\text{DOC}) = 11 \text{ mg/L}$): $r_H \approx 3,8 \text{ nm}$
 - **HO26** ($\rho(\text{DOC}) = 21 \text{ mg/L}$): $r_H \approx 6,5 \text{ nm}$
- explanation: coating of n-Ag particles with NOM molecules



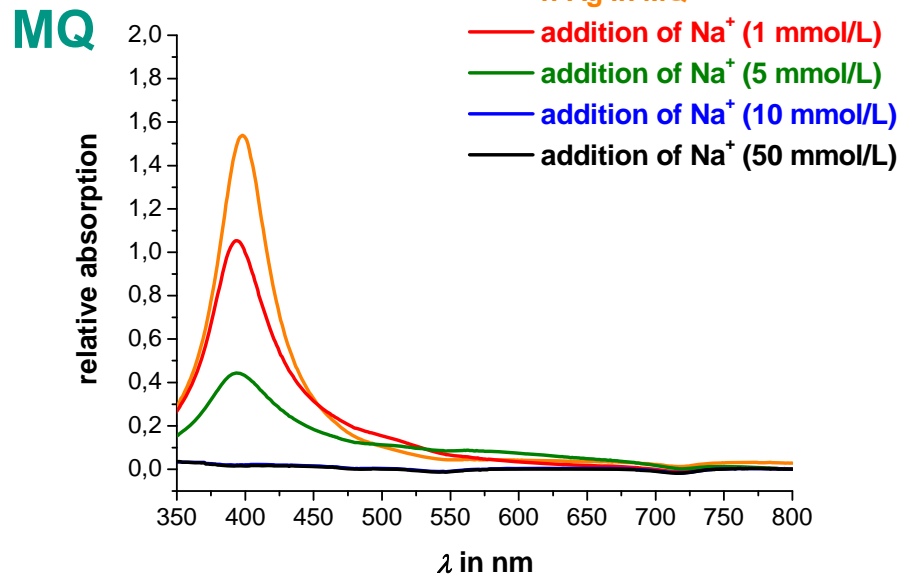
Stability of n-Ag suspensions

- Addition of NaNO_3 or $\text{Ca}(\text{NO}_3)_2$ (1 – 50 mmol/L)
- Suspension stability was investigated using UV/vis spectroscopy at 400 nm (light absorption of n-Ag due to the formation of a plasmon absorption band in the visible region [yellow])

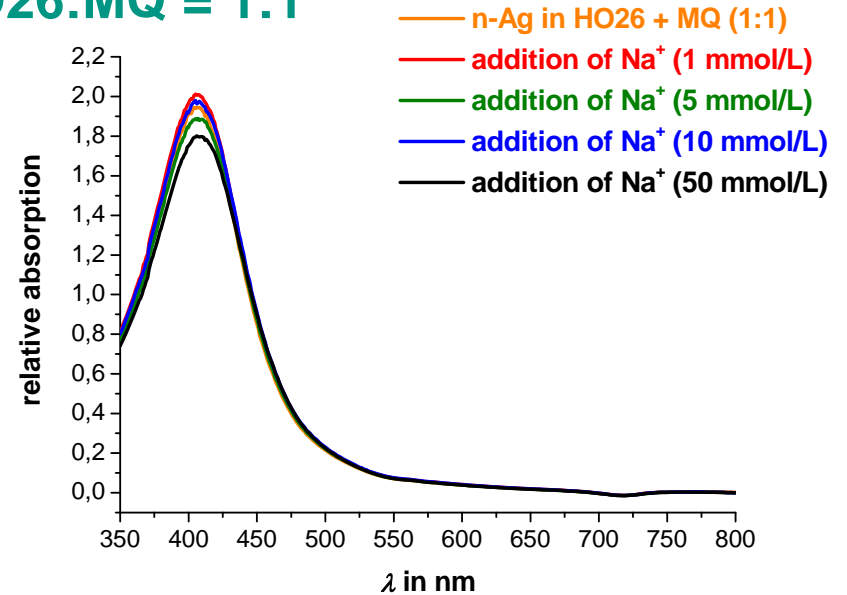


n-Ag in a teflon bottle

Addition of NaNO_3



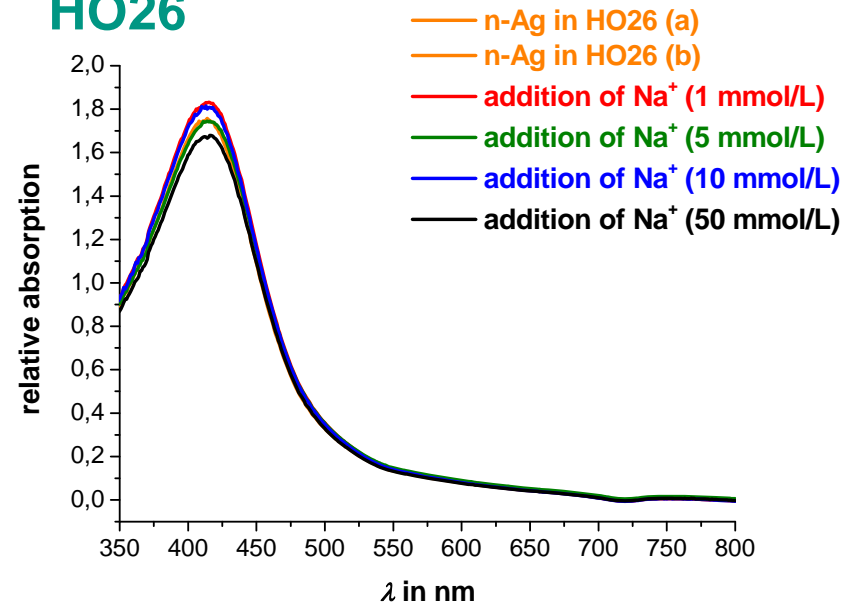
HO26:MQ = 1:1



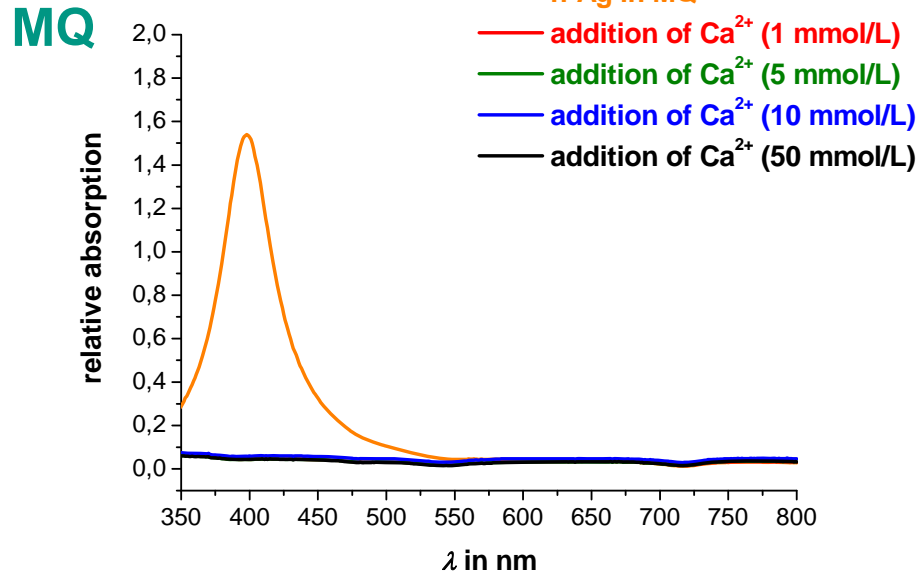
Addition of Na^+ :

- destabilization of n-Ag in MQ (compression of electrical double layer, aggregation)
- suspensions with HO26 remain stable
- NOM improves stability of n-Ag (surface coating, steric and charge stabilization)
[\[Cumberland and Lead 2009, J Chrom A, 1216, 9099–9105\]](#)

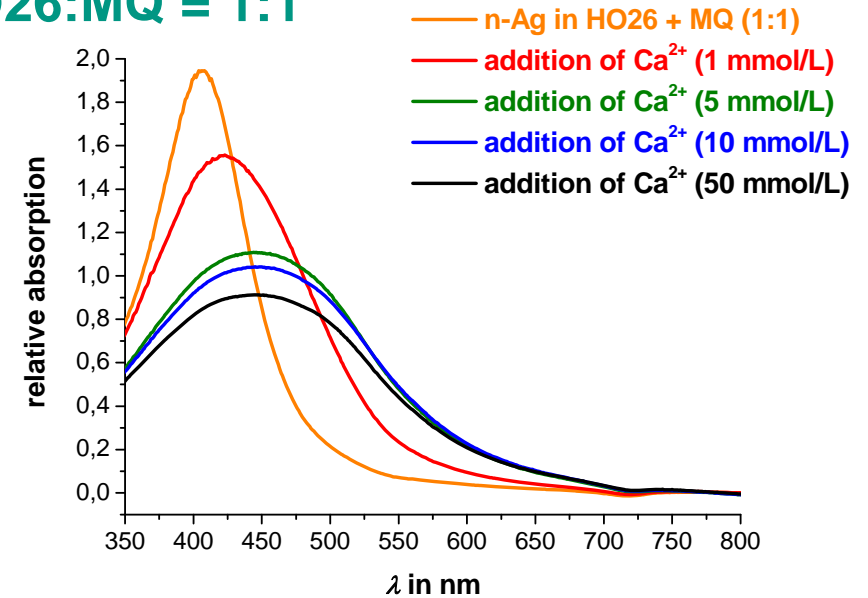
HO26



Addition of $\text{Ca}(\text{NO}_3)_2$



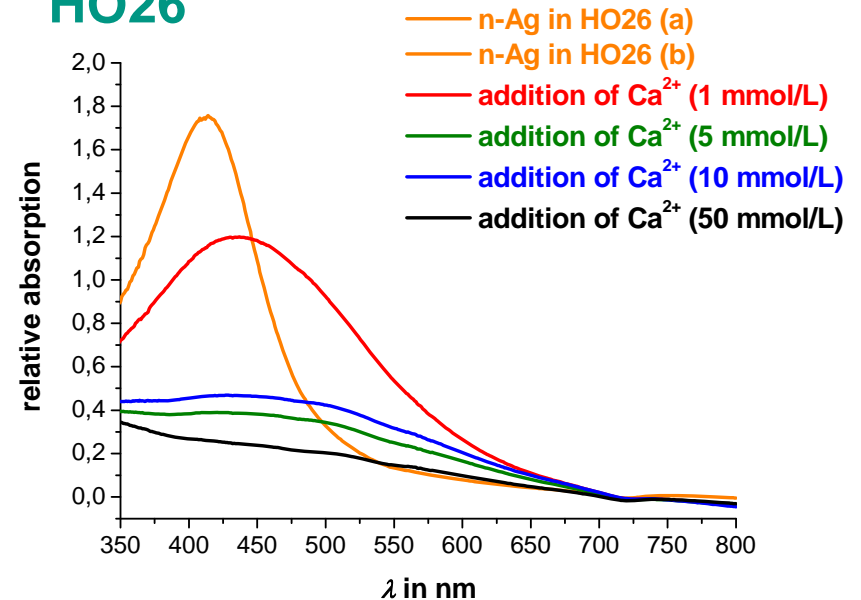
HO26:MQ = 1:1



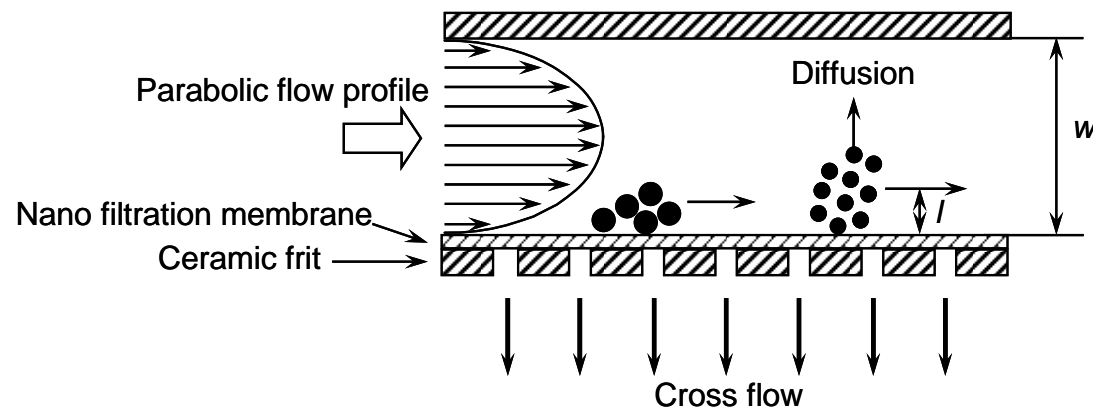
Addition of Ca^{2+} :

- destabilization of n-Ag in MQ, complete aggregation (higher ionic strength with Ca^{2+} than with Na^+)
- addition of HO26 enhances stability
- n-Ag + HO26: interaction of Ca^{2+} , NOM and n-Ag, formation of large aggregates (flocculation)

HO26



Asymmetrical Flow Field Flow Fractionation (AF⁴): Principle



Separation is based on the hydrodynamic diameter of the analyte particles.

Retention parameter λ_{AFFFF}

$$\lambda_{\text{AFFFF}} = \frac{l}{w} = \frac{kTV^0}{3\pi\eta\dot{V}_c d w^2}$$

k Boltzmann's constant

T Absolute temperature

V^0 Geometric volume of the channel

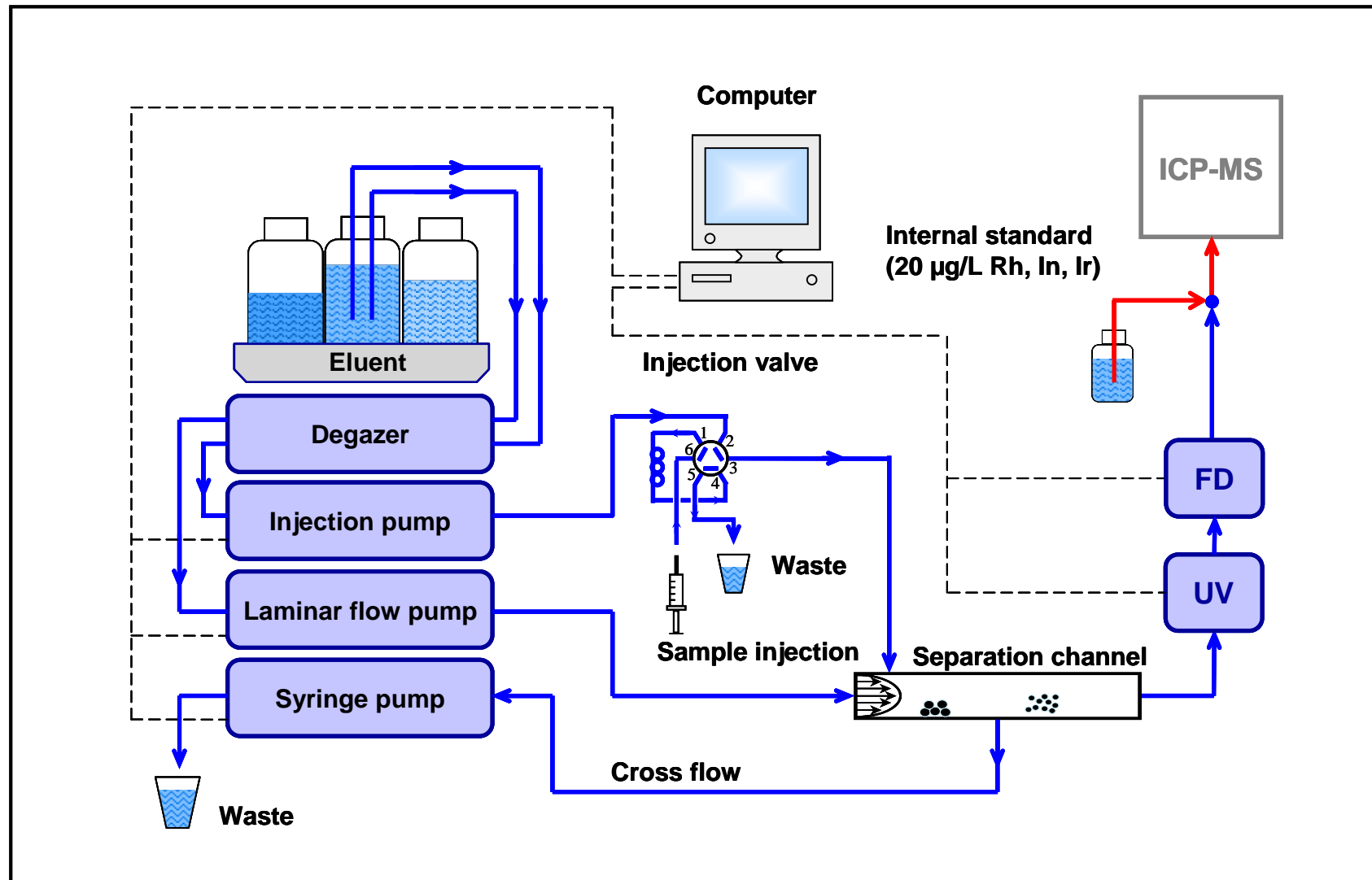
η Dynamic viscosity of the fluid

\dot{V}_c Volumetric rate of cross flow

d Hydrodynamic diameter of the particle

w Channel thickness

Coupling of a separation unit (here: AF⁴) with highly sensitive detectors



■ AF⁴ systems (separation):

■ **POSTNOVA HRFFF10.000**

(eluent: NaNO₃ (5 mmol/L); membrane: polyethersulfone, 300 Da MWCO; spacer: 350 μm; injection volume: 100 μL; detector flow: 0,3 mL/min)

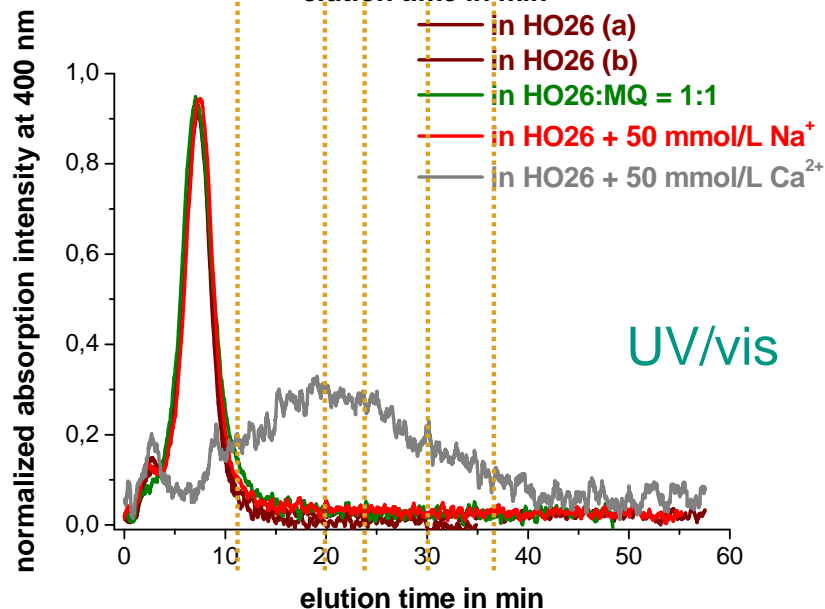
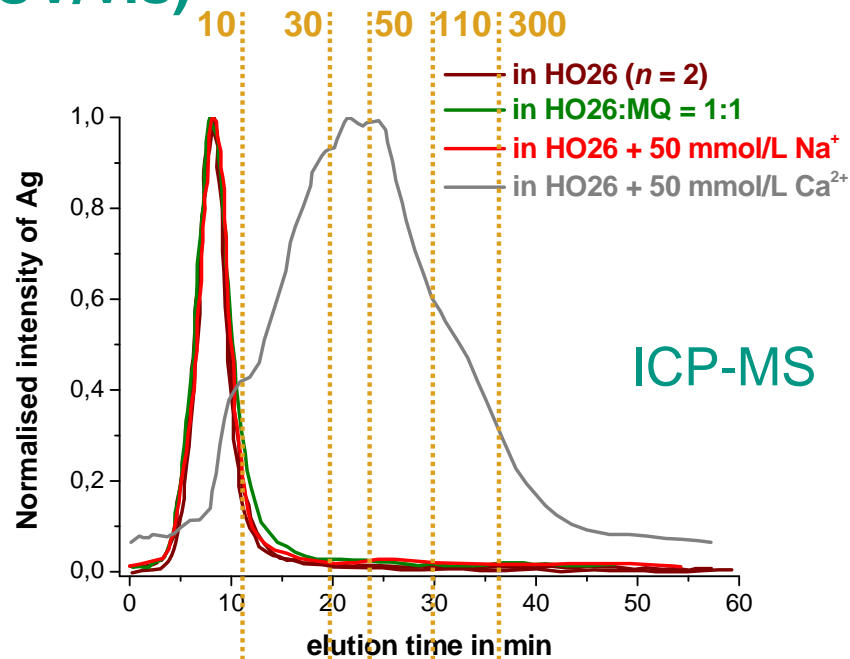
■ **WYATT Eclipse 3+ system**

(eluent: NaNO₃ (5 mmol/L); membrane: regenerated cellulose, 10 kDa MWCO; spacer: 350 μm; injection volume: 300 μL; detector flow: 0,5 mL/min) (measurements in cooperation with WYATT TECHNOLOGY EUROPE)

■ Detection systems (selection):

- UV/vis detectors ($\lambda = 400$ nm)
- *on-line* DLS
- ICP-MS

Fractogramms (HRFFF 10.000 coupled with ICP-MS and UV/vis)



■ Samples:

- (1) n-Ag in HO26
- (2) n-Ag in HO26:MQ = 1:1
- (3) n-Ag + Na⁺ (50 mmol/L)
- (4) n-Ag + Ca²⁺ (50 mmol/L)

■ Calibration with polystyrene standards ($r = 10 \text{ nm}, 30 \text{ nm}, 50 \text{ nm}, 110 \text{ nm}, 300 \text{ nm}$)

■ Eluting NP: n-Ag (ICP-MS)

■ UV absorption at $\lambda = 400 \text{ nm}$: alternative detection of n-Ag

■ n-Ag in the samples (1) – (3):

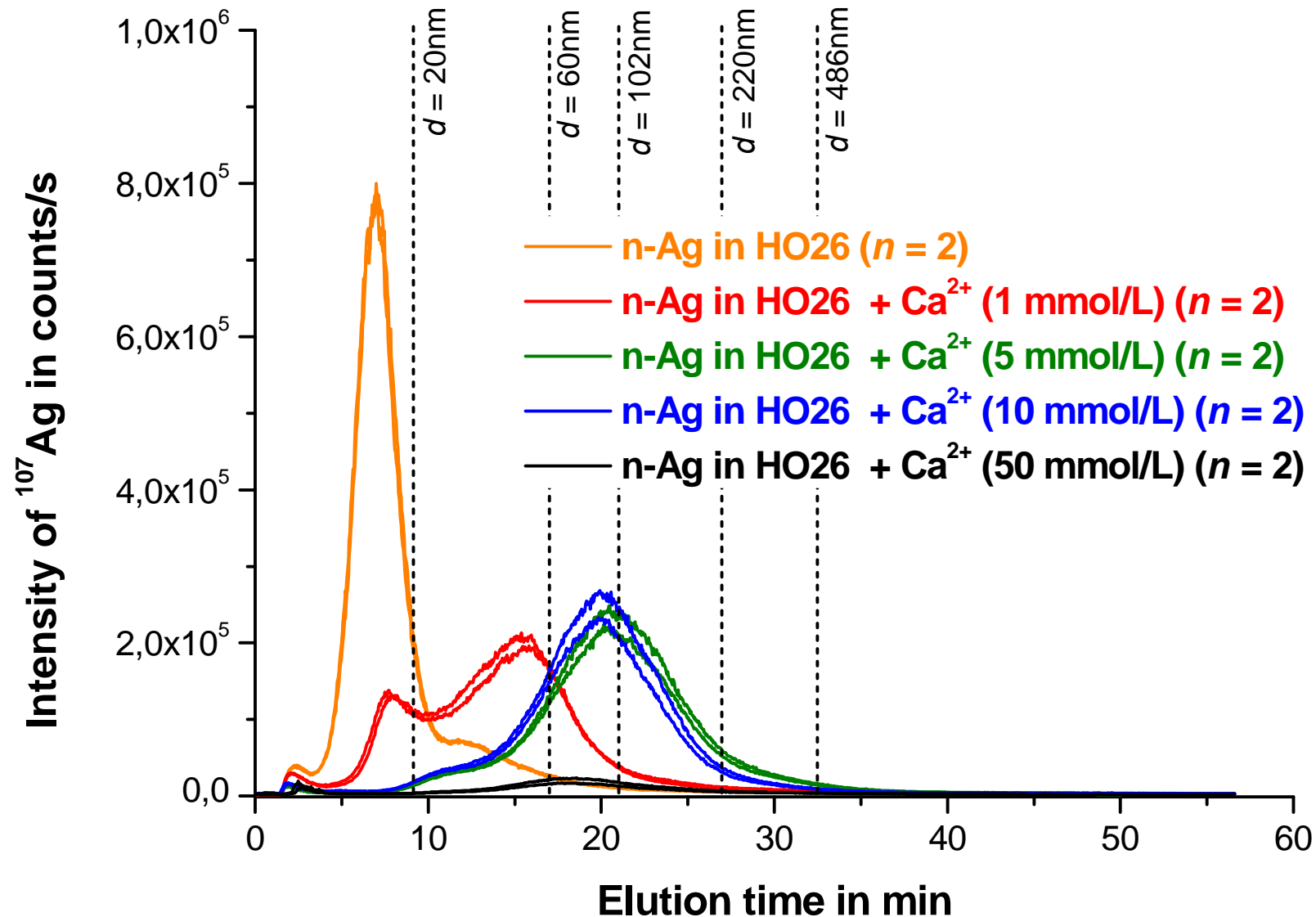
$r_H < 10 \text{ nm}$, good agreement with batch DLS measurements

■ Sample (4): Formation of aggregates including Ag

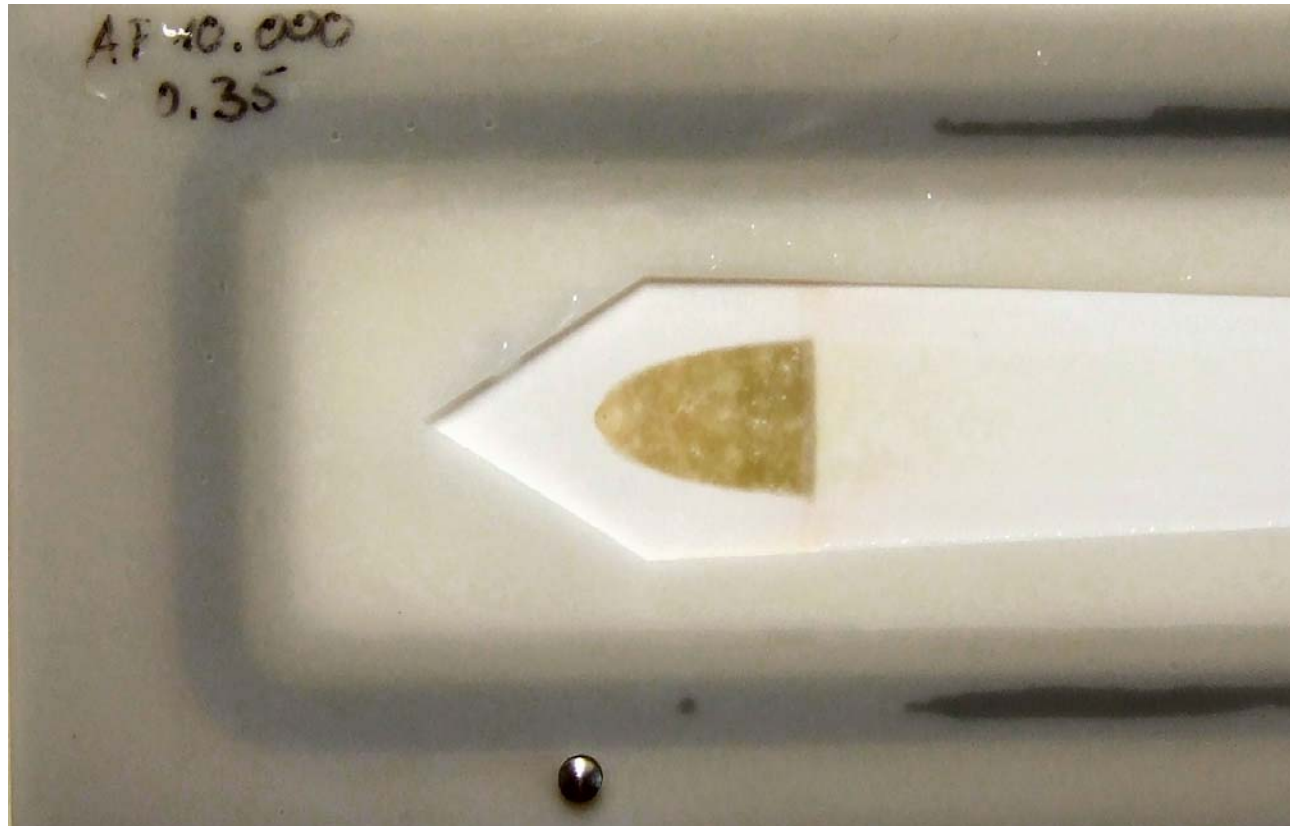
■ n-Ag in MQ: strong interaction with membrane material, separation not possible

Following the aggregation of n-Ag using AF⁴/ICP-MS

n-Ag in HO26

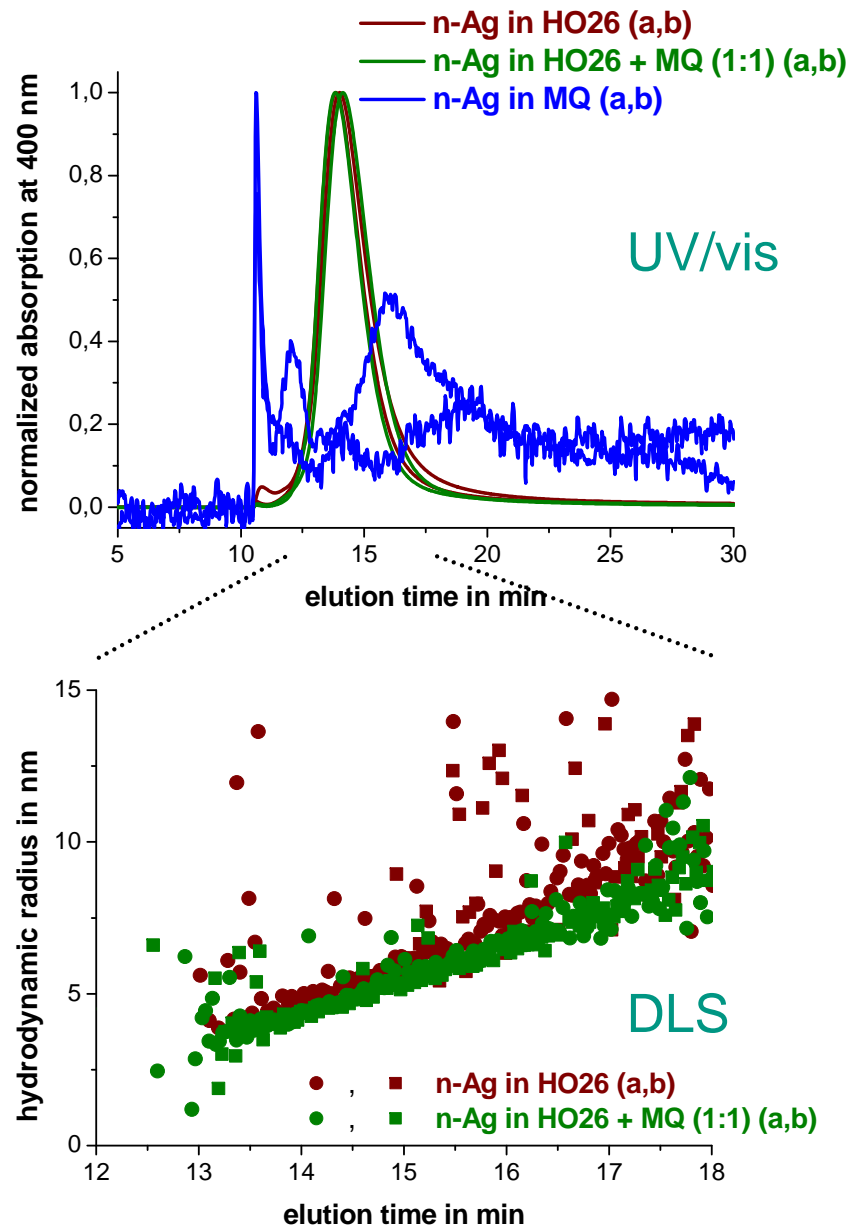


Interactions of n-Ag with membrane material



- membrane: polyethersulfone (MWCO: 300 Da)
- bare n-Ag in MQ

Fractogramms (Eclipse 3+ coupled with UV/vis and *on-line* DLS)



■ Samples:

- (1) n-Ag in HO26
- (2) n-Ag in HO26:MQ = 1:1
- (3) n-Ag in MQ

■ bare n-Ag in MQ:
interactions with membrane
material (poor recovery)

■ *on-line* DLS: good
agreement with batch DLS
measurements

■ NOM stabilizes n-Ag suspensions

- transport behavior, mobility
- bioavailability
- removal of n-Ag from the liquid phase (water treatment)
- analytical methods

■ Future investigations on n-Ag/NOM

- use of further n-Ag (different particle sizes, different surface functionalization)
- further studies on the role of metal ions (aggregation, sorption)
- application of AFM to study the interactions of n-Ag with functionalized surfaces (reversibility?): Collaboration with Prof. Th. Schimmel, KIT

■ Benefits

- separation of ENP from matrix
- highly sensitive detection of ENP directly in liquid samples, e.g. in environmental samples
- simultaneous information on particle size distribution and chemical composition (ICP-MS)

■ Limitations

- interactions of NP and membrane materials
- €!

■ Challenges

- optimization of methods and materials to avoid membrane–NP interactions
- detection of NP in environmental samples (low concentration)

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Metal oxides and metals

TiO ₂	Pigment, photo catalyst
Iron oxides	Pigment, pharmaceuticals, medical applications
ZnO / ZrO ₂	Surface hardener
SiO ₂	Additive for polymers
Ag / Au	Catalysts, electronic devices

Quantum dots

CdTe / GaAs	Semiconductors, electronic devices
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Carbon based nanomaterials (CBN)

Black carbon	Additive in wheels, pigment
Fullerenes	Additive in grease
Nano tubes	Additive in polymers, accumulators and liquid fuel-cells

Stability (> 7 days) as function of stirring time

Ionic strength



Energy input

	R	5	10	50
Stirring time (h)				
0		Yes	No	No
4		Yes	Yes	No
8		Yes	Yes	No
24		Yes	Yes	Yes