Nuclear Waste Management IEK-6
Institute of Energy and Climate Research

JÜLICH FORSCHUNGSZENTRUM

Microparticle Production as Reference Materials for Particle Analysis Methods in Safeguards

Stefan Neumeier[1*], R. Middendorp[1], A. Knott[1,2], M. Klinkenberg[1], F. Pointurier[3], D.F. Sanchez[4], V.-A. Samson[4], D. Grolimund[4], I. Niemeyer[1], D. Bosbach[1]

[1]Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
[2]European Commission, Joint Research Centre Karlsruhe (JRC), 76344 Karlsruhe, Germany
[3]CEA, DAM, DIF, F-91297 Arpajon, France
[4]Paul Scherrer Institute, 5232 Villigen, Switzerland
**E-mail: s.neumeier@fz-juelich.de*

MRS2017
Scientific Basis for Nuclear Waste Management Symposium 2017
29 Oct. - 03 Nov. 2017, Sydney, Australia

Introduction

Nuclear Safeguards Particle Analysis

- Treaty on non-proliferation of nuclear weapons signed by 191 countries
- Member-states declare not to develop nuclear weapons
- But, independent verification
  → IAEA
- Inspectors visit nuclear facilities
  - Bulk samples to verify declaration
  - Swipe samples to detect undeclared activities

Photo: Petr Pavlicek (IAEA)

- Swipe samples sent to dedicated laboratories ('NWAL')
- Analysis of isotopics of single microparticles (e.g. LG-SIMS)

- Analytical measurements require quality control measures to ensure correct results

- No microparticle reference materials available

Photo: D. Calma (IAEA)

Introduction

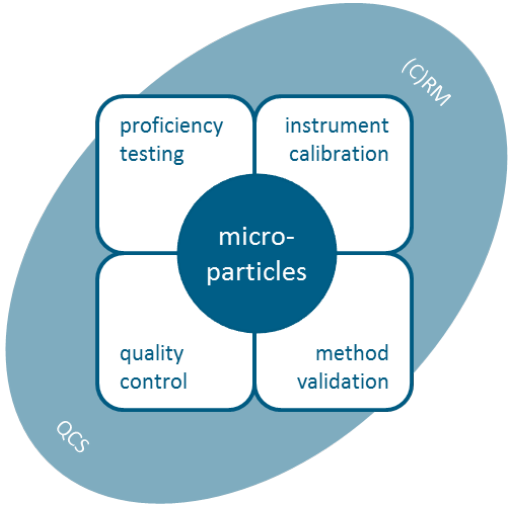
Since 07/2012 joint effort between
Forschungszentrum Jülich and IAEA-SGAS

Goal:

- Establishment of a production process for particles suitable as reference material and delivery of particles

Additional Goal:

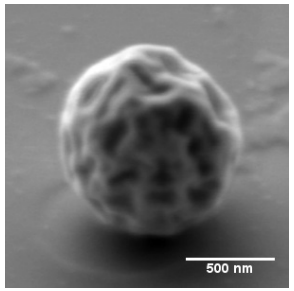
- Make production capacity available at FZ Jülich
- Final characterization and certification by other laboratories (IAEA-SGAS, JRC-IRMM,...)



Particle Reference Standard Production

Two step process:

1. Aerosol-based particle production and collection

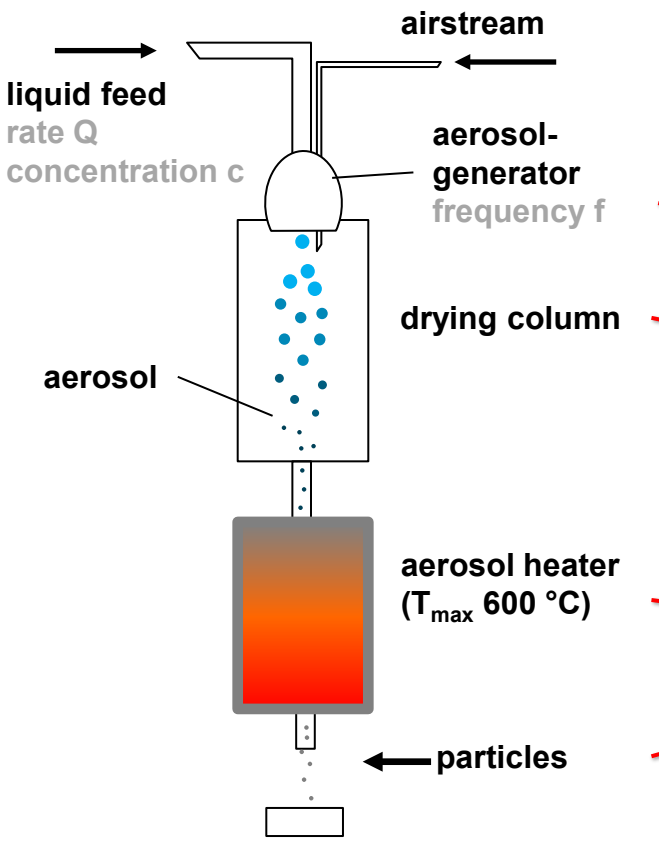


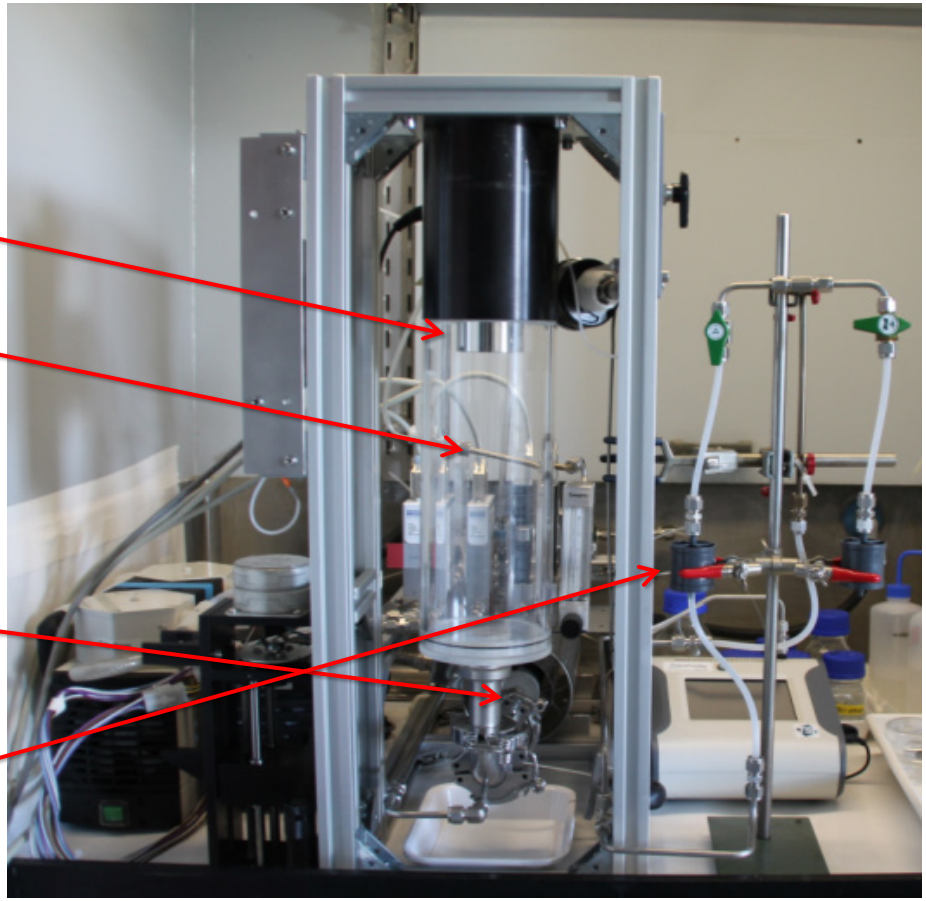
2. Particle distribution on substrates using suspensions

Production → Processing → Characterization → Distribution

Current set-up particle production

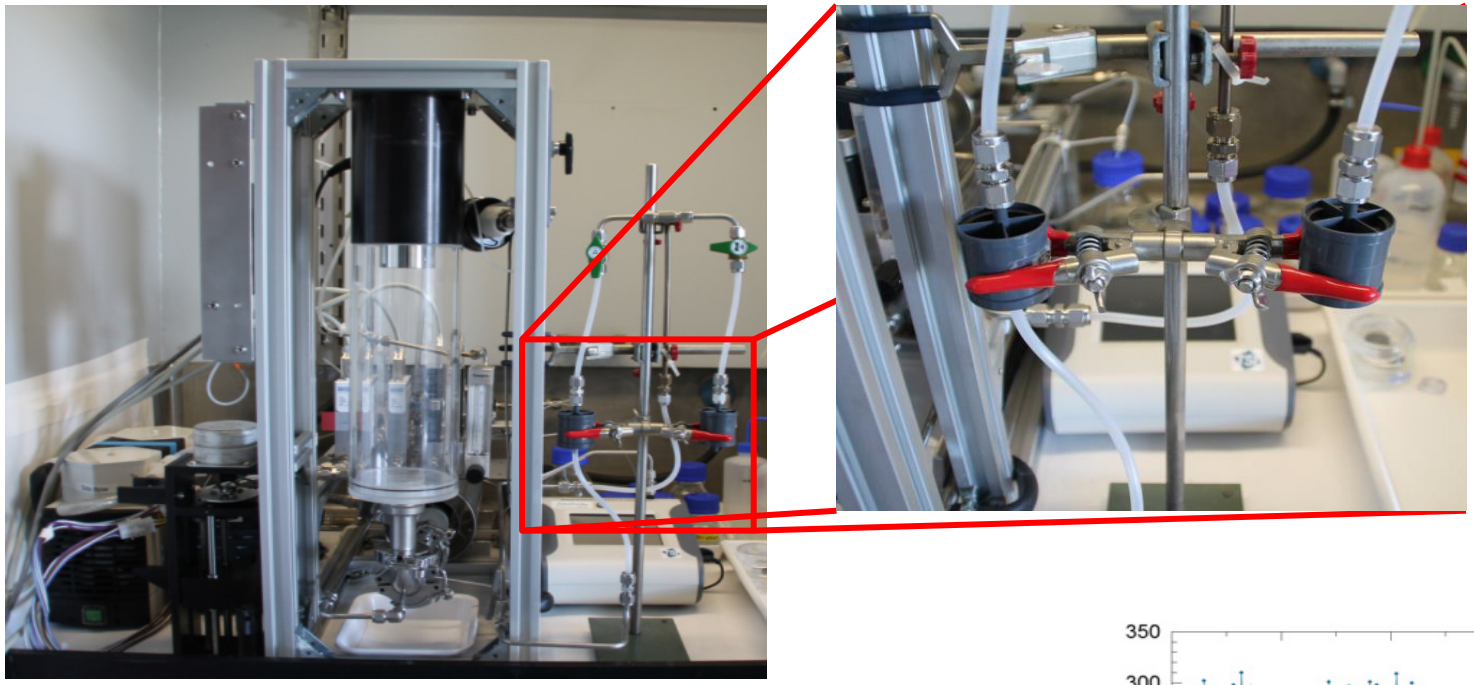
Vibrating Orifice Aerosol Generator (VOAG)





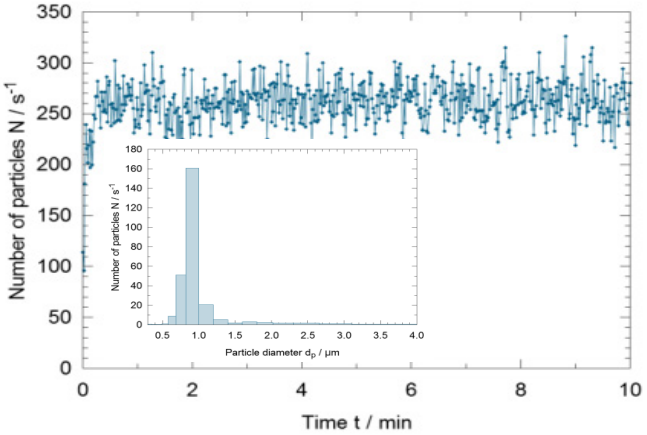
Current set-up particle production

Vibrating Orifice Aerosol Generator (VOAG)



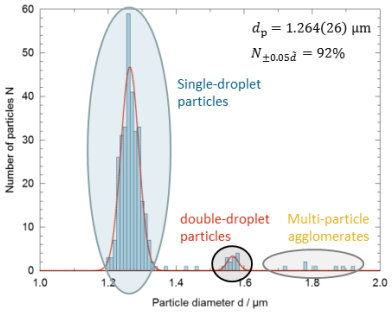
Process control

- Temperature of aerosol heater
- Air flow
- Liquid flow
  → Determination of el. content per particle
- Online monitoring with optical particle counter

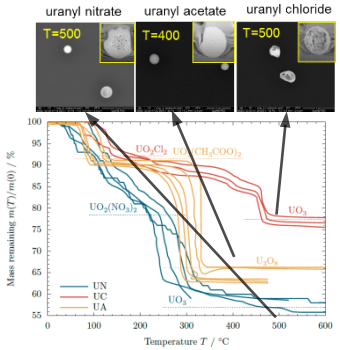


Particle characterization

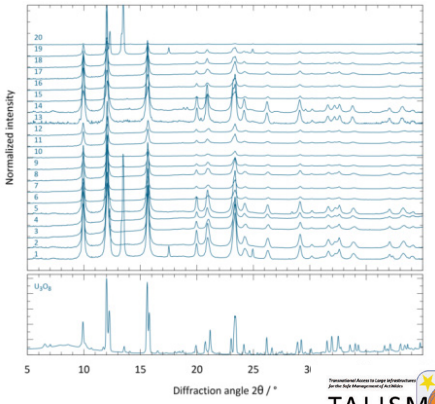
Size distribution



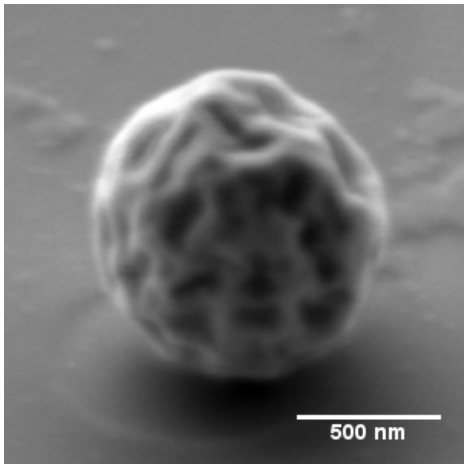
Heat treatment



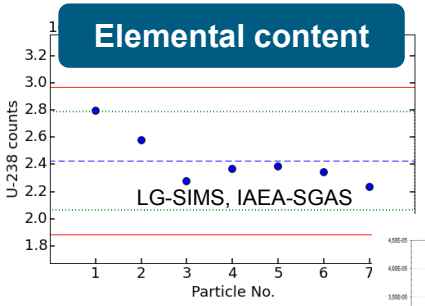
Crystal structure



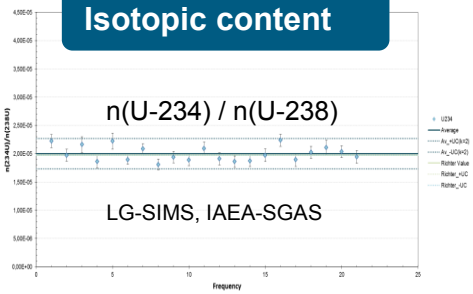
TALISMAn



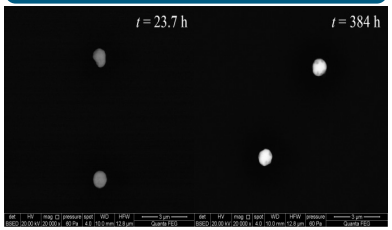
Elemental content



Isotopic content

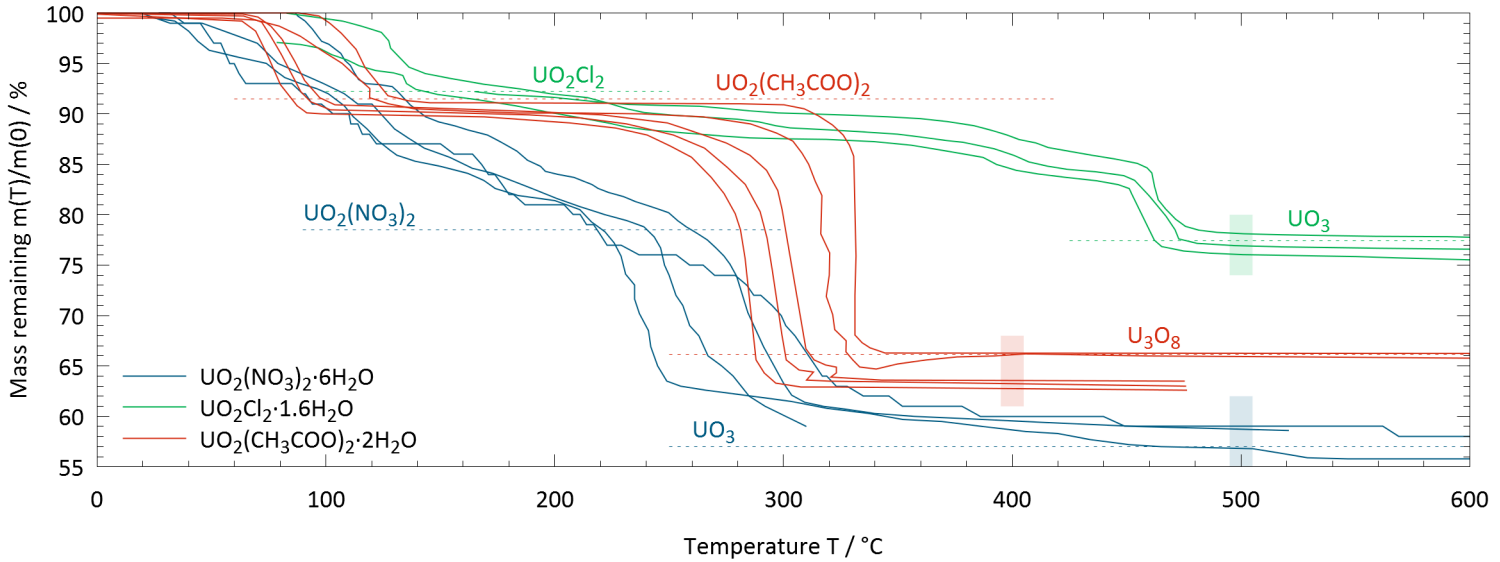


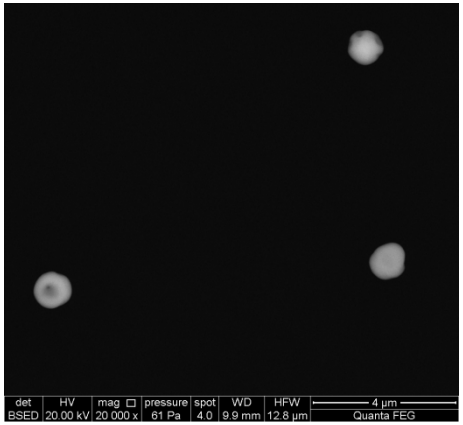
Stability in solutions



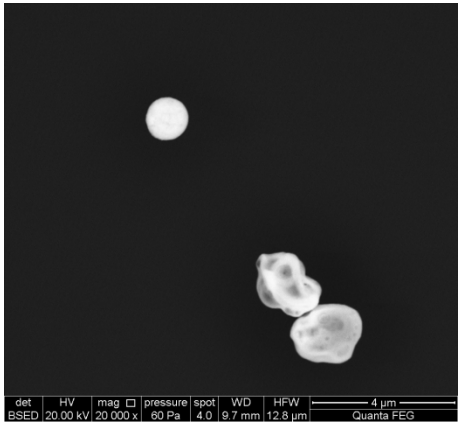
Particle Production

Precursor Solution

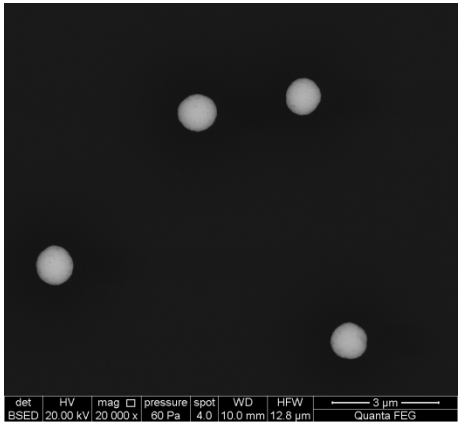




Uranyl nitrate
T = 500 °C



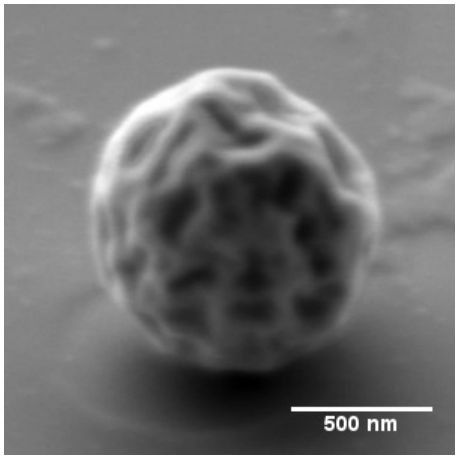
Uranyl chloride
T = 500 °C

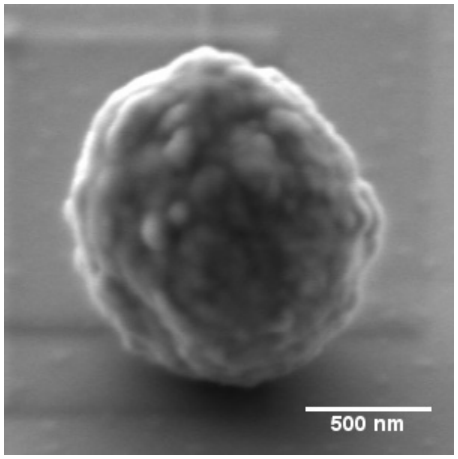


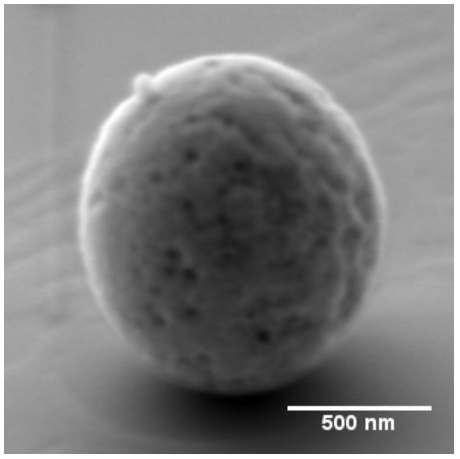
Uranyl acetate
T = 400 °C

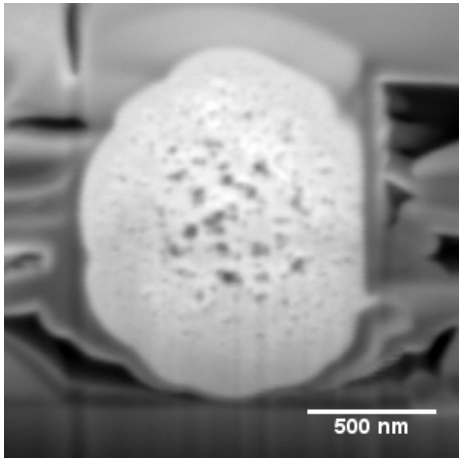
Particle Production

SEM/FIB

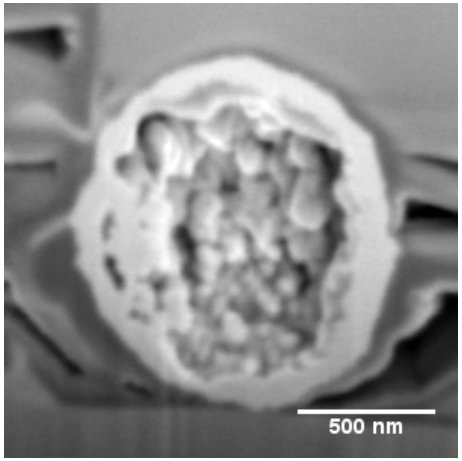




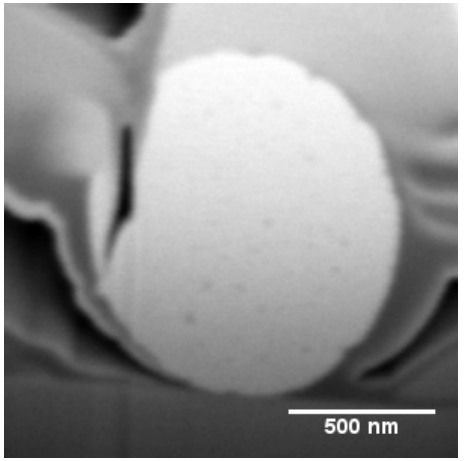




Uranyl nitrate
T = 500 °C



Uranyl chloride
T = 500 °C

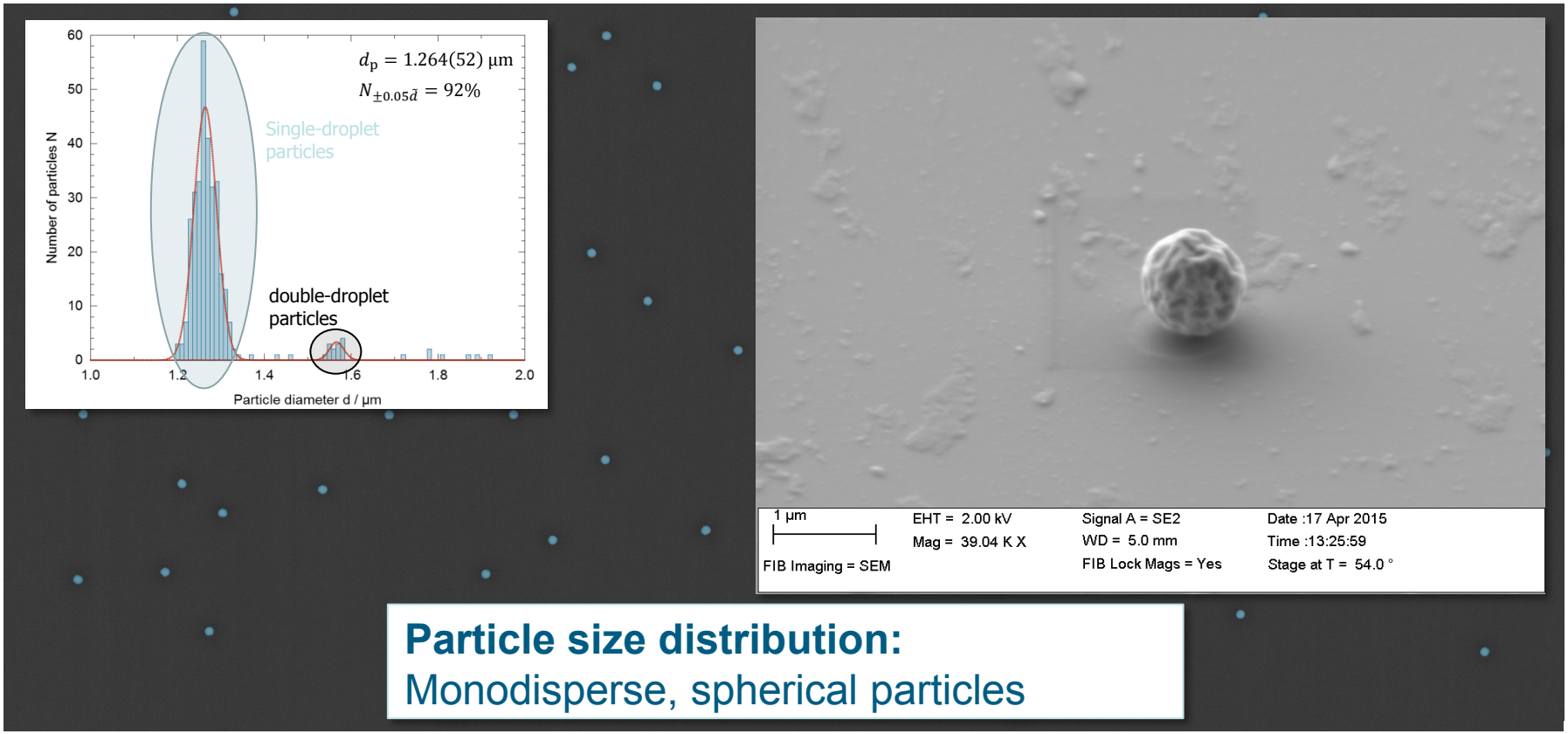


Uranyl acetate
T = 400 °C

Particle Production

Particle Size Distribution: SEM

- Scanning Electron Microscope (SEM) for particle size distribution



Particle size distribution:
Monodisperse, spherical particles

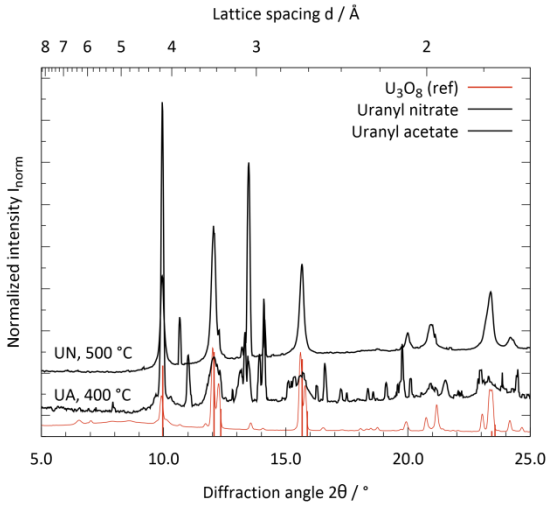
Particle Production

Characterization

X-ray diffraction, X-ray near-edge absorption spectroscopy and raman spectroscopy to determine structure

µ-XRD

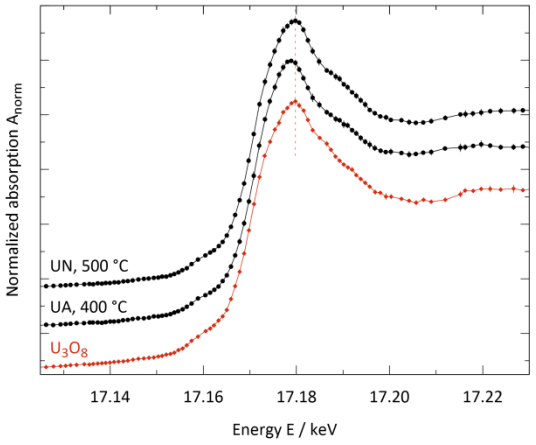
microXAS beamline (PSI)
4x1.5 µm beam (17.2 keV)



Orthorhombic U_3O_8 phase

µ-XANES

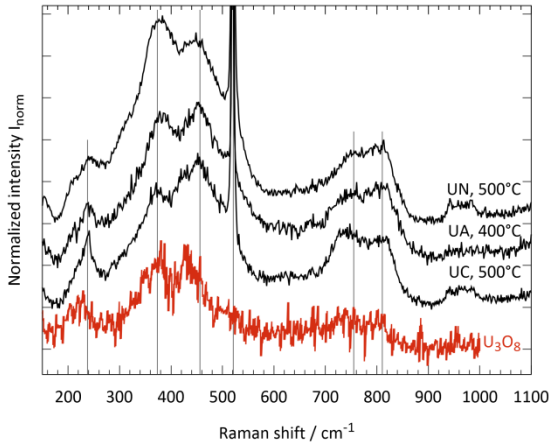
microXAS beamline (PSI)
300x300 µm beam (U L_3 edge)



U^V/U^{VI} mixture (U_3O_8)

µ-Raman

µ-Raman spectroscopy (CEA)
0.6 µm laser (514 nm)

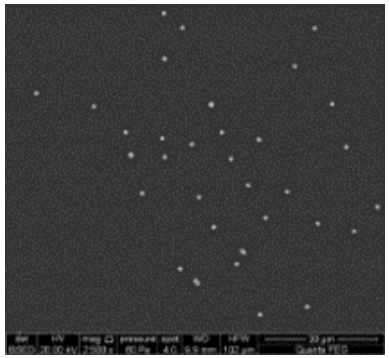


Particles suitable as standard

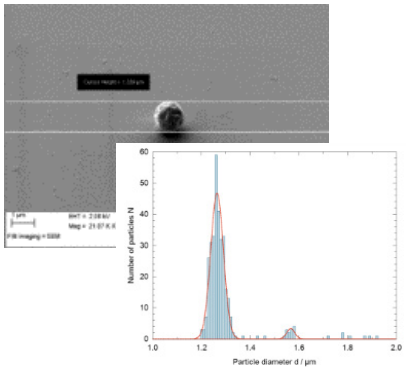
UN: Uranyl nitrate | UA: Uranyl acetate | UC: Uranyl chloride

R. Middendorp et al. *Anal. Chem.* 89 (**2017**) 4721-4728. DOI: 10.1021/acs.analchem.7b00631

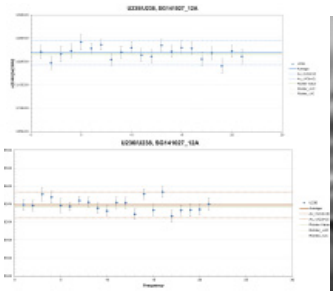
Status - Particle production 2015



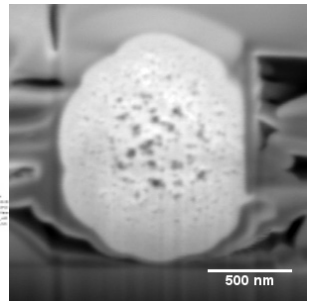
SEM



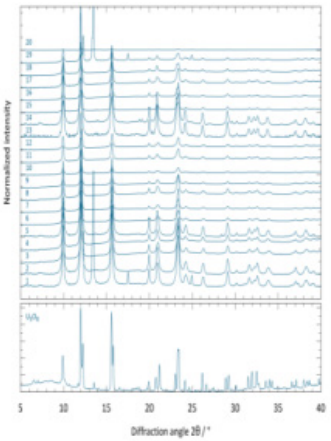
SEM



LG-SIMS



FIB/SEM



µ-XRD, µ-Raman
µ-XANES

✓ First in-depth characterization of particle formation process and final products

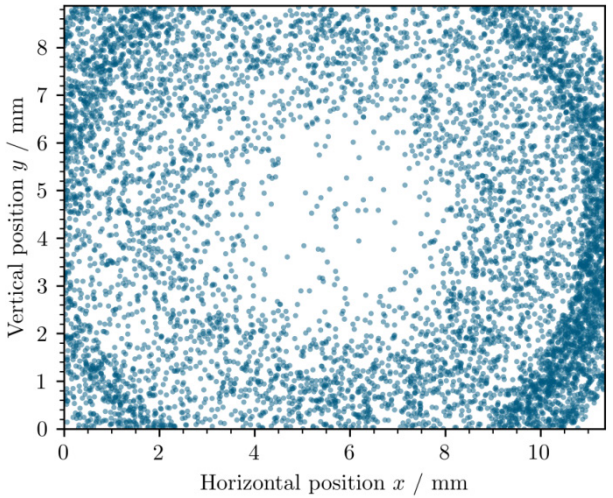
➢ Particles suitable for QC and interlaboratory comparisons

Particle suspensions

Present system

Particles are collected using vacuum impactors

+ Can be used without further handling
– Inhomogeneous deposition
– Requires solid substrate
– No mixing of particles possible
– Limited to ca. 50 samples/day



Spatial particle distribution obtained with single-stage inertial impactor

Problems can be overcome with intermediate processing step

Collection using inertial impactor → Particle transfer into suspension *ultrasonification* → Optional: Mixing of suspensions → Distribution on substrates *controlled drying*

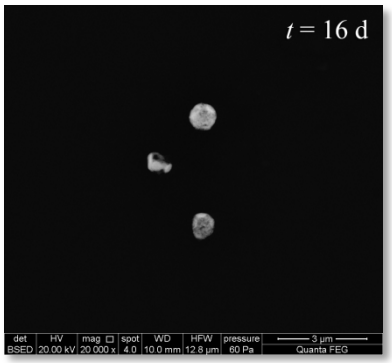
But stability of the particles in suspension has to be investigated

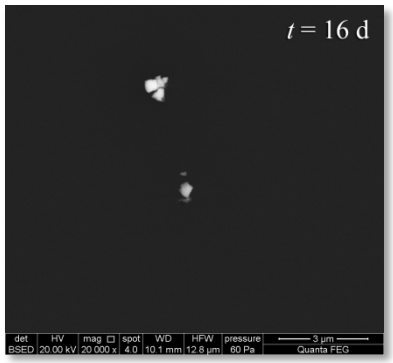
Particle suspensions

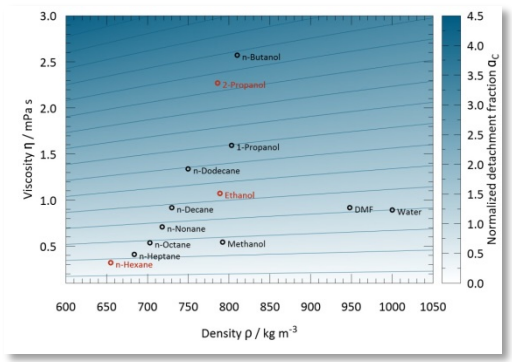
Medium selection

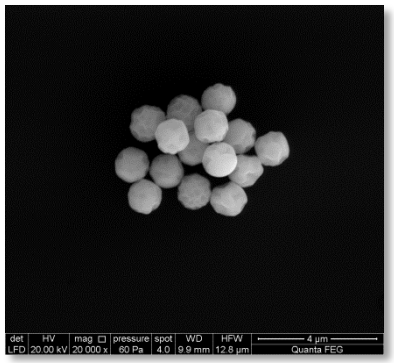
Various solvents were tested as medium:

- Water → dissolution
- Dimethyl formamide → particle break-up
- n-Decane and n-hexane → no detachment
- 2-Propanol → agglomeration
- Ethanol → most suitable









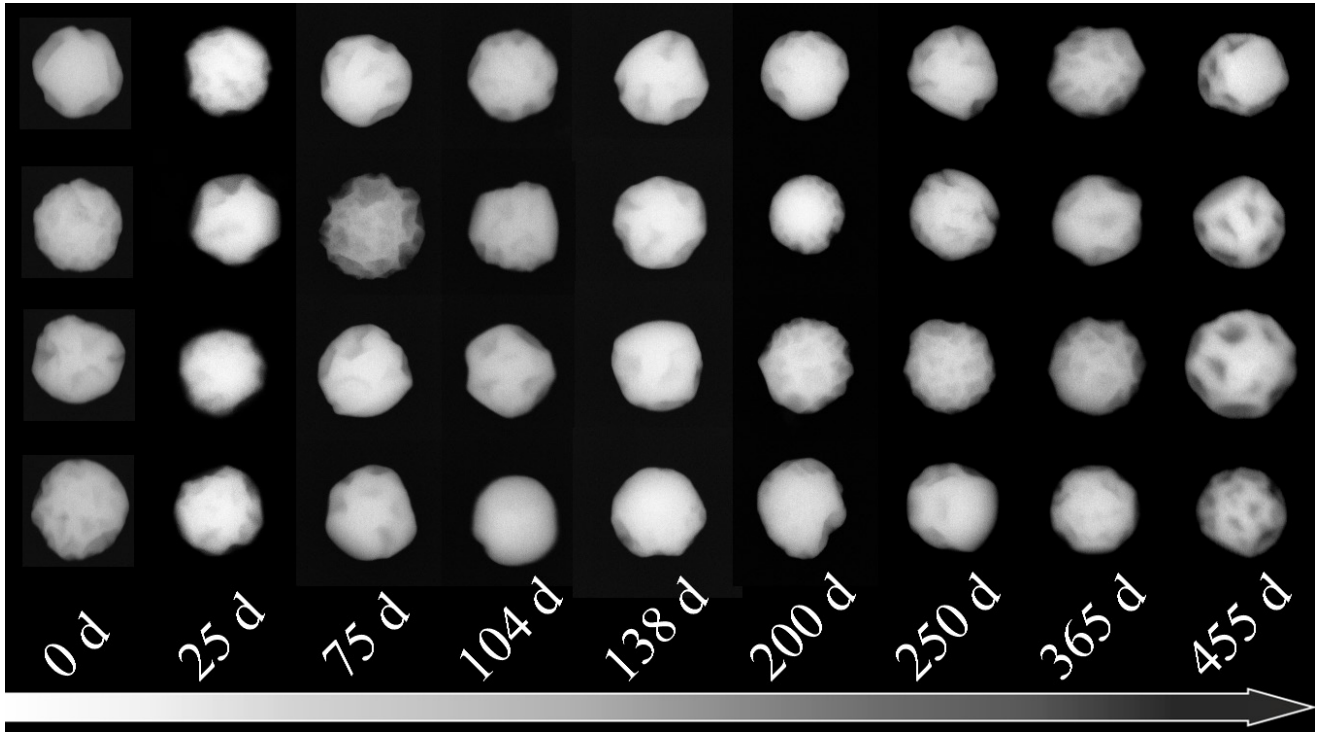
➢ **Ethanol used for further studies**

Particles suspensions

Dissolution in ethanol

Particles were stored in ethanol for 455 days

After 228 days: 0.132(22) % of particles were dissolved (Q-ICP-MS)



- **No significant dissolution measured after 228 days**
- **No significant dissolution after 455 days**

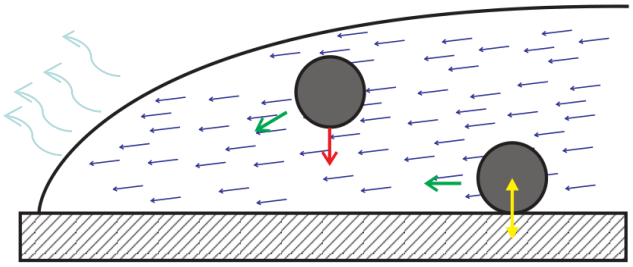
Particles suspensions

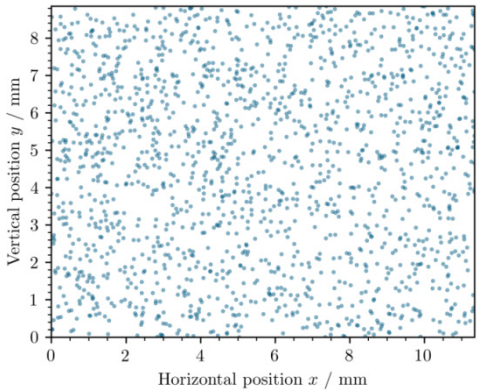
Distribution

Prepared suspensions are dried on substrates

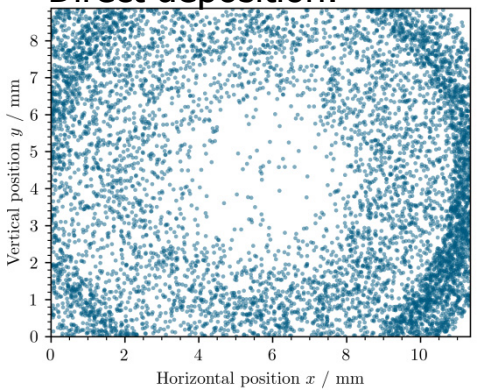
- Temperature (→evaporation rate) critical to control deposition

Drying on heating plate (50°C):





Direct deposition:



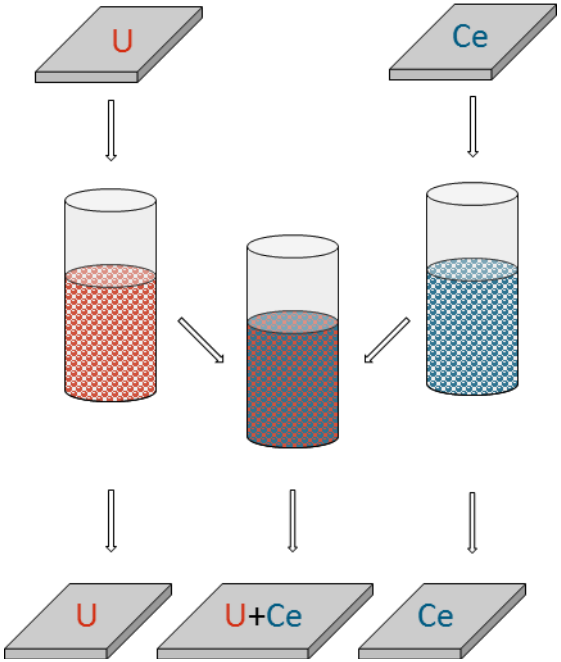
➢ **Homogeneous particle deposition achieved**

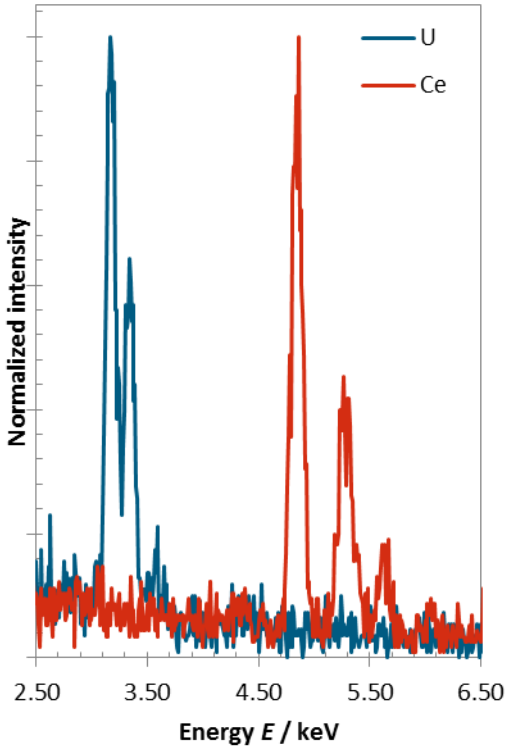
Particle suspensions

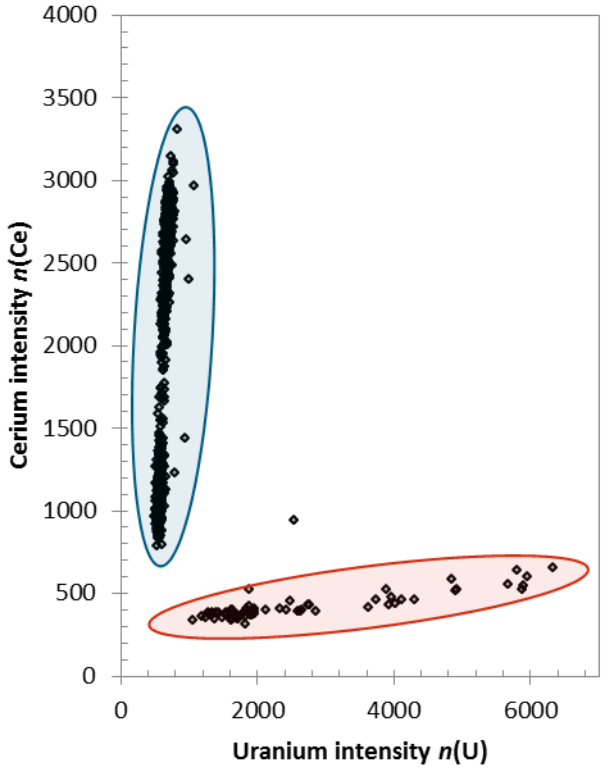
Application: Particle mixtures

Suspensions can also be mixed to produce particle mixtures

- Uranium and cerium particle suspensions mixed
- Substrates measured by SEM/EDX







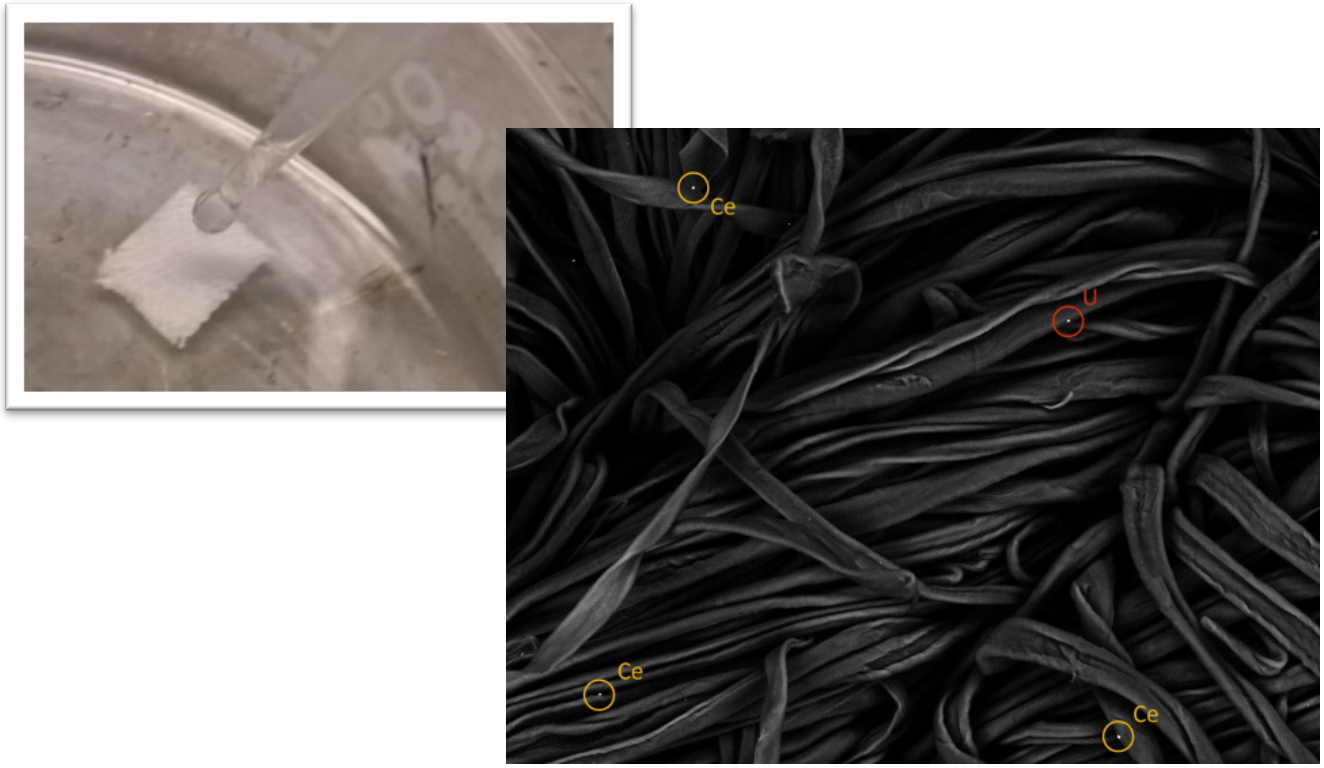
➢ **Production of particle mixtures feasible**

Particle suspensions

Application: Substrates

Suspensions can also be dried on other substrates

- U/Ce mixture dried on piece of cotton swipe



➢ **Production of “swipe samples” feasible**

Summary

Aerosol-based particle production method provides orthorhombic U_3O_8 microparticles:

- ✓ with average diameter of 0.9 – 1.4 µm and narrow size distribution
- ✓ with high density and some inner porosity
- ✓ with high chemical stability in ethanol
  - No visual signs of dissolution [455 days]
  - No significant dissolution [228 days]
  - No between-particle isotope exchange [202 days]

Particle suspensions in ethanol

- ✓ Homogeneous particle distribution on substrates
- ✓ Particle mixtures prepared
- ✓ Particles deposited onto cotton swipes
- ✓ Number of samples/day: 100 - 150