The Stability of Uranium Microspheres for Future Application as Reference Standards

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ESARDA 38th annual meeting, DA WG meeting
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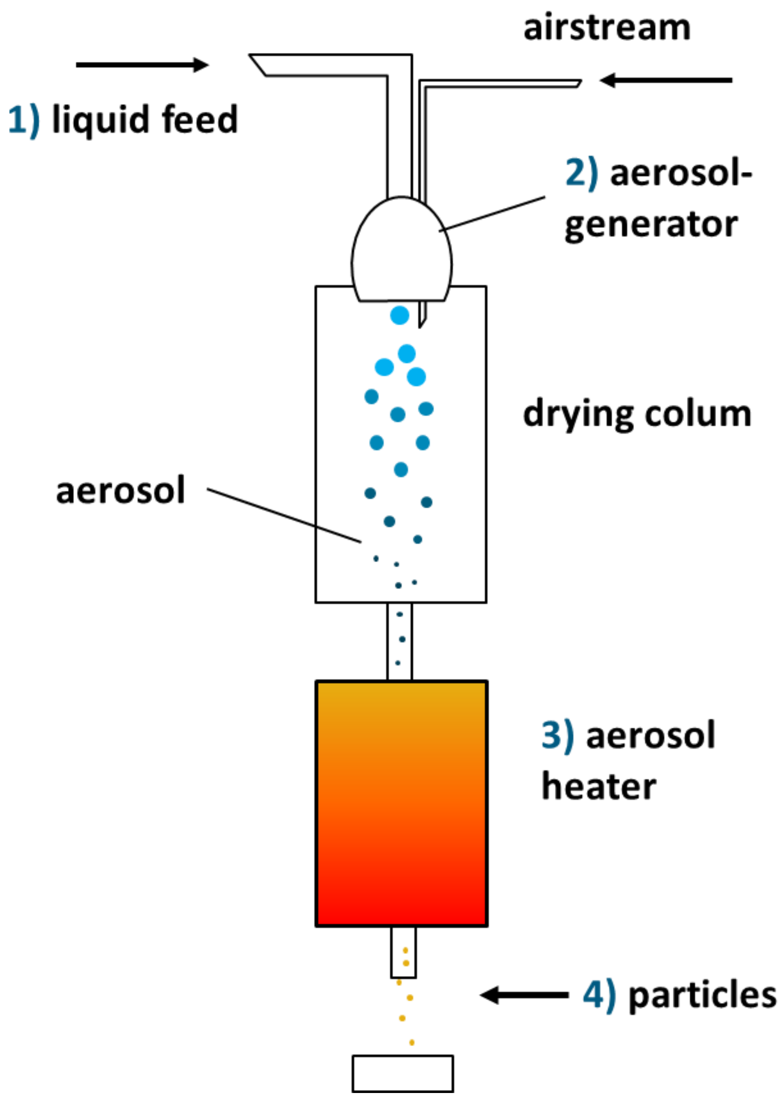
Introduction

Particle preparation

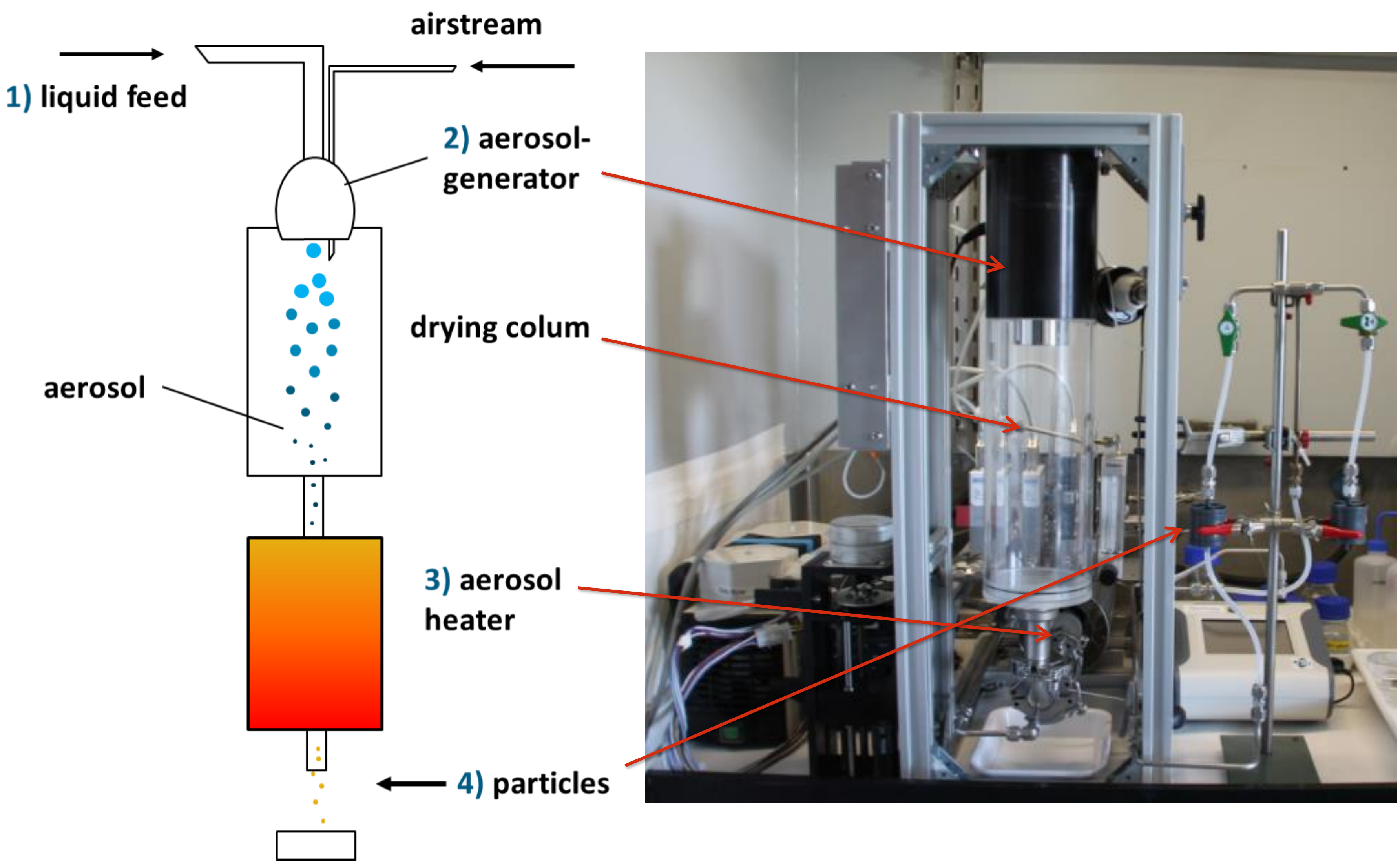


Particle production with vibrating orifice aerosol generator:

1) Liquid feed with known isotopic composition
2) Generation of monodisperse aerosol ($m_{\mathrm{U}} = Q/f \cdot c_{\mathrm{U}}$)
3) Drying & thermal treatment; conversion of uranium to UO_x
4) Particle collection by inertial impaction

Introduction

Particle preparation



Introduction

Particle preparation options

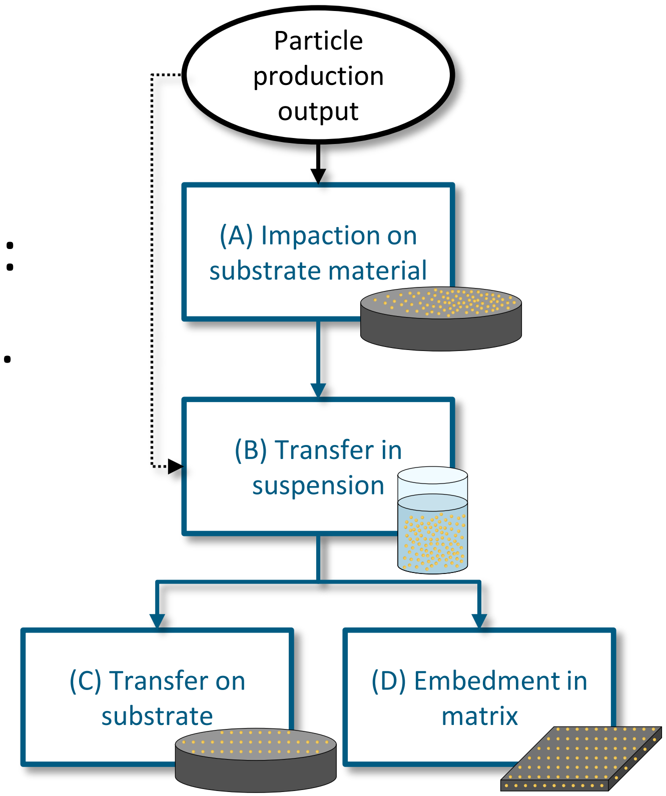
Currently: direct collection on substrates

Particle suspensions offer many advantages:

- e.g. particle mixtures, homogeneity, etc...

But, stability might be an issue

- e.g. dissolution, isotope exchange, etc...



Production → Processing → Characterization → Distribution

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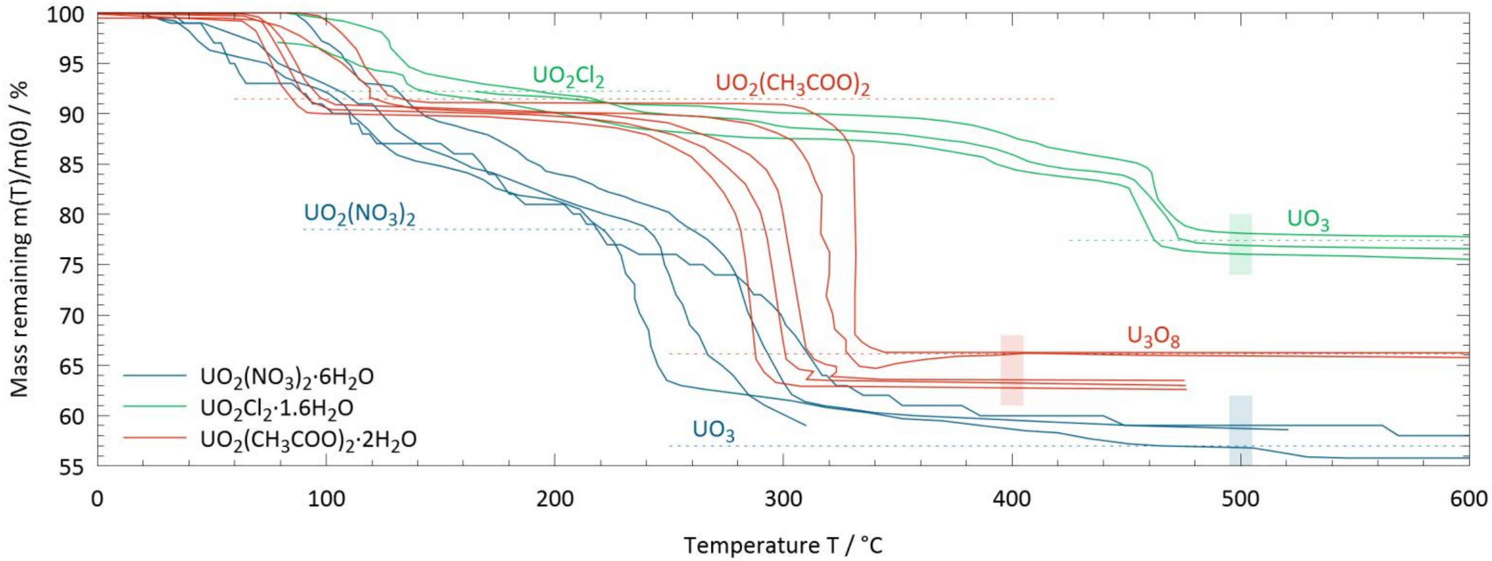
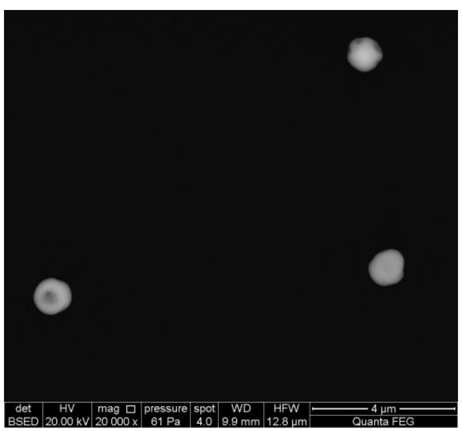
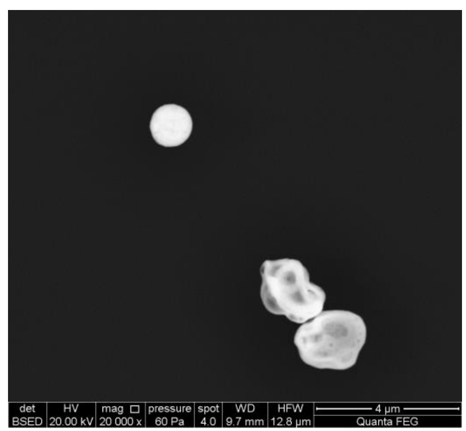
Precursor solution

TGA/SEM

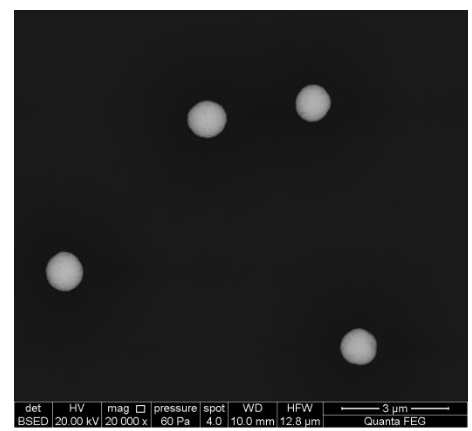




Uranyl nitrate
T = 500 °C



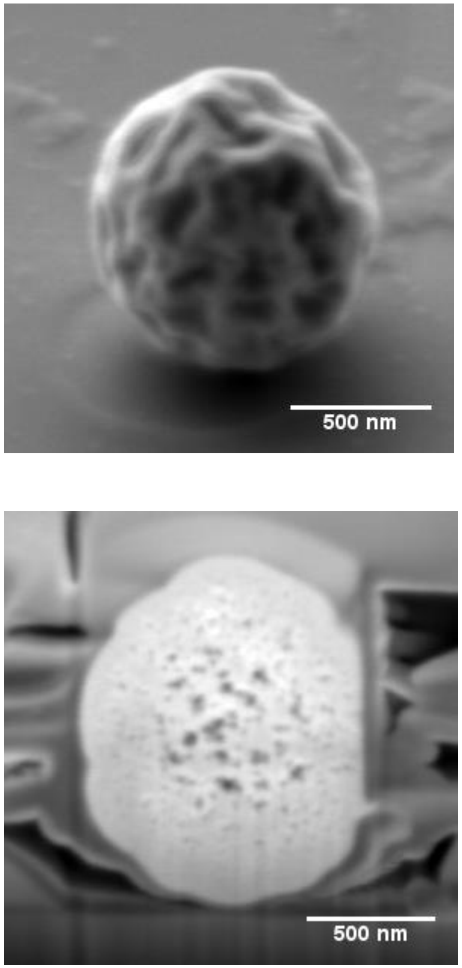
Uranyl chloride
T = 500 °C



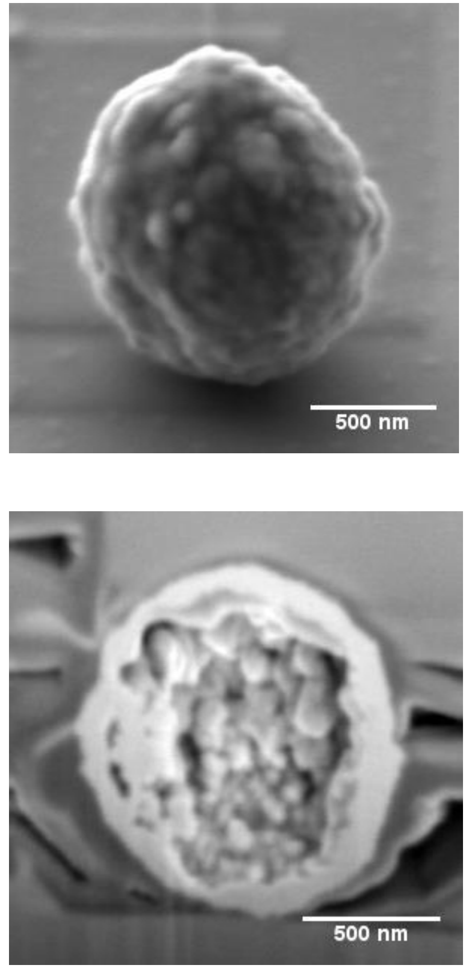
Uranyl acetate
T = 400 °C

Precursor solution

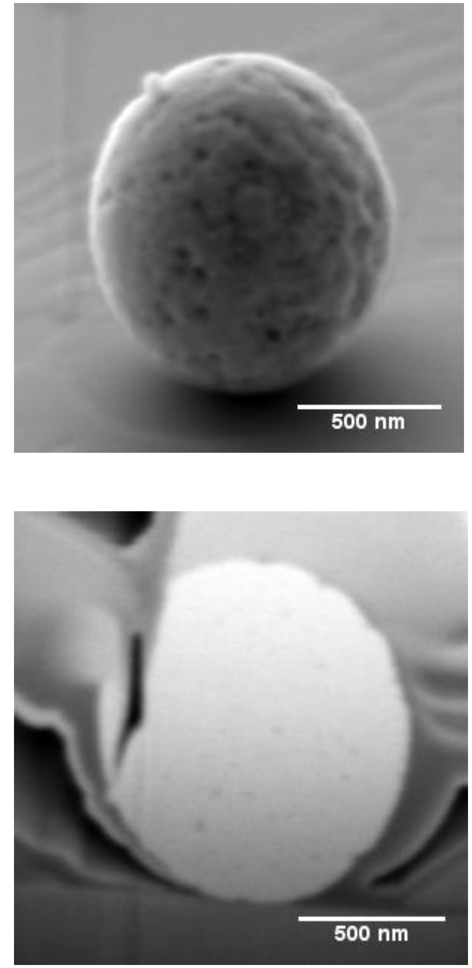
SEM/FIB



Uranyl nitrate
T = 500 °C



Uranyl chloride
T = 500 °C



Uranyl acetate
T = 400 °C

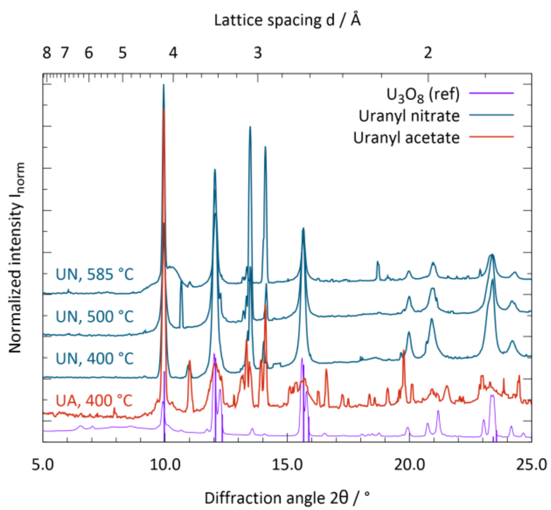
Precursor solution

Particle characterization

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

XRD

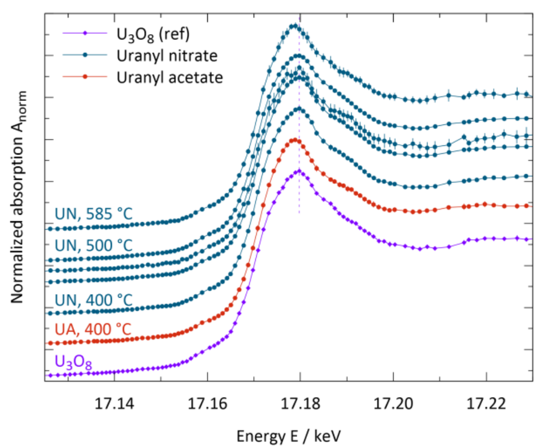
microXAS beamline (PSI)
4x1.5 µm beam (17.2 keV)



Orthorhombic U_3O_8 phase

XANES

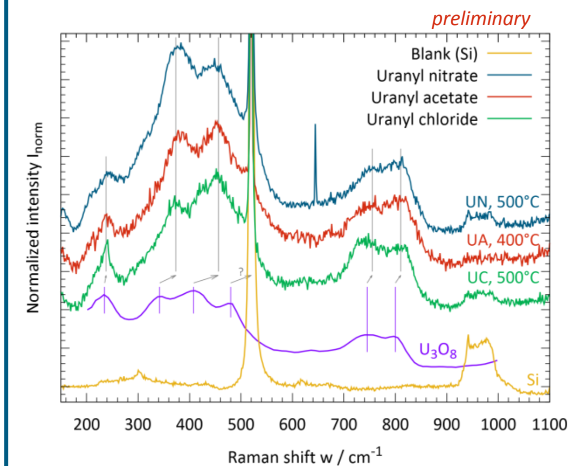
microXAS beamline (PSI)
300x300 µm beam (U L_3 edge)



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

Raman

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

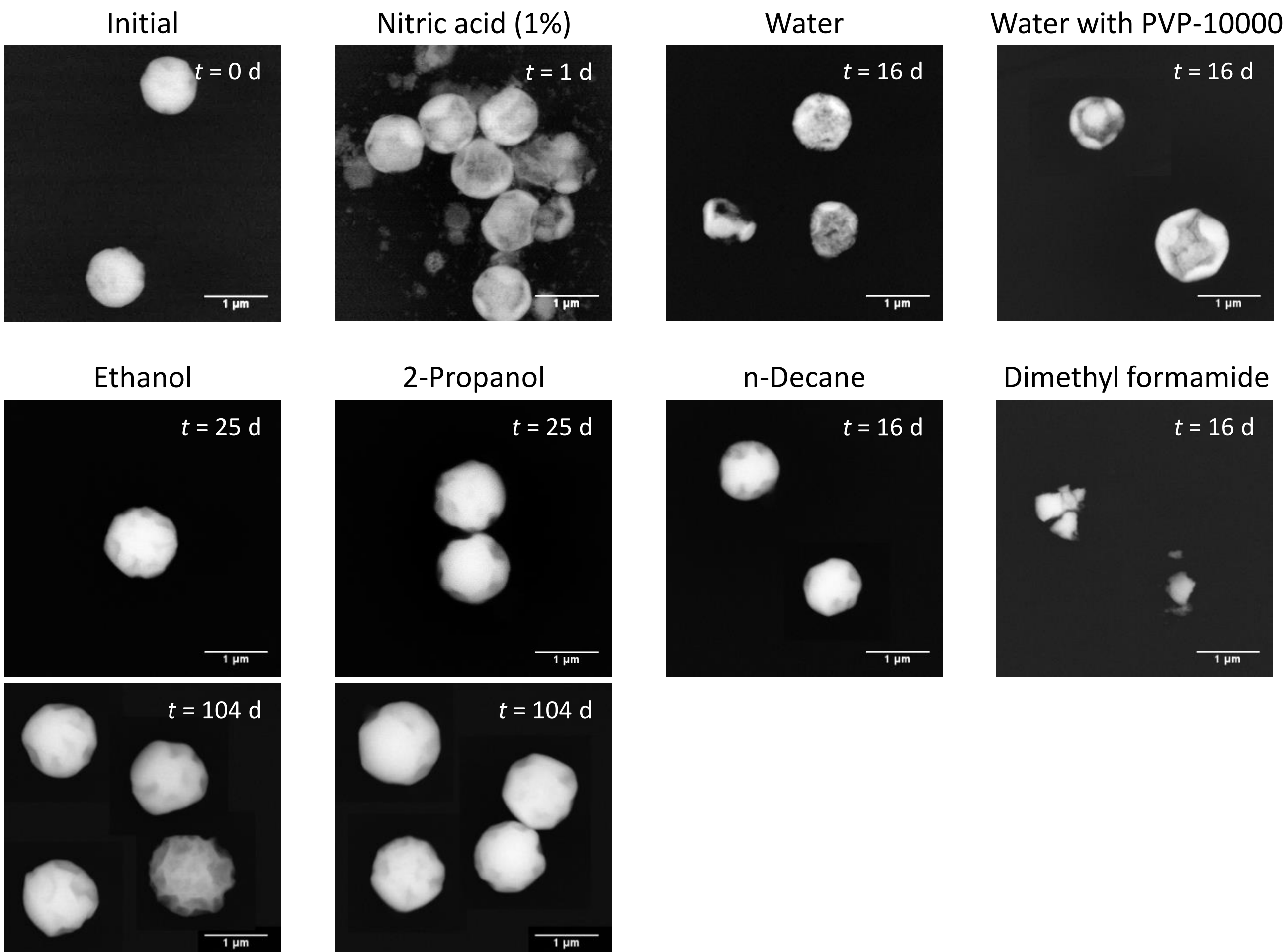


Uranyl chloride comparable

Particle dissolution

Solvent selection

Particles (still deposited on Si wafers) have been stored in solvents:



Images are collections of various micrographs taken under similar conditions

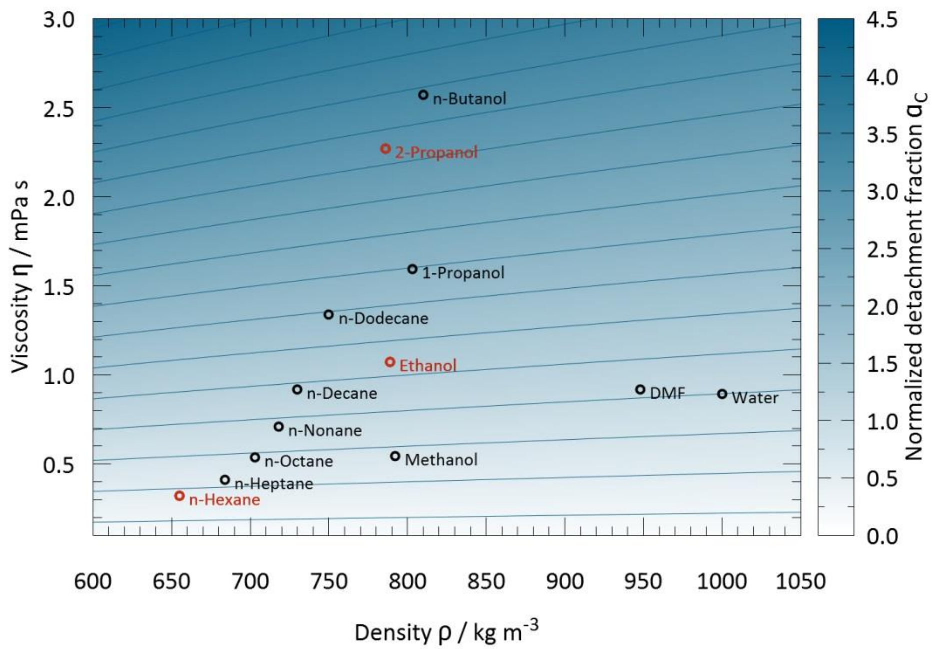
Particle dissolution

Particle detachment

Particles have been removed from substrate by ultrasonification

- Successful for ethanol and 2-propanol, but not for n-hexane

Particle detachment depends (mostly) on density and viscosity[1]:



[1] Awad S, Nagarajan R. Ultrasonic cleaning. In: Kohli R, Mittal KL, editors. Developments in Surface Contamination and Cleaning. 2010. p.225-280.

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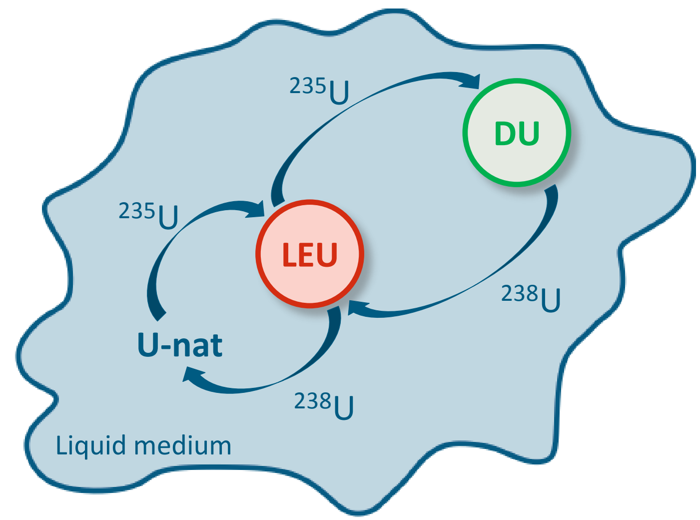
Uranium isotope exchange

Introduction

Exchange between traces of ^{nat}U in matrix and particles

Two reaction mechanisms[1]:

- Surface exchange ← major role
- Diffusion



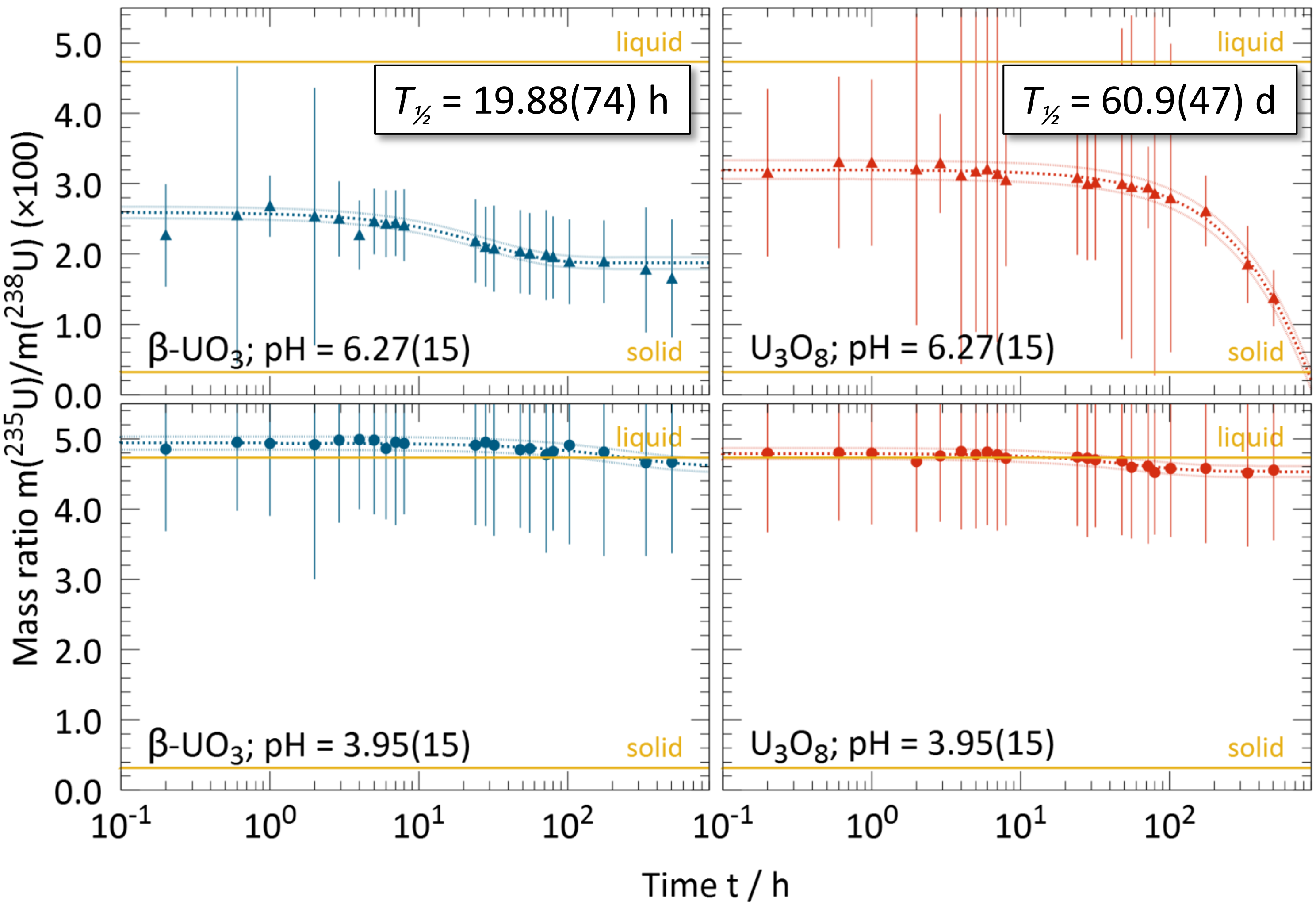
Experiments performed between $[LEU]UO_2^{2+}$ (aq) and $[DU]UO_x$ (s)

- Q-ICP-MS measurement of liquid phase

[1] Cole DR, Chakraborty S. Rates and Mechanisms of Isotopic Exchange. *Rev Mineral Geochem* 2001;**43**:83-140.

Uranium isotope exchange

Results



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Uranium isotope exchange

Results

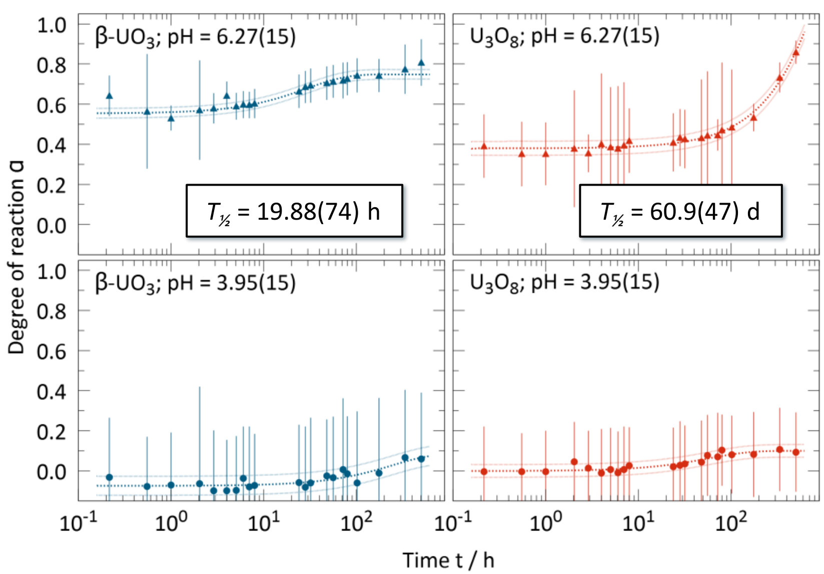
Exchange rate UO_3 faster than U_3O_8

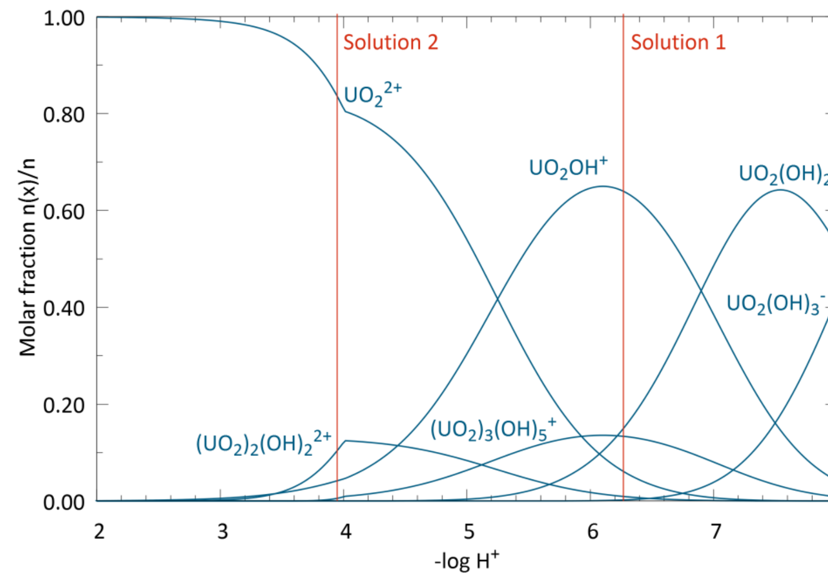
- Exchange via U(VI)

Faster exchange at higher pH

- Likely due to hydroxide formation[1]

$$\underbrace{\mathrm{UO_2^{2+}}}_{\text{liquid}} \rightleftharpoons \underbrace{\begin{bmatrix} \mathrm{UO_2OH^+} \\ \mathrm{UO_2(OH)_2} \\ \dots \end{bmatrix}}_{\text{surface}} \rightleftharpoons \underbrace{\mathrm{U(VI)}}_{\text{solid}}$$





[1] Szabó and Grenthe, *Inorg. Chem.*, **46**, 9372 (2007).

Conclusion

Particle production and characterization

Microparticles have been produced successfully

- Particles have been produced from IRMM-183 and IRMM-023

Optimization of production, production using:

- Uranyl nitrate ➢ Suitable; porous
- Uranyl chloride ➢ No advantages to uranyl nitrate
- Uranyl acetate ➢ Suitable; dense

Characterization with XRD, XANES and raman spectroscopy

- Uranyl nitrate ➢ U_3O_8 (even at 400 °C)
- Uranyl acetate ➢ U_3O_8
- Uranyl chloride ➢ only raman, similar to nitrate and acetate

Conclusion

Stability in suspension

Dissolution studied in various solvents:

- Solvent penetrates dense shell and reaches pores
- No dissolution in ethanol, 2-propanol (104 d) and n-decane (16 d)

Isotope exchange measured in aqueous solutions

- Significant exchange rates measured at neutral pH
- Exchange via U(VI) hydroxides
- For U_3O_8: $T_{½}$ = 60.9(47) d

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Thank you for your kind attention!

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