The Stability of Uranium Microspheres for Future Application as Reference Standard in Analytical Measurements

R. Middendorp*, M. Dürr, D. Bosbach

Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research,
*IEK-6: Nuclear Waste Management and Reactor Safety, 52425 Jülich, Germany, *e-mail: r.middendorp@fz-juelich.de*

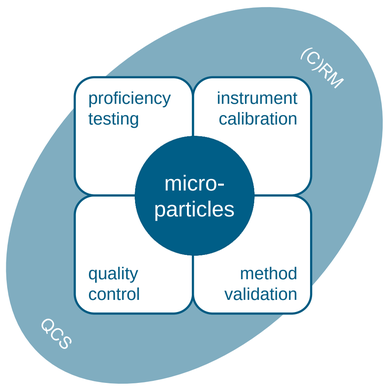
JÜLICH FORSCHUNGSZENTRUM

Supported by:
Federal Ministry of Economics and Technology
on the basis of a decision by the German Bundestag
PTKA Projektträger Karlsruhe im Karlsruher Institut für Technologie
TALISMAN

Reference Standards

Analytical measurements require dedicated reference standards

- e.g. nuclear safeguards particle analysis



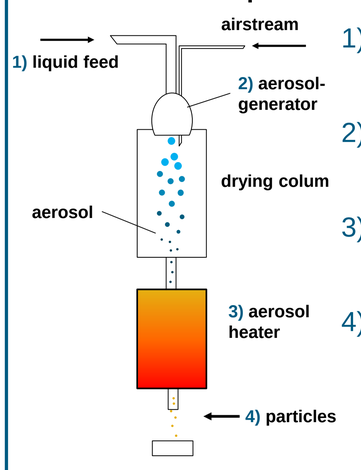
Reference materials have property values

- e.g. isotopic composition, content

Stability and homogeneity of value(s) should be fit for purpose (ISO Guide 34)

Particle Production and Characterization

Production of monodisperse uranium oxide microspheres[1]:



1) Liquid feed with known isotopic composition
2) Generation of monodisperse aerosol
3) Thermal treatment of droplets to UO_x particles
4) Collection of particles

Transfer of particles into suspension offer advantages:

- ➢ e.g. particles mixtures, handling

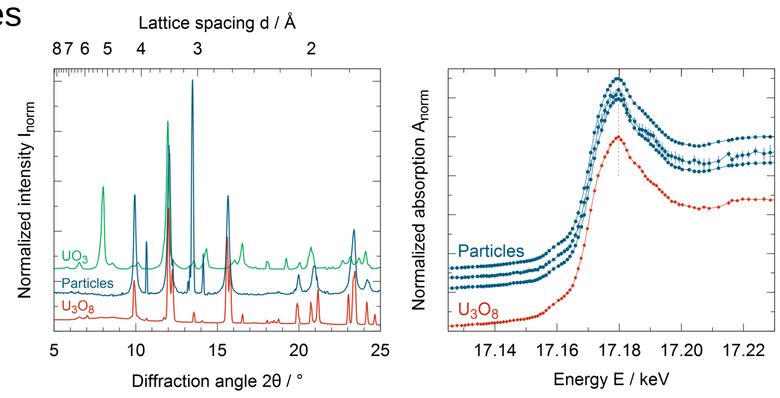
But, stability should be considered

Uranyl nitrate aerosol heated to 500 °C

- ➢ β-UO_3 expected[2]

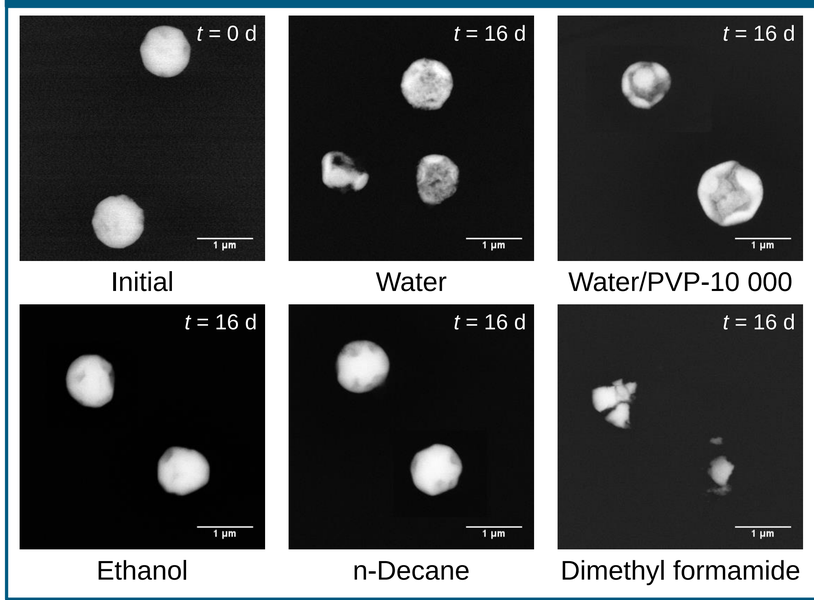
µ-XRD and µ-XANES measurements performed at single particles (PSI, CH)

- ➢ Orthorhombic U_3O_8 phase found for all measured particles



Monodisperse U_3O_8 microspheres produced

Microparticle Dissolution



Dissolution behavior of microparticles studied in various solvents:

- ➢ Partial dissolution in water, water with surfactant and dimethyl formamide
- ➢ No dissolution observed in ethanol and n-decane

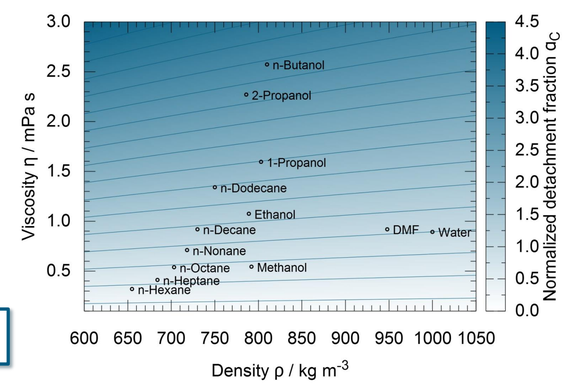
Dissolution leaves shell-shaped structures

- ➢ Indicating solvent penetration into pores

Ethanol determined as most suitable matrix material

Particle removal from Si wafer by ultrasonification

- ➢ Inefficient for n-hexane[3]

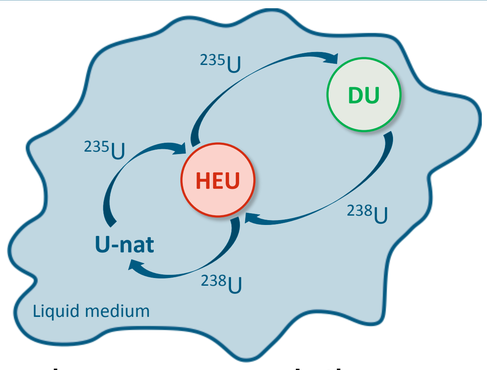


Detachment efficiency of microparticles from silicon wafer into various common solvents[3]

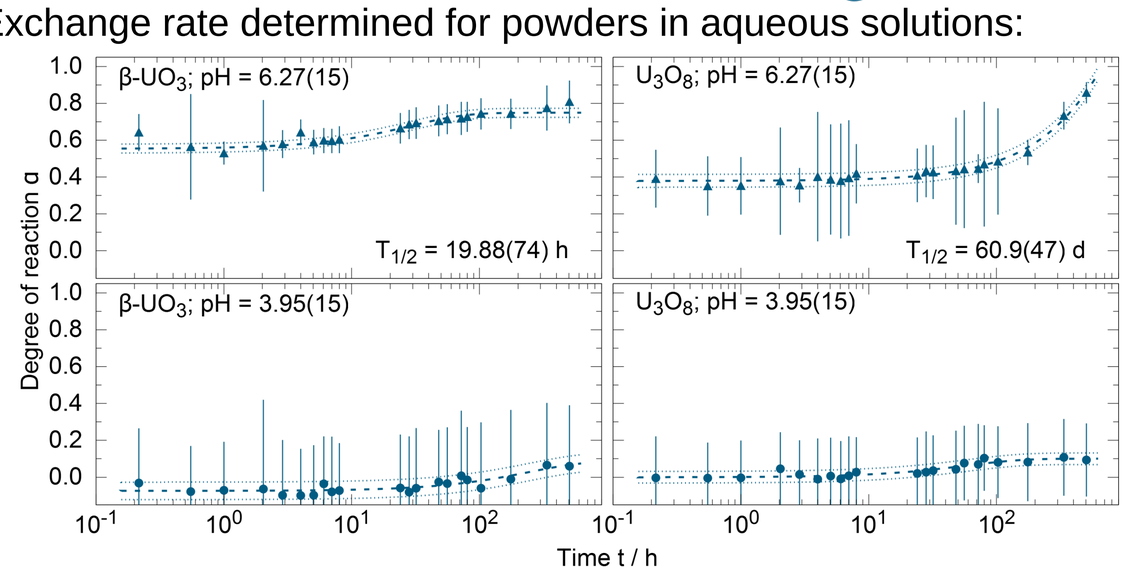
Uranium Isotope Exchange

Uranium exchange could alter composition:

- Between particles
- Between particles and traces of ^{nat}U in medium



Exchange rate determined for powders in aqueous solutions:



Faster exchange for UO_3 ➢ Exchange via U(VI)

No exchange at acidic conditions ➢ Exchange via hydroxides[4]

Uranium exchange proceeds via U(VI) hydroxides and has a reaction rate for U_3O_8 of 474(37) h^{-1}

Conclusion

Particle production and characterization:

- Monodisperse uranium microspheres have been produced
- XRD and XANES studies: orthorhombic U_3O_8 phase

Microparticle dissolution:

- Particle dissolution commences at particle core
- No dissolution observed in ethanol and n-decane
- Ethanol most suitable for particle suspensions

Uranium isotope exchange:

- Isotope exchange measured between UO_x (s) and UO_2^{2+} (aq)
- Exchange proceeds via U(VI) hydroxides
- Exchange rate for U_3O_8 of 474(37) h^{-1} determined

Outlook

Particle characterization:

1) Confirmation of particle phase by µ-raman

Dissolution behavior:

1) FIB/EM investigation of particle core
2) Longer contacting times

Uranium isotope exchange:

1) Rate determinations in ethanol
2) Between-particle exchange

[1] Middendorp, Knott, & Dürr, *ESARDA 37th Annual Meeting Proceedings,* 2015.
[2] Hoekstra & Siegel. *J. Inorg. Nucl. Chem.*, **18**, 154, 1691.
[3] Awad. & Nagarajan. *Developments in Surface Contamination and Cleaning*, 2010.
[4] Szabó, Z. & Grenthe, I. *Inorg. Chem.*, **46**, 9372, 2007.

- Thanks to F. Sadowski (Q-ICP-MS), Dr. M. Klinkenberg (SEM) and M. Güngör (SEM)
- Supported by Bundesministerium für Wirtschaft und Energie - “Neu- und Weiterentwicklung von Safeguardstechniken und –methoden” (FKZ 02W6263) and the German Support Programme to the IAEA