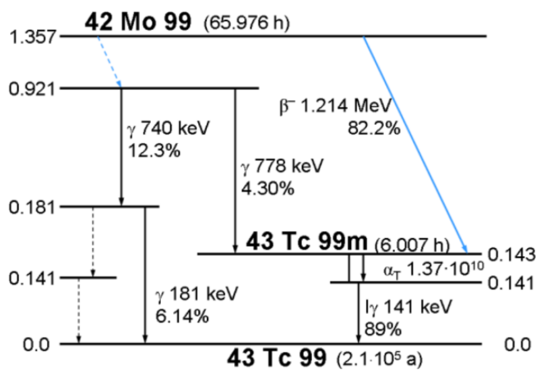
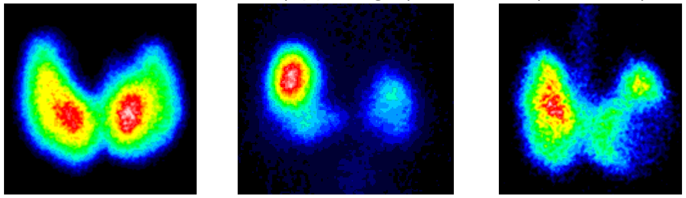
GHYHORSPHQW#RI#D#SODVPD#DIGHG#IOXRULQDWLRQ#
SURFHVV#IRU#PR0<<#VHSDUDWLRQ

WREIDV#FKHPQLW]

Rfwrehu3:/#5355
Ylhqqd

Why is ^{99}Mo of any importance?

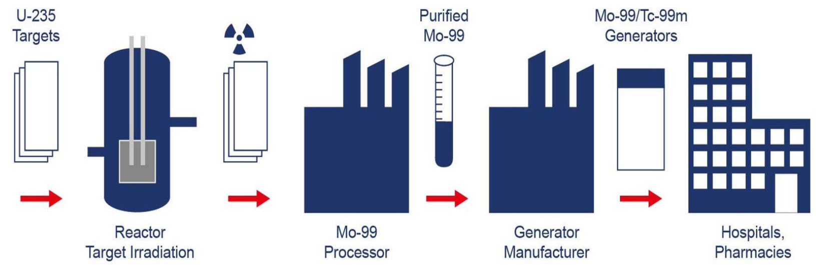




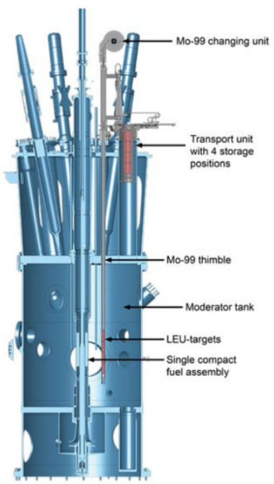
Source: Universitätsklinikum Marburg und Gießen GmbH

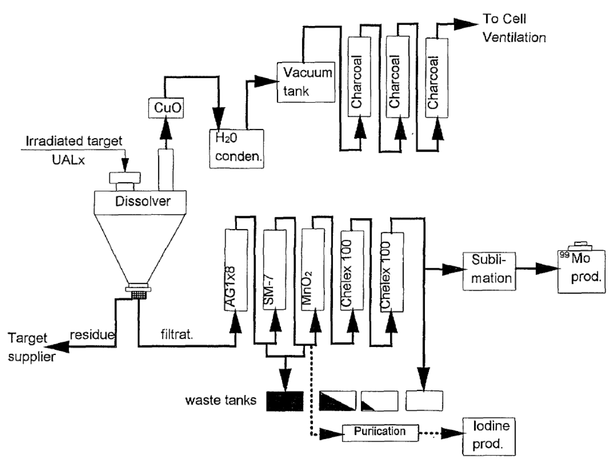
- ^{99m}Tc most widely used radioisotope in nuclear medicine
- 30 million procedures worldwide per year
- about 3 million procedures in Germany alone

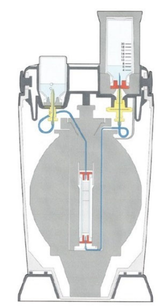
Mo-99/Tc-99m supply chain



Source: FRM II/TUM







Fission products in LEU targets (19.75%, 20g)

Nuclide vector after irradiation period of 180 h, 24 h after end of irradiation

element	mass [mg]	percentage
Xe	35.5	0.178
Zr	28.5	0.143
Ce	25.2	0.126
Mo	17.5	0.088
Nd	16.7	0.084
Ba	15.5	0.078
Ru	14.3	0.072
Sr	11.8	0.059
Cs	11.2	0.056
La	9.3	0.047
Pr	6.5	0.032
Y	5.0	0.025
Te	4.9	0.024
Tc	3.6	0.018
Pu	3.3	0.017
I	3.3	0.016
Kr	3.1	0.015
Rb	3.0	0.015
Sm	2.2	0.011

molybdenum

mass [mg]	percentage
17.5	0.088

uranium

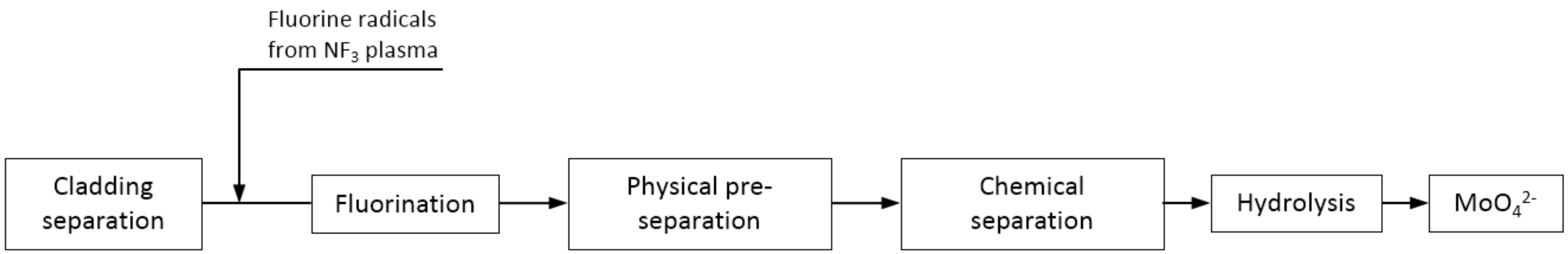
mass [mg]	percentage
19766.6	98.843

Alkaline dissolution process very efficient for HEU targets, BUT:

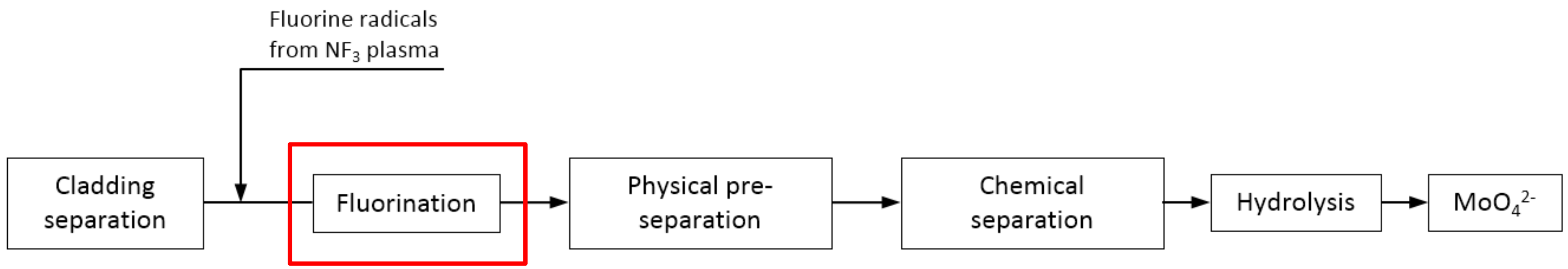
- significant increase in volume of intermediate level liquid waste (ILLW) for LEU targets by up to 200%
- corresponding to 15,000 l ILLW/year per 10,000 6-day Ci/wk fission ^{99}Mo

Source: Lee et al.,Development of Industrial-Scale Fission ^{99}Mo Production Process Using Low Enriched Uranium Target

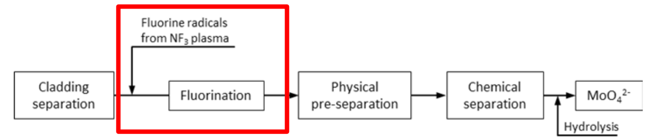
General Process



FLUORINATION



Hexafluoride separation



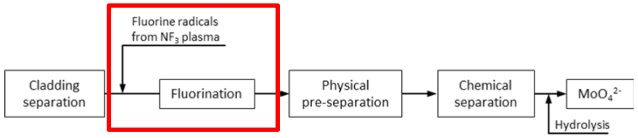
HF																	He
						MnF_3, MnF_4	FeF_3	CoF_3, CoF_2	NiF_2	CuF_2	ZnF_2	GaF_3	GeF_4	AsF_3, AsF_5	SeF_4, SeF_6	BrF_3	Kr, KrF_2
RbF	SrF_2	YF_3	ZrF_4	NbF_5	MoF_6	TcF_6	RuF_6, RuF_3	RhF_6, RhF_3	PdF_2	AgF, AgF_2	CdF_2	InF_3	SnF_4	SbF_5	TeF_6	IF_5, IF_7	Xe, $XeF_{2,4,6}$
CsF	BaF_2	LaF_3															

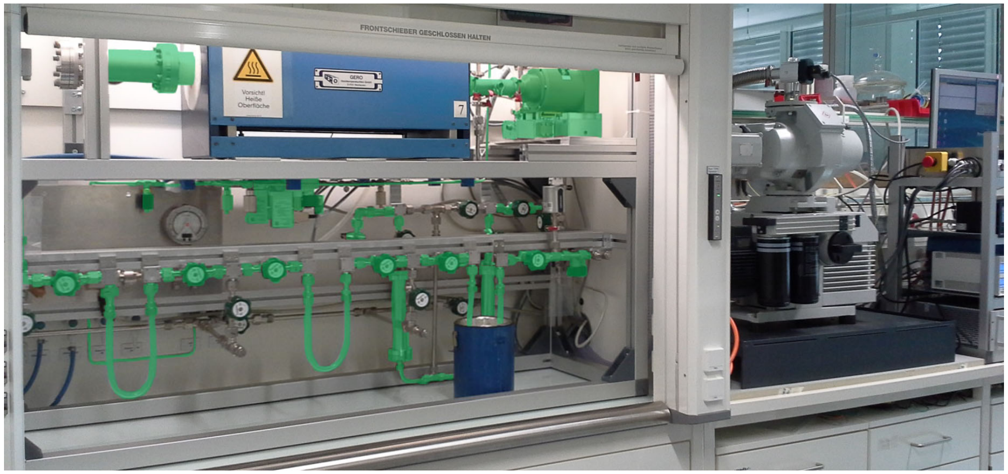
Lanthanoids	CeF_4	PrF_3	NdF_3	PmF_3	SmF_3	EuF_3	GdF_3	TbF_3	DyF_3	HoF_3	ErF_3			
Actinoids	ThF_4	PaF_3	UF_6	NpF_6	PuF_6	AmF_3	CmF_3							

Major volatile fluorides:

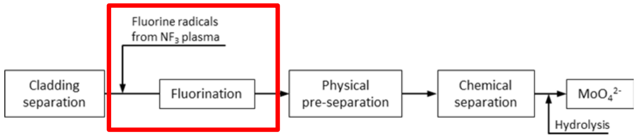
UF_6,
MoF_6,
TeF_6,
TcF_6,
PuF_6,
IF_5,
IF_7

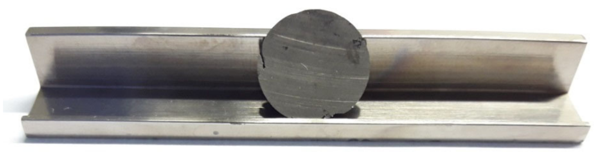
Microwave Plasma Fluorination Line





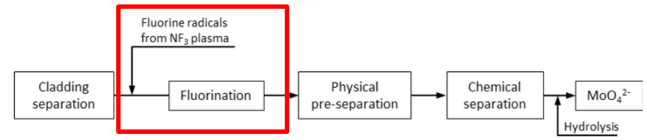
Surrogate Fluorination



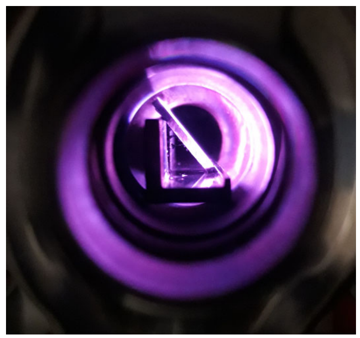


composition U/Mo	nominal [wt%]	MS [wt%]
99 : 1	1.00	1.144 ± 0.201
99.5 : 0.5	0.50	0.546 ± 0.040
99.9 : 0.1	0.10	0.123 ± 0.004

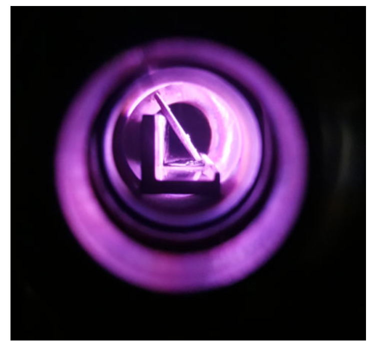
Surrogate Fluorination



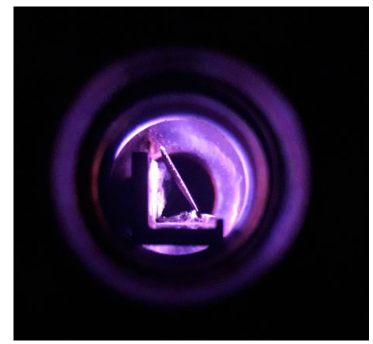
ignition
Ar plasma



t + 02:20 min
Ar/NF_3 plasma



t + 14:10 min
Ar/NF_3 plasma

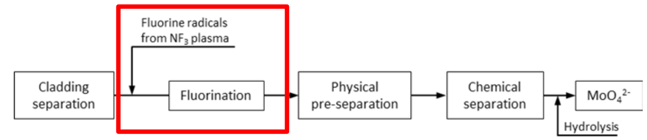


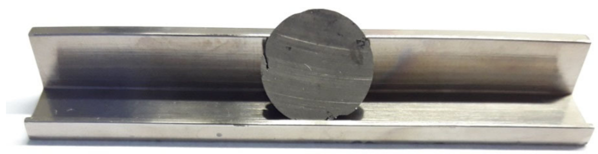
t + 36:30 min
Ar/NF_3 plasma

$$Mo + 2\,NF_3 \longrightarrow MoF_6 + N_2$$

$$U + 2\,NF_3 \longrightarrow UF_6 + N_2$$

Surrogate Fluorination

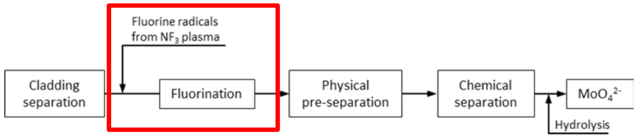


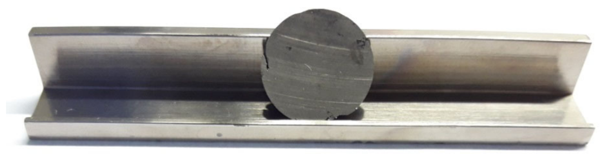


nuclide	mass [mg]	specific activity [Bq/g]	corr. activity [kBq]
^{238}U	2707.0 ± 0.2	$12.45 \cdot 10^3$	33.70 ± 0.01

center for
nuclear safety
and innovation

Surrogate Fluorination



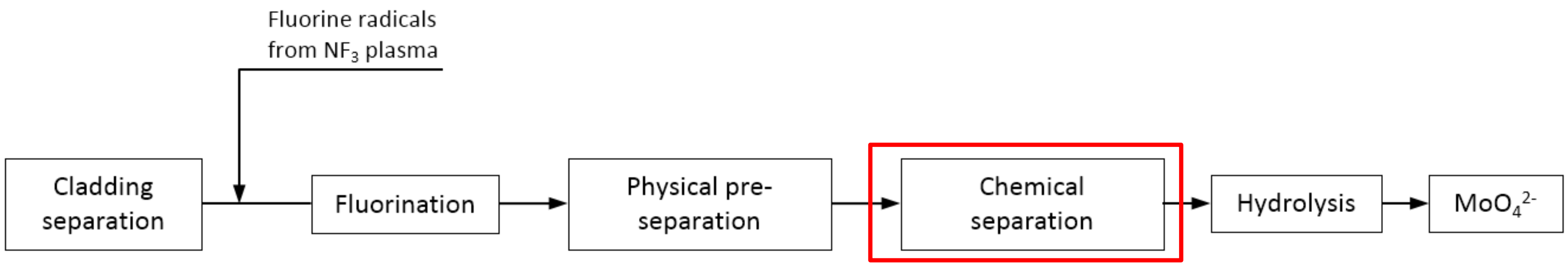


nuclide	mass [mg]	specific activity [Bq/g]	corr. activity [kBq]
^{238}U	2707.0 ± 0.2	$12.45 \cdot 10^{3}$	33.70 ± 0.01

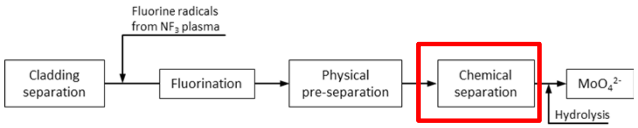
nuclide	activity [kBq]	specific activity [Bq/g]	corr. mass [mg]
^{234m}Pa	13.93 ± 0.45	$2.56 \cdot 10^{19}$	$(5.44 \pm 0.18) \cdot 10^{-13}$
^{234}Th	13.34 ± 0.97	$8.57 \cdot 10^{14}$	$(1.56 \pm 0.11) \cdot 10^{-8}$

→ significant amount (42 %) of non-volatile decay products stays behind

CHEMICAL UMO SEPARATION

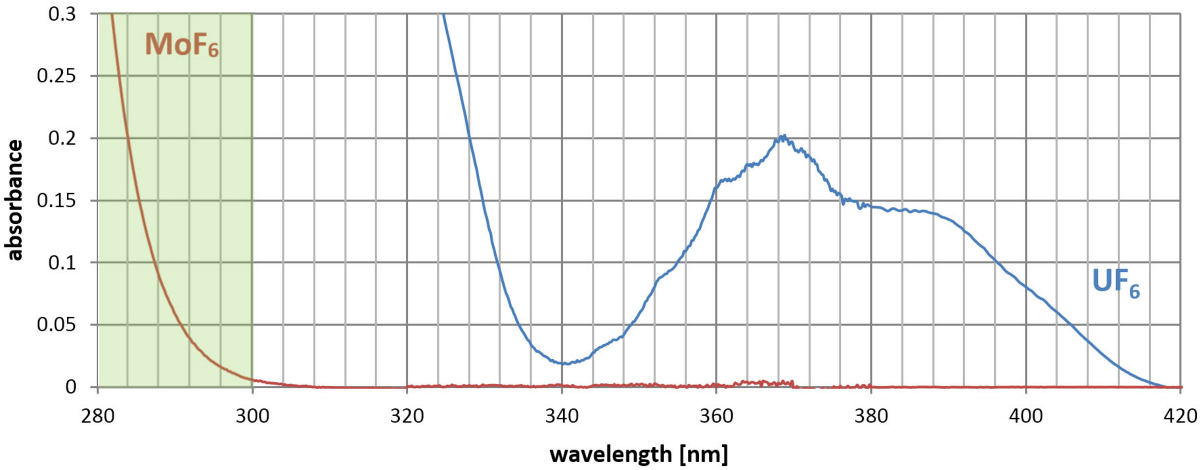


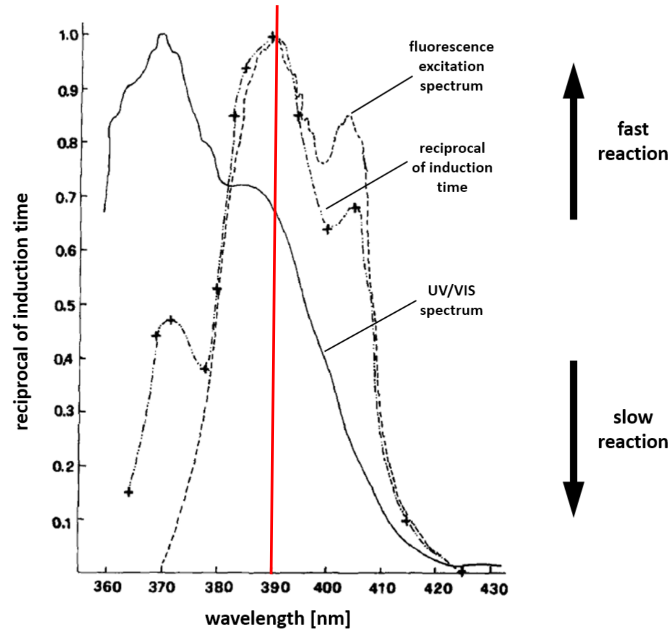
Photodissociation



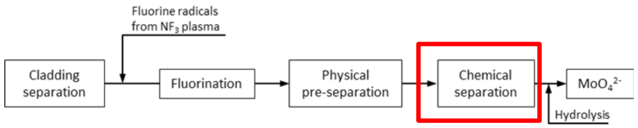
$$2\ UF_6 \xrightarrow{UV} 2\ UF_5 + F_2$$

$$2\ MoF_6 \xrightarrow{UV} 2\ MoF_5 + F_2$$



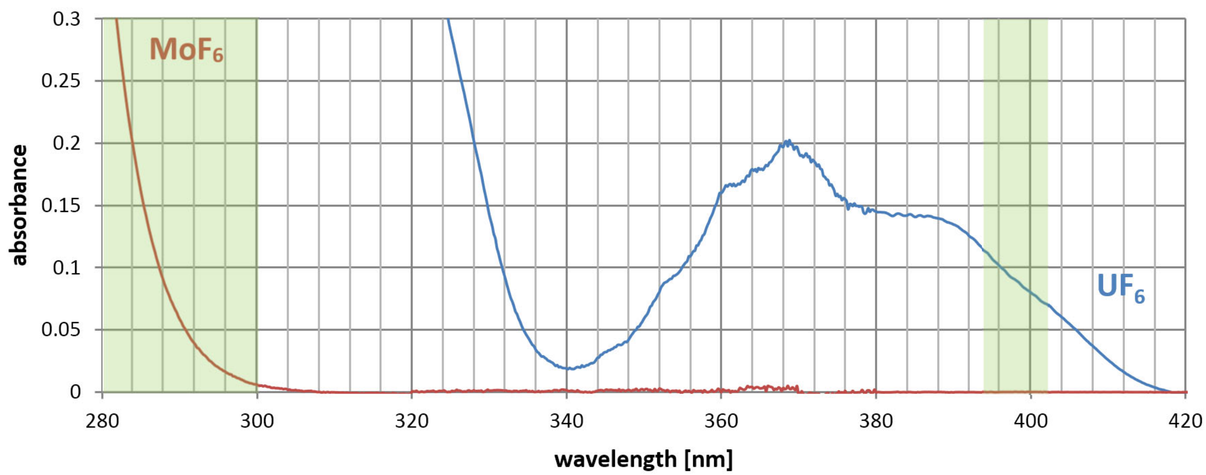


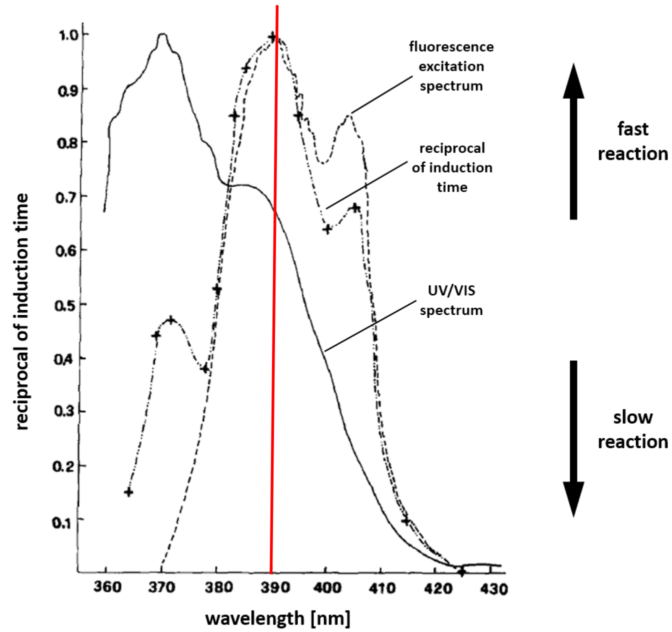
Photodissociation



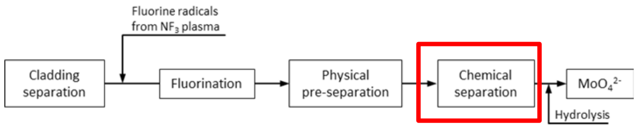
$$2\,UF_6 \xrightarrow{395\ nm} 2\,UF_5 + F_2$$

$$2\,MoF_6 \xrightarrow{\cancel{395\ nm}} 2\,MoF_5 + F_2$$





Chemical separation with gaseous CO (R. Stene)



$$2\ UF_6 \xrightarrow{395\ nm} 2\ UF_5 + F_2$$

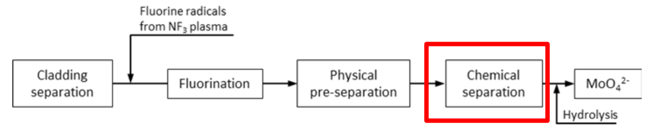
$$2\ UF_6 + CO \xrightarrow{395\ nm} 2\ UF_5 + COF_2$$

UF_6/MoF_6 mixture

UF_5/MoF_6 mixture

Source: Reductive photo-chemical sparation of the hexafluorides of uranium and molybdenum

Chemical separation with gaseous CO (R. Stene)



$$2\,UF_6 \xrightarrow{395\ nm} 2\,UF_5 + F_2$$

$$2\,UF_6 + CO \xrightarrow{395\ nm} 2\,UF_5 + COF_2$$

UF_6/MoF_6 mixture

UF_5/MoF_6 mixture

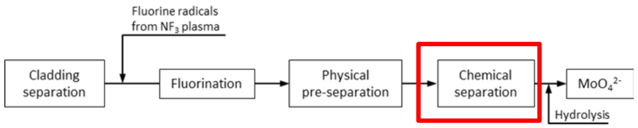
Source: Stene et al., Reductive photo-chemical separation of the hexafluorides of uranium and molybdenum

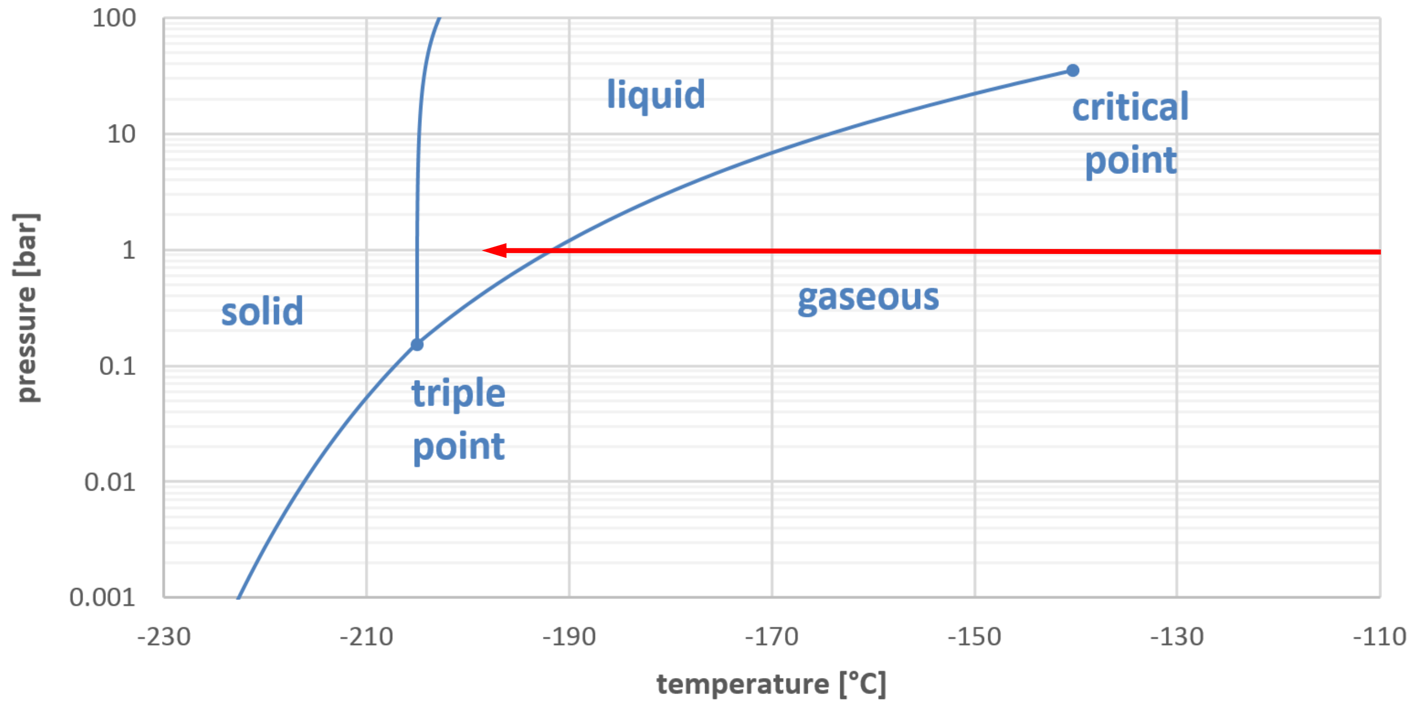
	mixture before	mixture after (Mo side)	mixture after (U side)
U [mg]	133.2	n.d.	39.3
Mo [mg]	91.5	29.14	0.16
wt% Mo	40.7	100	0.4

→ very good separation

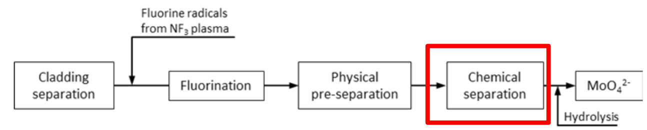
but:
total irradiation time 48 h

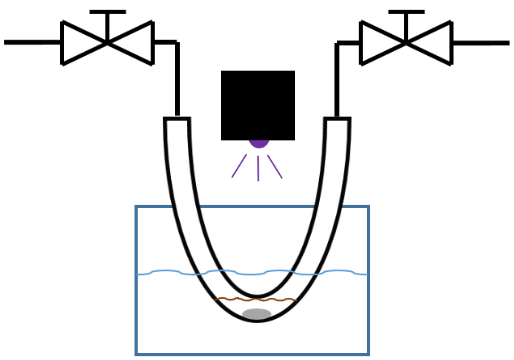
Phase diagram of CO

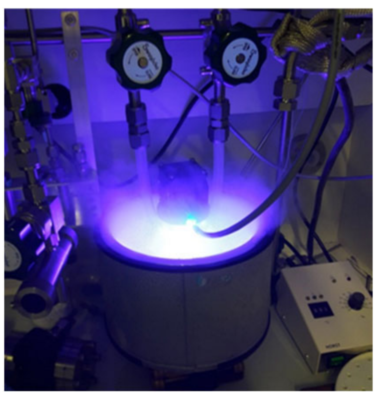


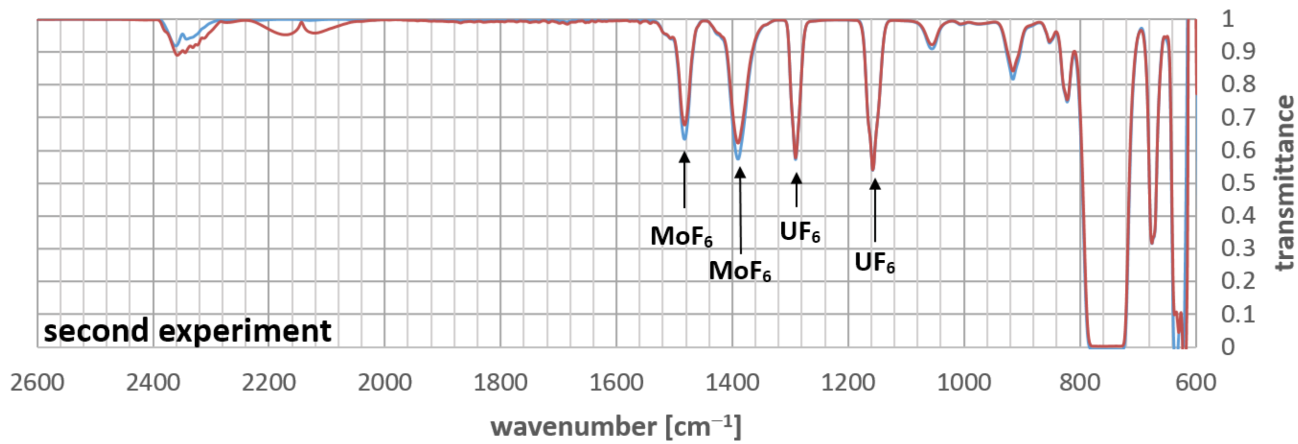


Chemical separation with liquid CO



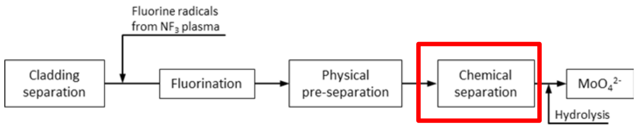


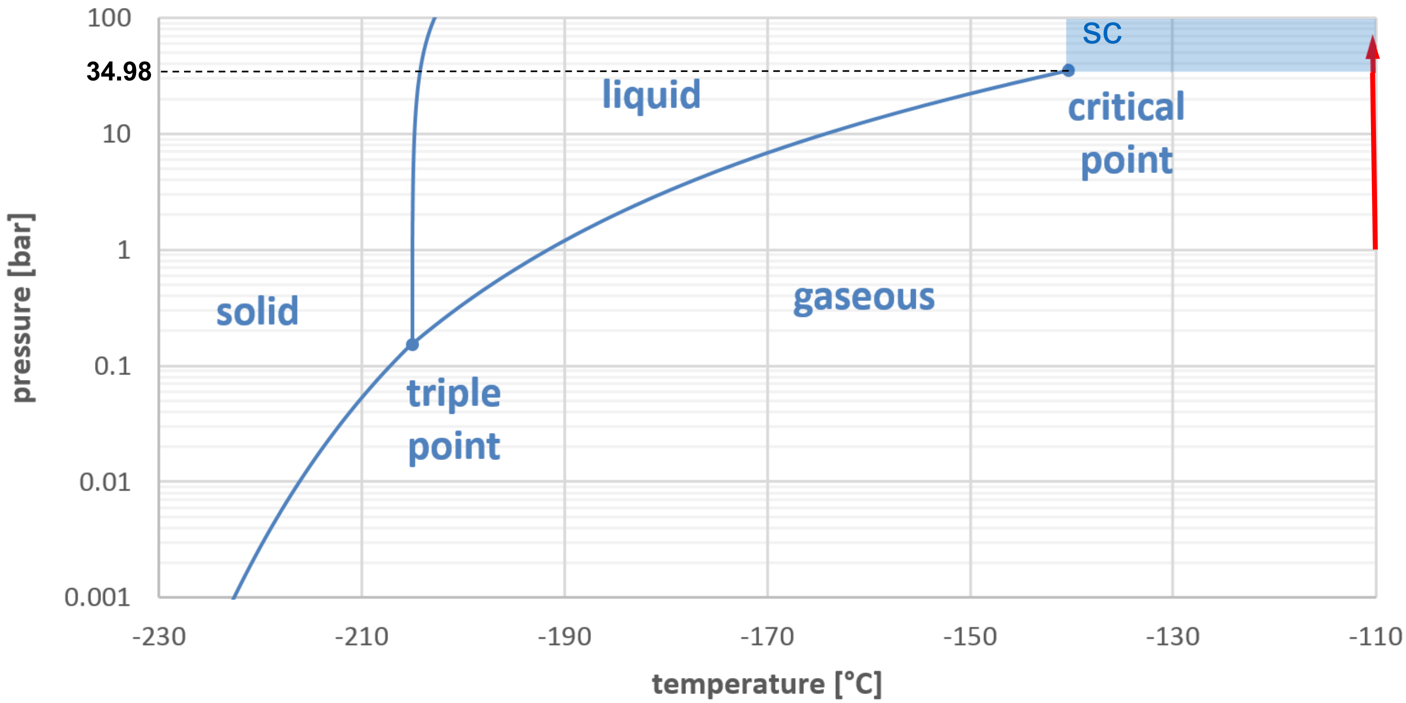




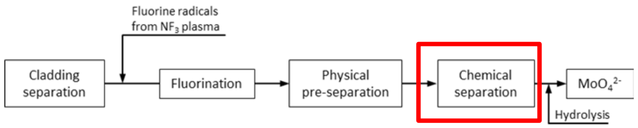
→ **no/insufficient separation**

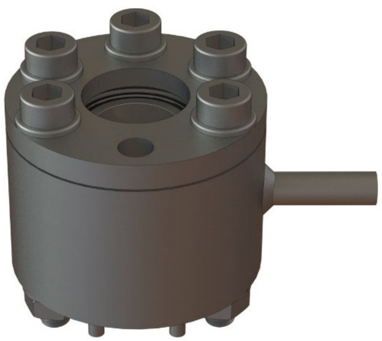
Phase diagram of CO



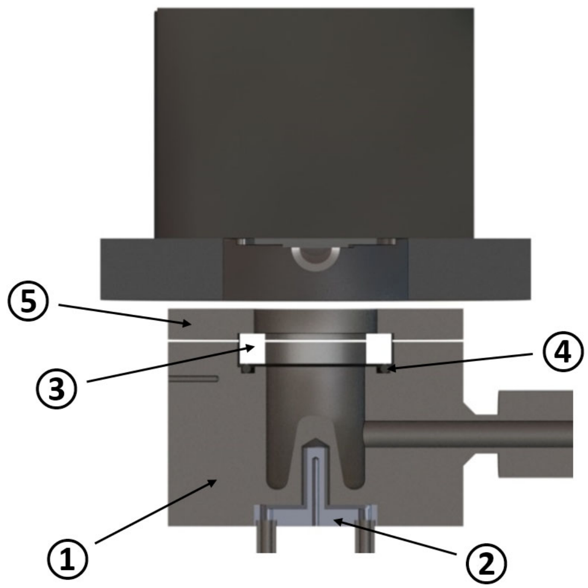


Chemical separation with supercritical CO



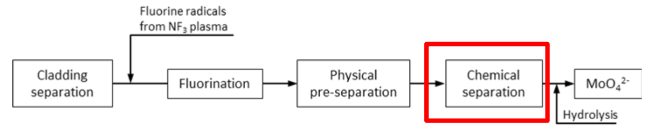


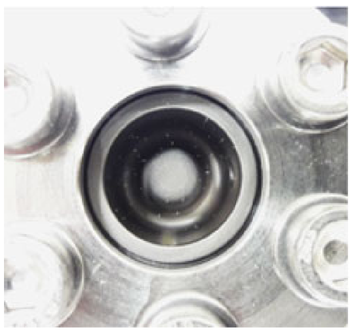
- p_{max} = 230 bar (SF = 4)
- tested with Ar at 80 bar for 6 h



- Irradiation for 60 minutes

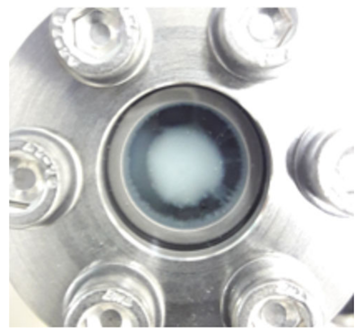
Chemical separation with supercritical CO



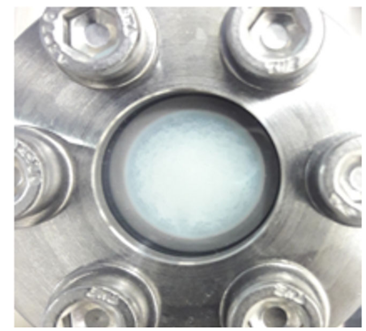


solid
UF_6/MoF_6

solid
UF_6/MoF_6 with
supercritical CO

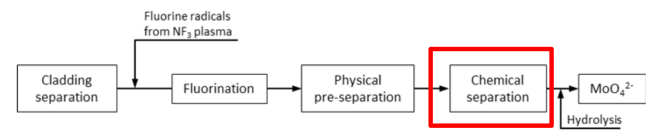


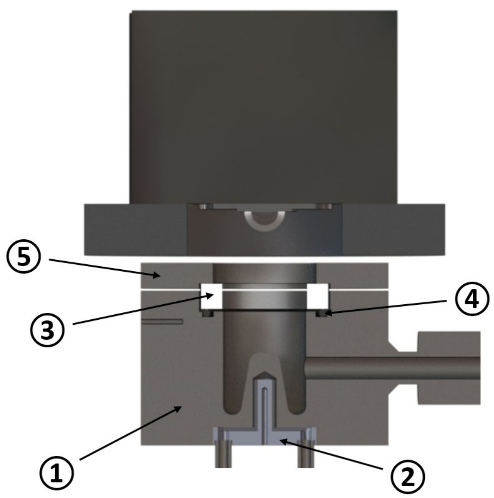
after irradiation
for 7 minutes

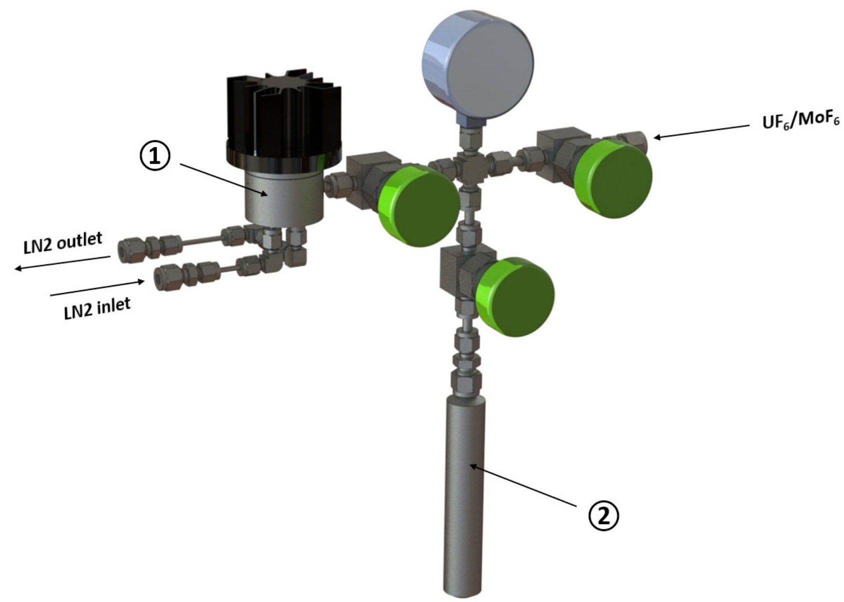


end of irradiation
after 60 minutes

Chemical separation with supercritical CO

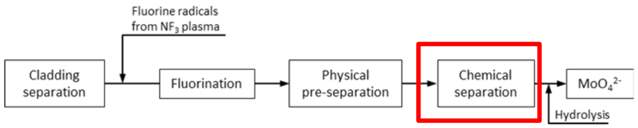


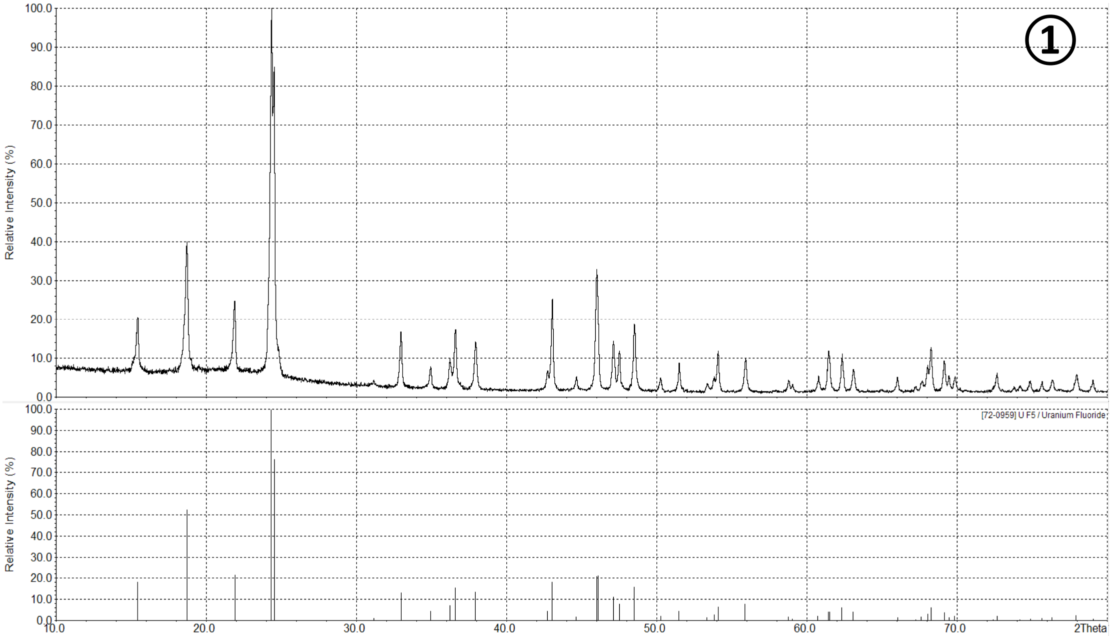


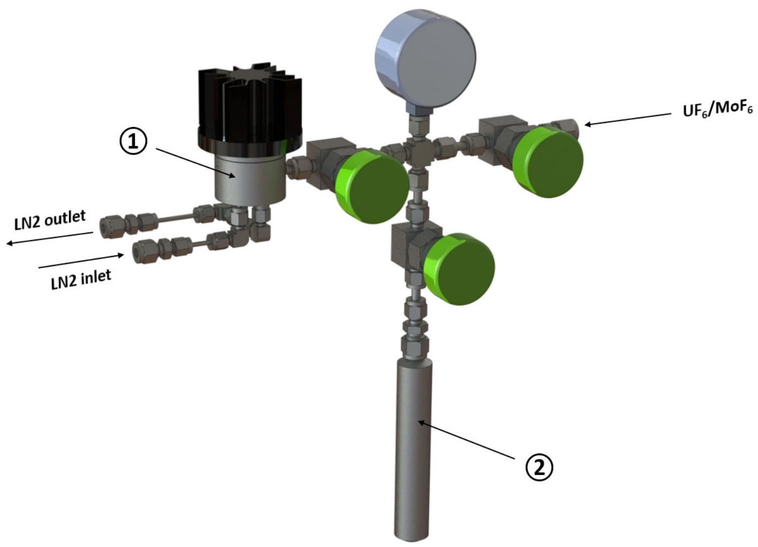


center for nuclear safety and innovation

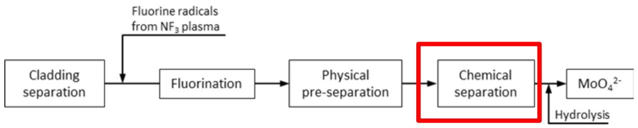
Chemical separation with supercritical CO

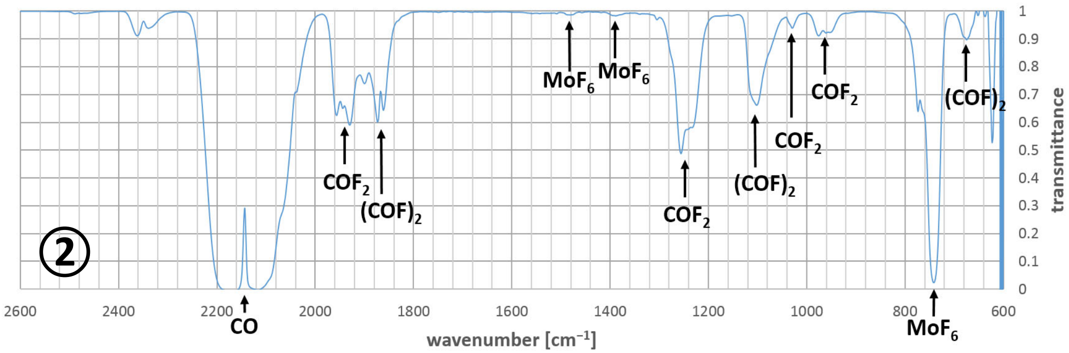


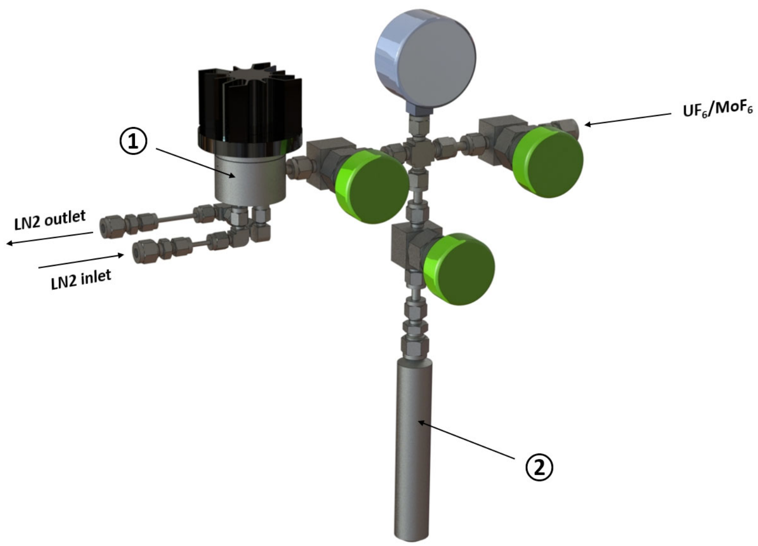




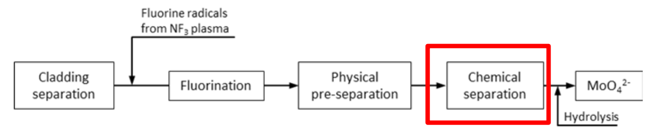
Chemical separation with supercritical CO







Chemical separation with supercritical CO

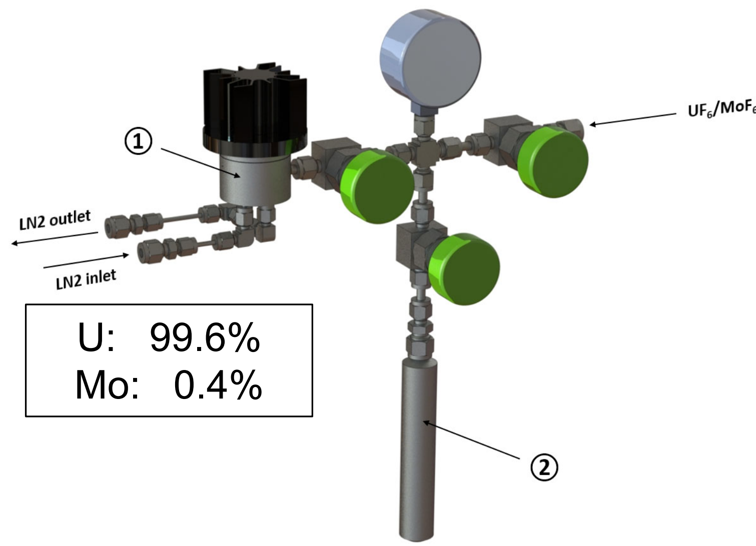


	mixture before	storage container ② (Mo side)	high-pressure container ① (U side)
U [mg]	26.8 ± 0.3	2.99 ± 0.60	20.96 ± 0.63
Mo [mg]	7.5 ± 0.3	7.35 ± 0.06	0.08 ± 0.06
wt% Mo	21.9 ± 0.7	71.2 ± 1.7	0.4 ± 0.3

Mo recovery 98.0%

U recovery 78.2%

→ good separation/ optimization necessary

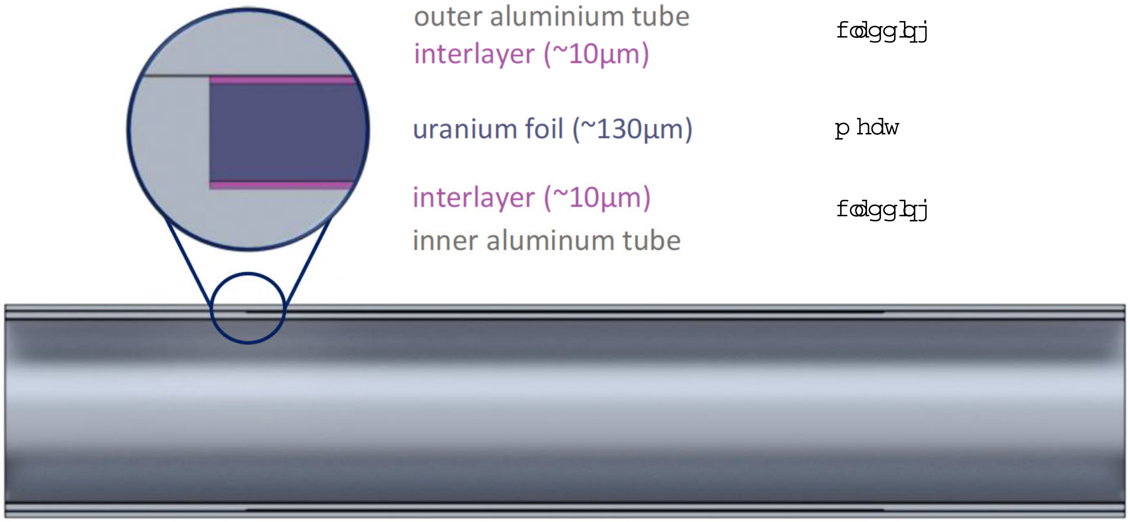


U: 99.6%
Mo: 0.4%

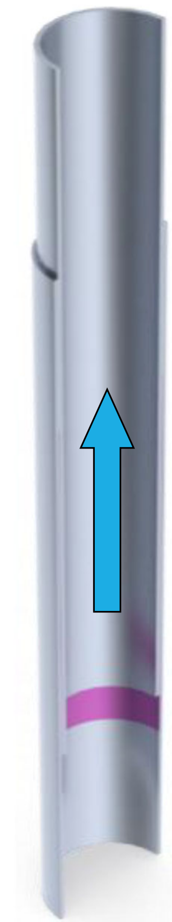
U: 29.8%
Mo: 71.2%

WKDQN \RX

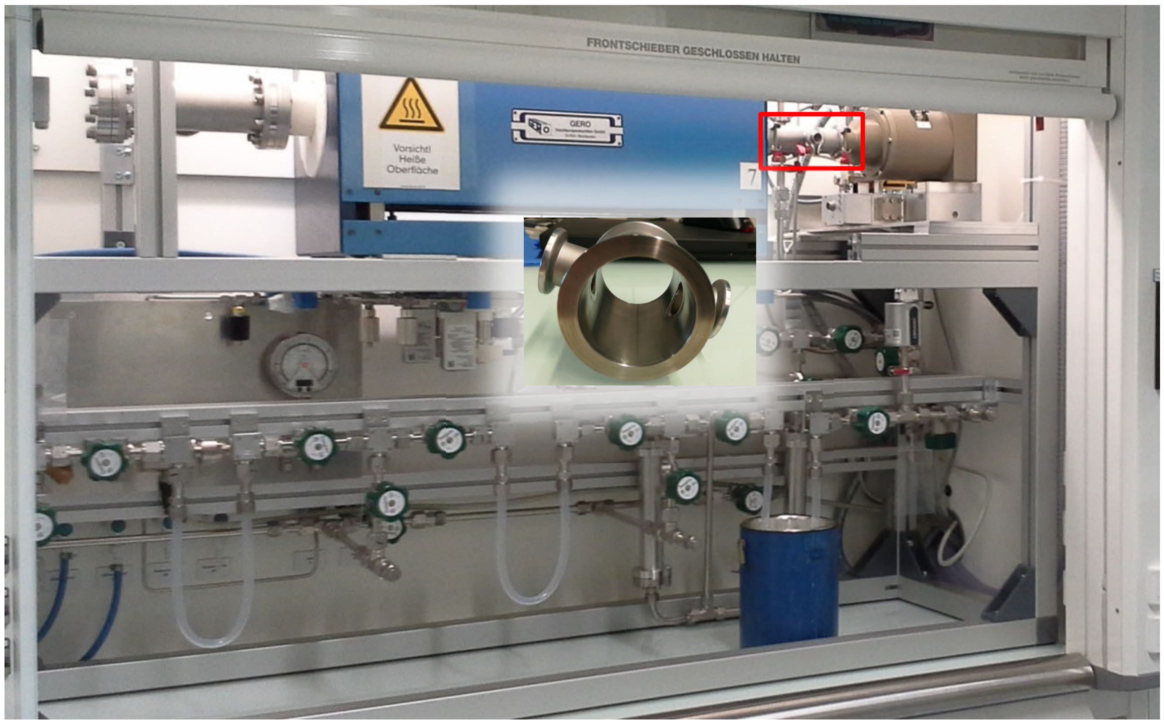
LUUDGLDWLRQ#WDUJHWV#+W1#KROOPHU,



Vrxufh=#Glvvhuwdwlrq#W1#Krop hu, Ghyhorsphqw#ri#SYG0edvhg pdqxidfwxulqj surfhvvhv iru prqrolwklf OHX#luudgldwlrq wdujhwv iru<<Pr#surgxfwlrq



FRUURVLRQ#DVSHFWV#,DIWHU#EHLQJ#LQVWDOOHG#IRU#5#\HDUV#



FRUURVLRQ#DVSHFWV#, DIWHU#EHLQJ#LQVWDOOHG#IRU#5#\HDUV#