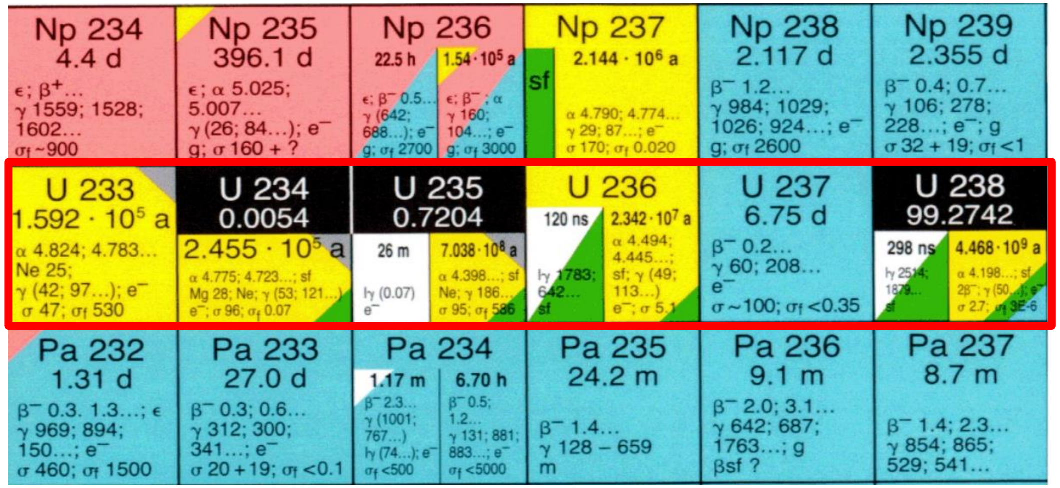
INCREASING THE IONIZATION YIELD FOR THE DETECTION OF ^{236}U AND ^{233}U BY AMS

PRESENTED BY MICHAEL KERN[1],

KARIN HAIN[1], TOMÁŠ PRÁŠEK[2], PETER STEIER[1], ANDREAS WIEDERIN[1] AND ROBIN GOLSER[1]
[1]UNIVERSITY OF VIENNA, FACULTY OF PHYSICS, AUSTRIA
[2]CZECH TECHNICAL UNIVERSITY IN PRAGUE, CZECH REPUBLIC

^{236}U and ^{233}U as fingerprint



Np 234 4.4 d ϵ; β^+… γ 1559; 1528; 1602… σ_f ~900	**Np 235** 396.1 d ϵ; α 5.025; 5.007… γ (26; 84…); e^- g; σ 160 + ?	**Np 236** 22.5 h | $1.54 \cdot 10^5$ a ϵ; β^- 0.5… | ϵ; β^-; α γ (642; | γ 160; 688…); e^- | 104…; e^- g; σ_f 2700 | g; σ_f 3000	**Np 237** $2.144 \cdot 10^6$ a sf α 4.790; 4.774… γ 29; 87…; e^- σ 170; σ_f 0.020	**Np 238** 2.117 d β^- 1.2… γ 984; 1029; 1026; 924…; e^- g; σ_f 2600	**Np 239** 2.355 d β^- 0.4; 0.7… γ 106; 278; 228…; e^-; g σ 32 + 19; σ_f <1
U 233 $1.592 \cdot 10^5$ a α 4.824; 4.783… Ne 25; γ (42; 97…); e^- σ 47; σ_f 530	**U 234** 0.0054 $2.455 \cdot 10^5$ a α 4.775; 4.723…; sf Mg 28; Ne; γ (53; 121…) e^-; σ 96; σ_f 0.07	**U 235** 0.7204 26 m | $7.038 \cdot 10^8$ a Iγ (0.07) | α 4.398…; sf e^- | Ne; γ 186… σ 95; σ_f 586	**U 236** 120 ns | $2.342 \cdot 10^7$ a Iγ 1783; | α 4.494; 642… | 4.445…; sf | sf; γ (49; 113…) e^-; σ 5.1	**U 237** 6.75 d β^- 0.2… γ 60; 208… e^- σ ~100; σ_f <0.35	**U 238** 99.2742 298 ns | $4.468 \cdot 10^9$ a Iγ 2514; | α 4.198…; sf 1879… | $2\beta^-$; γ (50…); e^- sf | σ 2.7; σ_f 3E-6
Pa 232 1.31 d β^- 0.3. 1.3…; ϵ γ 969; 894; 150…; e^- σ 460; σ_f 1500	**Pa 233** 27.0 d β^- 0.3; 0.6… γ 312; 300; 341…; e^- σ 20 + 19; σ_f <0.1	**Pa 234** 1.17 m | 6.70 h β^- 2.3… | β^- 0.5; γ (1001; | 1.2… 767…) | γ 131; 881; Iγ (74…); e^- | 883…; e^- σ_f <500 | σ_f <5000	**Pa 235** 24.2 m β^- 1.4… γ 128 – 659 m	**Pa 236** 9.1 m β^- 2.0; 3.1… γ 642; 687; 1763…; g βsf ?	**Pa 237** 8.7 m β^- 1.4; 2.3… γ 854; 865; 529; 541…

[Magill et al., EC. (7) 2006]

^{238}U ($t_{1/2} \approx 4.5 \times 10^9$ y)

^{235}U ($t_{1/2} \approx 7.0 \times 10^8$ y)

^{236}U ($t_{1/2} \approx 2.3 \times 10^7$ y)

→ Mainly anthropogenic radionuclide

^{236}U / ^{238}U = 10^{-6} – 10^{-12}

[Steier et al., NIMB. 2008]

^{233}U ($t_{1/2} \approx 1.5 \times 10^5$ y)

$$\frac{^{233}\text{U}}{^{236}\text{U}}$$

≥ 10^{-2} Nuclear weapons fallout

≪ 10^{-2} Civil nuclear industry

[Hain et al., Nat. Commun. 2020, this meeting]

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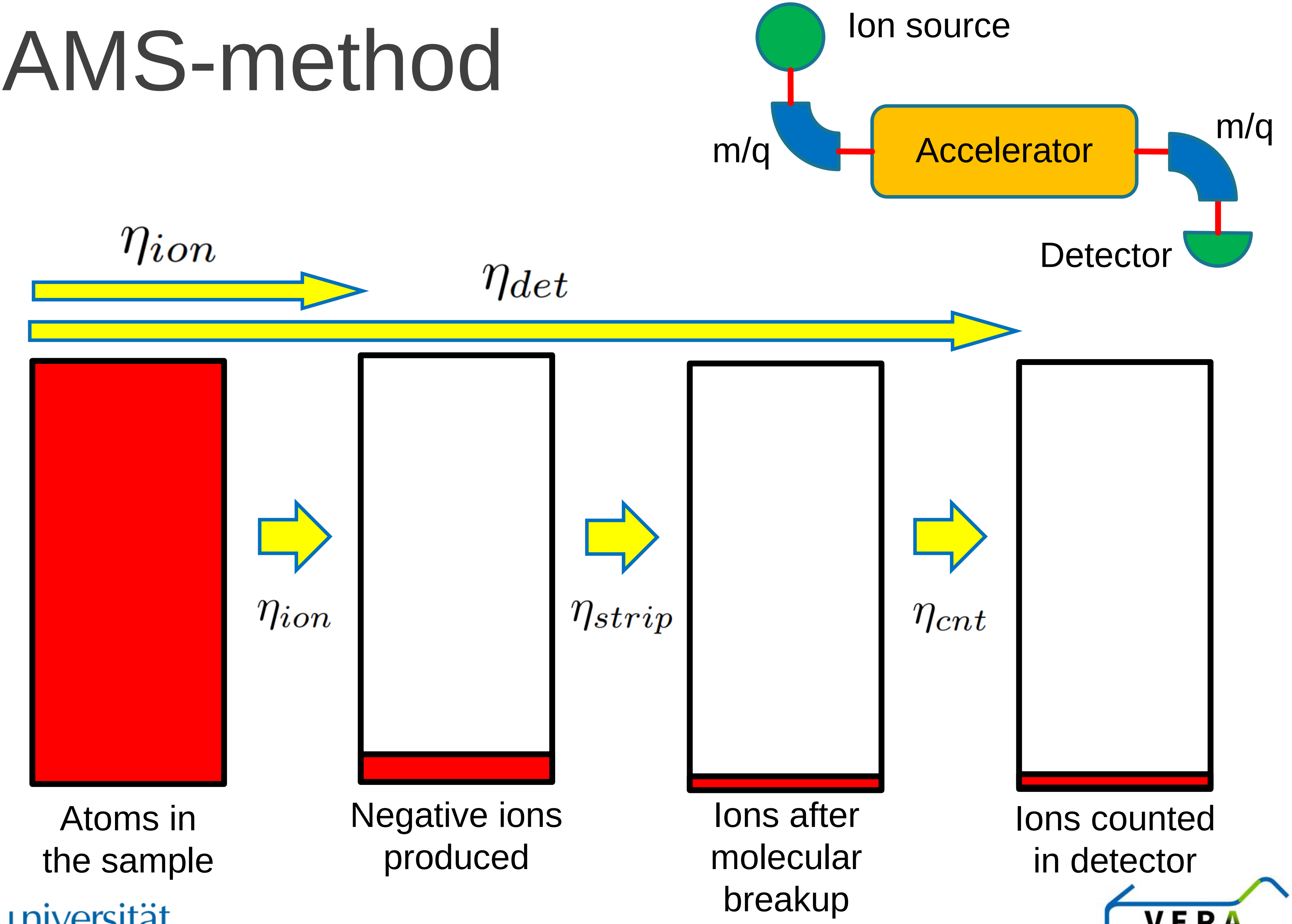
AMS-method



Ion source

m/q

Accelerator

m/q

Detector

η_{ion}

η_{det}

η_{ion}

η_{strip}

η_{cnt}

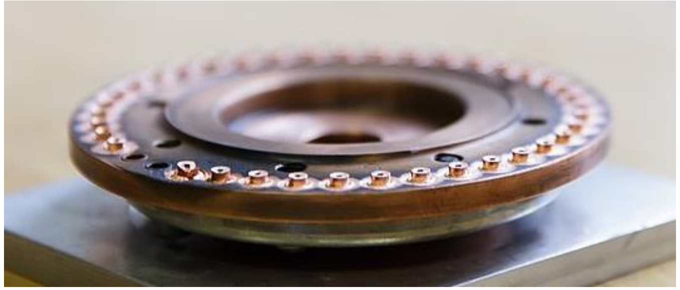
Atoms in the sample

Negative ions produced

Ions after molecular breakup

Ions counted in detector

UO^- for AMS



(~µg UO_x + 2 mg Fe_2O_3) → UO^-

- Slowly-rising UO^- current → time-consuming (~4-5 h)
- Low sample throughput
- Ionization yield ~0.3% $\eta_{ion} \propto \exp(E_A)$

Ion	E_A (eV)
UO^-	?
UO_3^-	2.125
UF_5^-	3.820

→ Strong UF_5^- (high E_A) current with excess fluorine (PbF_2) mixed with pure U metal [Zhao et al., NIMB. 2010].

(UO_x + Fe_2O_3) + PbF_2 → UF_5^- ?

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Results summary

- UF_5^- extraction 3 to 10-fold more efficient than UO^-
- Mixing ratio with PbF_2 of 1:9 (wt. ratio) is optimal
- ≥ 90% of extractable U within 2 h
- Direct application with sub-milligram Fe preparation
- UF_5^- extraction method validated with $^{236}U/^{238}U$ and $^{233}U/^{238}U$ levels of previously measured samples

Materials for UF_5^- extraction

I.

Dry Vienna-KkU-D30 powder (U:Fe = 1:30)

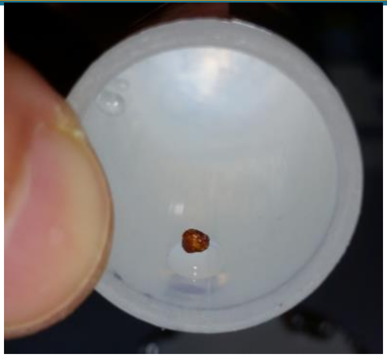
+

1:9 PbF_2 powder

II.

5 µg U in Vienna-KkU solution + 200 µg Fe solution

Dried + calcined (~6h)



+

1:9 PbF_2 powder

III.

Vienna-KkU solution co-precip. UF_4 with NdF_3 (U:Nd = 18)

+

1:9 PbF_2 powder

Materials for UF_5^- extraction

I.

Dry Vienna-KkU-D30 powder (U:Fe = 1:30)

+

1:9 PbF_2 powder

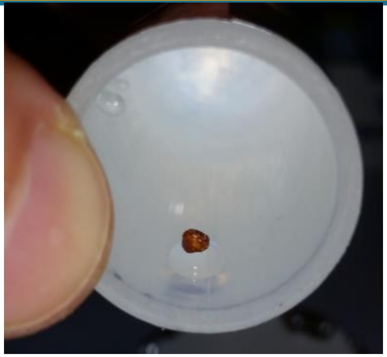
but at least 2 mg Fe using standard co-precipitation

$m_{samp} \geq 20$ mg!

II.

5 µg U in Vienna-KkU solution + 200 µg Fe solution

Dried + calcined (~6h)



+

1:9 PbF_2 powder

III.

Vienna-KkU solution co-precip. UF_4 with NdF_3 (U:Nd = 18)

+

1:9 PbF_2 powder

$m_{samp} \geq 20\text{-}30$ mg!

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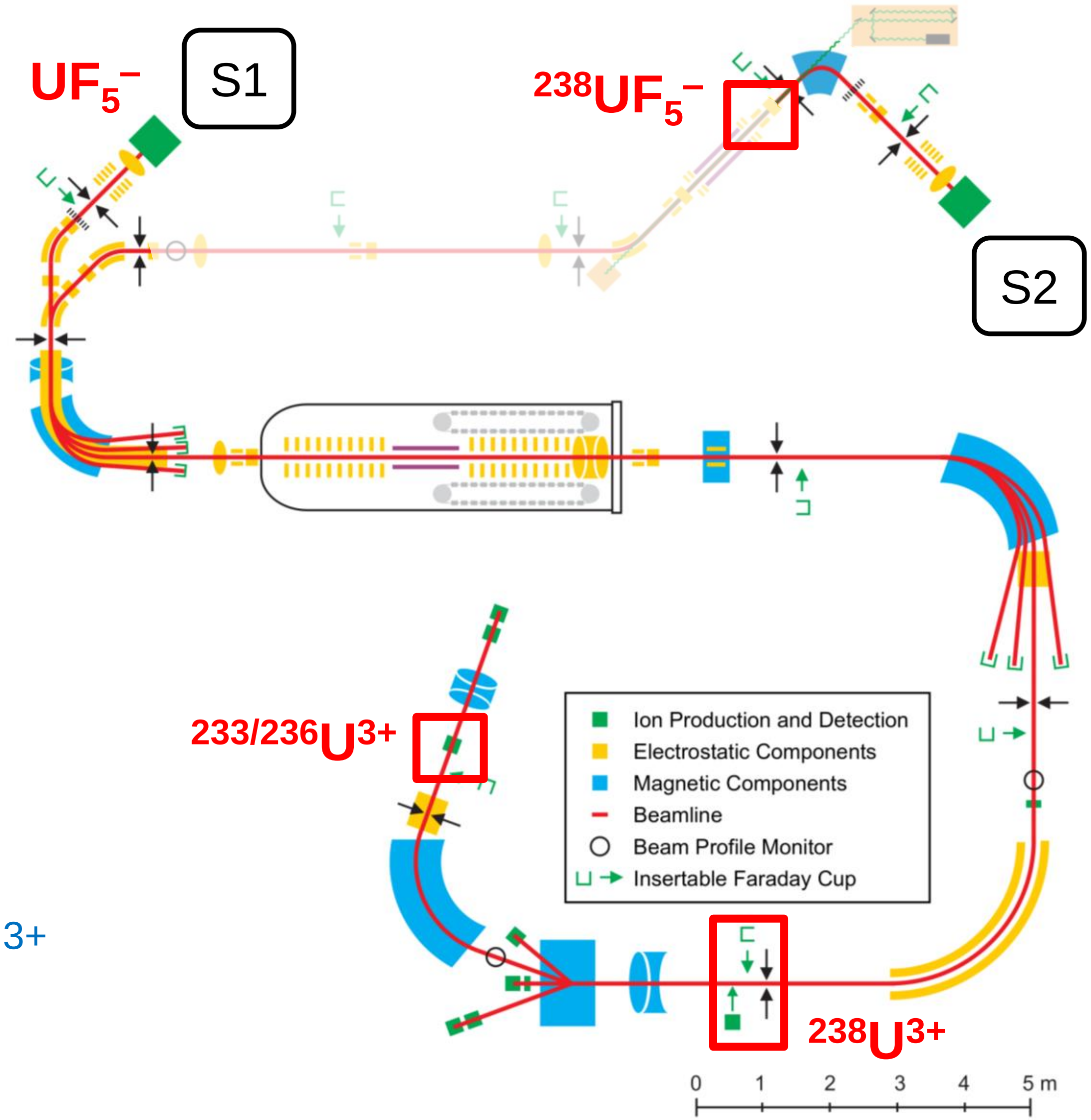
VERA Setup

S2: ionization efficiency experiments

→ $^{238}UF_5^-$

S1 + VERA: trace actinide detection

UF_5^- → $^{233}U^{3+}$, $^{236}U^{3+}$, $^{238}U^{3+}$



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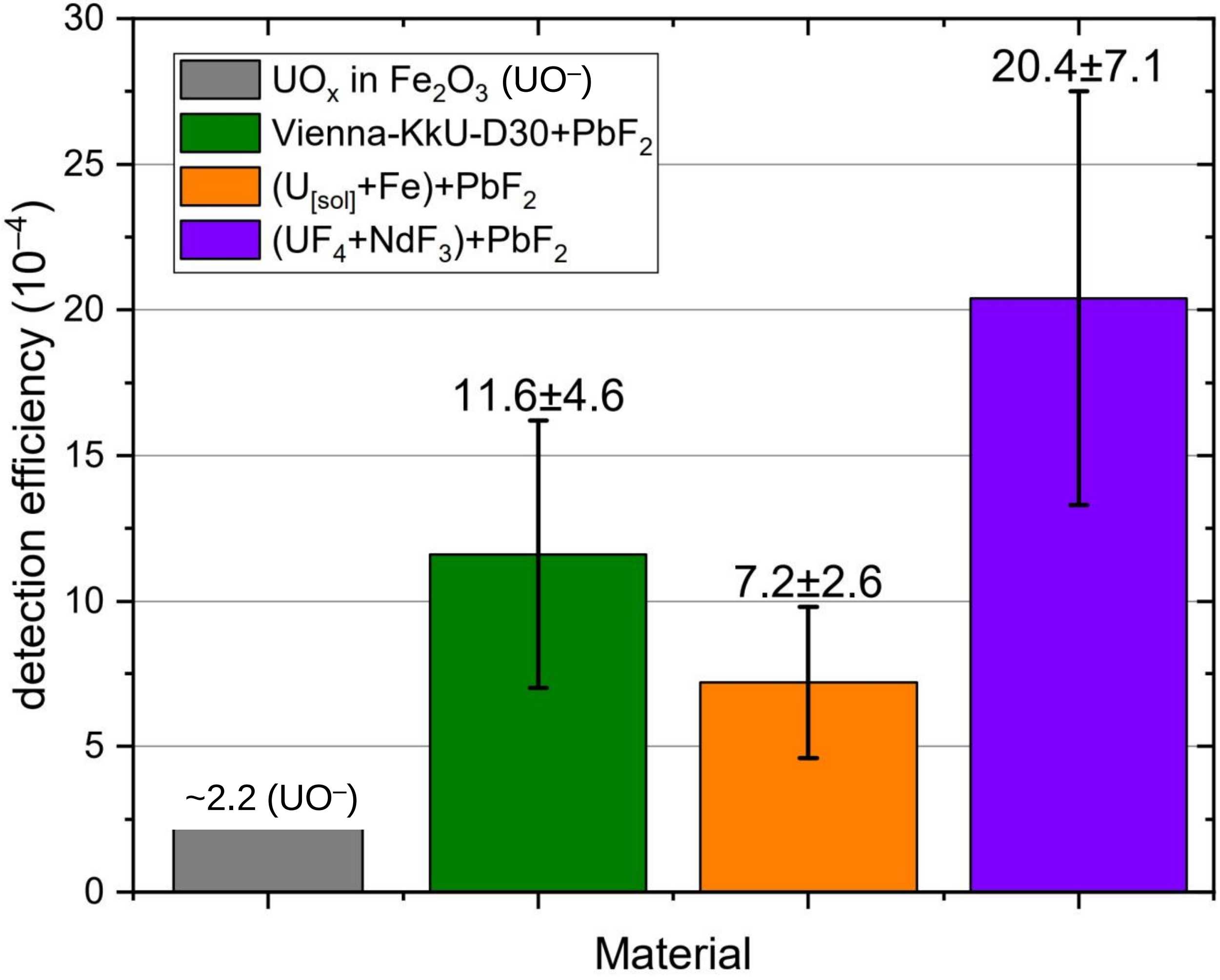
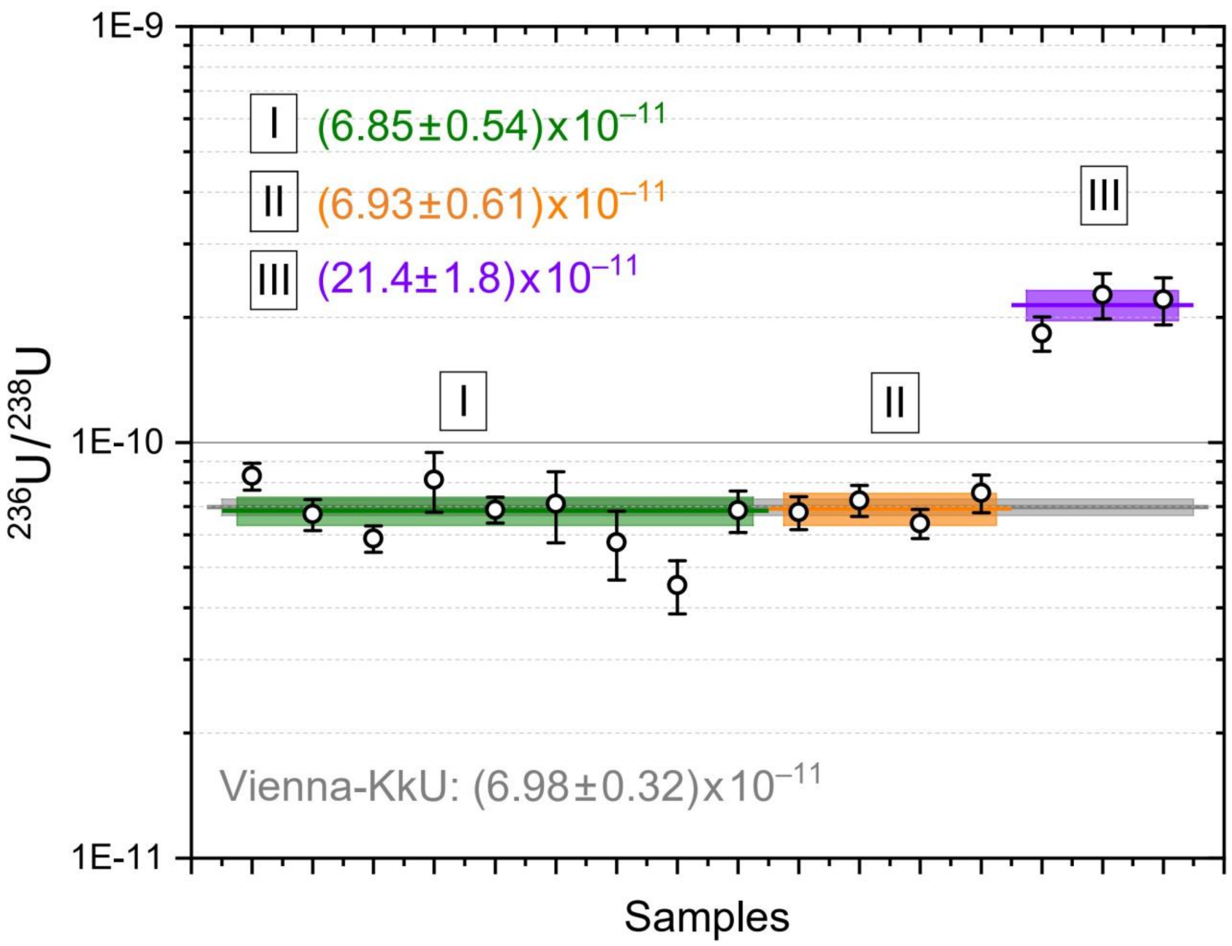
AMS detection efficiency of U using UF_5^-



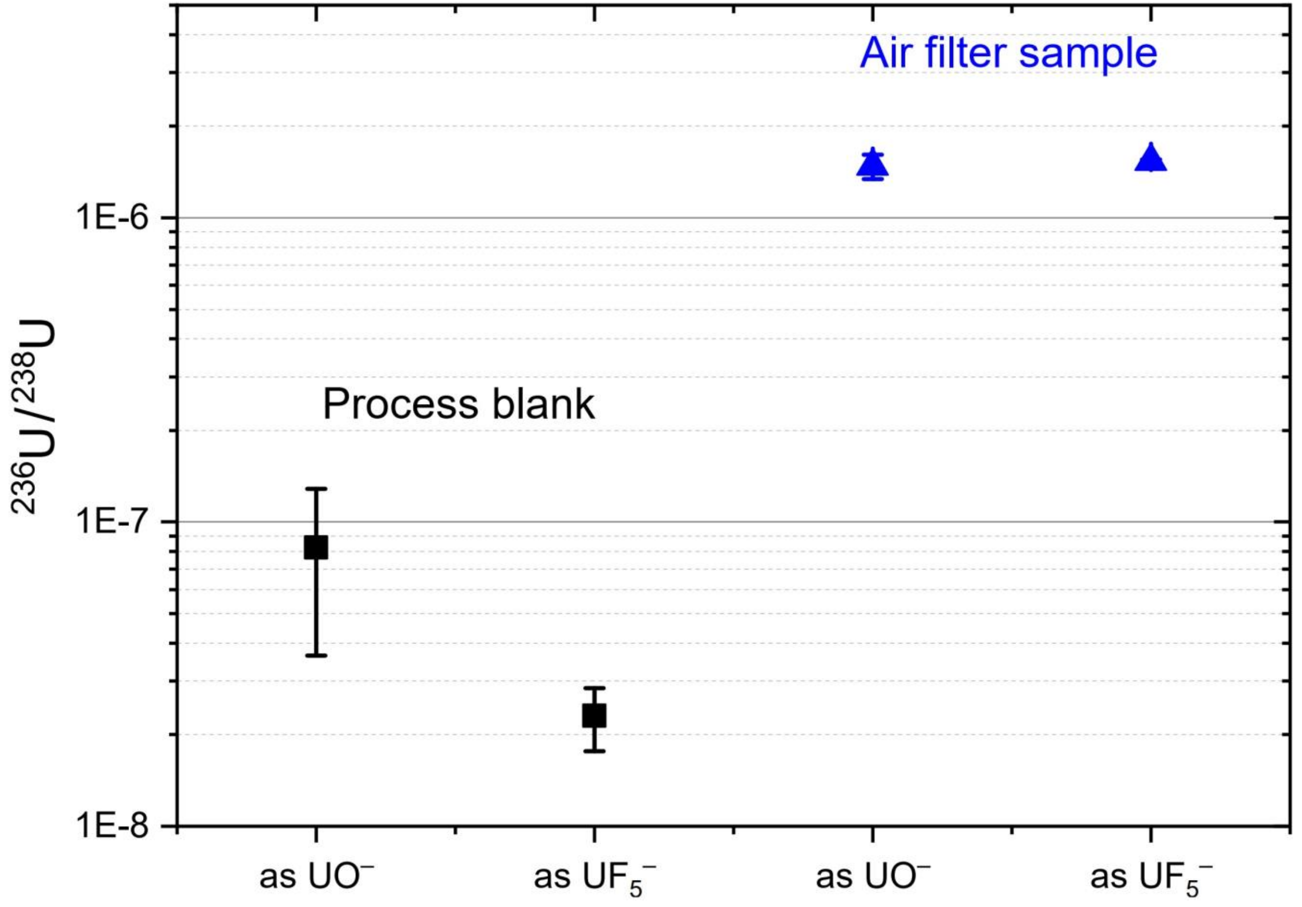
AMS analysis using UF_5^-



Validation with U-standard
[Steier et al., NIMB. 2008]

I : **Vienna-KkU-D30**+ PbF_2 ☑
II : **($U_{[sol]}$+Fe)**+PbF_2 ☑
III : **(UF_4+NdF_3)**+PbF_2 ☒

Method validation of AMS using UF_5^-



Previously measured isotope ratios of blank and sample confirmed ☑

Results summary

- UF_5^- extraction 3 to -10-fold more efficient than UO^-
- Mixing ratio with PbF_2 of 1:9 (wt. ratio) is optimal
- $\geq$ 90% of extractable U within 2 h
- Direct application with sub-milligram Fe preparation
- UF_5^- extraction method validated with $^{236}U/^{238}U$ and $^{233}U/^{238}U$ levels of previously measured samples

Thank You!

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Outlook

Application for environmental samples ☑

AF_m^- application for other actinides at VERA (Np, Pu, ..) ☑

C, Ag cathode material to further cut down low-energy background in future measurements ☐

Adjusting the UF4 + NdF3 co-precipitation to sub-milligram Nd amounts ☐

Long-lived U trace isotopes

⇒ ^{236}U

$^{235}U(n_{th},\gamma)^{236}U$ (~95 b)

$^{238}U(n_f,3n)^{236}U$ (~0.5 b @ E_n= 13 MeV)

^{236}U ($t_{1/2} \approx 2.3\text{x}10^7$ y)

→ mainly anthropogenic radionuclide by abundance

$^{236}U\,/\,^{238}U = 10^{-6} - 10^{-12}$

[Steier et al., NIMB. 2008]

⇒ ^{233}U

$^{232}Th(n_{th},\gamma)^{233}Th \rightarrow {}^{233}Pa \rightarrow {}^{233}U$ (~7 b)

$^{235}U(n_f,3n)^{233}U$ (~0.1 b @ E_n= 13 MeV)

$^{2}D + {}^{3}T \rightarrow {}^{4}He\ (3.5\ \text{MeV}) + n\ (14.1\ \text{MeV})$

^{233}U ($t_{1/2} \approx 1.5\text{x}10^5$ y)

→ Thermonuclear production, or Th-rich rocks

$^{233}U\,/\,^{236}U \approx 10^{-2}$

[Karin Hain et al., Nat. Commun. 2020]

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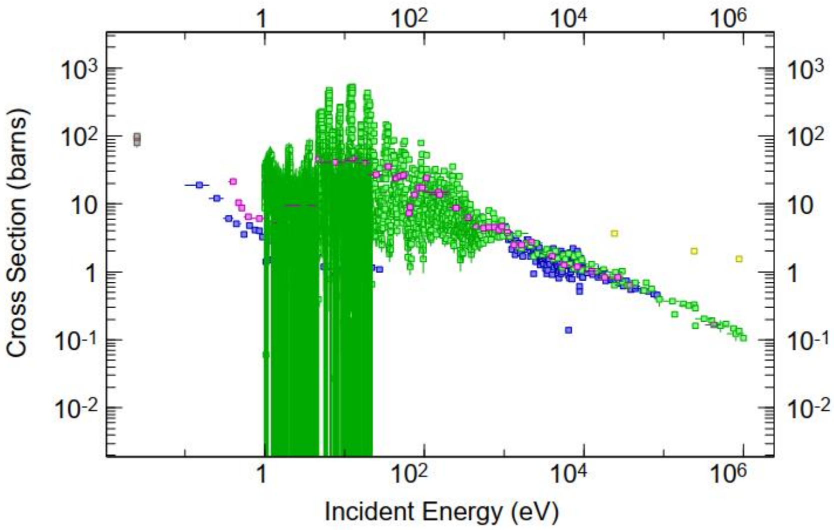
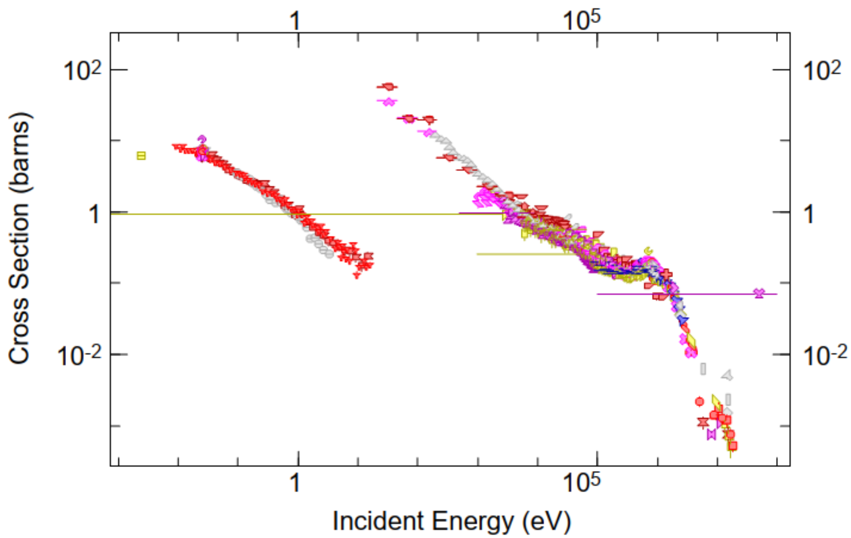
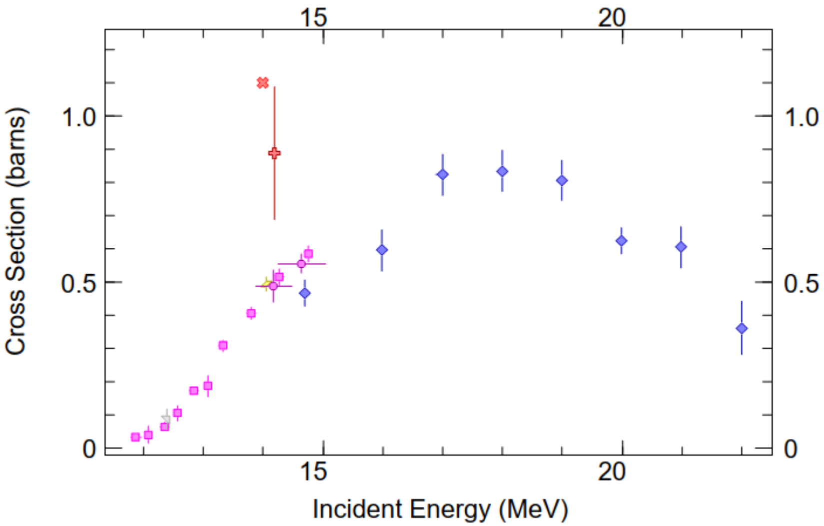
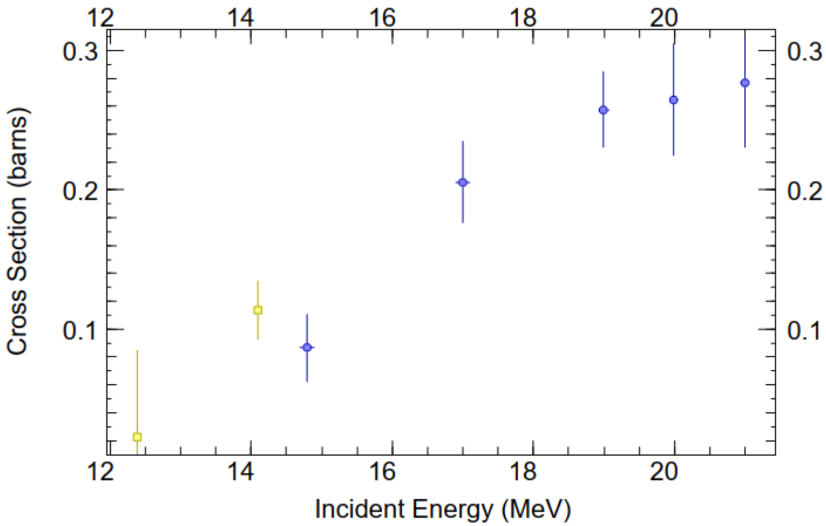
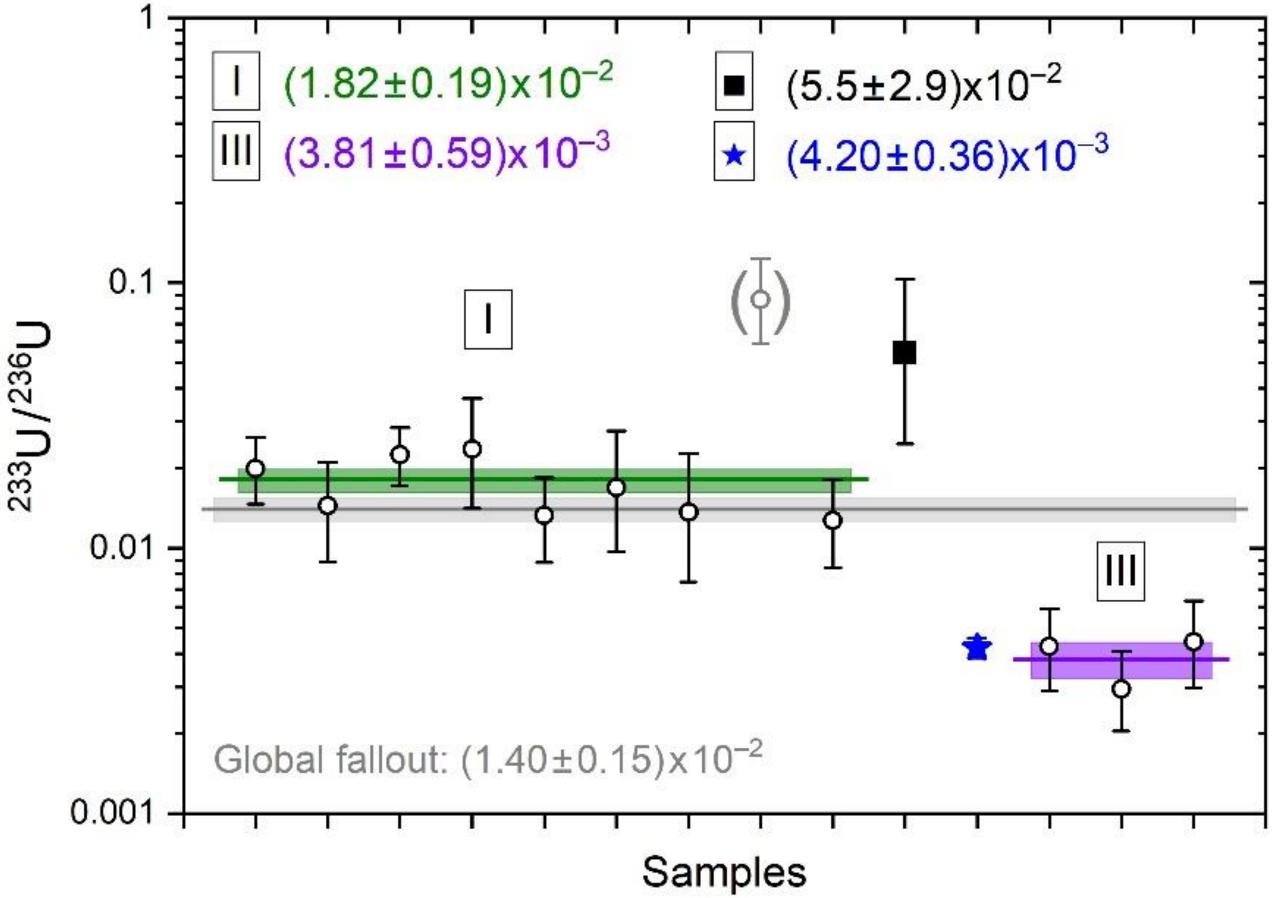

(92-U-235(N,G)92-U-236


90-TH-232(N,G)90-TH-233


92-U-238(N,3N)92-U-236


92-U-235(N,3N)92-U-233

$^{233}U/^{238}U$ AMS analysis using UF_5^-



Global fallout ratio: [Karin Hain et al., Nat. Commun. 2020, this meeting]

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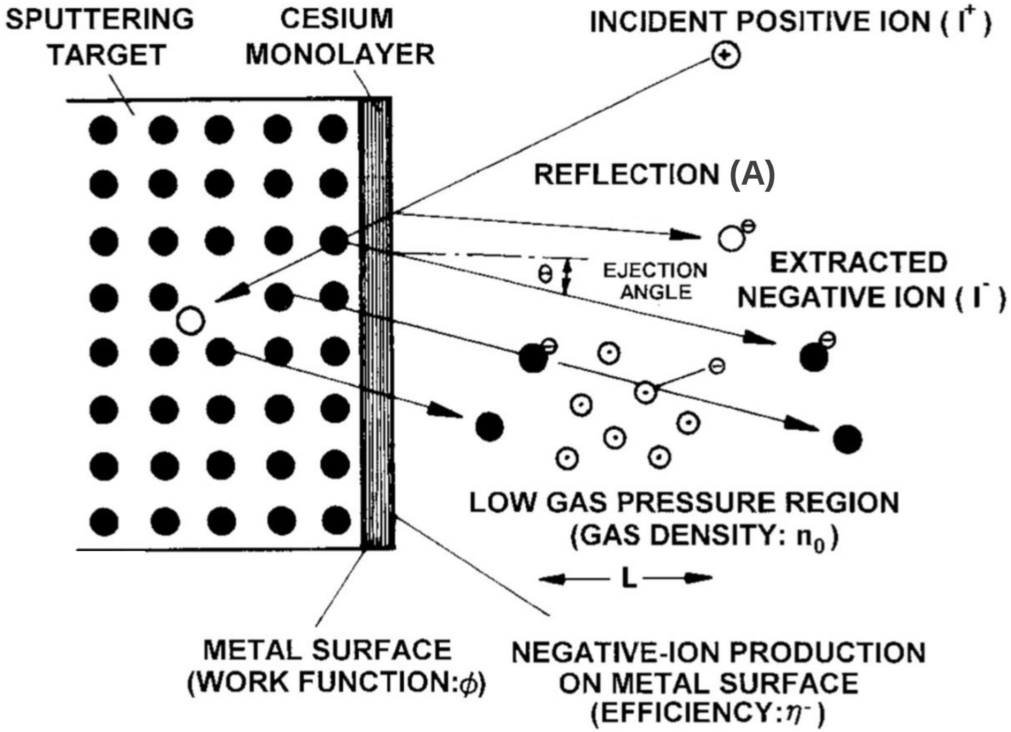
Ionization of negative ions



$$I^- = I^+ A \eta^- e^{-n_0 L \sigma_d}$$

$$\boxed{\eta^- = \int P^-(v) f(v) dv}$$

Ion	E_a (eV)
UO_3^-	2.125
$UO_2F_2^-$	3.356
UF_4^-	1.244
$UO_2F_3^-$	6.250
UOF_4^-	3.803
UF_5^-	3.820
UF_6^-	5.056

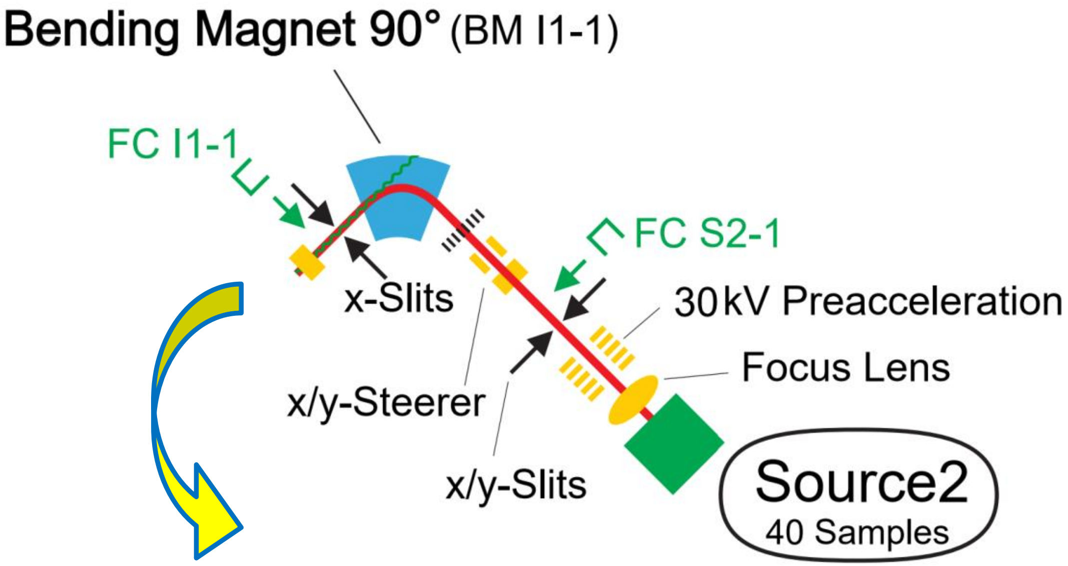
[NIST, 2020]

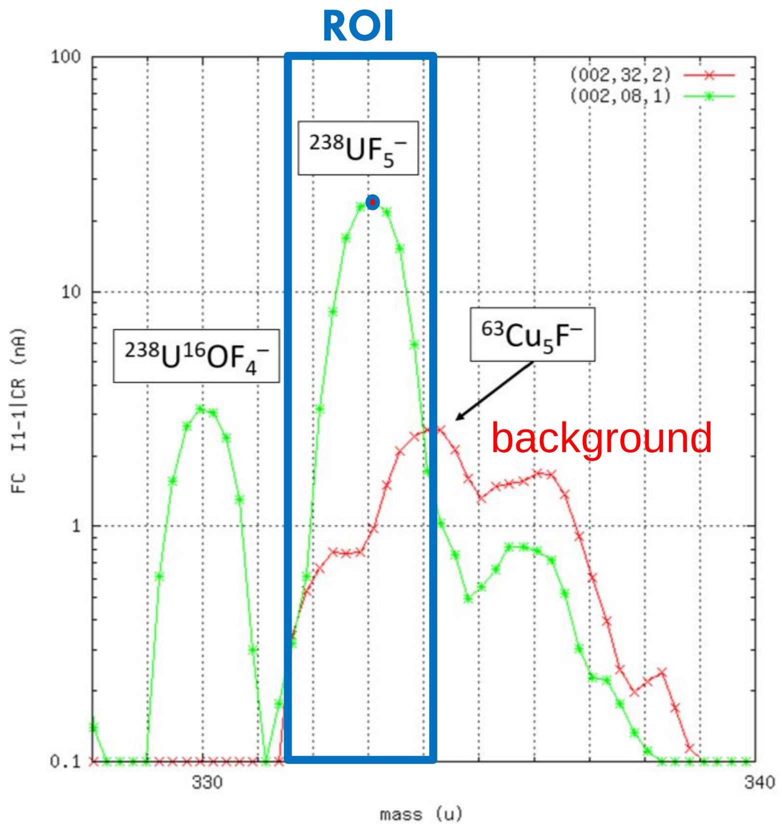
$$P^-(v) = \frac{2}{\pi} \exp\left[\frac{-(\phi - E_a)}{(2av\cos\theta)/\pi + k_B T_{\text{eff}}}\right]$$

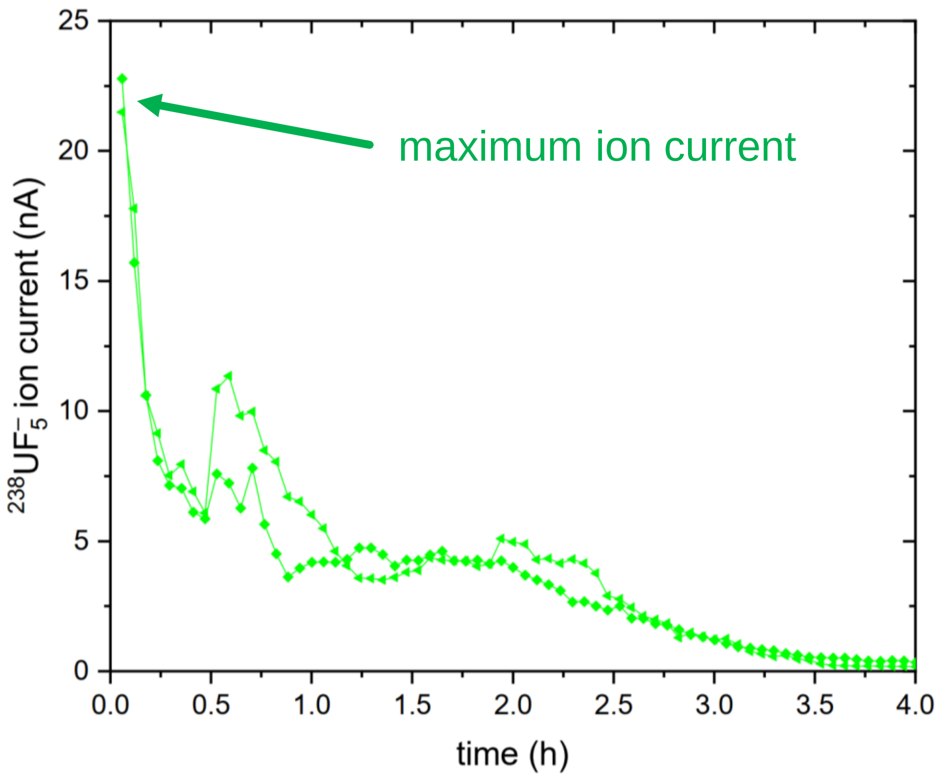
[Ishikawa et al., Rev. Sci. Instrum. 65(1732). 1994]

Ionization yield

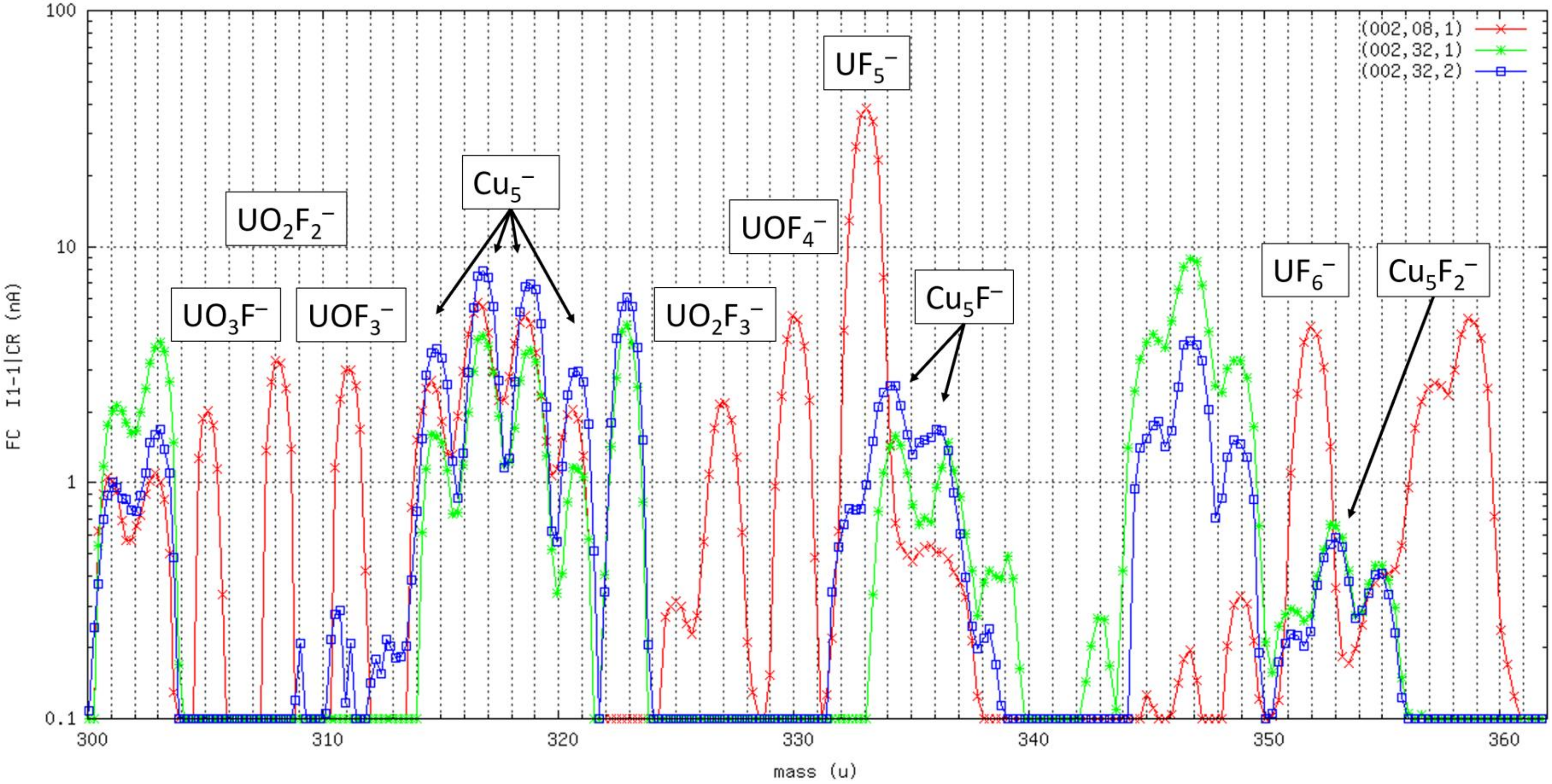
$$\eta_{ion} = \frac{\text{ions measured}}{\text{atoms in sample}}$$





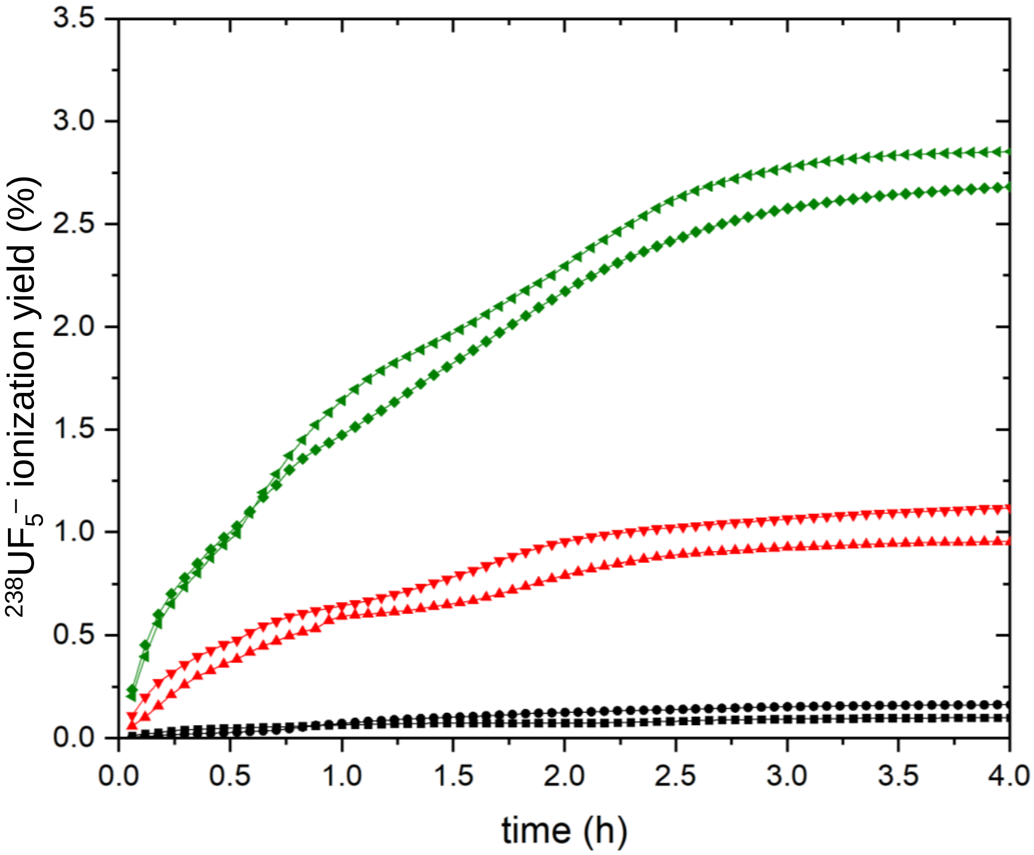


$$\eta_{ion} = \sum_i \frac{\tau_i \cdot I_i^q}{m_{\text{sample}} \cdot n_{iso} \cdot q \cdot e}$$



Materials for UF_5^- extraction

Vienna-KkU-D30 + PbF_2 powder by 1:X wt. ratio



$$\boxed{\eta_{\mathrm{UF}_5^-} = (2.49 \pm 0.12)\%}$$

(background corrected)

Optimal sample size for ionization efficiency ca. 200 µg Vienna-KkU-D30

→ difficult to handle environmental samples

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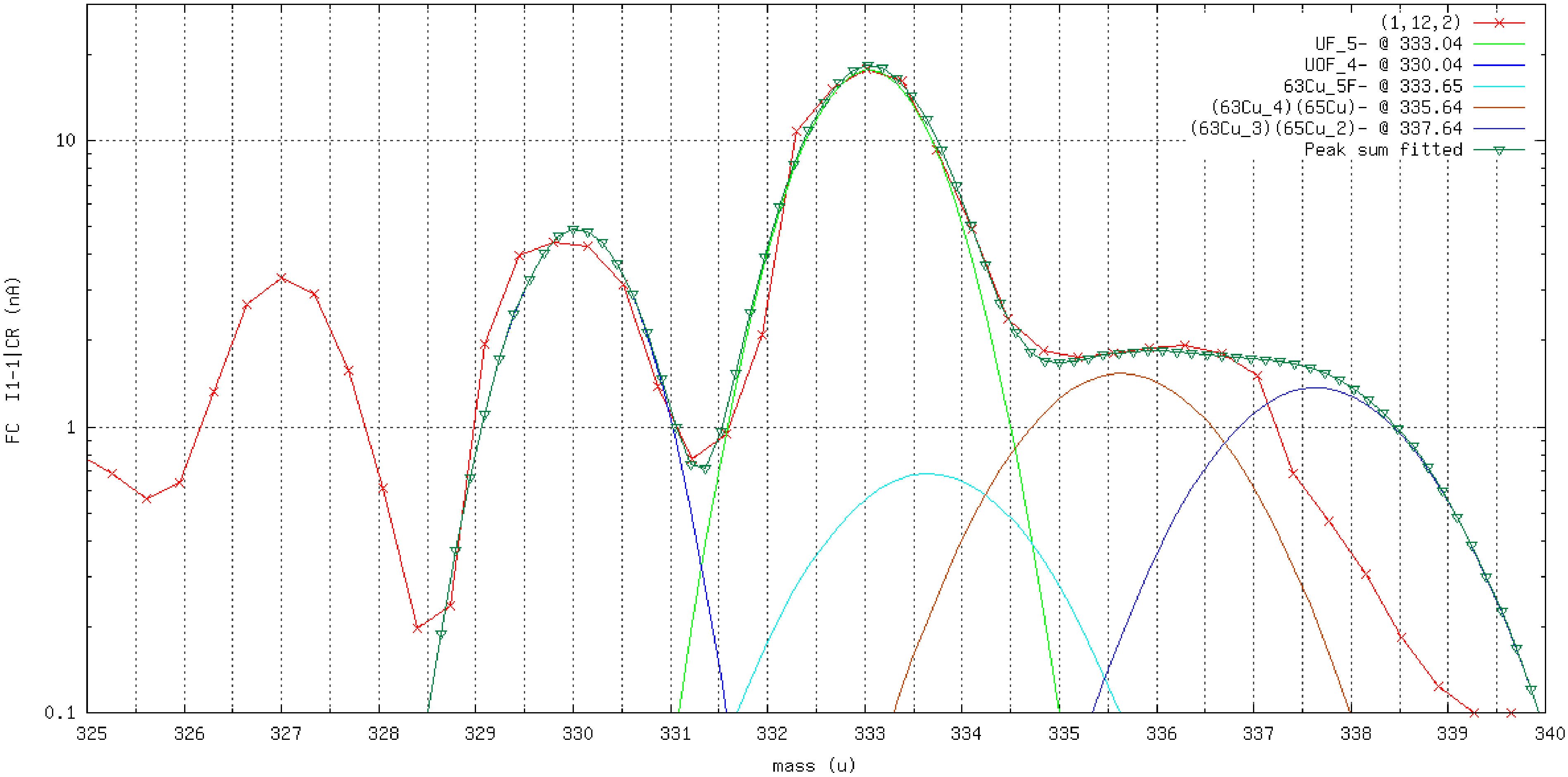
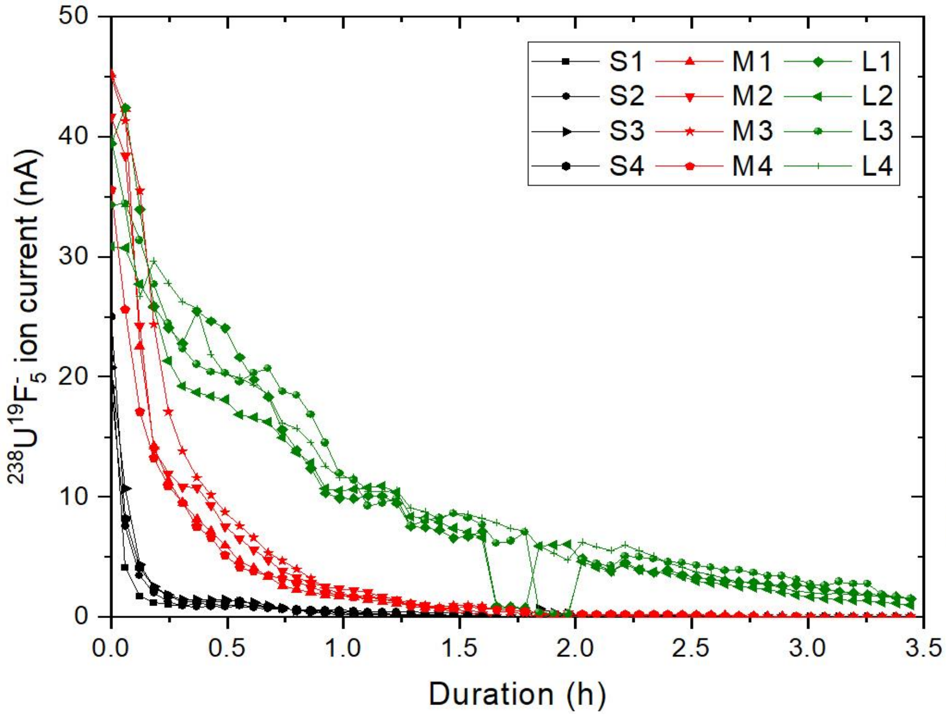
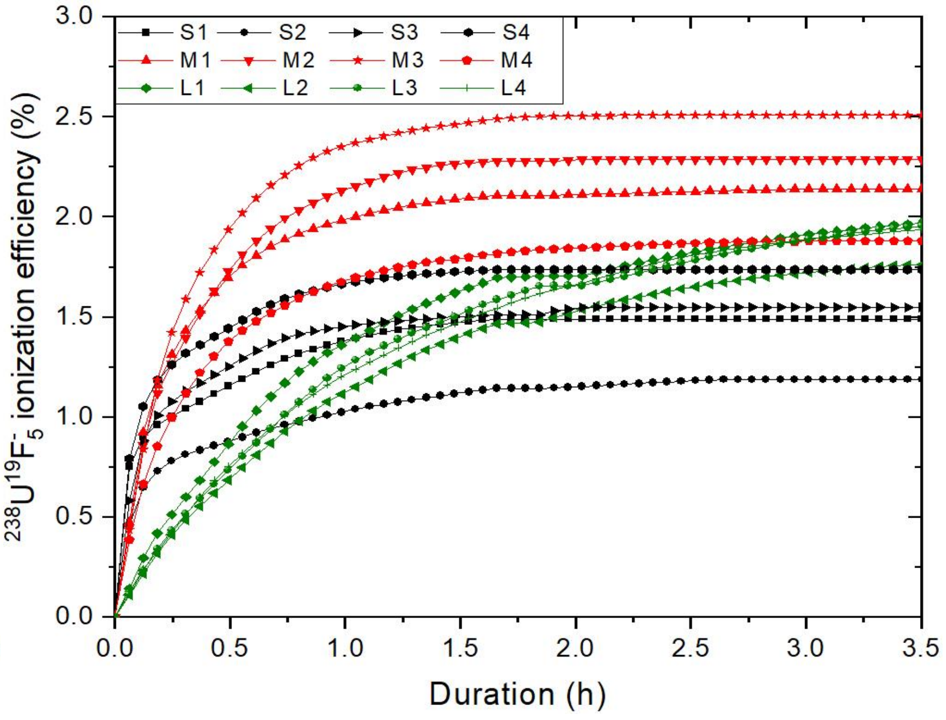
$$\text{normal}(x,\mu,\sigma) = \frac{1}{(\sigma\sqrt{2\pi})} \cdot \exp\frac{-(x-\mu)^2}{(2\sigma^2)} \tag{6.1}$$

$$\begin{aligned} f(x) = a_0 \cdot \text{normal}(x, x_0, \sigma_0) + a_r \cdot \text{normal}(x, x_l, \sigma_l) + 0.158 \cdot a_{cu}\text{normal}(x, x_{r1}, \sigma_r) \\ +0.353 \cdot a_{cu}\text{normal}(x, x_{r2}, \sigma_r) + 0.315 \cdot a_{cu}\text{normal}(x, x_{r3}, \sigma_r) \end{aligned} \tag{6.2}$$



Investigated sample sizes





S: 0.5 mg
M: 1.5 mg
L: 4.5 mg

Same relative U concentration!