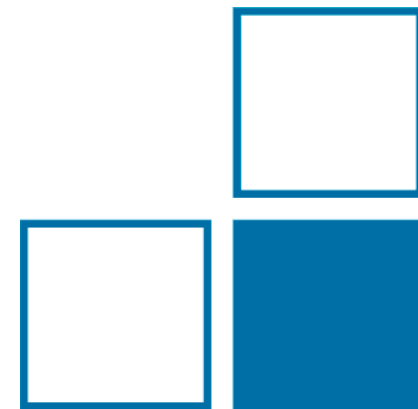
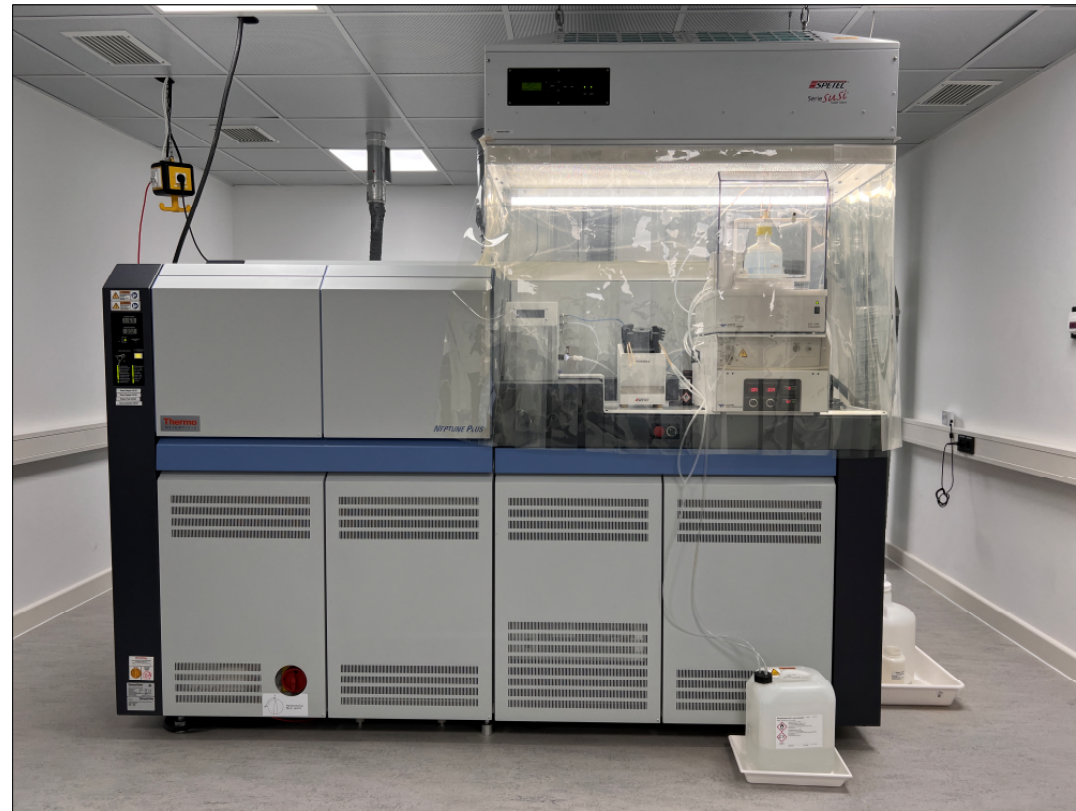


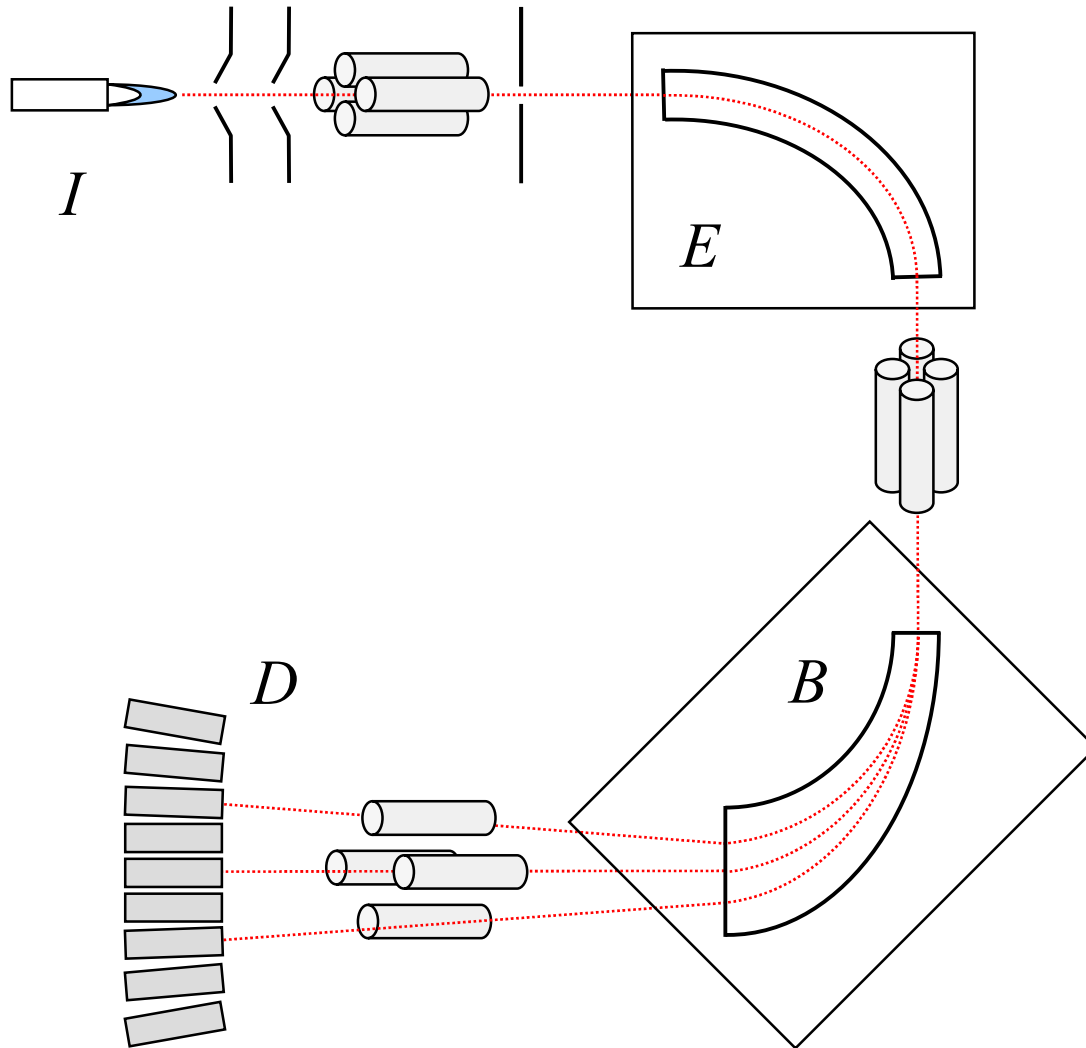
Radionuklid- Massenspektrometrie an der PTB

Janine Eberhardt, Lukas Flierl et al.
Physikalisch-Technische Bundesanstalt



- Multikollektor induktiv gekoppeltes Plasma Massenspektrometer (MC-ICP-MS):
Thermo Neptune Plus





- Ionenquelle (I)
 - Ionisierung im Plasma: hohe Effizienz
 - Diskriminierung
- Analysator (E + B)
 - Doppelfokussierend:
Elektrostatistischer Analysator (ESA) +
Magnetfeld
- Detektor (D)
 - Simultane Messung
 - Faraday-Cups
 - Hohe Präzision
 - Mittlere Sensitivität

- Kurze Messzeiten
- Niedrigste Messunsicherheit
- Gleichzeitige und separate Bestimmung von ^{239}Pu und ^{240}Pu
- Zertifizierung von Umweltprobenreferenzmaterialien für die absolute Isotopenzusammensetzung und Aktivitätskonzentration
- Bedarf an *ab-initio* Messungen: gravimetrische Isotopenmischungen
- Isotopenverhältnisse (R): fünf Größenordnungen
- Magnetisches Sektorfeld: K -Faktor unabhängig von R

- Ziel: Isotopenverhältnisse

Intensitätsverhältnisse		Isotopenverhältnisse
$R_{235/238}^{\text{mess}} = \frac{U(^{235}\text{U})}{U(^{238}\text{U})}$	\neq	$R_{235/238}^{\text{wahr}} = \frac{x(^{235}\text{U})}{x(^{238}\text{U})}$

„Mass bias“ ➡ Kalibration

$$R_{235/238}^{\text{wahr}} = K \cdot R_{235/238}^{\text{mess}}$$



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Directorate G – Nuclear Safety and Security
G.2 – Standards for Nuclear Safety, Security and Safeguards Unit

CERTIFIED REFERENCE MATERIAL IRMM – 184

CERTIFICATE OF ANALYSIS

Uranium in nitric acid solution		
	Isotope amount ratios	
	Certified value ¹⁾ [mol/mol]	Uncertainty ²⁾ [mol/mol]
$n(^{233}\text{U})/n(^{238}\text{U})$	< 0.000000002	/
$n(^{234}\text{U})/n(^{238}\text{U})$	0.000053138	0.000000032
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0072623	0.0000022
$n(^{236}\text{U})/n(^{238}\text{U})$	0.00000012446	0.00000000053

¹⁾ The certified values are traceable to the International System of units (SI).

²⁾ The uncertainty is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

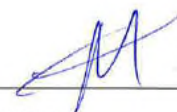
There is no minimum sample intake to be taken into account.

The certificate is valid for 3 years; the validity may be extended after further tests on the stability of the material are carried out.

The certificate is a revision of the original certificate of 1987, which was revised in 1993, 1999 and 2005.

Geel, September 2019

Signed: _____



18 SEP. 2019

Dr. Arjan Plompen
European Commission
Joint Research Centre
Directorate G – Nuclear Safety and Security
G.2 – Standards for Nuclear Safety, Security and
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Retieseweg 111
B-2440 Geel, Belgium

- Bestimmung von der Isotopenzusammensetzung von dem Uranaktivitätsnormal
- Kalibrierung: Intensitätsverhältnisse \neq Isotopenverhältnisse, externe Korrektur mit IRMM-184 (natürliches Uran)

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<p>CERTIFIED REFERENCE MATERIAL IRMM – 184</p>		
<p>CERTIFICATE OF ANALYSIS</p>		
<p>Uranium in nitric acid solution</p>		
<p>Isotope amount ratios</p>		
	Certified value ¹⁾ [mol/mol]	Uncertainty ²⁾ [mol/mol]
$n(^{233}\text{U})/n(^{238}\text{U})$	< 0.00000002	/
$n(^{234}\text{U})/n(^{238}\text{U})$	0.000053138	0.000000032
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0072623	0.0000022
$n(^{236}\text{U})/n(^{238}\text{U})$	0.0000012446	0.0000000053
<p>¹⁾ The certified values are traceable to the International System of units (SI).</p>		
<p>²⁾ The uncertainty is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.</p>		
<p>There is no minimum sample intake to be taken into account. The certificate is valid for 3 years; the validity may be extended after further tests on the stability of the material are carried out. The certificate is a revision of the original certificate of 1987, which was revised in 1993, 1999 and 2005.</p>		
<p>Geel, September 2019</p>		
<p>Signed:  18 SEP. 2019</p>		
<p>Dr. Arjan Plompen European Commission Joint Research Centre Directorate G – Nuclear Safety and Security G.2 – Standards for Nuclear Safety, Security and Safeguards Unit Reteseweg 111 B-2440 Geel, Belgium</p>		

$$R_3^{\text{wahr}} = R_3^{\text{mess}} \cdot K_3 \quad \text{mit} \quad K_3 = \frac{R_3^{\text{zert}}}{R_3^{\text{mess}}}$$



$$R_{\text{smp}}^{\text{wahr}} \left(\frac{{}^{235}\text{U}}{{}^{238}\text{U}} \right) = R_{\text{smp}}^{\text{mess}} \left(\frac{{}^{235}\text{U}}{{}^{238}\text{U}} \right) \cdot \left(\frac{R_{\text{IRMM-184}}^{\text{zert}} \left(\frac{{}^{235}\text{U}}{{}^{238}\text{U}} \right)}{R_{\text{IRMM-184}}^{\text{mess}} \left(\frac{{}^{235}\text{U}}{{}^{238}\text{U}} \right)} \right)$$

	Wert	U ($k=2$)	Einheit	U_{rel} in %
$n(^{234}\text{U})/n(^{238}\text{U})$	0.000053895	0.0000000035	mol/mol	0.065
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0072703	0.00000022	mol/mol	0.031
$x(^{234}\text{U})$	0.000053503	0.0000000036	mol/mol	0.067
$x(^{235}\text{U})$	0.0072174	0.00000022	mol/mol	0.030
$x(^{238}\text{U})$	0.9927291	0.00000022	mol/mol	0.00022
M	238.0288707	0.00000067	g/mol	2.8E^{-6}

Messung von Plutoniumisotopen

- Bestimmung von Pu-Isotopenverhältnissen in einem unbestrahltem Mischoxidbrennstoff (MOX fuel)
- Kalibrierung: externe Korrektur mit IRMM-184 (natürliches Uran) und Kross-Kalibrierung mit IRMM-184 und IRMM-3636a (synthetische Lösung, 1:1 Mischung von ^{233}U und ^{236}U)

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CERTIFIED REFERENCE MATERIAL IRMM – 184		
CERTIFICATE OF ANALYSIS		
Uranium in nitric acid solution		
	Isotope amount ratios	
	Certified value ¹⁾ [mol/mol]	Uncertainty ²⁾ [mol/mol]
$n(^{233}\text{U})/n(^{238}\text{U})$	< 0.000000002	/
$n(^{234}\text{U})/n(^{238}\text{U})$	0.000053138	0.000000032
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0072623	0.00000022
$n(^{236}\text{U})/n(^{238}\text{U})$	0.00000012446	0.00000000053
¹⁾ The certified values are traceable to the International System of units (SI).		
²⁾ The uncertainty is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.		
There is no minimum sample intake to be taken into account. The certificate is valid for 3 years; the validity may be extended after further tests on the stability of the material are carried out. The certificate is a revision of the original certificate of 1987, which was revised in 1993, 1999 and 2005.		
Geel, September 2019		
Signed:  18 SEP. 2019		
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CERTIFIED REFERENCE MATERIAL IRMM – 3636a		
CERTIFICATE OF ANALYSIS		
Uranium in nitric acid solution		
	Isotope amount content	
	Certified value ¹⁾ [μmol/g solution]	Uncertainty ²⁾ [μmol/g solution]
^{238}U	0.211906	0.000026
	Isotope amount ratios	
	Certified value ¹⁾ [mol/mol]	Uncertainty ²⁾ [mol/mol]
$n(^{233}\text{U})/n(^{238}\text{U})$	1.01906	0.00016
$n(^{234}\text{U})/n(^{238}\text{U})$	0.00036606	0.00000048
$n(^{235}\text{U})/n(^{238}\text{U})$	0.000045480	0.000000074
$n(^{236}\text{U})/n(^{238}\text{U})$	0.00023481	0.00000038
¹⁾ The certified values are traceable to the International System of units (SI). The reference date for the certified values is July 1, 2007.		
²⁾ The uncertainty is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.		
There is no minimum sample intake to be taken into account. The certificate is valid for 3 years; the validity may be extended after further tests on the stability of the material are carried out. The certificate is a revision of the original certificate of 2008, which was revised in 2009.		
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- Exponential Gesetz mit externem Uranstandard (IRMM-184)

$$R_4^{\text{wahr}} = R_4^{\text{mess}} \cdot \underbrace{\left(\frac{R_2^{\text{zert}}}{R_2^{\text{mess}}} \right)^{\gamma}}_{\substack{=K_2 \\ =K_4}} \quad \text{mit} \quad \gamma = \frac{\ln\left(\frac{M_4}{M_3}\right)}{\ln\left(\frac{M_2}{M_1}\right)}$$

$$\rightarrow R_4^{\text{wahr}} = R_4^{\text{mess}} \cdot \left(\frac{R_2^{\text{zert}}}{R_2^{\text{mess}}} \right)^{\left(\frac{\ln\left(\frac{M_4}{M_3}\right)}{\ln\left(\frac{M_2}{M_1}\right)} \right)}$$

- Exponential Gesetz mit externem Uranstandard (IRMM-184)

$$R_{\text{smp}}^{\text{wahr}} \left({}^{240}\text{Pu} / {}^{239}\text{Pu} \right) = R_{\text{smp}}^{\text{mess}} \left({}^{240}\text{Pu} / {}^{239}\text{Pu} \right) \cdot \underbrace{\left(\underbrace{\frac{R_{\text{IRMM-184}}^{\text{zert}} \left({}^{235}\text{U} / {}^{238}\text{U} \right)}{R_{\text{IRMM-184}}^{\text{mess}} \left({}^{235}\text{U} / {}^{238}\text{U} \right)}}_{=K_2} \right)^{\gamma}}_{=K_4}$$

mit

$$\gamma = \frac{\ln \left(\frac{M({}^{240}\text{Pu})}{M({}^{239}\text{Pu})} \right)}{\ln \left(\frac{M({}^{235}\text{U})}{M({}^{238}\text{U})} \right)}$$

➤ Isotopenverhältnisse und erreichte Messunsicherheiten

i	$R(^i\text{Pu}/^{239}\text{Pu})$ mol/mol	$U(R(^i\text{Pu}/^{239}\text{Pu}))$ mol/mol	$U_{\text{rel}}(R(^i\text{Pu}/^{239}\text{Pu}))$ %
240	0.4667	0.0037	0.80
241	0.10404	0.00095	0.92
242	0.1398	0.0013	0.96

- Erreichte Nachweisgrenzen ($\text{LOD} = y_{\text{Blk}} + 3 \times \sigma_{\text{Blk}}$) für den Massenanteil und für die Aktivität

i	$w(^i\text{Pu})$ fg/g	$A(^i\text{Pu})$ mBq/g
239	29	0.066
240	29	0.244
241	28	107
242	30	0.004

$$n = \frac{A \times T_{1/2}}{N_A \times \ln 2}$$

- CCQM-K178: Bestimmung des Uranmassenanteils in einer Bodenprobe (double IDMS, März 2023 bis März 2024)

- Metro POEM: Oktober 2022 bis September 2025

Metrology for the harmonisation of measurements of environmental pollutants in Europe

- Bestimmung der Plutoniumisotopenverhältnisse ($n(^{240}\text{Pu})/n(^{239}\text{Pu})$) und der Uranisotopenverhältnisse ($n(^{235}\text{U})/n(^{238}\text{U})$, $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{236}\text{U})/n(^{238}\text{U})$) in einer gespikten Meerwasserprobe und einem synthetischen Silikat



Danksagung für die Finanzierung

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- Grant number: 21GRD09 MetroPOEM