Increasing accuracy and precision of uranium isotope ratios by Thermal Ionization Mass Spectrometry using 10^{13} Ω amplifier technology

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Keywords

TIMS, uranium isotopes, total evaporation, 10^{13} Ω

Goal

To show improved precision of uranium isotope analysis by total evaporation of small sample amounts and minor isotopes using 10^{13} Ω amplifiers.

Summary

Technological developments have enabled high precision isotopic measurements of uranium with thermal ionization mass spectrometry (TIMS) using large sample amounts. The precision of isotope ratios from small sample sizes is restricted by the ion yield of the analytical technique and the noise of the detection system. This study reports precision and accuracy for minor uranium isotopes measured on a Thermo Scientific™ Triton™ XT TIMS equipped with Thermo Scientific™ 10^{13} Ω Amplifier Technology™.

Introduction

The measurement of small uranium samples and/or low intensity uranium ion beams is required in nuclear safeguards and industrial applications. Moreover, the accurate detection of minor uranium isotopes is a prerequisite. The measurement of small uranium samples and minor uranium isotopes is limited by high noise levels of standard 10^{11} Ω amplifiers, as well as the dynamic range and stability of ion counters. Using 10^{13} Ω amplifiers, both obstacles can be overcome and highly precise analysis of all uranium isotopes is enabled, including the minor isotopes ^{234}U and ^{236}U.

Materials and methods

Certified reference materials NBS U-010 and NBS U-500 (New Brunswick Laboratory, Argonne, IL, USA) were loaded onto zone-refined double rhenium filaments in sample amounts ranging from 0.5–20 ng. All uranium isotopes were detected on Faraday cups, equipped with either 10^{11} Ω or 10^{13} Ω amplifiers (Table 1).

Table 1. Amplifier arrangement for the analysis of NBS U-010 and NBS U-500 (0.5–20 ng total uranium loaded)

Cup	C	H1	H2	H3
Mass	^{234}U	^{235}U	^{236}U	^{238}U
NBS U-500				
Isotope Abundance (%)	0.5%	49.7%	0.1%	49.7%
20 ng U	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω
20 ng U	10^{13} Ω	10^{11} Ω	10^{13} Ω	10^{11} Ω
NBS U-010				
U [ng]	0.005%	1.004%	0.007%	98.98%
20 ng U	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω
20 ng U	10^{13} Ω	10^{13} Ω	10^{13} Ω	10^{11} Ω
1 ng U	10^{13} Ω	10^{13} Ω	10^{13} Ω	10^{11} Ω
0.5 ng U	10^{13} Ω	10^{13} Ω	10^{13} Ω	10^{11} Ω

Filaments were analyzed by Total Evaporation, a technique that is often used in nuclear applications when the abundance of uranium isotopes is unknown and no mass bias correction could be applied. It allows the analysis of all sample material by continuous and complete evaporation of the sample from the filament. All isotopes are collected during the entire period of evaporation. During the run, the evaporation filament current is continuously adjusted in order to follow a predefined and reproducible evaporation profile (Figure 1). The final isotope ratio is the averaged isotopic mean value at the end of the analysis.

Two experiments were performed:

- $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratio analyses of NBS U-500 and NBS U-010 were performed using classical 10^{11} Ω as well as 10^{13} Ω amplifiers to get a direct performance comparison. Total sample size was 20 ng
- $^{235}U/^{238}U$ analysis of NBS U-010 using 10^{13} Ω amplifier for ^{235}U. Total ^{235}U sample sizes were 0.2 ng, 10 pg and 5 pg

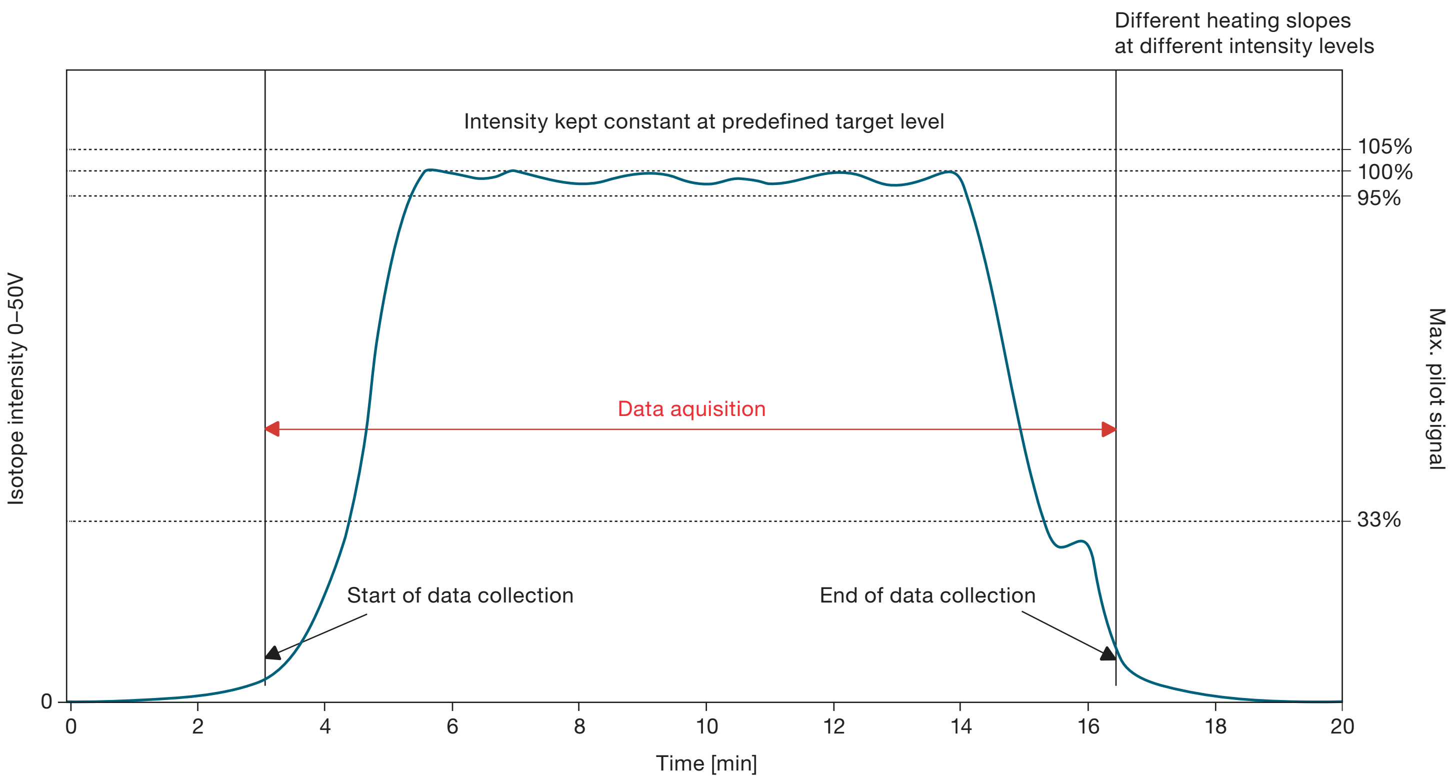

Figure 1. Schematic Procedure of the Total Evaporation Process

Results

Accuracy and precision for $^{234}U/^{238}U$ and $^{236}U/^{238}U$

Using the 10^{13} Ω amplifier for ^{234}U, the precision of $^{234}U/^{238}U$ in both NBS U-500 and NBS U-010 is improved by factor 4–5 compared to 10^{11} Ω amplifier measurements (0.05% vs 0.19% and 1.2% vs. 5.1% 1 RSD). For $^{236}U/^{238}U$ the improvement in precision is even up to a factor of 10 (0.08% vs. 1.08% and 0.6% vs. 7.3% 1 RSD, Table A1). Also, 10^{13} Ω amplifiers allow sample sizes of down to 1 pg to be analyzed with precisions between 0.6–1.2% (1 RSD).

Towards smaller sample sizes – accuracy and precision for $^{235}U/^{238}U$

The 10^{13} Ω Amplifier Technology allows extremely high precision analysis of $^{235}U/^{238}U$ in 20 ng total uranium sample loads (NBS U-010); the achieved precision is 0.018%, 1 RSD (Table 2). Lower sample sizes still provide good precision and accuracy. Even in 0.5 ng total uranium (corresponding to total ^{235}U amount of 5 pg, NBS U-010), a precision of 0.5% (1 RSD) on $^{235}U/^{238}U$ can be achieved using 10^{13} Ω amplifiers.

Table 2. Accuracy and precision of $^{235}U/^{238}U$ in NBS U-010. Total ^{235}U sample size ranging 0.2 ng down to 5 pg. Blue: both ^{235}U and ^{238}U detected on 10^{11} Ω amplifiers. Red: ^{235}U detected on 10^{13} Ω amplifier, ^{238}U on 10^{11} Ω amplifier.

	^{235}U	$^{235}U/^{238}U$	1 RSD	Amplifier	Reference value [1]
20 ng	0.2 ng	0.010143	0.065%	10^{11} Ω	0.010140(10)
20 ng	0.2 ng	0.010142	0.018%	10^{13} Ω	0.010140(10)
1 ng	10 pg	0.010152	0.21%	10^{13} Ω	0.010140(10)
0.5 ng	5 pg	0.010139	0.53%	10^{13} Ω	0.010140(10)

Conclusions

The attainable precision for uranium isotope ratios using total evaporation TIMS has been significantly improved using 10^{13} Ω amplifier technology. For NBS U-500 both $^{234}U/^{238}U$ and $^{236}U/^{238}U$ can be detected with a precision down 0.05% (1 RSD) in 20 ng total uranium sample loads. This is a factor of 10 better compared to conventional 10^{11} Ω amplifiers. For NBS-U010, 0.5% (1 RSD) on $^{235}U/^{238}U$ is routinely possible in 0.5 ng total uranium sample loads (i.e. 5 pg total ^{235}U).

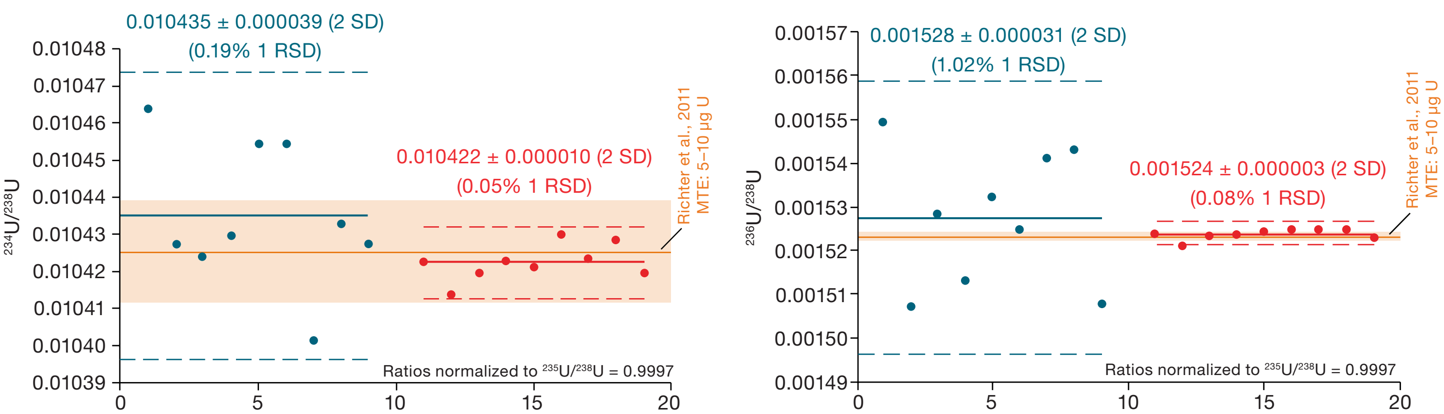

Figure 2. Precision and accuracy for $^{234}U/^{238}U$ (A) and $^{236}U/^{238}U$ (B) in 20 ng NBS U-500. Total ^{234}U and ^{236}U sample size were 104 and 15 pg. In blue: all U isotopes analyzed on 10^{11} Ω amplifiers, in red: ^{234}U and ^{236}U analyzed on 10^{13} Ω amplifiers.

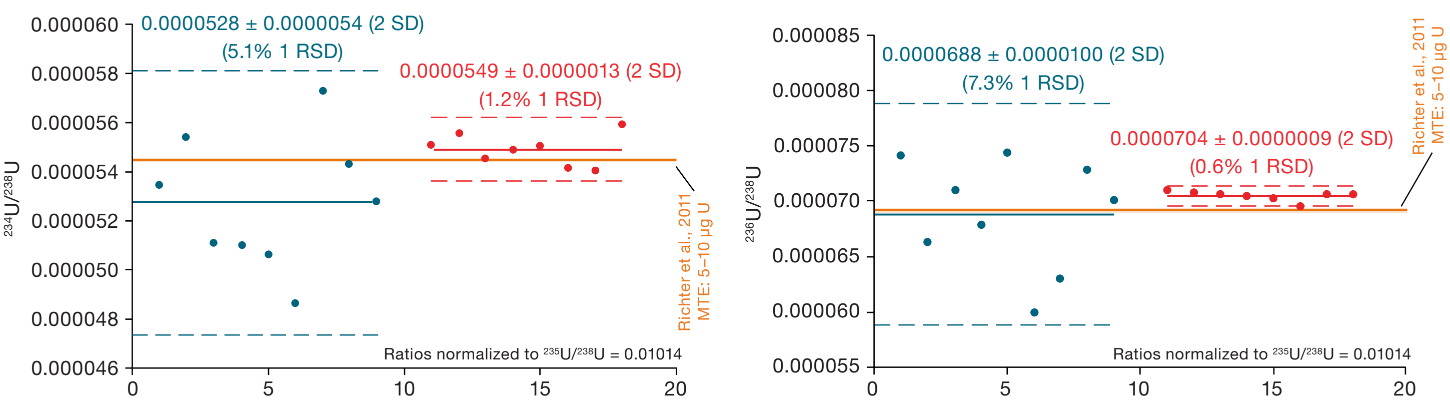

Figure 3. Precision and accuracy for $^{234}U/^{238}U$ (A) and $^{236}U/^{238}U$ (B) in 20 ng NBS U-010. Total ^{234}U and ^{236}U sample size were 1.08 and 1.36 pg. In blue: all U isotopes analyzed on 10^{11} Ω amplifiers, in red: ^{234}U and ^{236}U analyzed on 10^{13} Ω amplifiers.

References

1. Richter et al. (2011) *J. Anal. At. Spectrom.* V26, p550-564.

Appendix

Table A1. $^{234}U/^{238}U$ and $^{236}U/^{238}U$ of NBS U-500 and NBS U-010 (20 ng total uranium). Blue: all isotopes detected on 10^{11} Ω amplifiers. Red: minor isotopes detected on 10^{13} Ω amplifiers.

	Amplifier	^{234}U	$^{234}U/^{238}U$	1 RSD	Reference value [1]	^{236}U	$^{236}U/^{238}U$	1 RSD	Reference value [1]
NBS U-500 20 ng	10^{11} Ω	104 pg	0.010435	0.19%	0.010425(14)	15 pg	0.001528	1.02%	0.0015233(11)
	10^{13} Ω		0.010422	0.05%			0.001524	0.08%	
NBS U-010 20 ng	10^{11} Ω	1.08 pg	0.0000528	5.1%	0.000054484(77)	1.36 pg	0.0000688	7.3%	0.000069242(57)
	10^{13} Ω		0.0000549	1.2%			0.0000704	0.6%	

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