

TIMS: High Precision Cr TRITON *Plus* Isotope Analysis with Virtual Amplifier

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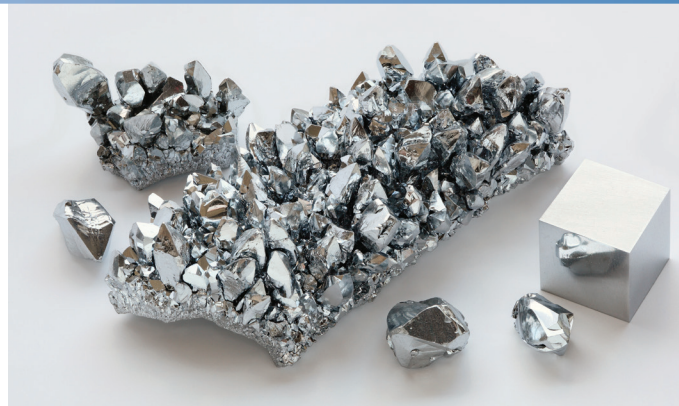
Keywords

Chromium, TRITON *Plus*, Thermal Ionization MS, static mode, virtual amplifier, $10^{11} \Omega$ amplifier

Introduction

Another Step Ahead in TIMS

Chromium is a transitional metal with four naturally occurring isotopes ^{50}Cr (4.35%), ^{52}Cr (83.79%), ^{53}Cr (9.50%) and ^{54}Cr (2.36%). Resolving Cr isotope anomalies at the ppm level is key to unraveling physico-chemical processing in planetary formation and environmental sciences. In the mid-2000's, Cr isotope Thermal-Ionization Mass Spectrometry (TIMS) analyses performed on the Thermo Scientific™ TRITON™ *Plus* instrument for the first time enabled resolution of ~ 10 ppm ^{54}Cr anomalies in geological samples from the KT-boundary and in meteorites, planetesimals and planetary objects. This impacted the understanding of the chronology of the early solar system formation.¹ In these studies, Cr analysis was performed in the static multicollection mode. Benefitting from the advances in ion optics (zoom optics), Cr isotope analyses were run in peak-jumping mode with 5 ion beam cup settings allowing isotopic ratios to be acquired with different axial masses and perfect peak overlap, without mechanically realigning the cups. This routine assessed and controlled in real time the stability of the ion optics, current amplifier system and Faraday cups by cross-checking isotopic ratios measured in the 5 cup settings. $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ isotope ratios reproduced to between 6 ppm and 12 ppm, respectively (2 SD).¹ Given the gain stability of Thermo Scientific Faraday cups, another way to average out stochastic amplifier gains is to use the rotation of the amplifier-cup association, the so-called virtual amplifier.



The present study on a Thermo Scientific TRITON *Plus* instrument is intended to assess precision and accuracy of Cr isotopic analyses in static mode using the virtual amplifier, $10^{11} \Omega$ current amplifiers, automated mode and >3 time shorter analyses compared to literature.

The Virtual Amplifier

By definition, in static acquisition mode, the uncertainty on amplifier gain calibration is a function of the gain relative uncertainty per measured isotope (ca. 5 ppm), the number of isotopes measured (n) and is approximately $5 \times \sqrt{n}$ (in ppm). This dictates that with 4 isotopes, the Cr system would reproduce to no better than 10 ppm/amu. However, if during analysis, n amplifiers are sequentially connected to n cups, each amplifier is exposed to each ion beam and the stochastic calibration biases of the amplifiers can be averaged out. The virtual amplifier thus reduces the propagation of the uncertainty from the gain calibration procedure. The switching of amplifier-cup association is performed as an inter-block action in a few ms. To ensure association of all Faraday cups with all amplifiers, the number of data blocks should be a multiple of the number of active amplifiers (for more details, see ref. 2).

Line No.	Mass Set	L4	L2	L1	RPO/IC1 C	H1	H2	H3	Integration Time(s)	Number of Integrations	Idle Time(s)	Control Cup Peakcenter	Control Cup Focus
1	Main	⁵⁰ Cr	⁵¹ V	⁵² Cr	⁵³ Cr	⁵⁴ Cr	⁵⁵ Mn	⁵⁶ Fe	8.389	1	5.000	⁵² Cr	⁵² Cr

Figure 1. Chromium Cup configuration.

Analytical Protocol

Chromium static analysis with virtual amplifier

Isotopic standard	MERCK Chromium ICP standard 170312
Filament assembly	Rhenium single filament
Outgasing	40 minutes at 3.2 A; 10 minutes at 3.5 A
Loading	Cr in 6M HCl
Additives	1.4 µl silica gel 4%; 1 µl H ₃ BO ₃ (5000 ppm B); 0.7 µL Al (1000 ppm) Dull red glow for 5 s
Amount and signal	500 ng Cr; 10 V on ⁵² Cr
Acquisition mode	Static, amplifier rotation ("virtual amplifier"), sequence
Baseline	157.5 s before each block
Temperature (°C)	1200–1250 °C
Normalized to	⁵² Cr/ ⁵⁰ Cr = 19.28323 (see ref. 3), exponential correction
Internal precision (2RSE)	6 ppm on ⁵³ Cr/ ⁵² Cr; 15 ppm on ⁵⁴ Cr/ ⁵² Cr (420 ratios)
External reproducibility (2 RSD)	4 ppm on ⁵³ Cr/ ⁵² Cr; 15 ppm on ⁵⁴ Cr/ ⁵² Cr (n=10)

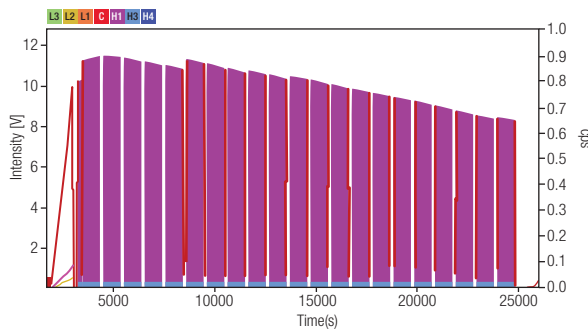


Figure 2. Typical Cr signal profile (V) during analysis.

Results

External Reproducibility

Cr isotope ratios corrected for instrumental mass bias are plotted in Figure 3. With ≥ 3 cycles of amplifier-cup rotation, the external reproducibility of Cr isotope ratios is similar to that obtained in literature¹ but with shorter analyses (≥ 2.5 h instead of ≥ 8 h).

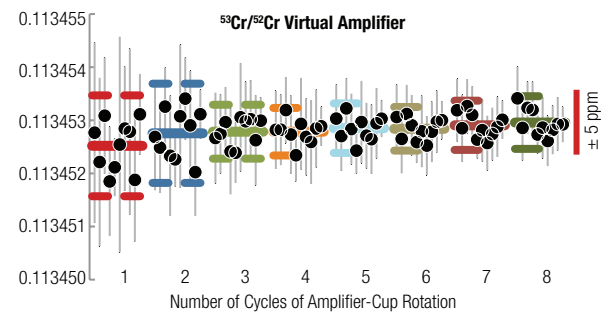


Figure 3. ⁵³Cr/⁵²Cr 2 SD external reproducibility of 10 Cr analyses vs. the number of cycles of amplifier-cup rotation. From 3 cycles of rotation on, ⁵³Cr/⁵²Cr isotope ratios are reproducible to 4 ppm (2 SD, 420 ratios). Error bars are 2 se.

⁵³Cr/⁵²Cr - ⁵⁴Cr/⁵²Cr Residual Correlation?

Reported non-ideal fractionation effects on Cr isotopes¹ are not observed in this study (Figure 4). However this study being limited to 10 analyses, only a thorough investigation over months of analysis will enable one to assess if such correlations are still present.

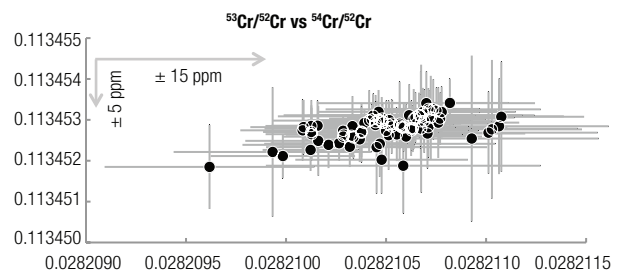


Figure 4. ⁵³Cr/⁵²Cr vs ⁵⁴Cr/⁵²Cr of all Cr measurements (with 1 to 8 cycles of amplifier-cup rotation, see Figure 3). Within the error bar envelope, there is no analytically resolvable residual correlation between ⁵³Cr/⁵²Cr and ⁵⁴Cr/⁵²Cr ratios corrected for mass-dependent fractionation using the normalizing ratio ⁵²Cr/⁵⁰Cr. Error bars are 2 se.

Conclusion

Fast Analyzing with High Reproducibility

>3 time shorter Cr isotopic analyses compared to literature can be achieved in static mode with virtual amplifier. They yield 2 SD external reproducibility of 4 to 7 ppm/amu, similar to that obtained in literature. This validates the stability of the current amplifier system and the Faraday cup multiple collection system and holds promise for analysis of smaller sample loads to high precision.

References

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