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Plasma Note **NP09**

Precise and Accurate Determination of Chromium Isotope Ratios

- **Pseudo resolution capability**
- **Use of mixed 1011 and 1012 ohm resistors**
- **Excellent mass fractionation stability**
- **Precise and accurate static Cr isotope determination**

A 500 ppb solution of the international chromium standard NIST SRM 979 [$Cr(NO_3)_{3.9}H_2O$] was used in this study. Solution was introduced into the mass spectrometer in 2% HNO_3 under 'dry plasma' conditions, using a DSN-100 Desolvating Nebuliser System with a 100 µL/min glass concentric nebuliser and the Enhanced Sensitivity interface (see Nu Instruments Application Note AN27).

Data was collected using static analysis. Each analysis consisted of two blocks of 20 integrations of 5 seconds on-peak measurements; baselines were obtained by a 30 seconds ESA deflection at the beginning of each analysis. The analysis duration was approximately 4.5 minutes. 53 repeat analyses were performed, equating to ca. 4 hours of data collection. No tuning of the instrument or nebuliser was made once the measurement had started.

Cr isotopes have several polyatomic interferences. In order to partially resolve these interferences, measurements were carried out on the oxide, carbide and nitride interference-free plateaus of the Cr peaks, in the Pseudo-High Resolution mode (50 µm source defining slit, medium resolution) with a resolving power of approximately 8,500 (5, 95% Edge Resolving Power). The ^{49}Ti, ^{51}V and ^{56}Fe beam intensities were simultaneously monitored during the course of measurement to correct for the irresolvable isobaric interferences of ^{50}Ti, ^{50}V on ^{50}Cr and ^{54}Fe on ^{54}Cr, using $^{49}Ti/^{50}Ti$ = 1.04320, $^{50}V/^{51}V$ = 0.002503 and $^{54}Fe/^{56}Fe$ = 0.063703 (IUPAC database). It is suggested that such isobaric interference correction would lead to inaccurate Cr ratios when one or more of the Ti, V, Fe concentrations are higher than 2% relative to the Cr concentration[1]. In this case, concentrations of Fe, Ti and V were measured to be less than 0.008%, 0.0005% and 0.00004% respectively, relative to the Cr concentration, proving the validity of this correction for the SRM 979 standard.

As will be mentioned in a later paragraph, all Cr isotope ratios were normalised to $^{50}Cr/^{52}Cr$ for the mass fractionation correction. It was therefore crucial to minimize any error propagation of the isobaric interference correction of ^{50}Cr. Therefore, ^{49}Ti was measured in a Faraday collector connected to a pre-amplifier fitted with a 1012 ohm resistor, in order to increase the signal to noise ratio thus reduce the measurement uncertainty. Due to its polyatomic interferences, ^{56}Fe was measured on the interferencefree plateau. A Cr solution spiked with Fe was used to set up the coincidence of the leading edges (Figure 1).

The zoom optics maintain good peak shapes and flat interference free plateaus (Figure1), which allows precise measurements of Cr isotope ratios.

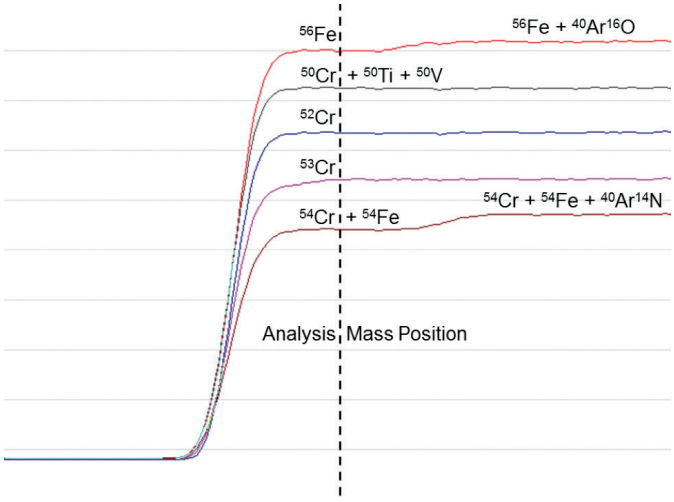

Figure 1: Chromium isotopes ^{50}Cr, ^{52}Cr, ^{53}Cr and ^{54}Cr and iron isotope ^{56}Fe partially resolved from their respective polyatomic interferences in the Pseudo-High Resolution mode using the 50 µm source defining slit.

It is reported that the presence of more than 10% of one or more matrix elements relative to the concentration of Cr, could significantly affect the accurate determination of Cr isotope ratios on MC-ICP-MS[1]. Concentrations of the major and trace elements (Ca, Al, Mg, Mn, Fe, Ti, Na, K, Sr, Ba, V, Ni, Cu, Pb, U) in the SRM 979 solution used in this study have been checked and were all less than 0.01% relative to the Cr concentration, eliminating any possible matrix effect.

The total Cr sensitivity achieved in the Pseudo-High Resolution mode was approx. 65 volts/ppm, at a 10% transmission. The signal intensity remained relatively stable over the course of measurement, with a loss of < 5% after 4 hours.

For the mass fractionation correction, two different approaches were adopted for comparison. The first one was internal normalisation, with the measured $^{53}Cr/^{52}Cr$, $^{54}Cr/^{52}Cr$ ratios being normalised to the certified reference value of $^{50}Cr/^{52}Cr$ = 0.05186 using the Exponential Law.

The mass fractionation corrected $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ ratios are reported in Table 1, in comparison with the IRMM certified reference values. For both ratios, the corrected values agree with the certified values within measurement errors.

	Corrected	IRMM Certified
$^{53}Cr/^{52}Cr$	0.11342 (1 RSD = 0.015‰, n = 53)	0.11339 ± 0.00015
$^{54}Cr/^{52}Cr$	0.028228 (1 RSD = 0.025‰, n = 53)	0.028220 ± 0.000060

Table 1: Fractionation corrected $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ ratios of the SRM 979 standard using $^{50}Cr/^{52}Cr$ = 0.05186, in comparison with the certified reference values. Certified values in blue were obtained from the IRMM database, measurements performed on a thermal ionization mass spectrometer.

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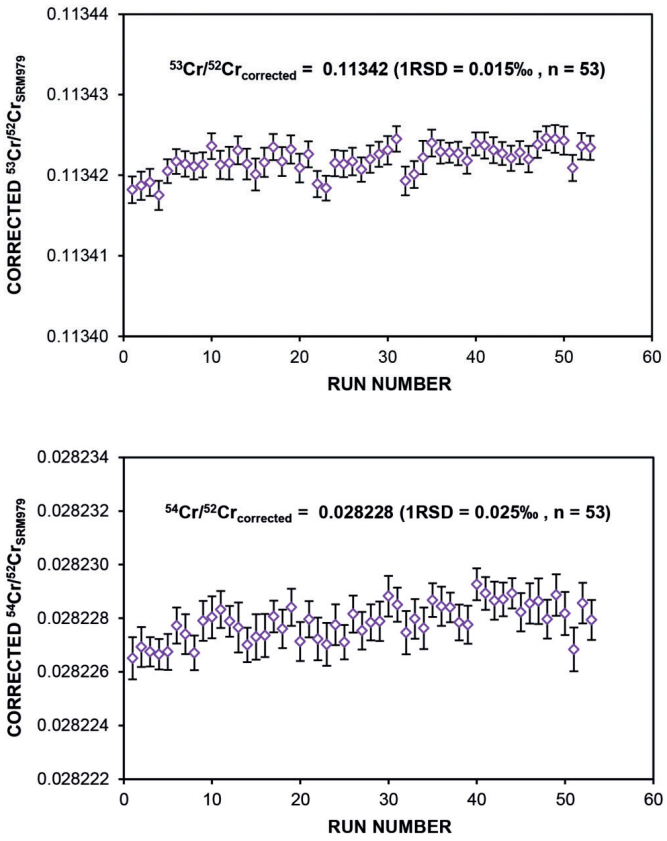

Figure 2: Corrected $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ ratios of the 500 ppb SRM 979 standard solution measured over the course of 4 hours. Error bars are 2 SE.

Repeat analyses are plotted in Figure 2.

For each analysis of 40 integrations, the internal precisions for $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ were 0.007‰ and 0.013‰ (1 RSE) respectively, highlighting the low noise of the pre-amplifiers, stability of baselines and excellent peak flatness.

Figure 3 shows the log-log plot of the uncorrected $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ ratios for the 53 repeat analyses. The two display a linear correlation and the slope of the fractionation line is within error of the theoretical value of 0.5, showing no evidence of mass-independent fractionation over the course of measurement.

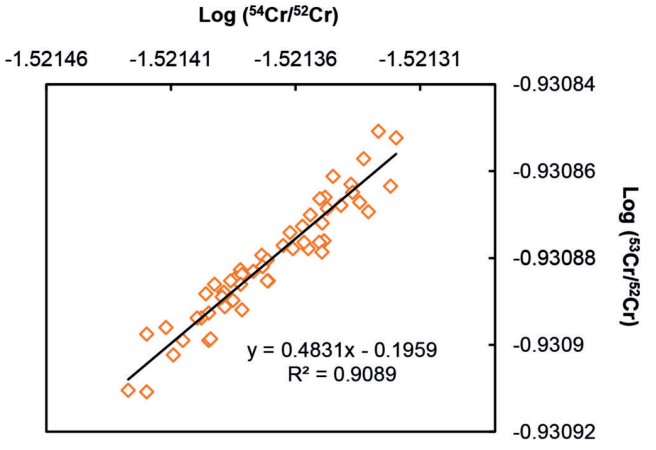

Figure 3: Log ($^{53}Cr/^{52}Cr$) and log ($^{54}Cr/^{52}Cr$) of the 53 repeat analyses display a linear correlation. The slope of the fractionation line is within error of the theoretical 0.5.

The second mass fractionation correction approach adopted here was standard bracketing. This approach assumes a linear mass fractionation drift over the course of measurement. Results are reported in Table 2, where δ denotes the per mil deviation of an uncorrected ratio relative to the average of the two ratios measured before and after. For all three uncorrected Cr isotope ratios, the average δ values of 26 brackets are within errors of the theoretical 0‰. The precisions are comparable to those achieved using internal normalisation.

	$^{50}Cr/^{52}Cr$	$^{53}Cr/^{52}Cr$	$^{54}Cr/^{52}Cr$
Average δ (‰)	0.001	-0.002	-0.001
1SD (‰)	0.030	0.015	0.033

Table 2: Standard bracketing results of 53 repeat analyses of a 500 ppb SRM 979 standard solution.

For the mass fractionation correction of Cr isotope ratios, it is demonstrated that the internal normalisation method and the standard bracketing method can both produce accurate and precise results.

References

[1] Halicz, L., Yang, L., Teplyakov, N., Burg, A., Sturgeon, R., & Kolodny, Y., 2008. High precision determination of chromium isotope ratios in geological samples by MC-ICP-MS. J. Anal. At. Spectrom., 23, 1622-1627.