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Highly Precise Vanadium Isotope Determination of Small Samples

Vanadium (V) isotope compositions of terrestrial samples have been widely used to constrain variations of redox conditions during many geological processes[1]. V isotope measurements were carried out using Thermal Ionization Mass Spectrometry (TIMS) in early studies with large uncertainties (>1%). Multi-Collector ICP-MS (MC-ICP-MS) has shown promise in high precision V isotope measurements due to its high ionization efficiency and fast sample throughput. However, this technique is limited by the presence of the $^{36}Ar^{14}N^+$ and $^{38}Ar^{12}C^+$ ion beams which inhibit the measurement of $^{50}V^+$. On a standard MC-ICP-MS instrument, measurements are carried out on the interference-free plateau of the V peaks, in the pseudo-high resolution mode, in order to partially resolve polyatomic interferences. This inevitably sacrifices 90% of the beam intensity. In addition, there are irresolvable isobaric interferences on ^{50}V from ^{50}Ti and ^{50}Cr which require an efficient chemical separation prior to mass spectrometry, and any residual of these two needs to be corrected for mathematically.

In this study, the Nu Sapphire was used for V isotopic measurements. The Nu Sapphire, is a novel MC-ICP-MS instrument equipped with a dual-path design including both a conventional MC-ICP-MS (high-energy) path and a hexapole collision cell (low-energy) path. For the low-energy path, following extraction of the ions from the ICP at 6 kV, the ions are deflected off-axis and decelerated to enter the collision cell. In the cell, the ions mix with gases to remove interfering species and are then re-accelerated to 6 kV on exiting the cell and focused back onto the high-energy path.

Using the low-energy path of the Sapphire, polyatomic species can be removed through charge exchange with H_2 gas. As a result, V isotopes may be measured in the low resolution mode. The $^{49}Ti^+$ and $^{52}Cr^+$ beams were simultaneously monitored during the course of measurement to correct for the irresolvable isobaric interferences of $^{50}Ti^+$, and $^{50}Cr^+$ on $^{50}V^+$, using $^{49}Ti^+/^{50}Ti^+ = 1.04320$, $^{52}Cr^+/^{50}Cr^+ = 19.2832$ (IUPAC database). Note that $^{52}Cr^+$ is normally subject to $^{36}Ar^{16}O^+$ and $^{38}Ar^{14}N^+$ interferences on a standard MC-ICP-MS but they are both eliminated in the collision cell via charge exchange with H_2.

A 100 ppb solution of the SpexCertiprep standard was used in this study. Solution was introduced into the mass spectrometer in 2% HNO_3 under 'dry plasma' conditions, using an Apex Omega Desolvating Nebuliser system with a PFA nebuliser with a 0.1 ml/min uptake rate and the Enhanced Sensitivity (ES) interface (see Nu Plasma Application Note NP05). 3 sccm He and 5 sccm H_2 were injected into the cell to remove Ar species.

Data was collected using static analysis. Each analysis consisted of one block of 420 integrations of 1 second on-peak measurement, equaling to 70 ng V consumption. The measurement sequence was preceded with a 2 min 'on peak' zero measurement in 2% HNO_3, and each analysis was followed by a 3 min wash in 2% HNO_3. No tuning of the instrument or nebuliser was made once the measurement batch had started.

The collector configuration on the Sapphire instrument is displayed in Table 1. Typical V peak alignment is displayed in Figure 1.

Table 1 displays the Sapphire collector configuration used in this study. Blue represents Faraday cups, yellow dummy cups. V isotopes are in green. The collector array also includes 3 Daly detectors, 3 electron multipliers, 2 additional Faraday cups – not shown below.

Collector	H9	X	H8	X	H7	X	H6	X	H5	H4	H3	H2	H1	Ax	L1	L2	L3	X	L4
Isotope										$^{52}Cr^+$		$^{50}Ti^+$ $^{50}V^+$ $^{50}Cr^+$	$^{51}V^+$						$^{49}Ti^+$

The variable zoom optics maintain good peak shapes and flat interference-free plateau (Figure 1), allowing highly precise measurements of V isotopes.

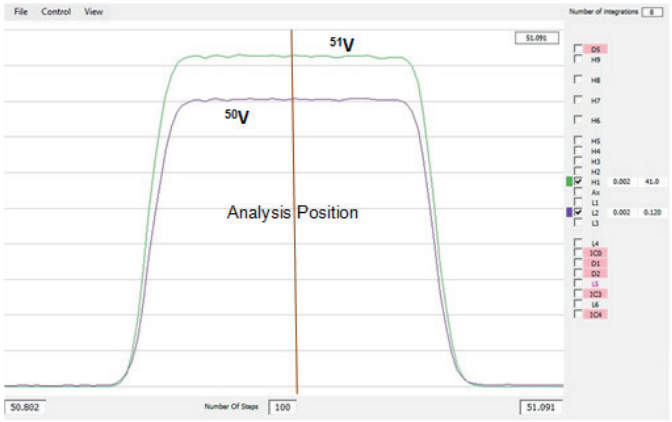

Figure 1: Vanadium peaks ^{50}V, ^{51}V in coincidence in the low resolution mode using the Sapphire collision cell.

The V signal remained very stable over the course of measurement, with a loss of < 1% over the course of 3.5 hours.
For each individual analysis, the uncertainty for $^{51}V/^{50}V$ was 0.04‰ (1 RSE), highlighting the low noise of the pre-amplifiers, stability of baselines and excellent peak flatness.

The mass fractionation correction approach adopted in this study was sample-standard bracketing. This approach assumes a linear mass fractionation drift over the course of the measurement sequence. Results are reported in Table 2, where $\delta^{51}V$ denotes the per mil deviation of the $^{51}V/^{50}V$ ratio relative to the average of the two $^{51}V/^{50}V$ ratios measured immediately before and after. Using less sample, this study produces a better reproducibility (2σ=0.06‰, 70 ng V) comparing to the best published results to date (2σ=0.10‰, 112 ng V) [1].

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Table 2 displays the Standard bracketing results of 19 repeat analyses of a 100 ppb V SpexCertiprep standard solution. The average $\delta^{51}V$ value of 9 brackets is within errors of the theoretical 0‰.

	$\delta^{51}V$ (‰)
Average	-0.02
2 SD	0.06

The V isotopic results have demonstrated the capability of the Nu Sapphire dual-path MC-ICP-MS to provide highly precise V isotope data using small samples. The collision cell greatly benefits V isotopic measurements, by efficiently removing Ar-based spectral interferences, thus enabling V measurement in low resolution mode and reducing the sample size. This new technique also provides time efficiency as setting up pseudo resolution is no longer required.

References

[1] Wu. F, Qi. Y, Yu. H, Tian. S, Hou. Z, Huang. F, 2016. Vanadium isotope measurement by MC-ICP-MS. Chemical Geology 421, 17-25.