

Determination of vanadium in graphite samples by high-temperature ashing pretreatment followed by inductively coupled plasma mass spectrometry

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ABSTRACT

Direct determination of vanadium (V) in graphite by mixed-acid digestion and inductively coupled plasma mass spectrometry (ICP-MS) is hindered by matrix effects and polyatomic interferences, resulting in limited trueness. Conventional methods for geological materials often have high detection limits (LODs) and low throughput. This study presents a high-temperature ashing pretreatment combined with mixed-acid digestion and ICP-MS for the true and precise quantification of V in graphite. Key parameters, including ashing temperature, sample mass, and digestion protocol, were optimized. Ashing at 950 °C efficiently removed the carbon matrix and minimized analyte loss, particularly in high-carbon samples. Polyatomic interference from $^{35}\text{Cl}^{16}\text{O}^+$ on the $^{51}\text{V}^+$ signal was effectively eliminated using the kinetic energy discrimination (KED) mode. The method achieved an LOD of 0.62 µg/g, a limit of quantitation (LOQ) of 2.48 µg/g, and excellent linearity ($R^2 = 0.9994$) over 0–1,000 µg/L. Spike recoveries ranged from 94% to 103.5%, with relative standard deviations (RSDs) below 3.8%. Compared with direct acid digestion, the proposed approach significantly improves trueness, precision, and robustness, offering a reliable, high-throughput solution for V analysis in graphite. This protocol provides an effective analytical tool for geological exploration and resource assessment.

Keywords: High-temperature ashing; Graphite; Mixed-acid digestion; Kinetic energy discrimination; Inductively coupled plasma mass spectrometry.

1. INTRODUCTION

Graphite is a critical strategic mineral with irreplaceable applications in high-temperature refractories, conductive materials, and new energy storage systems [1–3]. Recent explorations have revealed that certain types of graphite deposits are often associated with economically significant concentrations of vanadium (V) [4–6]. For instance, a key study by LIU *et al.* [1] on a V-bearing graphite ore reported a V_2O_5 content of 0.51% (equivalent to approximately 2860 µg/g of V), which was explicitly identified as having ‘comprehensive recovery value’. This example helps to define ‘economically significant’ concentrations, which can range from several hundred to a few thousand µg/g in such deposits. This concentration level firmly places vanadium in the trace-to-minor element category, not as a major element. The formation of these V-bearing graphite deposits is closely linked to the synergistic enrichment of V and the recrystallization of carbonaceous materials during hydrothermal events [7, 8]. V, often called the “vitamin of modern industry,” is experiencing growing demand for its use in high-strength alloys and all-V redox flow batteries. Consequently, the accurate determination of V content and its mode of occurrence in graphite ores has become crucial for geological prospecting and resource evaluation.

Currently, methods for determining V in rocks and ores include spectrophotometry, inductively coupled plasma-optical emission spectrometry (ICP-OES), and X-ray fluorescence (XRF) spectrometry [9–13]. Notably, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has become a premier technique for the accurate determination of trace to minor concentrations of vanadium in complex geological matrices, including various

rock types and reference materials [10, 11]. However, while effective for conventional geological samples, these methods exhibit significant limitations when applied to high-carbon graphite matrices. For instance, spectrophotometry is prone to interference from undigested carbon particulates, leading to incomplete color development and biased results. XRF spectrometry [12, 13], while non-destructive, often suffers from matrix absorption-enhancement effects and lacks the sensitivity required for accurately quantifying trace levels of V. Additionally, sample preparation methods such as alkaline fusion, often used in traditional spectrophotometry, introduce high salt loads that cause severe matrix effects in ICP-MS, making them unsuitable for trace-level quantification [14, 15]. Furthermore, the complete decomposition of the carbonaceous matrix is a well-established challenge in graphite analysis due to its highly stable chemical structure [16–20], a point consistently emphasized in studies exploring various advanced digestion techniques such as microwave-induced combustion and microwave-assisted acid digestion [17, 18]. This incomplete digestion leads to residual carbon particles that can block the instrument's sample introduction system and cause signal drift [16]. Secondly, the complex matrix of graphite can generate severe polyatomic interferences in inductively coupled plasma mass spectrometry (ICP-MS), compromising analytical accuracy [21, 22]. Although ICP-MS offers advantages such as multi-element capability and ultra-low detection limits (LODs), the elimination of interferences during the analysis of high-carbon matrices remains a primary obstacle [16].

This study aims to develop a robust method for the accurate determination of trace V in graphite. The proposed strategy involves a systematically optimized high-temperature ashing procedure to efficiently remove the organic matter and fixed carbon from the graphite matrix. This is followed by an optimized mixed-acid digestion protocol to ensure the complete dissolution of the target analyte. To address spectral interferences, kinetic energy discrimination (KED) mode in ICP-MS was employed to mitigate polyatomic interferences, such as $^{35}\text{Cl}^{16}\text{O}^+$, on the ^{51}V signal. The trueness, precision, and robustness of the method were validated through rigorous testing and application to real-world samples, with the goal of providing reliable analytical support for the genetic study of graphite deposits and the comprehensive evaluation of associated strategic resources.

2. EXPERIMENTAL

2.1. Instruments and reagents

2.1.1. Instrumentation

A NexION 350D ICP-MS system (PerkinElmer, Waltham, MA, USA), equipped with a Meinhard® nebulizer and a quartz cyclonic spray chamber, was employed for all elemental measurements. Sample digestion was carried out on a temperature-controlled graphite hotplate (DF-101S, 3 kW, Gongyi Yuhua Instrument, Gongyi, China), while drying was performed using a DHG-9140A electric blast oven (Shanghai Jinghong, Shanghai, China). Ashing was conducted in a Nabertherm L3/11 muffle furnace (Nabertherm GmbH, Germany). An FA-series analytical balance (precision ± 0.0001 g, Shanghai Precision Scientific Instrument, Shanghai, China) was utilized for weighing. Porcelain crucibles (approximately 50 mL capacity) were used for ashing, and 25 mL polytetrafluoroethylene (PTFE) crucibles (Nanjing Binzhenghong, Nanjing, China) were employed for acid digestion.

2.1.2. Reagents and standards

All acids used, including hydrofluoric acid (HF), nitric acid (HNO_3), and hydrochloric acid (HCl), were of trace-metal grade (Merck, Darmstadt, Germany). High-purity deionized water (resistivity ≥ 18.2 M Ω ·cm), produced using a Milli-Q purification system (Merck Millipore, Burlington, MA, USA), was employed for all dilutions, in compliance with the GB/T 6682-2008 Grade 1 specification (equivalent to ASTM Type I).

A certified vanadium (V) stock solution (1,000 $\mu\text{g/mL}$, P/N N9300175, PerkinElmer, USA), traceable to NIST SRM 3165, was used to prepare calibration standards by serial dilution with 1% (v/v) HNO_3 . Calibration standards were prepared at concentrations of 0, 2.00, 5.00, 20.0, 100, 200, 500, and 1,000 $\mu\text{g/L}$.

A certified rhodium (Rh) stock solution (1,000 $\mu\text{g/mL}$, P/N N9300144, PerkinElmer, USA), traceable to NIST SRM 3144, was diluted to 10.0 $\mu\text{g/L}$ with 1% (v/v) HNO_3 and employed as an internal standard.

Graphite reference materials (GBW03118, GBW03119, and GBW03120) were obtained from the National Research Center for Geoanalysis (Beijing, China), an ISO 17034-accredited producer of certified reference materials. These materials do not have certified values for vanadium but were used as real-world samples to validate the method's applicability. Trueness was assessed using spike recovery. Five graphite samples (labeled 1# to 5#), collected from a deposit in Heilongjiang Province, China, were used for method development and validation. All samples were ground to pass through a <75 μm sieve to ensure homogeneity.

2.3. Sample pretreatment

2.3.1. High-temperature ashing

An aliquot of the graphite sample ($0.10 \text{ g} \pm 0.0001 \text{ g}$), previously dried to a constant weight at 105°C , was weighed into a porcelain crucible and spread thinly. The crucible was placed in a muffle furnace, and the temperature was ramped from ambient to 950°C over 45 minutes. The furnace door was left slightly ajar to ensure a sufficient supply of air, promoting complete carbon combustion. The temperature was held at 950°C for 1–2 h until no black particles remained. The crucible was then cooled to room temperature in a desiccator. The fixed carbon and ash content of samples 1#–4# were determined according to the ASTM D5142 standard method.

2.3.2. Digestion of ash residue

The ash residue was quantitatively transferred to a 25 mL polytetrafluoroethylene (PTFE) crucible. A 5 mL volume of mixed acid ($\text{HF} : \text{HNO}_3 = 2 : 1$, v/v) was added, and the crucible was heated on a hotplate at a low temperature ($\sim 120^\circ\text{C}$) until near dryness to remove silicates. This step was repeated with another 5 mL of the mixed acid. Next, 3 mL of HNO_3 was added, and the solution was heated to near dryness to expel residual HF. Finally, 5 mL of diluted aqua regia (prepared by mixing 3 mL concentrated HCl , 1 mL concentrated HNO_3 , and 4 mL deionized water) was added. This step, a standard procedure for complex geological samples, ensures the complete dissolution of any refractory minerals potentially hosting vanadium. The crucible was covered with a watch glass and heated gently ($\sim 90^\circ\text{C}$) for approximately 30 minutes to ensure complete dissolution of the residue. After cooling, the crucible walls and watch glass were rinsed with deionized water, and the solution was quantitatively transferred to a 25 mL volumetric flask and diluted to the mark. An aliquot of this solution (1.00 mL) was then quantitatively transferred to a 10.00 mL volumetric flask and diluted to the mark with deionized water for ICP-MS analysis. The total dilution factor from the original 0.1 g sample was 2500-fold.

2.4. ICP-MS measurement

The ICP-MS was initialized and optimized according to the manufacturer's protocol (see Table 1 for operating parameters). After plasma ignition, the system was stabilized by aspirating a 1% (v/v) HNO_3 solution for at least 30 minutes. Instrument performance was tuned in Standard Mode using a tuning solution to optimize nebulizer gas flow, torch position, and QID voltage. All sample measurements were performed in KED mode. The signal intensities of ^{51}V and the ^{103}Rh were acquired. A calibration curve was constructed, and the instrument software automatically calculated the V concentration in the samples. The final V content in the original graphite sample (in $\mu\text{g/g}$) was calculated based on the instrument reading, sample mass, final volume, and dilution factor.

Table 1: ICP-MS operating parameters.

PARAMETER	SETTING	PARAMETER	SETTING
RF power (W)	1350	Scan mode	Peak hop
Plasma gas flow (L/min)	18	Dwell time (ms/AMU)	50
Auxiliary gas flow (L/min)	1.2	Scan repetition times	20
Nebulizer gas flow (L/min)	0.90 (optimized)	Rinse time (s)	10
Collision gas (He) flow (mL/min)	3.0 (optimized)	Sampler cone aperture (mm)	Ni, 1.0
Measurement mode	KED	Skimmer cone aperture (mm)	Ni, 0.7

2.5. Traditional spectrophotometric analysis

For method comparison, samples were also analyzed using a traditional spectrophotometric method. Sample decomposition was achieved by alkaline fusion. The V concentration was determined by measuring the absorbance of the phosphotungstovanadic acid complex using a 721-type UV-Vis spectrophotometer at a wavelength of 400 nm. A calibration curve was prepared using a series of V standard solutions subjected to the same color development procedure. The final V content was calculated based on this calibration.

3. RESULTS AND DISCUSSION

3.1. Optimization of sample pretreatment

3.1.1. Comparison of pretreatment methods

In this study, we compared direct mixed-acid digestion (Method A) with high-temperature ashing followed by mixed-acid digestion (Method B). Six parallel experiments ($n = 6$) were performed on graphite samples 1#–4# and reference materials GBW03118 and GBW03120. The results are presented in Table 2.

Table 2: Comparison of results from different pretreatment methods (n = 6).

SAMPLE ID	FIXED C (%)	ASH (%)	METHOD A: DIRECT ACID DIGESTION		METHOD B: ASHING + ACID DIGESTION		F-TEST
			MEAN (MG/G)	RELATIVE STANDARD DEVIATION (RSD) (%)	MEAN (MG/G)	RSD (%)	F VALUE
1#	6.81	90.87	460	5.23	460	3.29	2.51
2#	7.07	90.43	670	2.27	670	3.11	1.91
3#	11.64	81.82	870	14.67	990	4.79	7.26
4#	18.65	76.17	1,920	13.70	1,970	3.16	17.79
GBW03118	2.91	91.36	330	10.84	320	10.54	1.13
GBW03120	76.5	21.04	170	29.12	320	5.86	24.7

Note: The critical F-value at $p = 0.05$ ($df_1 = 5$, $df_2 = 5$) is 5.05. Values in bold indicate a significant difference in variance. ASH (%) refers to the mass percentage of the inorganic residue remaining after high-temperature combustion of the graphite sample.

As shown in Table 2, for samples with low fixed carbon content (<10%; samples 1#, 2#, GBW03118), the mean values and RSDs obtained by Method A and Method B were not significantly different. This was confirmed by an F-test, indicating that direct digestion is adequate for low-carbon samples. However, for high-carbon samples (3#, 4#, and GBW03120), Method A yielded significantly lower mean values and drastically higher RSDs. For instance, with GBW03120 (76.5% C), the result from Method A (170 µg/g) represented a recovery of only 53% compared to Method B (320 µg/g), with a very poor RSD of 29.12%. For sample 4#, the high F-value (17.79) indicates a statistically significant improvement in precision with the proposed method. This severe negative bias confirms that the carbon matrix encapsulates the analyte, preventing its complete liberation. Therefore, high-temperature ashing is indispensable for the accurate analysis of V in carbon-rich graphite.

3.1.2. Optimization of ashing conditions

Sample 5#, a typical flake graphite with a fixed carbon content of 14.45%, was selected to optimize the ashing temperature [19]. The effect of different temperatures (400, 500, 700, 900, 950, 1,000, and 1,100 °C) on the V signal intensity was investigated with a fixed ashing time of 1 hour. The results are shown in Figure 1.

The results indicated that at temperatures ≤500 °C, the sample appearance remained unchanged (Figure 2a), signifying negligible carbon oxidation and resulting in a low and unstable V signal. At 700 °C, incomplete ashing was identified by the visible presence of residual black carbon particulates (Figure 2b), which corresponded to a highly variable V signal. Between 900 °C and 1,000 °C, the ashing was effective, yielding a high V signal that formed a stable plateau (Figure 1) and a loose, grayish-white powder (Figure 2c). Within this optimal range, the signal at 950 °C exhibited the highest stability (i.e., the smallest data variance). Crucially, at 1,100 °C, the sample began to sinter (Figure 2d), which would impede subsequent acid dissolution. Therefore, considering the combined factors of signal stability, the physical state of the ash, and energy efficiency, 950 °C was selected as the optimal ashing temperature.

3.1.3. Optimization of acid digestion and sample mass

An HF-HNO₃ mixture was chosen for digestion to decompose residual silicates and dissolve metal oxides in the ash [20]. A sample mass of 0.10 g was selected to ensure homogeneity while keeping the total dissolved solids (TDS) in the final analytical solution below 0.1% to minimize matrix effects. This sample mass is consistent with the recommended minimum sample size (≥100 mg) for the graphite reference materials to ensure a representative aliquot. A factorial study was conducted on the ash of sample 5# to optimize the digestion parameters, including the HF : HNO₃ volume ratio, total acid volume, and number of digestion cycles. The optimization and data visualization were performed using OriginPro 2021 (OriginLab, USA). The results (Table 3 and Figure 3) showed that a single digestion with 2 mL of acid was insufficient for complete silicate removal. Figure 3 illustrates that the first digestion step (A) was insufficient, while the second digestion step contributed significantly to the total signal (B), ensuring complete analyte recovery. Increasing the acid volume to 10 mL (5 mL HF + 5 mL HNO₃) resulted in complete dissolution. Two digestion cycles with 5 mL of a 2 : 1 HF : HNO₃ mixture provided the most robust and complete dissolution. Therefore, the final optimized procedure was set to two digestion cycles, each with 5 mL of a 2 : 1 (v/v) HF : HNO₃ mixture.

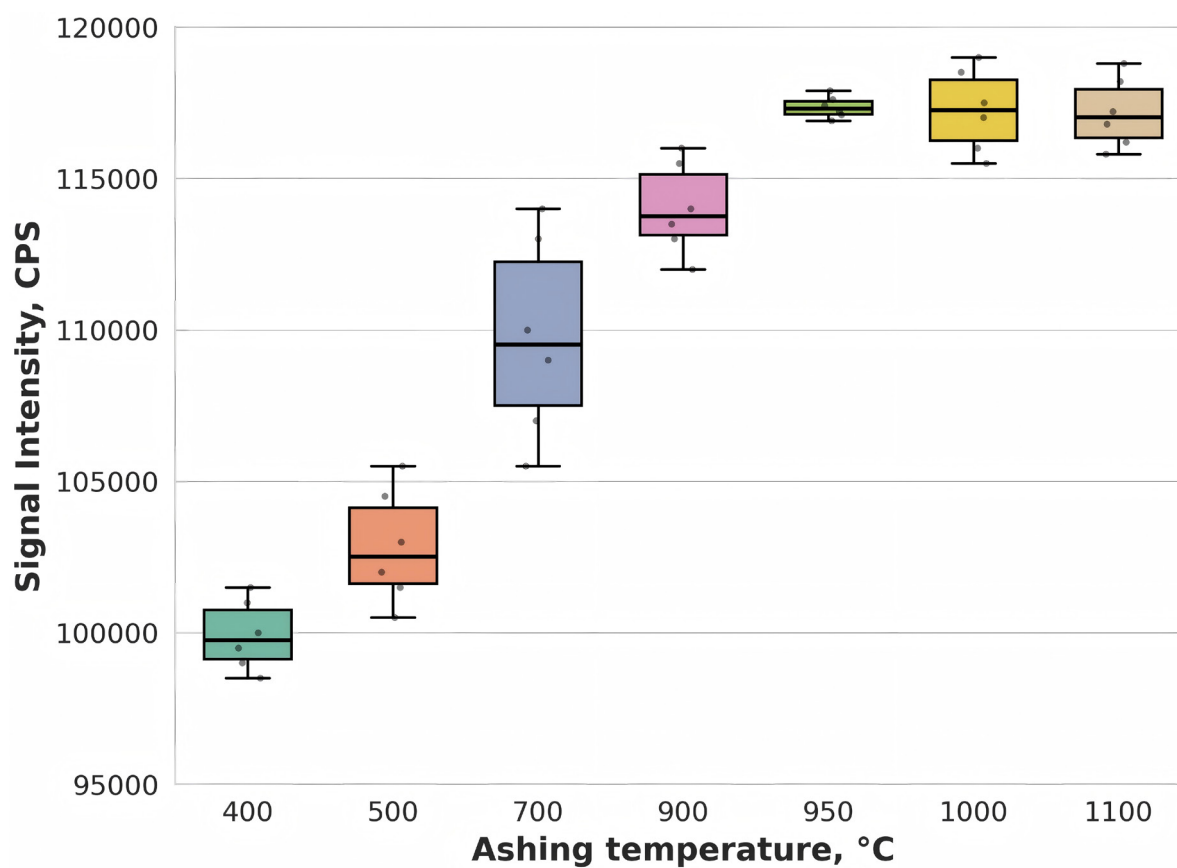


Figure 1: Influence of ashing temperature on the signal intensity of V.

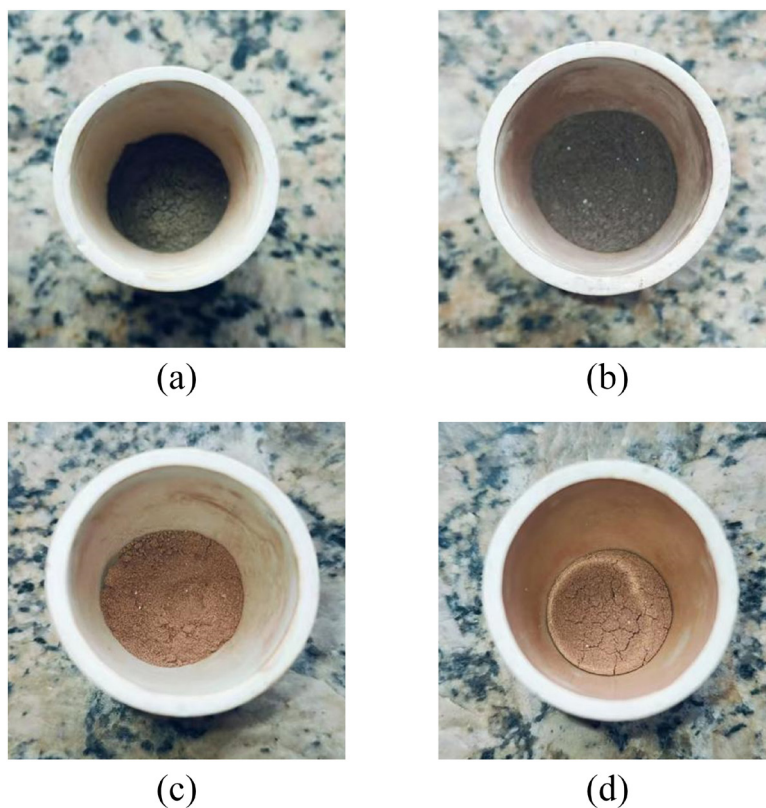
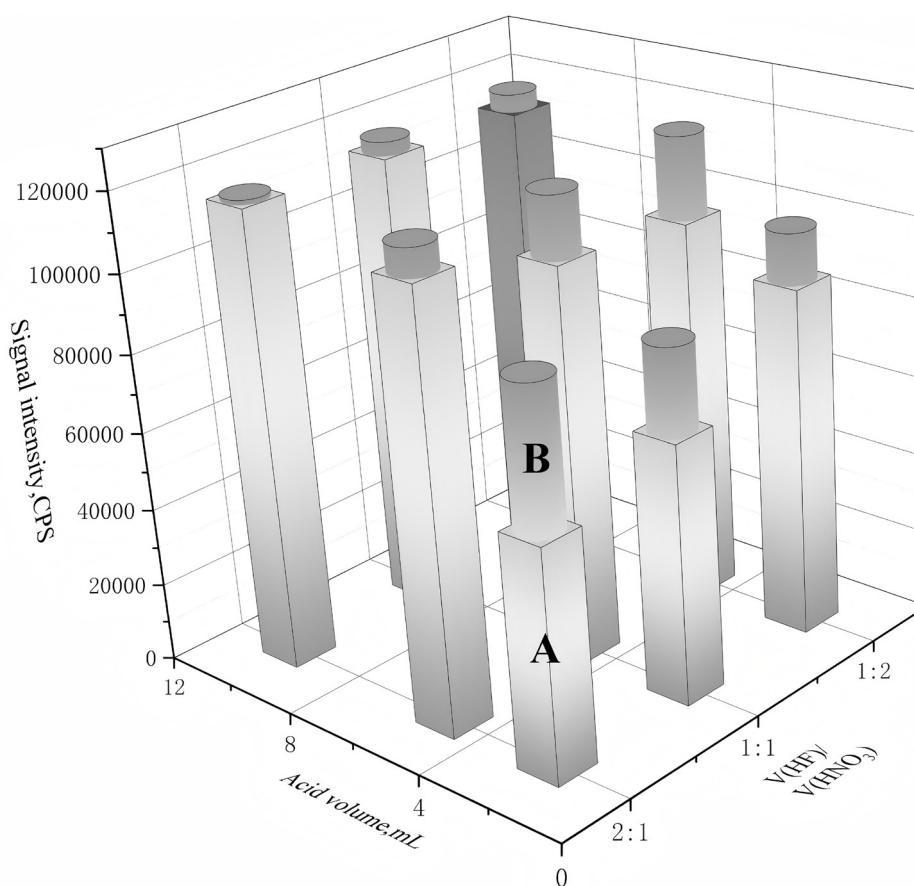


Figure 2: Ashing effects at different temperatures: (a) original sample at 500 °C, (b) incomplete ashing at 700 °C, (c) complete ashing at 950 °C, (d) sintered sample due to overheating at 1,100 °C.

Table 3: Optimization of acid digestion parameters (values are V signal intensity in counts per second (CPS)).

V(HF)/ V(HNO ₃)	ACID VOLUME PER DIGESTION (ML)					
	2		5		10	
	CYCLE 1	CYCLE 2	CYCLE 1	CYCLE 2	CYCLE 1	CYCLE 2
1 : 2	87,859	100,523	97,248	117,952	115,145	119,576
1 : 1	65,724	87,534	100,579	116,277	115,876	113,259
2 : 1	58,462	94,515	110,275	117,266	116,479	117,549

**Figure 3:** Comparison of V signal intensity under different digestion conditions. A represents the signal from the first digestion step alone; B represents the total signal after the second, cumulative digestion step, highlighting the contribution of the second dissolution.

3.2. Interference and its elimination

The interference in ICP-MS analysis is mainly divided into mass spectral interference and non-mass spectral interference. The first type of interference can be divided into four types: isobaric interference, polyatomic ion interference, insoluble oxide interference, and doubly charged ion interference. The second type is mainly matrix effects caused by high salt content [16].

3.2.1. Mass spectral interference

The primary spectral interference on ^{51}V is the polyatomic ion $^{35}\text{Cl}^{16}\text{O}^+$, arising from the HCl used in the digestion. While a mathematical correction equation can be applied, its effectiveness is limited in the presence of high chloride concentrations [17, 18].

To demonstrate the most effective interference removal strategy, we compared the background equivalent concentration (BEC) of V under three modes: Standard, Mathematical Correction, and KED. As shown in

Table 4, in Standard Mode, the BEC increased dramatically with HCl concentration, rendering the analysis unreliable. Mathematical correction provided only a marginal improvement. In contrast, KED mode, using He as a collision gas, effectively eliminated the $^{35}\text{Cl}^{16}\text{O}^+$ interference, reducing the BEC to a consistently low level ($<0.5 \mu\text{g/L}$) even at high HCl concentrations. This occurs because the larger polyatomic ions (e.g., $^{35}\text{Cl}^{16}\text{O}^+$) undergo more collisions with the inert He gas in the collision cell than the smaller analyte ions ($^{51}\text{V}^+$). Consequently, the polyatomic ions lose more kinetic energy. An energy barrier at the cell exit then filters out these lower-energy ions, preventing them from reaching the quadrupole mass filter and detector (Figure 4). KED mode was therefore deemed essential for true and precise analysis.

Table 4: Influence of measurement mode on the BEC of ^{51}V .

AQUA REGIA VOLUME PERCENTAGE (%) (HCL CONCENTRATION IN THE FINAL SOLUTION)	STANDARD MODE BEC ($\mu\text{g/L}$)	MATH CORRECTION BEC ($\mu\text{g/L}$)	KED MODE BEC ($\mu\text{g/L}$)
0 (1% HNO_3 only)	0.5	0.3	0.242
0.2 (equivalent to 0.08% HCl in the final solution)	6.4	1.2	0.262
0.5 (equivalent to 0.2% HCl in the final solution)	15.7	7.8	0.375
1.0 (equivalent to 0.4% HCl in the final solution)	33.3	11.3	0.431
2.0 (equivalent to 0.8% HCl in the final solution)	65.1	50.6	0.274
5.0 (equivalent to 2.0% HCl in the final solution)	165.6	135.7	0.243

Note: The final HCl concentration in the sample solution was calculated to be approximately 0.4% (v/v) (from 5 mL of 1+1 aqua regia diluted to 25 mL and then diluted 10-fold).

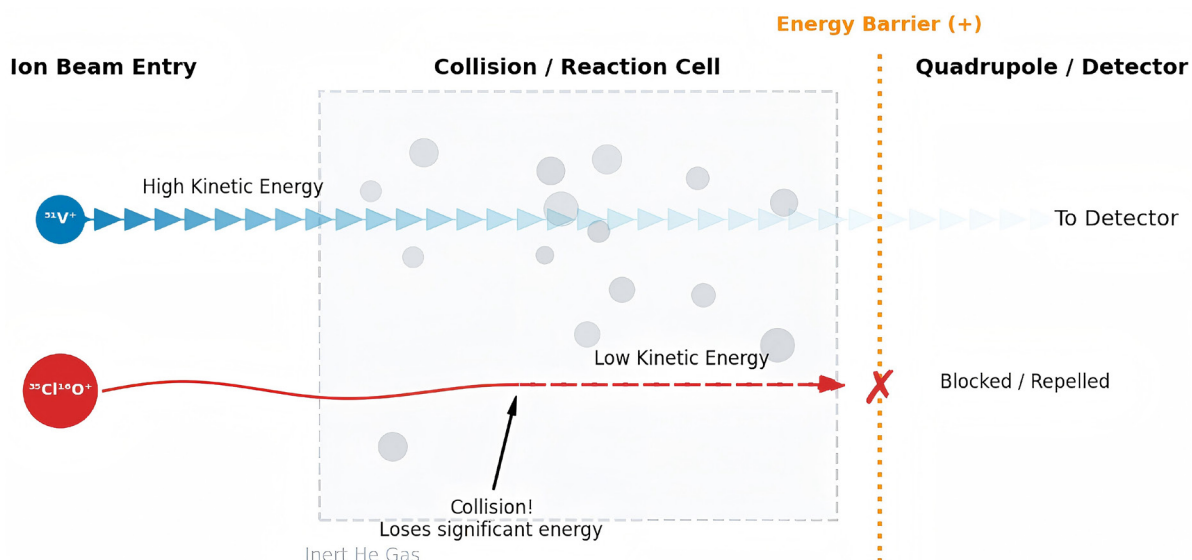


Figure 4: Schematic diagram illustrating the principle of Kinetic Energy Discrimination (KED). Larger polyatomic interfering ions (e.g., $^{35}\text{Cl}^{16}\text{O}^+$) undergo more collisions with the inert He gas than the smaller analyte ions ($^{51}\text{V}^+$). This causes the interferences to lose significantly more kinetic energy. A discriminating potential barrier at the cell exit then filters out these lower-energy ions, allowing only the higher-energy analyte ions to pass through to the detector, thus greatly reducing interferences and enhancing measurement trueness.

3.2.2. Non-MS interference

Non-MS interference (matrix effects) were minimized by the high-temperature ashing step [23], which reduced the TDS of the final solution to approximately 0.04%. To correct for any residual matrix effects and instrument drift, ^{103}Rh was used as an internal standard. In a stability test with 100 consecutive measurements of sample 5#, the RSD of the ^{51}V signal was 5.32%. After Rh correction, the RSD of the $^{51}\text{V}/^{103}\text{Rh}$ ratio improved to 2.03%, demonstrating effective correction.

3.3. Method validation

The developed method was validated by evaluating its linearity, limit of detection (LOD), limit of quantitation (LOQ), precision (repeatability), and trueness (recovery). The acceptance criteria were established based on common requirements for geochemical analysis in geological surveys: linearity ($R^2 > 0.999$), precision ($RSD < 5\%$), and recovery (90–110%).

3.3.1. Linearity and LODs

Under the optimized conditions, the calibration curve for V showed excellent linearity in the range of 0–1,000 $\mu\text{g/L}$, with a coefficient of determination (R^2) of 0.9994. The curve was constructed using eight concentration levels, with each point measured in triplicate. The calibration function was a linear regression model ($y = mx + c$) where the intercept was statistically insignificant ($p > 0.05$). The method LOD, calculated as 3 times the standard deviation of 12 replicate blank measurements and adjusted for the dilution factor, was 0.62 $\mu\text{g/g}$. The quantitation limit (LOQ), calculated as 10 times the standard deviation of the blank, was 2.48 $\mu\text{g/g}$.

3.3.2. Precision and trueness

The precision and trueness of graphite samples 1#–5# and standard materials GBW03118, GBW03119, and GBW03120 were evaluated. Since the graphite standard materials used did not have a certified value for V, the spike recovery method was used to evaluate trueness. A known amount of V standard solution was added during the ash digestion step. The results are shown in Table 5. The spike recovery of this method was between 94% and 103.5%, meeting the acceptance criterion of 90–110%. The precision, evaluated as the repeatability of six replicate analyses for each sample, was between 1.16% and 3.77% (RSD), well within the acceptance criterion of $RSD < 5\%$. Both of these results met the technical requirements for geological sample analysis.

Table 5: Method precision and trueness ($n = 6$).

SAMPLE ID	MEAN VALUE (MG/G)	SPIKED AMOUNT (MG/G)	MEASURED TOTAL (MG/G)	RECOVERY (%)	RSD%
1#	440	200	631	95.6	1.91
2#	700	200	888	94.0	3.19
3#	1,100	200	1,297	98.9	1.56
4#	2,010	1,000	3,021	101.1	1.46
5#	1,930	1,000	2,965	103.5	1.16
GBW03118	320	200	511	95.5	3.37
GBW03119	520	200	713	96.5	2.74
GBW03120	320	200	512	96.0	3.77

Note: Recovery (%) = [(measured total - mean value) / spiked amount] $\times$ 100%.

3.3.3. Method comparison

The proposed method was compared against a traditional method (alkaline fusion followed by phosphotungstovanadic acid spectrophotometry) using samples 1#–5# [19, 20]. As shown in Table 6, the mean values obtained by the proposed ICP-MS method and the traditional spectrophotometry method showed no statistically significant difference (t -test, $p > 0.05$), indicating comparable accuracy for the determined concentration range. However,

Table 6: Comparison of results from different analytical methods.

SAMPLE ID	PROPOSED METHOD (ICP-MS)		TRADITIONAL METHOD (SPECTROPHOTOMETRY)	
	CONTENT (MG/G)	RSD%	CONTENT (MG/G)	RSD%
1-#	440	1.91	410	3.56
2-#	700	3.19	700	2.87
3-#	1,100	1.56	1,110	3.45
4-#	2,010	1.46	1,950	1.56
5-#	1,930	1.16	1,910	3.21

the proposed method demonstrates a marked improvement in precision, with RSDs consistently below 3.2% for all samples, significantly lower than those from the traditional method (up to 3.56%). This enhanced precision, combined with a much lower LOD and the inherent high-throughput capability of ICP-MS, establishes its clear superiority for routine analysis of large sample batches in geological surveys.

3.3.4 Estimation of Measurement Uncertainty

The measurement uncertainty was estimated according to the Guide to the Expression of Uncertainty in Measurement (GUM). The main sources of uncertainty were identified as: (1) preparation of the standard solutions (u_{cal}), (2) the calibration curve fitting (u_{fit}), (3) sample mass (u_{m}), (4) final dilution volume (u_{vol}), and (5) method repeatability (u_{rep}). The combined standard uncertainty (u_{c}) was calculated using the law of propagation of uncertainty. For a sample with a vanadium concentration of $\sim 500 \mu\text{g/g}$, the combined relative uncertainty was estimated to be 4.2%. The expanded uncertainty (U), using a coverage factor (k) of 2 (providing a confidence level of approximately 95%), was 8.4%.

4. DISCUSSION

The analysis of vanadium (V) in graphite samples presents significant challenges due to matrix effects and polyatomic interferences, which can compromise the accuracy of inductively coupled plasma mass spectrometry (ICP-MS) [21, 22]. This study developed an analytical method employing a high-temperature ashing pretreatment followed by acid digestion to overcome these limitations.

4.1. Optimization of sample pretreatment

Sample pretreatment is a critical step for ensuring analytical accuracy. For high-carbon samples, direct acid digestion methods were found to be inadequate, leading to lower results and higher variability [16–20]. This is likely due to the encapsulation of the analyte within the carbon matrix, which prevents its complete liberation. High-temperature ashing at 950°C proved essential for effectively removing the carbon matrix, ensuring the success of the subsequent acid digestion. The optimized acid digestion procedure, using a 2:1 (v/v) mixture of HF:HNO₃ applied in two cycles, ensured the complete dissolution of vanadium from the ash residue.

4.2. Interference elimination

A significant obstacle in the ICP-MS analysis of vanadium is the polyatomic interference from $^{35}\text{Cl}^{16}\text{O}^+$, which originates from the hydrochloric acid (HCl) used in digestion [17, 18]. While mathematical correction methods exist, their effectiveness is limited. The use of kinetic energy discrimination (KED) mode proved essential for eliminating this interference. KED mode effectively reduces the background equivalent concentration (BEC) to a consistently low level, even in the presence of high HCl concentrations, thereby greatly enhancing analytical accuracy. To mitigate non-spectrometric matrix effects and instrument drift, rhodium (^{103}Rh) was used as an internal standard, further improving the precision of the results.

4.3. Method validation and comparison

The developed method demonstrated excellent analytical performance, including a low limit of detection (LOD) of $0.62 \mu\text{g/g}$, excellent linearity ($R^2 = 0.9994$), and satisfactory trueness (recoveries 94%–103.5%). The precision of the method, with relative standard deviations (RSDs) consistently below 3.8%, is notably superior to that of traditional methods, such as spectrophotometry [19, 20]. Although the mean values obtained by the proposed method and spectrophotometry showed no statistically significant difference, the superior precision and lower LOD of the ICP-MS method, combined with its high-throughput capability, establish its superiority for the routine analysis of large sample batches.

In conclusion, the developed method offers a robust, true, and precise approach for the determination of vanadium in graphite samples. The sample preparation protocol, centered on high-temperature ashing, could potentially be adapted for the simultaneous determination of other valuable elements associated with graphite, providing a more comprehensive tool for integrated mineral resource assessment.

5. CONCLUSION

This study successfully developed and validated a robust method for the determination of trace V in graphite samples using high-temperature ashing pretreatment combined with mixed-acid digestion and ICP-MS analysis in KED mode. The key findings are as follows:

- Optimal ashing: The optimal ashing temperature was determined to be 950°C , which effectively removed the carbon matrix and minimized matrix effects.

- Complete digestion: An optimized digestion protocol using a 2 : 1 (v/v) mixture of HF : HNO₃ (5 mL added twice) ensured the complete dissolution of V from the ash residue.
- Interference elimination: The use of KED mode with He as a collision gas successfully eliminated the ³⁵Cl¹⁶O⁺ polyatomic interference on the ⁵¹V signal, greatly enhancing analytical accuracy.
- Excellent performance: The method demonstrated a low LOD (0.62 µg/g), excellent linearity (R² = 0.9994), satisfactory recoveries (94%–103.5%), and high precision (RSD < 3.8%).
- Compared to traditional methods, the proposed approach is simpler, consumes fewer reagents, and provides higher trueness and precision. It is highly suitable for the routine, high-throughput analysis of V in graphite samples. Finally, while this study focused on V, the developed sample preparation protocol shows promise for future adaptation. Subsequent research could investigate its applicability for the simultaneous determination of other valuable associated elements in graphite, such as molybdenum, uranium, and nickel, thereby providing a more comprehensive tool for the integrated assessment of mineral resources.

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