

Distribution of vanadium(V) species between soil and plants in the vicinity of vanadium mine

N. Panichev*, K. Mandiwana, D. Moema, R. Molatlhegi, P. Ngobeni

Department of Chemistry, Tshwane University of Technology, Private Bag X31, Rosslyn 0200, South Africa

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Abstract

The distribution of vanadium(V) species between soil and plants around the vanadium mine have been studied. The mine dam spilled water around this area after collapsing some time ago. V(V) species were determined by electrothermal atomic absorption spectrometry (ETAAS) after leaching of vanadium(V) compounds with 0.1 M of Na₂CO₃, with a limit of detection 0.2 μg g⁻¹. The validity of V(V) determination had been confirmed by the spike recovery and of the total amount of vanadium by the analysis of CRM's with good correspondence of found to certified values. The concentration of V(V) species were found to be in the range of 620–1680 μg g⁻¹ in soil and 4–6 μg g⁻¹ in grass samples, respectively. The total amount of vanadium in soil varied from 1570 to 3600 μg g⁻¹ and from 8 to 13 μg g⁻¹ in grass. The results indicate that considerable amount of vanadium (about 50%) in soils and plants is present as V(V) species.

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Keywords: Vanadium(V) speciation; Soil; Plants; Leaching; Sodium carbonate; Electrothermal atomic absorption spectrometry

1. Introduction

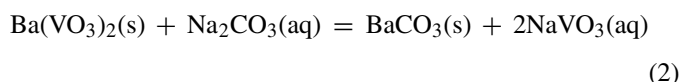
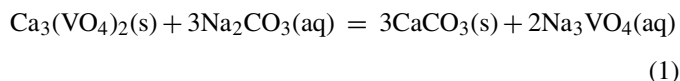
The average concentration of vanadium in soils around the world ranges from trace amounts to 400 μg g⁻¹, with an average of 150 μg g⁻¹ [1]. One of the main sources of vanadium in soil is the parent rock from which it is formed [2].

In spite of the fact that V(V) is the most toxic vanadium species [3], little attention has been paid to the determination of V(V) species in soil and plants. The United States of America's Environmental Protection Agency (EPA) has not listed vanadium as a pollutant requiring urgent research and legislation, because "there is no evidence that the general population is at risk, either through deficiency of, or over-exposure to vanadium"[4]. Consequently, there are few countries, where standards and regulations for environmental pollution in soil with vanadium are accepted, for example, Russia, where the maximum of 150 μg g⁻¹ allowed in agricultural soil [5].

The development of reliable methods for the speciation of vanadium remains a challenging field of analytical chemistry,

especially for solid samples. Many investigations that have been dedicated to the determination of vanadium in soils were mainly concentrating on the determination of total vanadium concentration [6–8]. However, to assess vanadium in plants and its impact on animals that consume plants, it is important to verify vanadium valency speciation [9,10].

Because V(V) and Cr(VI) have similar chemical properties [11], they can exist under natural environmental conditions in corresponding anionic forms, as VO₄³⁻ and CrO₄²⁻ ions, respectively. Both of them can be separated from V(IV) and Cr(III) compounds by treatment with Na₂CO₃ solution [12]. A solution of Na₂CO₃, when heated with solid samples yields insoluble carbonates of common metals and releases anions present in the solution, according to following equations:



Even if solubility differences are moderately unfavourable, increased concentration of carbonate ion will assure adequate conversion.

* Corresponding author. Tel.: +27 12 521 0603; fax: +27 12 521 0820.
E-mail address: panichevn@tut.ac.za (N. Panichev).

The chromium speciation in solid samples by leaching with alkaline Na_2CO_3 solution has been described. US EPA method 3060A [13] of leaching Cr(VI) compounds with $\text{Na}_2\text{CO}_3/\text{NaOH}$ in combination with a spectrophotometric detection (US EPA 7196A) [14], provide satisfactory results in the quantitative determination of Cr(VI). The leaching of Cr(VI) from soil [15] and plants [16] was successfully achieved with 0.1 M Na_2CO_3 . But such methods of leaching have never been tested and applied for vanadium speciation in soil and plants.

The soil near existing South African vanadium mines might be contaminated with vanadium as a pollutant [17] since about 30% of the current vanadium global output [18] are produced in that country. The presence of V(V) compounds in plants at concentrations higher than $2 \mu\text{g g}^{-1}$ may cause chlorosis and limit growth [19]. Due to the structural analogy between vanadate (H_2VO_4^-) and phosphate (H_2PO_4^-) ions [20], the accumulation of vanadium by plants reduces the amount of phosphate that plays a very important physiological role. The consumption of such vanadium enriched contaminated grass by mammals including cattle, would ultimately lead to the replacement of PO_4^{3-} in their bones.

The present article is devoted to the determination of V(V) species in soil and plants by ETAAS after the leaching of V(V) species with Na_2CO_3 .

2. Experimental

2.1. Materials

A Perkin-Elmer Atomic Absorption Spectrophotometer model AAnalyst 600 with Zeeman background correction system was used for all measurements. The Analyst 600 spectrophotometer was equipped with AS-800 autosampler and the whole system was controlled by means of AAWinlab control software running under Microsoft Windows program. All determinations were carried out at characteristic wavelength of V 318.4 nm, with a 0.7 nm band pass using hollow cathode lamp of vanadium (Perkin-Elmer), operating at 25 mA. Tubes of a transversely heated graphite atomizer (THGA) with integrated L'vov's platforms (Perkin-Elmer, Part Number B050-4033) were used for atomization of vanadium. Argon (Afrox, South Africa) was used as a protective gas throughout.

2.2. Reagents and standard solutions

To avoid possible reduction of V(V) to V(IV) compounds, V(V) standard solutions were prepared by appropriate dilution of stock solution, containing 1000 mg l^{-1} of V(V) as NH_4VO_3 (Merck) with 0.1 M Na_2CO_3 . Ultra-pure water (with a resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was obtained with a Milli-Q water purification system (Millipore Corp., USA) and was used for sample preparation and dilutions. Certified standard reference materials (CRM's) MESS-3 and PACS-2 (Marine sediments for trace metals), obtained from the National Research Council of Canada, (Ottawa, Canada), as well as BCR CRM 414 (Trace elements in plankton) were used for the evaluation of analytical results for the determination of total vanadium concentration.

3. Analytical procedure

3.1. Samples

Soil and grazing grass samples (*Chloris gayana*, *Digitaria eriantha* and *Eragrostis curvula*) were collected at a distance about 2 km from a vanadium mine in the North West Province of South Africa, on the field, where cattle died, presumably from V(V) poisoning [21]. The soil representing 20 cm of the upper soil layer and grass (without roots) were collected into plastic bags. *Chloris gayana*, *Digitaria eriantha* and *Eragrostis curvula* are the most widely distributed grass species in southern Africa and regarded as the best natural and cultivated pastures [22]. The samples were dried and ground in a tungsten carbide milling system to a grain size less than $200 \mu\text{m}$.

3.2. Sample preparation for the determination of V(V)

Twenty-five milliliter of 0.1 M Na_2CO_3 solution was added to approximately 0.25 g of soil or plant sample, accurately weighed in a 50 ml glass beaker. The contents was boiled for 15 min and, after cooling, transferred into 50 ml plastic tubes. The final volumes of sample solutions were adjusted to 25.0 ml with deionized water. Before the analysis, samples were filtered through a $0.45 \mu\text{m}$ filter and transferred into the sampling cups of the autosampler.

3.3. Sample preparation for the determination of total amount of vanadium

3.3.1. Soil samples

Because the soil may hold vanadium within the crystal lattice structure of specific minerals, in order to determine the total content of vanadium, complete digestion of samples was carried out. For this purpose, approximately 0.25 g of soil was first dissolved in a 10:1 mixture of concentrated HF (5 ml) and concentrated H_2SO_4 (0.5 ml), and heated till near dryness. Furthermore, 1 ml concentrated HClO_4 and 2 ml concentrated HF were added and again the mixture was heated to near dryness. Finally, 1 ml concentrated HClO_4 was added, and the sample was evaporated until the appearance of white fumes. The residue was then dissolved in 5 ml of 6 M HCl and diluted to 50.0 ml with deionized water. The resulting solution was then analyzed by ET-AAS.

3.3.2. Plant samples

0.25–0.50 g of the finely ground grass sample was placed in a muffle furnace in porcelain crucible. The temperature of the furnace was slowly increased from room temperature to 650°C in 1 h. The samples were ashed at this temperature for approximately 2.5 h, until a white or grey ash residue was obtained. The residue was dissolved in 0.5 ml of a mixture of 1:1 concentrated HNO_3 and concentrated HCl. The product was diluted to the mark in a 25.0 ml volumetric flask and filled to the volume.

Table 1
Temperature program for vanadium determination

Step	Temperature (°C)	Ramp (s)	Hold (s)	Internal gas flow (ml min ⁻¹)
1	100	1	10	250
2	250	5	15	250
3	1600	10	20	250
4	2600	0	5	0
5	2600	1	3	250

4. Results and discussion

4.1. Analytical results of V determination

Vanadium is not a simple element for the ET-AAS determination. It is a refractory element, which requires a high rate of heating and the use of freshly pyrolytically coated graphite tubes [23]. Problems like tailing of the absorbance signal, carbide formation and acid interferences have been encountered [24,25]. Atomization of vanadium from a matrix with a relatively high amount of Na₂CO₃ was carried out using the temperature program presented in Table 1. The absorption signals of vanadium obtained at different pyrolysis temperatures are shown in Fig. 1. Sixteen hundred degree Celsius was chosen as the optimum temperature. It was observed that after the treatment of samples at 1600 °C for a relatively long time (20 s), the atomization of vanadium could be completed in less than 5 s [17]. Atomization of V from standard solutions, which were obtained after the treatment of soil or plant samples with Na₂CO₃ do not differ in time of appearance and in time of complete atomization (Fig. 2). Possibly, this phenomenon can be explained by the complete separation of V(V) compounds from all other metals, which were initially present in solutions, but have been precipitated as insoluble carbonates or hydroxides during the treatment with Na₂CO₃.

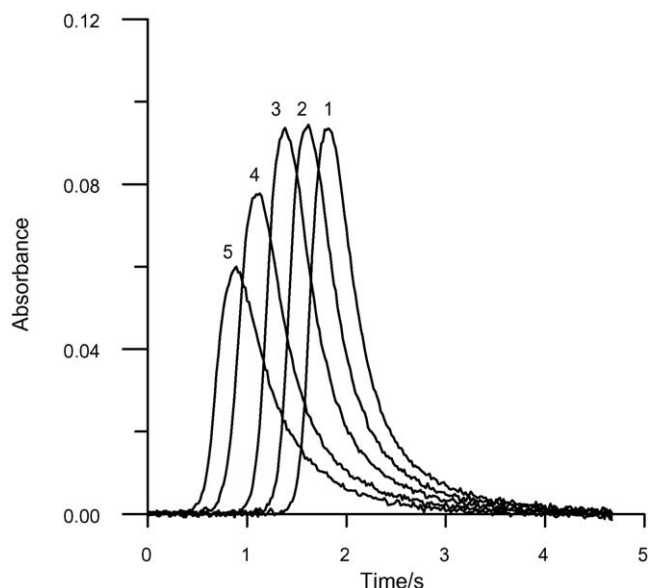


Fig. 1. Optimization of the pyrolysis temperature for V(V) determination: (1) 1400 °C; (2) 1600 °C; (3) 1800 °C; (4) 2000 °C; (5) 2200 °C.

The calibration graph (integrated absorbance versus concentration) was described by the equation $y = 0.0002x + 0.001$ with regression coefficient, $R^2 = 0.9978$ and the graph is linear up to 2000 $\mu\text{g l}^{-1}$ of vanadium.

The limit of detection (LOD) for vanadium determination calculated as the concentration corresponding to a signal equal to three times the standard deviation of the integrated absorbance for the blank solution, has been established using solutions of 0.1 M Na₂CO₃ as a blank. LOD was found to be about 2 $\mu\text{g l}^{-1}$ for a 10 μl sample aliquot ($n = 11$). With respect to the solid samples, assuming that 0.25 g of soil or plant sample after digestion has been adjusted to 25.0 ml, the LOD for vanadium determination in solid samples was estimated to be 0.2 $\mu\text{g g}^{-1}$.

4.2. Validation of results for V(V) determination

The leaching of V(V) compounds from plants has been tested by boiling plant samples with Na₂CO₃ for 1–20 min. The results showed that the extraction of V(V) could be completed after 15 min of boiling (Fig. 3). The repeatability of extraction of V(V) from the same plant sample, expressed as R.S.D., was found to be 7.6%.

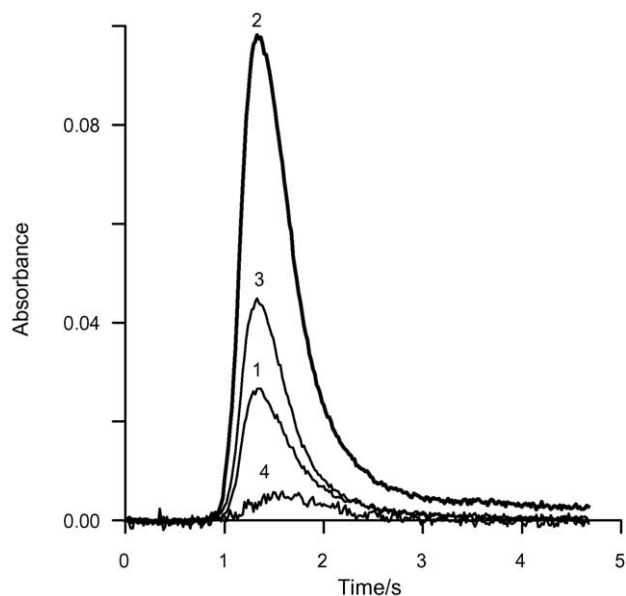


Fig. 2. Atomization of vanadium in THGA from V(V) standard solutions: (1) 125 $\mu\text{g l}^{-1}$; (2) 500 $\mu\text{g l}^{-1}$; (3 and 4) from the grass species *Chloris gayana* growing on contaminated field (13 $\mu\text{g g}^{-1}$) and from the uncontaminated area (0.8 $\mu\text{g g}^{-1}$).

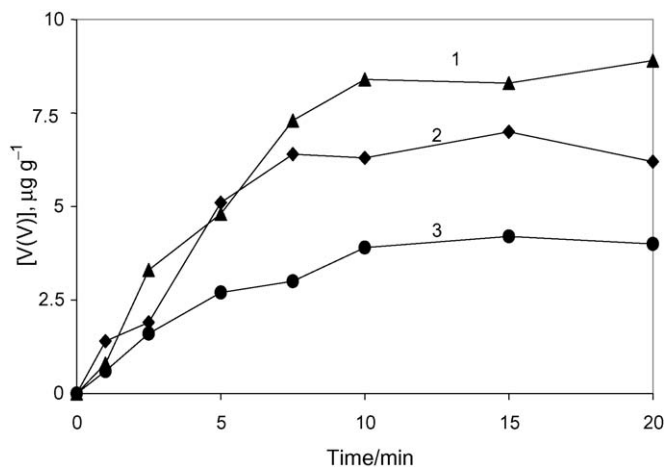


Fig. 3. Kinetic of V(V) extraction from plant species with 0.1 M Na₂CO₃: (1) *Chloris gayana*; (2) *Digitaria eriantha*; (3) *Eragrostis curvula*.

Since the CRM's with known amount of V(V) in soil are not available at present, validation of the method using certified reference material was not possible. In order to validate the method, recoveries of the spiked sample, were tested. For this purpose, the calculated volumes of V(V) standard stock solution were added to 0.25 g of soil samples to create concentrations of 7.5 and 15.0 µg g⁻¹. The recoveries of the added amount were found to be quite satisfactory, between 98 and 105%. Alternatively, the method of V(V) determination was validated by comparing the sum of concentrations of vanadium species with the total vanadium concentration. The results in Table 2 shows that the sum of [V(IV)] and [V(V)] is the same as total [V], in all samples at 95% level of confidence and therefore, the applied method has been validated.

4.3. Validation results for determination of total amount of vanadium

Results of total amount of vanadium determination in soil and plant samples were validated by using set of the CRM's: CRM 414, PACS-2 and MESS-3. Results for total vanadium determination in CRM's are in a good agreement with certified values (Table 2).

4.4. Results of V(V) determination in soil and plant samples

The results of the total amount and V(V) determination in soil and grass samples shown in Table 3 reveal very interesting information about distribution of V(V) species in analyzed samples. For example, soil samples were found to contain high

Table 2
Results of total vanadium determination in CRM's

CRM	Certified value (µg g ⁻¹)	Found value (µg g ⁻¹) (n=6, P=0.95)
CRM 414	8.10 ± 0.18	7.9 ± 0.4
MESS-3	243 ± 10	245 ± 12
PACS-2	133 ± 5	130 ± 8

Table 3
The distribution of V(IV) and V(V) in the samples

Sample	[V(IV)] (µg g ⁻¹)	[V(V)] (µg g ⁻¹)	Total [V] (µg g ⁻¹)
Grass 1	3.9 ± 0.04	2.6 ± 0.05	7.5 ± 0.15
Grass 2	4.5 ± 0.07	5.9 ± 0.10	10.9 ± 0.30
Soil 1	1790 ± 100	1660 ± 89	3505 ± 320
Soil 2	1500 ± 90	640 ± 13	2200 ± 210

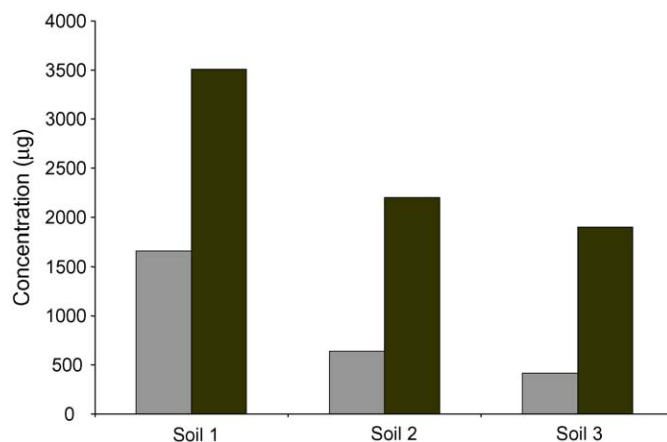


Fig. 4. Comparison of the distribution of V(V) content in soil samples: (■), [V(V)]; (■), [V].

concentration of total amount of vanadium, ranging from 1570 to 3600 µg g⁻¹ as well as high concentrations of V(V) species, in the range of 620–1680 µg g⁻¹. The highest content of V(V) compounds in soil was approximately 50% as shown in Fig. 4. The concentration of V(V) species in plants varied between 4 and 6 µg g⁻¹, while total amount of vanadium was higher, in the range 8–11 µg g⁻¹.

5. Conclusions

It has been found that vanadium speciation in soil and plants, based on classical analytical chemistry procedure of anion determination is easily achieved by the treatment of analyzed samples with 0.1 M Na₂CO₃ followed by the ETAAS determination.

Very good reproducibility of V(V) extraction from plant samples with 0.1 M Na₂CO₃ had been achieved, with the mean value of 7.6% (R.S.D.). LOD for vanadium determination in soil and plant samples was found to be 0.2 µg g⁻¹.

The results obtained in this study indicate that considerable amount of vanadium in soils is present as V(V) species (1640 µg g⁻¹), while total amount of vanadium was 3500 µg g⁻¹. The concentration of vanadium in plants was 4.3 ± 0.5 µg g⁻¹ for V(V) species and 11 ± 2 µg g⁻¹ for total amount of vanadium, respectively. Contaminated plants were visibly smaller in size as compared with the same plants growing on the areas that are remote from the vanadium mine where only 1.1 ± 0.3 µg g⁻¹ of total amount of vanadium were found.

The case of acute cattle's poisoning which had happened in the area some time ago [21], could be connected with ingestion of vanadium from the surface of grass, as the amount of V(V) in

grass itself (about $11 \mu\text{g g}^{-1}$) is not enough to poison the cattle in 48 h.

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