

Electrothermal atomic absorption spectrometric determination of vanadium(V) in soil after leaching with Na_2CO_3

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Abstract

Vanadium(V) is a potentially dangerous chemical pollutant, which coexists in the natural environment with V(IV) species. A method of selectively leaching V(V) species from soil is presented in this work, wherein samples are treated with 0.1 M Na_2CO_3 . The amount of V(V) species “liberated” is proportional to the concentration of CO_3^{2-} ions; 0.1 M Na_2CO_3 was found to be optimum. It was also shown that V(V) compounds are leached from soil in the presence of CO_2 .

The sum of V(V) and V(IV) in all soil samples was found to be in good agreement with the total content of vanadium in all soil samples after $\text{HF-H}_2\text{SO}_4\text{-HClO}_4$ digestion. The limit of detection for determination of vanadium in soil by electrothermal atomic absorption spectrometry was found to be $0.5 \mu\text{g g}^{-1}$. The method was applied to the determination of V(V) in Certified Reference Material Marine Sediments MESS-3 and PACS-2 (National Research Council of Canada). Of a total vanadium content of 243 and $133 \mu\text{g g}^{-1}$, 15 and $8 \mu\text{g g}^{-1}$ is present as V(V) species in CRM MESS-3 and PACS-2, respectively.

Results of V(IV) and V(V) determination in soils, taken near a vanadium mine in the North West Province of South Africa show that the concentration of V(V) species in some samples is relatively high, up to $2700 \mu\text{g g}^{-1}$, and varies from 0.6 to 50.8% of the total amount of vanadium.

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1. Introduction

The determination of contaminants in polluted soils has changed over the years from simple determination of the total concentrations of a specific element to a more sophisticated fractionation or “speciation” of its chemical forms. It is well established that speciation measurements are necessary for the study of toxicity, bio-availability, bio-accumulation and mobility of a specific element in the environment [1–3].

Vanadium in trace amounts (at the $\mu\text{g l}^{-1}$ level) is essential for normal cell growth, but can be toxic when present at higher, mg l^{-1} concentrations [4]. Of the two dominant chemical forms of vanadium, viz. V(IV) and V(V), it is recognized that V(V) as vanadate is more toxic than V(IV) present as vanadyl ion [5]. The toxicity of vanadium to-

wards plants and all living organisms arises from the structural analogy between vanadate (H_2VO_4^-) and phosphate (H_2PO_4^-) ions. The accumulation of vanadium in soil reduces the amount of phosphate that plays a very important physiological role on plants.

Although the global concentration of vanadium in soil ranges from trace levels to 400 mg kg^{-1} , with an average of 150 mg kg^{-1} , its concentration in soil depends mostly on the parent material from which the soils were formed [6]. Most minerals of vanadium are V(V) compounds [7].

In spite of the fact that V(V) is more toxic, little attention had been paid to the determination of V(V) species in soil. The US Environmental Protection Agency has not listed vanadium as a pollutant requiring urgent research and legislation. Consequently, there are few international standards and regulations relating to environmental pollution by vanadium.

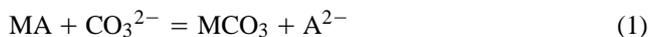
Because V(V) and Cr(VI) have similar chemical properties [8], they can exist under natural environmental

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conditions in corresponding anionic forms, as VO_3^- and CrO_4^{2-} ions. Both of them can be separated from V(IV) and Cr(III) compounds by treatment with a solution of Na_2CO_3 . The solution of Na_2CO_3 , when heated with solid samples, yields insoluble carbonates of many common metals or their hydrolysis products and releases anions present into solution according to the general equation:



Soluble carbonates and hydrogen carbonate-ion complexes are limited to a few elements (Na^+ , K^+ , Be^{2+} , Co^{3+} , HfO_2^+) and none is significant as an oxidizing agent.

When it comes to chromium speciation analysis in solid samples, a number of methods using an alkaline Na_2CO_3 solution for leaching Cr(VI) have been described [9]. Leaching with Na_2CO_3 (US EPA 3060A) [10] combined with a spectrophotometric detection method (US EPA 7196A) [11] provides satisfactory performance in quantifying the amount of Cr(VI). The results of Panichev et al. indicate that leaching of Cr(VI) from soil can be achieved with 0.1 M of Na_2CO_3 [12]. However, such methods of leaching have never been tested and applied to the speciation analysis of vanadium in soil samples. The development of reliable methods for the determination of V(V) in solid samples remains a challenging field of effort and improvement.

South Africa is one of the world's leading producers of vanadium minerals and accounts for about 30% of the current global output [13]. As such, soil near existing vanadium mines might be naturally enriched with vanadium or as a result of pollution. In the present study, a method was developed for the speciation analysis of vanadium in soil, based on the leaching of V(V) compounds with Na_2CO_3 and applied in the determination of vanadium species in soils near vanadium mine of the North West Province of South Africa.

2. Experimental

2.1. Materials

A Perkin-Elmer atomic absorption spectrometer model AAnalyst 600 with a Zeeman background correction system was used for all measurements. The spectrometer was equipped with an AS-800 autosampler and the entire system has been controlled by means of AAWinlab control software running under Microsoft Windows. All measurements were made at the 318.4 nm analytical line, with a 0.7 nm band pass using a hollow cathode lamp source (Perkin Elmer), operating at 25 mA. Transversely heated graphite furnace tubes (THGA) with integrated L'vov platforms (Perkin-Elmer, part N B050-4033) were used for atomization. Argon (Afrox, South Africa) was used as a sheath gas throughout.

2.2. Reagents and standard solutions

A standard stock solution containing 1000 mg l^{-1} V(V) as NH_4VO_3 (Merck) was used for preparation, by appropriate dilution, of working standards. Ultra-pure water (resistivity $18.2 \text{ M}\Omega\text{cm}$) was obtained from a Milli-Q water purification system (Millipore Corp.) and was used for all dilutions and samples preparation.

Certified standard reference materials (CRMs) MESS-3 and PACS-2, marine sediments for trace metals, obtained from the National Research Council of Canada (Ottawa) were used for the evaluation of analytical results for determination of vanadium.

3. Analytical procedure

3.1. Samples

Soil samples were collected from an area around the vanadium mine in North West Province of South Africa. The samples were dried and ground in a tungsten carbide milling system to a grain size less than $200 \mu\text{m}$. The soil samples represent the upper soil layer with a thickness of 20 cm.

3.2. Sample preparation

3.2.1. Determination of water-soluble fraction of V(V)

Approximately 0.25 g of the soil was accurately weighed into plastic tubes. To each of them 25.0 ml of deionized water was added and the contents periodically shaken for 24 h. Before analysis, the solution was filtered through a hydrophilic PVDF $0.45 \mu\text{m}$ filter.

3.2.2. Determination of V(V) extracted with CO_2

Approximately 1.0 g of soil was accurately weighed into a plastic bottle to which 250.0 ml of deionized water was added and the mixture was periodically shaken for 24 h. Before bubbling CO_2 , the samples of water, containing only the water-soluble fraction of V(V), were taken for analysis. CO_2 was bubbled through the suspension of soil at a flow rate of 50 ml min^{-1} . Filtered samples for analysis (1 ml) were taken every 10 min for periods of time ranging from 1 to 3 h. For the studies connected with the influence of pH on the efficiency of V(V) extraction, the pH of the soil suspension was gradually changed by the addition of increasing amounts of ammonia solution during continuous bubbling of CO_2 . For the determination of the equilibrium amount of V(V) released from soil to a solution at a specific pH, samples were taken 30 min after addition of each portion of ammonia.

3.2.3. Determination of V(V) extracted with Na_2CO_3

A 25.0 ml volume of 0.1 M Na_2CO_3 was added to approximately 0.25 g of soil, accurately weighed in a glass beaker. The contents were boiled for 15 min and filtered through a Whatman no. 1 filter paper. The precipitates were washed

several times with 0.1 M Na₂CO₃ and after that with deionized water. The final volumes of sample solutions were adjusted to 25.0 ml with deionized water.

3.2.4. Determination of V(IV)

The precipitates which were left after the filtration of samples treated with 0.1 M Na₂CO₃ were transferred on the filter paper to a platinum crucible and ashed in a muffle furnace at 600 °C for about 1 h. Because the residual solid may hold vanadium within the crystal structure of specific minerals, in order to evaluate the content of vanadium in this residual fraction, digestion was undertaken using the last step of Tessier's procedure [14]. The solid residue was first dissolved with a 10:1 mixture of HF (5 ml)–H₂SO₄ (0.5 ml) and heated till near dryness. Subsequently, a second addition of HClO₄ (1 ml) and HF (2 ml) was made and again the mixture was evaporated to near dryness. Finally, HClO₄ (1 ml) alone was added, and the sample was evaporated until the appearance of white fumes. The residue was then dissolved with 5 ml of 6 M HCl and diluted to 50.0 ml with deionized water. The resulting solution was then analyzed by electrothermal atomic absorption spectrometry (ET-AAS).

3.2.5. Determination of total amount of vanadium

The digestion of soil for the determination of total vanadium was accomplished using the last step of Tessier's procedure [14]. To approximately 0.25 g of soil sample, accurately weighed into a platinum crucible, 10 ml of conc. HF and 2 ml of conc. HClO₄ were added and heated to evaporate excess acid. To eliminate the remaining organic matrix, 2 ml of HClO₄ was added and heated to dryness. The residue was dissolved in 5 ml of 6 M HCl and diluted to 50.0 ml.

4. Results and discussions

4.1. Analytical results of V determination

Vanadium is not a simple element to determine by ET-AAS, as it is refractory and requires a high rate of heating and the use of a fresh pyrolytic graphite coating [15]. The peaks usually tail for 6 s or more. To minimize that problem, the furnace program summarized in Table 1 was used.

The total vanadium concentration in the soil samples was determined in digests obtained using the decomposition pro-

cedure described in Section 3.2.5. This technique was validated using two CRMs: PACS-2 and MESS-3. Results for total vanadium are in good agreement with the certified values, for example, for MESS-1, the certified value is 243 ± 5 j.Lg g⁻¹, and the found value was 245 ± 12 j.Lg g⁻¹.

4.2. Mechanism of the speciation analysis of V

The proposed procedure of V(V) speciation analysis is based on the chemical properties of V(V) species, which are of anionic origin, e.g. VO₅³⁻, V₂O₇⁴⁻ or VO₃⁻, that can exist as different minerals in non-soluble fractions of soil. In order to convert non-soluble compounds of V(V) to the soluble forms, soil samples can be treated with Na₂CO₃. In this case all non-soluble V(V) compounds form soluble sodium metavanadate, Na₂VO₃, while V(IV) compounds remained in the precipitates. The analysis of the residue would give the amount of V(IV) in the sample. Even if solubility differences are moderately unfavourable, an increased concentration of carbonate ion assures adequate conversion [16].

4.3. Extraction of V(V) from soil

In order to obtain the maximum level of V(V) which can be extracted from soil, various concentrations of Na₂CO₃ ranging from 1 × 10⁻³ to 1 M were utilized. The results of the conventional extraction of V(V) from soil are presented in Fig. 1. The efficiency of extraction strongly depends on the concentration of the extractant. The highest and the same amount of V(V) was extracted with 0.1 M Na₂CO₃ and 1 M Na₂CO₃. Since the application of 1 M Na₂CO₃ is less practical owing to the introduction of a large amount of matrix into the graphite furnace over a prolonged period of time, 0.1 M Na₂CO₃ was chosen.

In order to ensure that V(V) is completely extracted with 0.1 M Na₂CO₃ and that this amount may be used for determination of "total" V(V) in soil for speciation analysis, multiple extractions of V(V) were conducted using fresh portions of 0.1 M Na₂CO₃ on the same sample of soil. After a single extraction with 0.1 M Na₂CO₃, about 97% of the available V(V) goes into solution, while the second extraction accommodates the remaining fraction.

The effect of the soil weight-to-volume ratio of 0.1 M Na₂CO₃ on the amount of V(V) extracted from soil was also studied. This was achieved by keeping the volume of 0.1 M Na₂CO₃ solution constant while changing the soil weight. The ratios investigated were 1:400, 1:200, 1:100 and 1:50. Fig. 2 shows that at a ratio of 1:400 to 1:100 the extracted amount was practically the same, while at a ratio of 1:50 the extracted amount of V(V) was statistically lower.

4.4. Influence of pH

In a solution saturated with CO₂ under normal atmospheric pressure, the concentration of CO₃²⁻ ions is pH

Table 1
ET-AAS furnace programme for atomization of vanadium

Step	Temperature (°C)	Ramp (s)	Hold (s)	Internal gas flow (mlmin ⁻¹)
1	120	1	10	250
2	250	5	10	250
3	1800	5	20	250
4	2600	0	5	0
5	2600	1	3	250

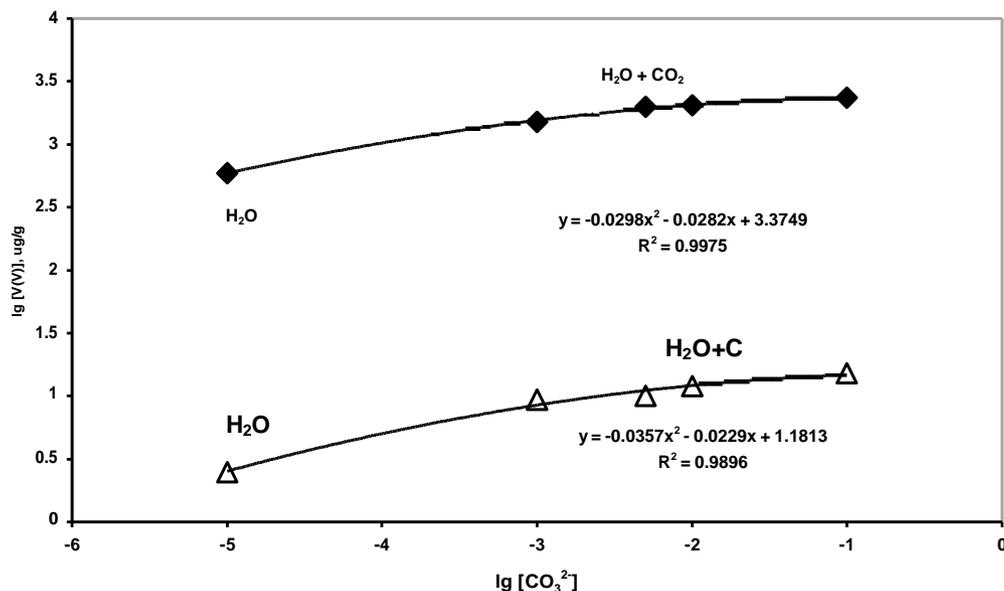


Fig. 1. Extraction of V(V) from soil by Na₂CO₃: (+), Soil 2; (6), Soil 4; H₂O is water-soluble fraction of V(V); H₂O + CO₂ is amount of V(V) extracted with bubbling CO₂; the remaining are for Na₂CO₃ of increasing concentration.

dependent, and can be described [17] by the following equations:

$$\begin{aligned}
 [\text{H}^+]^2[\text{CO}_3^{2-}] &= K = 7.24 \times 10^{-19} \text{ or } [\text{CO}_3^{2-}] \\
 &= \frac{7.24 \times 10^{-19}}{[\text{H}^+]^2} \quad (2)
 \end{aligned}$$

The increase in solubility of V(V) species with an increase in the pH of the saturated CO₂ solution is expected. The influence of the pH of a saturated solution of CO₂ on the level of V(V) extracted from soil is shown in Fig. 3. It has been found that the amount of V(V) extracted is proportional to the pH, with the highest amounts corresponding to the pH of 0.1 M Na₂CO₃.

4.5. Validation of the analytical method

Since certified reference materials for V(IV) and V(V) in soil are not available at present, validation of the method for vanadium speciation analysis using this approach was not possible. In order to validate the method, the sum of V(IV) and V(V) determined from several soil samples was checked for correlation with the total concentration of vanadium determined by an independent method. From the results, presented in Table 2, the sum of V(IV) and V(V) concentrations perfectly correlate with the total concentration of vanadium determined after complete decomposition of the soil samples.

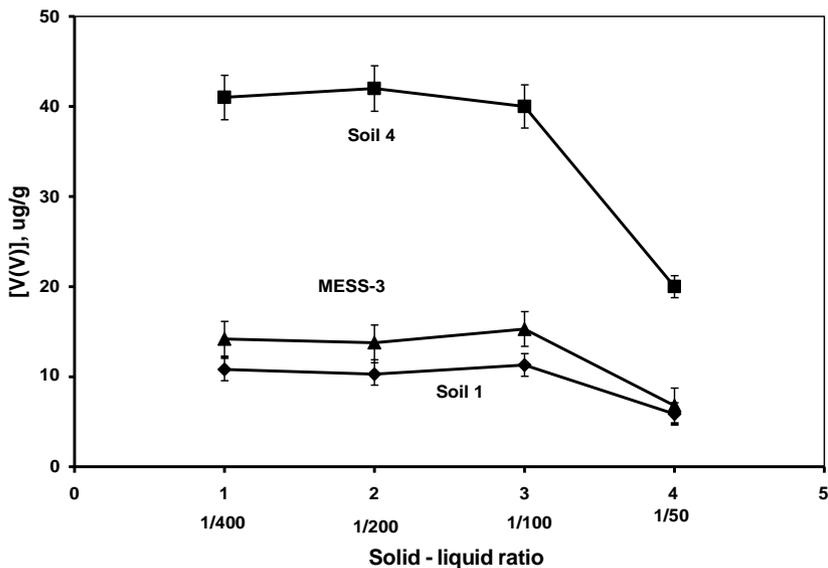


Fig. 2. The influence of sample mass-to-extractant volume ratio on the extraction efficiency of V(V).

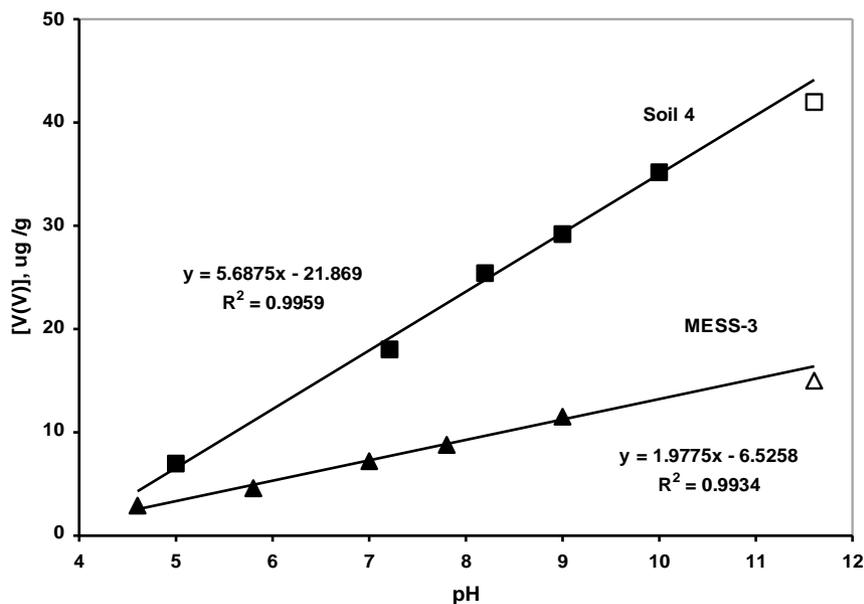


Fig. 3. Influence of pH of the saturated CO_2 solution on the extraction of V(V) from soil: (\bullet), (\blacktriangle), with continuous bubbling of carbon dioxide at different pH; (\square), (\triangle), corresponding to the pH of 0.1 M Na_2CO_3 taken from the previous experiments.

Table 2

Results for V(IV), V(V) and total V determination in soil samples and CRMs ($\mu\text{g g}^{-1}$)

Sample	Water-soluble V[V]	[V(V)] ^a	[V(IV)] ^a	{[V(IV)] + V(V)} ^b	{Total [V]} ^c	V(V) (%)
Soil 1	0.9 ± 0.2	11.2 ± 1.0	520.1 ± 30	533	548 ± 39	2.0
Soil 2	590 ± 25	2710 ± 150	2846 ± 155	5556	5340 ± 267	51
Soil 3	2.6 ± 0.4	17.0 ± 1.2	646 ± 25	646	678 ± 32	2.5
Soil 4	1.3 ± 0.2	42.0 ± 0.6	7120 ± 200	7150	7160 ± 215	0.6
MESS-3	0.6 ± 0.1	14.5 ± 0.4	221 ± 15	236	243 ± 12	6.0
PACS-2	≤ 0.5	8.8 ± 0.4	^d		129 ± 6	6.8

^a Average of three replicates for each sample.

^b Sum of [V(IV)] and [V(V)] in each sample.

^c Total [V] determined by an independent method.

^d Not measured.

4.6. Analysis of real samples

Results for the determination of V(V), V(IV) and total vanadium are summarized in Table 2. The concentration of V(V) in the water-soluble fraction of soil was found to be rather small, with an average value ranging from 2 to $8 \mu\text{g g}^{-1}$, except for Soil 2. The equilibrium concentration of V(V) in the water-soluble fraction does not change with time, even after 3 months of storage of the soil samples as a water slurry.

The concentration of V(V) in the soils, extracted with 0.1 M Na_2CO_3 was found to be quite different, with respect to the total amount of vanadium. For example, Soil 1 and Soil 4 were found to contain 11.2 ± 1.0 and $42.0 \pm 0.6 \mu\text{g g}^{-1}$ out of the total vanadium concentration of 548 ± 39 and $7160 \pm 215 \mu\text{g g}^{-1}$, respectively, i.e. 2.3% in Soil 1 and 0.6% in Soil 4. In Soil 2, in contrast to all other samples, about 51% of total vanadium is present as V(V) compounds. This soil sample was taken from the grazing land after the vanadium mine dam collapsed some years ago. This may be

the reason for the enrichment of soil with V(V) species. The toxic properties of V(V) compounds could be the reason for the poisoning of cattle grazing in the area [18].

5. Conclusions

The sequential extraction procedure developed by Panichev et al. [12] for Cr(VI) was examined for the speciation analysis of vanadium in soil. It has been found that vanadium speciation analysis in soil samples is easily achieved by treatment with 0.1 M Na_2CO_3 followed by the ET-AAS determination of V(V). It was also shown that the presence of CO_2 in the soil–water system leaches V(V) from soil with high efficiency at higher pH. The highest extraction efficiency was obtained with 0.1 M Na_2CO_3 .

The results obtained in this study indicate that some soils near the vanadium mine of North West Province of South Africa have very high levels of total vanadium (up to $7160 \mu\text{g g}^{-1}$) and that considerable vanadium, up to 50.8%,

is present as V(V). Because V(V) species are more soluble, they can be leached out of soil to the ground water.

For the first time the concentration of V(V) was determined in the CRMs MESS-3 and PACS-2.

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