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Hazardous impact and translocation of vanadium (V) species from soil to different vegetables and grasses grown in the vicinity of thermal power plant

Sumaira Khan [1], Tasneem Gul Kazi*, Nida Fatima Kolachi [1], Jameel Ahmed Baig [1], Hassan Imran Afridi [1], Abdul Qadir Shah [1], Sham Kumar, Faheem Shah

Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan

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ABSTRACT

The distribution of vanadium (V) species in soil (test soil), vegetables and grasses, collected from the vicinity of a thermal power plant has been studied. For comparison purpose soil (control soil), same vegetable and grass samples were collected from agricultural land devoid of any industrial area. A simple and efficient ultrasonic assisted extraction method has been developed for the extraction of V^{5+} species from soil, vegetable and grass samples using Na_2CO_3 in the range of 0.1–0.5 mol/L. For comparison purpose same sub samples were also extracted by conventional heating method. The total and V species were determined by electrothermal atomic absorption spectrometry using different modifiers. The validity of V^{5+} and V^{4+} determination had been confirmed by the spike recovery and total amount of V by the analysis of CRM 1570 (spinach leave) and sub samples of agricultural soil. The concentration of total V was found in the range of 90–215 and 11.4–42.3 μg/g in test and control soil samples, respectively. The contents of V^{5+} and total V in vegetables and grasses grown around the thermal power plant were found in the range of 2.9–5.25 and 8.74–14.9 μg/g, respectively, which were significantly higher than those values obtained from vegetables and fodders grown in non exposed agricultural site ($P < 0.01$). Statistical evaluations indicate that the sum of concentrations of V^{5+} and V^{4+} species was not significantly different from total concentration of V in same sub samples of vegetable, grass and soil of both origins, at 95% level of confidence.

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1. Introduction

Vanadium is an essential trace element, with specific physiological functions [1] and has been found to possess the properties that reduce the effects of different chronic physiological disorders [2,3]. However, numerous reports have warned about its carcinogenic and toxic effects from excessive exposure [4,5]. The compounds of V are released in atmosphere by burning of fossil fuels and from various industrial processes [6,7]. In soil, V accompanies with iron oxides and organic fraction. An average amount of V in soils ranges from 10 to 220 mg/kg. Soils from industrial areas can have more V due to anthropogenic activities such as emission by petroleum refineries, metal plants and phosphorite treating factories [8]. The biological and physiological characteristics of V are depending upon its oxidation states. Generally, V exists in two oxidation states (tetravalent and pentavalent) in the environmental samples. The high concentrations of V^{5+} in water are toxic to both plants and animals [9,10], because it is more toxic than V^{4+} [11,12]. Therefore, the separation and quantification of V^{5+} species is important for evaluating the potential risk to the environmental and biological systems rather than determining total V contents [13,14].

In spite of the fact that V^{5+} is the most toxic species [15], little attention has been paid to the determination of V^{5+} species in soil and plants. The United States of America's Environmental Protection Agency (EPA) has not listed V as a pollutant requiring urgent research and legislation, because there was no evidence about the toxic risk on population, either through deficiency or over exposure to V [16]. Consequently, there are few countries where standards and regulations for environmental pollution in soil with V are accepted. For example, in Russia the maximum tolerance limit of V is 150 μg/g for agricultural soil [17].

Several analytical techniques have been used to determine V and its species at trace levels in various samples [18,19]. Electrothermal atomic absorption spectrometry (ETAAS) is mostly the technique of choice for trace element analysis due to its high sensitivity, low sample consumption, simplicity in operation and reduced matrix effects [20]. Most publications concerning the speciation of V in environmental samples deal with liquid samples such as water

* Corresponding author. Tel.: +92 022 92134729; fax: +92 022 9213431.
E-mail addresses: skhanzai@gmail.com (S. Khan), tgkazi@yahoo.com, kazitg@ceacsu.edu.pk (T.G. Kazi), nidafatima6@gmail.com (N.F. Kolachi), jab_mughal@yahoo.com (J.A. Baig), hassanimranafridi@yahoo.com (H.I. Afridi), aqshah07@yahoo.com (A.Q. Shah).
[1] Tel.: +92 022 92134729; fax: +92 022 9213431.

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[21,22], while selective determination of V species in solids, till now requires additional efforts [8,23,24]. Finally, there is no official method of V speciation in solid samples.

Conventional heating method is extremely time consuming. There has been considerable recent interest in the use of ultrasonic energy to improve the extraction of analyte from environmental and biological samples. Ultrasonic energy can be considered as an alternative for solid sample pre-treatment because this energy facilitates and accelerates some steps, such as dissolution, fusion and leaching among others [25]. The use of ultrasound power has been investigated to speed up the different extraction methods because it has long been recognized that, the cavitational effect created by ultrasound waves can break down the particle size, exposing a fresh surface and aggressively agitating the solution system [26]. Ultrasonic effects have been exploited for sample preparation in agricultural, biological and environmental applications [27].

In present work, the translocation of vanadium species (V^{4+} and V^{5+}) from soil to different vegetables and grasses grown in the vicinity of thermal power plant was evaluated. For this purpose a rapid, efficient and economic method was developed for the speciation of V in soil and plants. So, the levels of this pollutant can easily be monitored in routine analysis. The analytical methodologies for extraction of V species from all under study samples were based on ultrasonic assisted extraction method, which is less time-consuming as compared to conventional heating system on electric hot plate. The soil, vegetables and grasses were collected from agricultural field near thermal plant as test soil and crop samples. For comparative purposes soil, same vegetable and grass samples were collected from agricultural field devoid of any industrial activity termed as control soil and crop samples. The water and EDTA extractable V were also determined from soil samples of both origins.

2. Experimental

2.1. Instrumentation

The ultrasonic extractions were carried out with a Sonicor, Model No. SC-121TH (Sonicor Instrument Corporation Copiague, NY, USA) with technical specifications; timer 0–30 min, 220 V, 50/60 Hz, intensification frequency 35. Centrifugation was carried out to separate the supernatant from the sample extracts by, WIROWKA Laboratoryjna type WE-1, no. 6933 centrifuge; speeds range 0–6000 rpm, timer 0–60 min, 220/50 Hz (Mechanika Phecyzyjna, Poland). A WTW pH meter was employed for the determination of pH in soil and reagents. A Perkin Elmer model AAnalyst 700 atomic absorption spectrometer equipped with a deuterium background correction system and electrothermal atomizer, HGA-400 was used. The V was measured at 318.5 nm with a V hollow cathode lamp and a slit width of 0.7 nm. The pyrocoated graphite tubes with an integrated L'vov platform and peak area integration were used. The graphite furnace program for V determination was, temperature (°C)/ramp time (s)/hold time (s) for drying (100–150/1/10), ashing (1600/15/20) and atomization (2600/0/4), respectively, with 200 mL/min of argon flow rate.

2.2. Reagents

The chemicals used were of analytical grade, and all solutions were prepared with ultrapure water. Ultrapure water obtained from ELGA lab water system (Bucks, UK), was used throughout the work. To avoid possible reduction of V^{5+} to V^{4+} compounds, V^{5+} standard solutions were prepared by dilution of stock solution, containing 1000 mg/L of V^{5+} as NH_4VO_3 (Fluka Kamika) with 0.1 mol/L Na_2CO_3. Extractant solution 0.05 mol/L, EDTA at pH 7 was prepared by dissolving disodium dihydrogenethylenediaminetetraacetate salt dihydrate ($Na_2EDTA{\cdot}2H_2O$ Merck). The BaF_2 was used as chemical modifier by dissolving 1 g of the salt (99.99% purity, Aldrich, Milwaukee WI, USA) in 100 mL of ultrapure water. The palladium nitrate solution of 1000 mg/L was prepared by dissolving 106.6 mg Pd $(NO_3)_2$ (Merck) in 50 mL of 0.1% (v/v) HNO_3. A 1.0 mol/L solution of $Mg(NO_3)_2$ (Merck) was prepared by dissolving 14.8 g $Mg(NO_3)_2$ in 100 mL of deionized water [28]. All glassware and polyethylene bottles were kept overnight by soaking in 10% HNO_3, and cleaned by rinsing repeatedly with ultrapure water prior to use.

2.3. Sampling of soil, vegetable and grass

Six batches of surface soils, grazing grass and vegetable samples were collected from agricultural soil around 4–5 km of the thermal power plant, situated in Jamshoro, Sindh (Pakistan), with the help of stainless steel auger during 2008–2009. For comparative purpose soil, same vegetable and grass samples were also collected from Mehrabpur, Pakistan (agricultural area) devoid of any power plant and industries. Grass samples included lucerne (*Medicago sativa*) and berseem (*Trifolium alexandrinum*), while vegetables sampled included bitter gourd (*Momordica charantia* L.), carrot (*Daucus carota* L.), cluster beans (*Cyamopiss tetragonoloba* L.), coriander (*Coriandrum sativum* L.), okra (*Abelmoschus esculentus* L.), onion (*Allium cepa* L.), pepper mint (*Mentha piperita* L.), potatoes (*Solanum tubersum* L.), spinach (*Spinacia oleracea* L.), sponge gourd (*Luffa cylindrica* L.) and peas (*Pisum sativum* L.) (twenty samples of each) collected from the vicinity of thermal power plant, as test crop samples (TCS). The same vegetables and grass samples were collected from agricultural sites of Mehrabpur as control samples (CCS). After delivery to the laboratory, samples of vegetables and grasses were stored at 4 °C till further analysis. All crop samples were put through a three steps washing sequence, which involved agitating and rinsing first with distilled water followed by three separate washings with deionized water. The clean vegetable and grass samples were air-dried, and placed in an electric oven at 70 °C for 48–72 h depending on the sample size. All soil samples were spread on plastic trays in fume cupboards and allowed to dry at ambient temperature for 8 days. The dried soil, grass and vegetable samples were homogenized by grinding in an agate mortar and sieved through a nylon sieve (<75 μm mesh size). The final samples were kept in labeled polypropylene containers at ambient temperature before analysis.

2.4. Analytical procedures

2.4.1. Physico-chemical characteristics of soil samples

The physicochemical parameters such as pH, organic matter (OM) and cation exchange capacity (CEC) for soil samples of both agricultural fields were determined by using standard methods [29]. The pH was determined for each batch, using a ratio of soil to ultra-pure water of 1:2.5 (w/v). The OM content was obtained by ashing triplicate samples of each batch in muffle furnace at 540 °C for 6 h. The change in the dry weight of soils before and after ashing was used to calculate the OM content [30]. The CEC was determined by ammonium acetate at pH 7 using standard methods [31]. All analyses were performed in triplicate. Blanks were run simultaneously. The results are shown in Table 1. The resulted data indicated that there is no significant difference in understudy physico-chemical parameters, except the pH of test soil samples was lower than control soil samples.

Table 1
Physico-chemical characteristics of the agricultural soil samples collected from the vicinity of thermal power plant (test soil) and non-industrial area (control soil).

Parameters	Test soil	Control soil
pH of soils	6.8–7.6	7.4–8.2
Organic matter (%)	23.8 ± 2.13	24.7 ± 2.23
Sand (%)	42.5 ± 3.12	41.0 ± 2.5
Silt (%)	32.1 ± 1.84	29.2 ± 1.48
Clay (%)	3.4 ± 0.67	3.9 ± 0.58
CEC (mequiv./100 g)	14.3 ± 1.2	14.8 ± 2.40

2.4.2. Water-soluble fraction of V

Triplicate samples of each batch of air-dried soil samples (1 g) were weighed into extraction bottles. Added 20 mL of ultrapure water and shaken on a mechanical end-over-end shaker at a speed of 30 rpm for 1 h at room temperature. The extract was separated by centrifuging at 3000 rpm and the supernatant liquid was filtered through Whatman 42 filter paper and stored in polyethylene bottles at 4 °C until analysis.Extraction of V by 0.05 mol/L EDTA

Triplicate 0.5 g of soil samples of each batch were weighed directly in the extraction bottles (250 mL polypropylene bottles) and 50 mL of 0.05 mol/L EDTA [32,33] was added. The mixture was shaken in a mechanical end-over-end shaker at a speed of 30 rpm for 1 h at room temperature. The extract was separated by centrifuging at 3000 rpm, and the supernatant liquid was filtered and stored in polyethylene bottles at 4 °C until analysis.

2.4.4. Extraction procedure of V^{5+} from soil, vegetable and grass samples

0.5 g and 0.25 g of replicate six sub samples of dried crops and soil samples, respectively were weighed in 100 mL flasks, and 25.0 mL of 0.1–0.5 mol/L Na_2CO_3 was added. All flasks were shaken energetically and the mixtures were subjected to an ultrasound water bath for different time intervals (2–10 min) at constant temperature (80 °C), while replicate six sub samples of same plant and soil were treated with 25 mL of 0.1–0.5 mol/L of Na_2CO_3 and heated on an electric hot plate at 80 °C for 10–60 min. The contents of the flasks were cooled and transferred into a 50 mL plastic tube and subjected to centrifugation at 3000 rpm (5 min). The supernatant aliquots of each sample were transferred to 25 mL volumetric flasks and made volume with deionized water, then subjected to electrothermal atomic absorption spectrometer with different modifiers.

2.4.5. Determination of V^{4+} and total V in soil, vegetable and grass samples

The residue of each samples was obtained after extraction with Na_2CO_3, while weighed triplicate 0.25 g of soil and 0.5 g of vegetable and grass samples of both origins and treated with 6 mL of mixture of concentrated acid HF:H_2SO_4:HNO_3:H_2O_2 (1:1:1:1), kept at room temperature for 15 min, then heated on a electric hot plate till semi dried mass. The residue was dissolved in 5 mL of 6 mol/L HCl and diluted to 25 mL with deionized water.

2.5. Validity and applicability

The calibration curve for both V species was linear in the range of 10–50 μg/L and is described by the following equations, $y = (0.13[V^{5+}] + 0.0026)$ and $y = (0.11[V^{4+}] + 0.0031)$ with correlation coefficient of 0.998 and 0.993, respectively. The limit of detection (LOD) for both species of V determination has been established using blank solutions of 0.2 mol/L of Na_2CO_3. The limit of detection (LOD), calculated as the amount of V required to yield signal-to-noise ratio of (3σ) was 2 μg/L for both species. The results of these standards indicated that the calibration of V can be performed using any V standard irrespective of the oxidation state.

Table 2
Validation of vanadium by standard addition method in a control soil samples extracting with 0.2 mol/L Na_2CO_3 (μg/g) using ultrasonic assisted extraction (UAE) and conventional heating method (CHM).

V^{5+}/V^{4+}	V^{5+}		V^{4+}
	CHM	UAE	CHM
0.0	1.67 ± 0.42[a]	1.70 ± 0.39	17.53 ± 3.17
5.0	6.48 ± 0.52 (97.1)[b]	6.52 ± 0.58 (97.3)	21.8 ± 2.02 (96.8)
10.0	11.4 ± 1.04 (97.7)	11.5 ± 0.92 (98.3)	26.8 ± 2.18 (97.3)
20.0	21.4 ± 1.85 (98.8)	21.6 ± 1.72 (99.5)	36.7 ± 3.24 (97.8)
SRM1570 (spinach) certified total vanadium 0.57 (μg/g)			
0.0	0.24 ± 0.014	0.244 ± 0.012	0.32 ± 0.026
2.0	2.20 ± 0.17 (98.2)	2.22 ± 0.19 (98.9)	2.28 ± 0.20 (98.3)
5.0	5.20 ± 0.45 (99.2)	5.21 ± 0.41 (99.4)	5.30 ± 0.43 (99.6)
10.0	10.21 ± 0.81 (99.7)	10.23 ± 0.92 (99.9)	10.29 ± 0.83 (99.7)

[a] Average value ± confidence interval ($P = 0.05$).
[b] ( ): values in parenthesis %recovery.

In present study the validation of extraction methods by conventional heating method (CHM) and ultrasonic assisted extraction method (UEA), using certified reference material of soil was not possible because certified reference material with known amount of V^{5+} and V^{4+} in soil is not available. While for plant samples SRM 1570 (spinach leave) with certified value of total V was used. In order to validate the method, recoveries of the spiked sub samples of soil and SRM 1570 were tested. For this purpose, known amount of V^{5+} and V^{4+} was added at three concentration levels in a sub sample of soil and SRM extracted with optimum concentration of Na_2CO_3 (0.2 mol/L) and heated with CHM and UAE. The recoveries of the added amount were found to be quite satisfactory, between 97 and 99% (Table 2). It was observed that with the use of UAE the recovery was enhanced 1–2% of those values obtained by CHS. For subsequent extractions of V^{5+} in soils and crops, UAE method was used. Alternatively, the method of V determinations was validated by comparing the sum of concentrations of both V species with the total V concentration. The results in Tables 3 and 4 indicated that no significant difference at 95% confidence level was observed between sum of (V^{5+} and V^{4+}), total V in soil and understudy crop samples of both origins.

3. Results and discussion

The distribution of V between different oxidation states plays an important role in environmental chemistry. The two most common forms, V^{5+} and V^{4+} have different toxicity, so speciation analysis of this element is necessary for environmental and biological samples.

3.1. Optimization of extraction of V^{5+} from soil and crop samples

The performance of UAE procedure with respect to conventionally heating was assessed by the extraction of sub samples of agricultural soil. After optimizing parameter of the UAE method such as sonication time, the full extraction experimental was carried out on replicate six sub sample of a soil after three point

Table 3
Determination of total, extractable and different species of V in soil samples collected from different agricultural fields (μg/g).

Total/extractable V	Test soil	Control soil
V^{5+}	35.9 ± 4.8[a]	1.67 ± 0.02
V^{4+}	76.34 ± 9.5	17.53 ± 3.17
$V^{5+} + V^{4+}$	112 ± 13.4	19.2 ± 4.95
Total V	110 ± 12.4	18.7 ± 3.85
Water extractable	2.23 ± 0.28	0.56 ± 0.12
EDTA extractable	2.56 ± 0.23	1.12 ± 0.01

[a] Average values reported as mean ± standard deviation.

Table 4
The distribution of V^{5+} and V^{4+} in the vegetable and grass samples (μg/g).

Vegetables/grasses English name (botanical name)	Jamshoro				Mehrabpur			
	V^{5+}	V^{4+}	$V^{5+}+V^{4+}$	Total V	V^{5+}	V^{4+}	$V^{5+}+V^{4+}$	Total V
Lucerne (*Medicago sativa*)	3.43 ± 0.21	5.42 ± 0.43	8.85 ± 0.71	9.57 ± 0.08	1.23 ± 0.09	1.87 ± 0.15	3.09 ± 0.03	3.43 ± 0.03
Berseem (*Trifolium alexandrinum*)	4.52 ± 0.23	8.23 ± 0.66	12.75 ± 1.02	13.65 ± 0.11	1.62 ± 0.12	2.84 ± 0.23	4.45 ± 0.04	4.86 ± 0.04
Bitter gourd (*Momordica charantia* L.)	3.21 ± 0.29	5.85 ± 0.45	9.06 ± 0.72	9.78 ± 0.08	1.12 ± 0.09	1.95 ± 0.16	3.09 ± 0.03	3.12 ± 0.02
Carrot (*Daucus carota* L.)	5.25 ± 0.47	8.74 ± 0.70	13.99 ± 1.12	14.9 ± 0.12	1.88 ± 0.14	3.01 ± 0.24	4.89 ± 0.04	4.98 ± 0.04
Cluster beans (*Cyamopiss tetragonoloba* L.)	2.95 ± 0.27	4.78 ± 0.38	7.73 ± 0.42	8.74 ± 0.07	1.05 ± 0.08	1.65 ± 0.13	2.70 ± 0.02	2.95 ± 0.02
Coriander (*Coriandrum sativum* L.)	3.42 ± 0.31	5.85 ± 0.47	9.27 ± 0.64	10.12 ± 0.08	1.22 ± 0.09	2.02 ± 0.16	3.24 ± 0.03	3.45 ± 0.03
Okra (*Abelmoschus esculentus* L.)	4.32 ± 0.39	6.69 ± 0.54	11.01 ± 0.88	12.53 ± 0.10	1.54 ± 0.12	2.31 ± 0.18	3.85 ± 0.03	4.15 ± 0.03
Onion (*Allium cepa* L.)	4.82 ± 0.43	8.34 ± 0.67	13.16 ± 1.05	13.98 ± 0.11	1.72 ± 0.13	2.88 ± 0.23	4.60 ± 0.04	4.85 ± 0.02
Pepper mint (*Mentha piperita* L.)	3.86 ± 0.35	6.32 ± 0.51	10.18 ± 0.81	10.85 ± 0.09	1.38 ± 0.10	2.18 ± 0.17	3.56 ± 0.03	4.47 ± 0.03
Potatoes (*Solanum tubersum* L.)	4.65 ± 0.42	7.82 ± 0.63	12.47 ± 1.00	13.54 ± 0.11	1.66 ± 0.12	2.70 ± 0.22	4.36 ± 0.04	4.55 ± 0.03
Spinach (*Spinacia oleracea* L.)	3.45 ± 0.31	4.87 ± 0.46	8.32 ± 0.67	9.15 ± 0.07	1.23 ± 0.09	1.68 ± 0.13	2.91 ± 0.02	3.83 ± 0.02
Peas (*Pisum sativum* L.)	3.12 ± 0.28	5.78 ± 0.52	8.9 ± 0.71	9.82 ± 0.08	1.11 ± 0.08	1.99 ± 0.16	3.11 ± 0.03	4.13 ± 0.03

addition of standards of both V species (5–20 μg/L) (Table 2). Several concentrations of (Na_2CO_3) were used to extract V^{5+} from soil, ground vegetable and grass samples to obtain the most appropriate concentration of the reagent solution that can transfer the total concentration of the analyte species into solution. Precautions were made so as not to use extremely concentrated solution of Na_2CO_3 to avoid introducing severe matrix into the graphite tube. It was observed that 0.2 mol/L Na_2CO_3 was the least concentration of reagent to extract the optimum amount of V^{5+} from soil and crop samples. The method was also optimized by conventionally heating on a hot plate at different time intervals (10–60 min). The results of this investigation presented in Fig. 1, show that 0.2 mol/L of Na_2CO_3 extracts optimum amount of V^{5+} species from soil and vegetables at 25 and 15 min, respectively after CHM. Our results are not consistent with other researcher who used 0.1 mol/L Na_2CO_3, because at lower concentration of extracting solution 30–35% recovery was reduced [12,13,18]. The V^{5+} was extracted in ultrasonic bath within 10 and 5 min from soil and crop samples as compared to those obtained by CHM in 25–30 min, respectively. The repeatability of extraction of V^{5+} from the same soil and vegetable samples, expressed as R.S.D. was found <10%.

3.2. Bioavailable fractions of vanadium in soil

To know the potential risk of V to plants, animals and human beings, it is necessary to evaluate its mobile and/or available fractions in vicinity of thermal power plant (Jamshoro) and agricultural (Mehrabpur) soil samples. Researchers have been tried to measure the plant-available fraction of metals in soils using different extraction procedures. The mobility of trace metals, their bioavailability and related eco-toxicity to plants, depend strongly on their specific chemical forms or ways of binding [34,35]. The lixiviation of metals from soils using selective extractants gives valuable information,

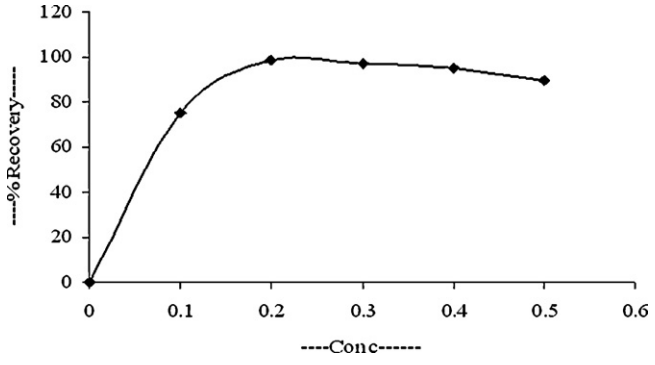

Fig. 1. Effects of the concentrations of extracting reagents (Na_2CO_3) on the recovery of V^{5+} in soil samples.

especially for agricultural purposes. The method was validated by a group of European researchers coordinated by the Measurements and Testing Program of the Commission of the European Community, in single extraction procedures [36] are EDTA 0.05 mol/L, in either di-sodium or di-ammonium salt form has been used extensively as an extractant of potentially plant available metals. In some trials, EDTA was found to give a very good indication of the toxic metal pollution hazard in soils as well as being a reliable test for predicting plant-available metals [37]. Neutral salt extractants are generally weaker extractants than EDTA and give an indication of the immediately exchangeable (therefore immediately plant-available) metals.

In this work, deionized water and 0.05 mol/L EDTA (pH 7) were chosen as the extracting solutions. The pH value of soil samples collected from the vicinity of thermal power plant and agricultural field was found in the range of 6.85–7.6 and 7.4–8.2, respectively (Table 1). Results for the determination of V^{5+}, V^{4+}, total V and extractable V in soil samples are summarized in Table 3, all results are expressed on dried weight basis. The average value was achieved using triplicate measurements of real samples ($n = 36$). The concentration of V in the water-soluble fraction of soil was found to be rather small, ranging from 1.56 to 2.65 and 0.36 to 0.85 μg/g, in test soil and control soil samples. In fact, there were statistically significant correlations were observed between total concentrations of V in both soil samples with those values obtained from water soluble and EDTA extractant ($R^2 = 0.742–0.851$).

3.3. Predicting the uptake of total and species of V in vegetable and grass samples

Results for the determination of V^{5+}, V^{4+} and total V in grass and vegetable samples are summarized in Table 4. These results show that the concentration of V^{5+} in vegetables and grass samples grown around the thermal power plant ranges between 2.95–5.25 and 3.54–4.35 μg/g, while the total V contents found in the range of 8.74–14.9 and 9.57–13.6 μg/g, respectively. In all test crop samples and more than 50% of control crops, the total V concentrations exceed 2 μg/g (upper limit recommended in literature value for safe V levels), which may cause chlorosis and limit the growth of plants [38]. These may affect animal grazing in the area. The constant consumption of grass and vegetables with these levels of V^{5+} by animals and human may result in the accumulation of V in their cells, which may results in symptoms of V poisoning in the long-term.

On the basis of these results, individual transfer factors (T_f) were calculated as the ratio between the concentrations of V in understudy vegetables and grasses with respect to the concentration of V in EDTA extracts of soils (Table 5). As can be observed, T_f of V in underground vegetables, potato, carrot and onion were higher

Table 5
Transfer factor of V in test crop samples (TCS) and control crop sample (CCS) vegetables and grasses with related to 0.05 M EDTA soil extracts.

Grasses/vegetable samples	TCS[a]	CCS[b]
	T_f[c]	
Lucerne	3.74	3.06
Berseem	5.33	4.34
Bitter gourd	3.82	2.79
Carrot	5.84	4.45
Cluster beans	3.41	2.64
Coriander	3.95	3.08
Okra	4.89	3.71
Onion	5.46	4.33
Pepper mint	4.24	3.99
Potatoes	5.29	4.06
Spinach	3.57	3.42
Peas	3.84	3.68

[a] Crops grown in soil samples from the vicinity of thermal power plant.
[b] Crops grown in soil of agricultural field.
[c] Transfer factor (T_f) = total V in crops/EDTA extractable V in soil.

than other vegetables ($P < 0.01$), while a grass sample, berseem also shows the higher uptake of V.

V presence in the soil is not neutral for the plants and its influence on the plants depends on concentration and pH. Due to structural analogy between vanadate (H_2VO^{4-}) and phosphate (H_2PO_4) ions [39], the accumulation of V by plants reduces the amount of PO_4^{3-}, which plays a very important physiological role. The consumption of such V enriched contaminated grass by mammals including cattle, would ultimately lead to the replacement of PO_4^{3-} in their bones. V is present in most cells of plants and animals. Intercellularly, it tends to be present as vanadyl, bound to glutathione, catecholamines or other small peptides [40]. V^{5+} and V^{4+} in these cells are capable of reacting with phosphate and sugar alcohol groups of nucleotides to form complexes that inhibit or stimulate the activity of many DNA or RNA enzymes.

3.4. Matrix modifiers

A number of matrix modifiers were testing for V determination by ETAAS in different kinds of samples [41,42]. V is a refractory element; meanwhile it is carbide forming element and its atomization is carried out at very high temperatures in the graphite tube. The atomization efficiency could be obviously improved by increasing the atomization temperature, but at the same time, the deterioration of graphite tube occurred and frequently changes of graphite tubes were required. For improving the V signal, different modifiers, $Mg(NO_3)_2$, $Pd(NO_3)_2$, BaF_2 and mixtures of $Pd(NO_3)_2$ and BaF_2 (1:1) were tested. Fig. 2 shows that the use of BaF_2 as chemical modifier was more efficient than that of the other two modifiers. The positive effect on sensitivity is probably caused by the formation of volatile compounds between V and fluoride [43]. The maximum experimental atomization temperature ensuring optimum sensitivity with BaF_2 was obtained at 2600 °C, and further increase of the temperature did not improve the signal intensity. Integrated absorbance values were enhanced with 5–10%, when mixture of $Pd(NO_3)_2$ and BaF_2 was injected with standards and samples into the furnace. The ashing step (1500–1600 °C) was not significantly influenced by the investigated modifiers, but the intensity of the signal was increased in the atomic curve, and an atomization temperature of 2600 °C was selected. For subsequent work, mixture of two modifiers ($Pd(NO_3)_2$ and BaF_2) was used.

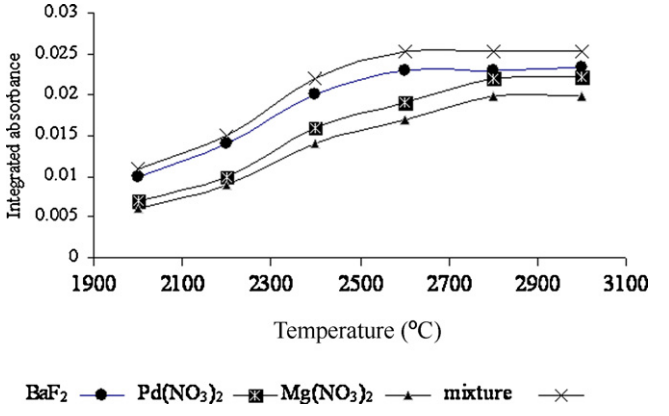

Fig. 2. Integrated absorbance values of V^{5+} (10 μg/L) obtained with various chemical modifiers at different atomization temperatures.

4. Conclusion

It can be concluded that V species, viz. V^{5+} and V^{4+}, can be determined successfully with ETAAS after their separation, by treating the soil, vegetable and grass samples with 0.2 mol/L Na_2CO_3. The method of extracting V^{5+} was validated by standard addition methods at three concentration levels in sub samples of a soil and certified reference material of vegetable. The statistical resulted data indicated that the sum of concentrations of V species is same as the total concentration of V at 95% level of confidence. The results obtained in this study indicate that considerable amount of V in agricultural soil collected from the vicinity of thermal power plant and non-industrial field was present as V^{5+} species while total amount of V was 5 time higher in test soil as compared to control soil samples. The plant samples collected around the vicinity of thermal power plant have twice the level of V species and total content as compared to those values obtained in same crops grown in agricultural field, devoid of any industrial activity. Contaminated vegetables and grass may impact human as well as animal.

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