Analytical Methods

Evaluation of modifiers for determination of V in parsley by GF AAS

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ABSTRACT

The thermal behaviour of vanadium in the absence and presence of BaF_2, W and Rh as modifiers were evaluated for the direct determination of V in parsley slurries by GF AAS. For the sequence BaF_2, no modifier, W and Rh, the characteristic masses were 16, 17, 58 and 37 pg, and the RSD were 1.3%, 0.6%, 9.8% and 10.8%, respectively. BaF_2 and absence of modifier furnished the best thermal stability, signal profile, repeatability and characteristic mass. For slurries containing 0.5% (m/v), 0.2% (v/v) HNO_3, 0.05% (v/v) Triton X-100, the pyrolysis and atomisation temperatures were 1700 and 2600 °C, respectively. The method was applied for V in digests and slurries and results agreed at 95% confidence level. Spinach and tomato leaves standard reference materials were analysed and results agreed with certified values. Recoveries from 93% to 108% were obtained. The graphite tube lifetime and LOD was 250 firings and 0.94 μg L^{-1}, respectively.

1. Introduction

Vanadium and its compounds are of interest in analytical chemistry because they may be classified as essential or toxic to humans depending on the element concentration in foods and the amount ingested. According to the Food and Drug Administration, the recommended amount of vanadium for adult humans is 1.8 mg per day (Lesniewicz, Jaworska, & Zyrnicki, 2006), while the initial level of toxicity is higher than 3.0 mg per day (Sabbioni, Kuéera, Pietra, & Vesterberg, 1996). Although the functions of vanadium in higher animals and humans have been investigated, it is known this element mimics insulin, stimulates cell proliferation and differentiation and regulates hormones, glucose and lipid metabolism (Ahmad, Isab, Ali, & Al-Arfaj, 2006; Baran, 2003; Sigel & Sigel, 1995; Wang, Yuen, & McNeill, 2001; Willsky et al., 2001). Indeed, deficiency of vanadium in goats was correlated to increased abortion rate and lower milk production (Mertz, 1987).

The presence of vanadium in foods is mainly related to their origin, raw-materials employed and industrial processing (Myron, Givand, & Nielsen, 1977). Some foods have the ability to accumulate high amounts of vanadium, such as mushroom, shellfishes, dill seed, black pepper, radish and parsley plants (Myron et al., 1977; Sigel & Sigel, 1995; Teissèdre et al., 1998). As the level of vanadium in plants depends on the geochemical factors (Aloway, 1990), some vegetables may be more nutritionally complete than others. For

mineral deficient soils, the commercial production of enriched vegetables and functional foods is an alternative to increase the number and concentration of beneficial nutrients for human consumption (Roberfroid, 1999, 2002). Due to the narrow concentration interval between nutritional and toxic effects, the accurate determination of vanadium in foodstuffs is important.

Among analytical techniques available for determination of vanadium at trace levels, graphite furnace atomic absorption spectrometry (GF AAS) is a suitable and widely used technique due to its selectivity, simplicity, high sensitivity and capability for direct analysis with minimal sample preparation (Jackson, 1999; Welz & Sperling, 1999). Graphite atomisers may be used to decompose solid samples (Welz & Sperling, 1999; Rosa, Moraes, Neto, Nóbrega, & Nogueira, 2002). However, the reaction between vanadium and carbon producing high-melting carbides inhibits the atomisation of vanadium, and is considered the main difficulty associated with vanadium determination by GF AAS. This problem can usually be circumvented by using pre-treated graphite tubes and chemical modifiers (Flores, Perez, & Arruda, 2005; Saavedra, Fernández, & González, 2004).

Studies dealing with electrothermal behaviour of vanadium in different modifiers are important parameters to be considered in analytical methodologies employing solid sampling. Previous works related on vanadium determination in milk (Bermejo-Barrera et al., 2000) and urine (Fernandes, Nogueira, Neto, & Nóbrega, 2004) using BaF_2 as chemical modifier were proposed. The main advantage of this modifier was the pronounced increase on vanadium sensitivity due to the formation of volatile compounds

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between vanadium and fluoride. Permanent chemical modifiers have also been investigated for the determination of vanadium in different samples (Meeravali & Kumar, 2001; Nakamoto, Ishimaru, Endo, & Matsusaki, 2004; Thomaidis & Piperaki, 1996). Tungsten and Rh were applied as permanent modifiers for the determination of vanadium in heavy oils (Nakamoto et al., 2004) and in oils and water (Thomaidis & Piperaki, 1996), respectively. The W-coated tube increased the graphite tube lifetime in firings compared with other tested modifiers and precise results were obtained using an oil standard reference material. For the second case, the Rh-coated platform prevented pre-atomisation losses, which increased significantly the vanadium sensitivity. Among main advantages of permanent modifiers are shorter analytical cycle, lower blanks and limits of detection, higher lifetime of graphite tube and lower background (Oliveira, Oliveira, & Neto, 2007). Little attention has been given to the influence of different modifiers on the electrothermal behaviour of vanadium in plant slurries. Likewise, procedures involving solid sampling for direct determination of vanadium in plant materials are also scarce in the literature.

This study reports the electrothermal behaviour of vanadium in slurries of parsley samples in different conditions: (a) without modifier; (b) W as permanent modifier; (c) Rh as permanent modifier and (d) BaF_2 as conventional modifier. The performance of the method for the direct determination of vanadium in parsley using electrothermal atomic absorption spectrometry with Zeeman-effect background corrector was checked after analysis of acid digests and slurries of parsley, tomato leaves and spinach.

2. Experimental

2.1. Reagents and analytical slurries

High purity deionised water obtained using a Millipore Rios 5® reverse osmosis and a Millipore Milli-Q Academic® deioniser system (resistivity 18.2 MΩ cm), and Suprapur® nitric acid (Merck, Darmstadt, Germany) were used throughout the work to prepare all solutions.

A $1.0 \, g \, L^{-1}$ W stock solution used as permanent modifier was prepared by dissolving 0.1794 g of $Na_2WO_4 \cdot 2H_2O$ (Merck, Darmstadt, Germany) in 100 mL water.

A $1.0 \, g \, L^{-1}$ Rh stock solution ($RhCl_3$; Fluka, Milan, Italy) was used as permanent chemical modifier without previous dilution.

A $1.0 \, g \, L^{-1}$ BaF_2 stock solution used as a conventional chemical modifier was prepared by dissolving 100 mg of the salt (99.99% purity, Aldrich, USA) in 100 mL of deionised water.

Vanadium working standards slurries containing 0.5% (m/v) of dried and powdered vegetables were prepared daily in the 5.0–50.0 µg L^{-1} V range by appropriate dilution of the Normex® $1.0 \, g \, L^{-1}$ stock solution (Carlo Erba, Milan, Italy) in 0.2% v/v HNO_3 plus 0.05% v/v of Triton X-100 (Merck, Darmstadt, Germany).

2.2. Hydroponics experiments

A 1000 mg L^{-1} V stock solution used in the hydroponics experiments to enrich parsley plants was prepared by dissolution 1.15 g NH_4VO_3 (99% purity, Vetec, Rio de Janeiro, Brazil) in 500 mL of water. This experiment was conduced in a greenhouse with relative humidity and temperature controlled. Parsley seeds (*Petroselinum* sp.) were put in an ISOPOR® plate with own holes for germination and growing, containing PLANTIMAX® as substrate. After germination, seedlings with approximately 10 cm height were collected from the ISOPOR® plates, washed with deionised water and transferred to reservoirs containing the Hoagland nutritive solution (Hoagland & Arnon, 1950): 6.0 mmol L^{-1} KNO_3, 4.0 mmol L^{-1} $Ca(NO_3)_2 \cdot 4H_2O$, 1.0 mmol L^{-1} $NH_4H_2PO_4$,

2.0 mmol L^{-1} $MgSO_4 \cdot 7H_2O$, solution Fe–EDTA (40.0 µmol L^{-1} $FeCl_3 \cdot 6H_2O$ plus 40.0 µmol L^{-1} Na_2EDTA), 19.0 µmol L^{-1} H_3BO_3, 2.0 µmol L^{-1} $ZnSO_4 \cdot 7H_2O$, 0.6 µmol L^{-1} $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 0.5 µmol L^{-1} $CuSO_4 \cdot 5H_2O$ and 7.0 µmol L^{-1} $MnCl_2 \cdot 4H_2O$. A volume of 3.2 L of this solution was transferred to 3.5 L capacity opaque plastic vases, covered with plastic lids containing two holes. The seedlings were fixed in the central hole while in the side hole a hose was inserted to oxygenate the nutritive solution. Plants were cultivated in 0, 1.5 and 3.0 mg L^{-1} NH_4VO_3 solution. All vases remained closed under regular oxygenation conditions for 30 days. Each treatment was done in four replicates, and was randomly distributed over the greenhouse bench. The pH of solutions was adjusted to 6.0 ± 0.2 with a 0.1 mg L^{-1} NaOH solution.

2.3. Samples and SRMs preparation

After harvest, all leaves and root samples were dried at 50 °C for 48 h in a forced air oven and grounded in a cutting mill fitted with a 20 mesh screen at the bottom of the cutting chamber and thereafter powdered again in a Spex 6750 cryogenic mill (Metuchen, NJ, USA). A mass of 1.0 g of sample was added in a grinding vial, a polycarbonate cylinder supplied with two end plugs, immersed in liquid nitrogen and ground with a magnetically driven impactor. Samples were pulverised by the impact between parsley samples and the magnetic bar submitted to an oscillating magnetic field of 20 impacts s^{-1}. A time of 4 min was required to pulverise each sample. The grinding procedure was implemented with a first step of 2 min for sample freezing followed by two cycles with two stages of pulverisation and cooling, with a total time of 4 min, in order to obtain particles with diameter ⩽50 µm (Miller-Ihli, 1998). A mass of 0.25 g of enriched parsley samples cryogenically powdered was dispersed in 50 mL of 0.2% (v/v) HNO_3 + 0.05% v/v Triton X-100 solution. The flasks containing slurries were placed on an ultrasonic bath during 15 min for homogenisation. Thereafter, ca. 1.5 mL slurry was transferred to the autosampler cup. Immediately before sampling, slurries were stirred during 10 s by means of a Ti ultrasound probe at 80% ultrasound amplitude. Slurries of standard reference materials (1573a Tomato Leaves; 1570a Trace Elements in Spinach Leaves) from the National Institute of Standards and Technology (Gaithersburg, MD, USA) were similarly prepared, unless the final volume that was 10 mL.

Parsley samples and SRMs were mineralised with nitric acid in triplicate in a Perkin–Elmer–Anton Paar Multiwave™ microwave oven digestion system (Graz, Austria). A volume of 2.5 mL HNO_3 conc. and 0.5 mL of 30% v/v H_2O_2 were added to 250 mg of dried powdered materials placed into PTFE tubes, which were closed and placed on the microwave oven cavity. Thereafter, the following power/time programme was run: *step 1: 100–500 W (5 min); step 2: 800–800 W (15 min); step 3: 0–0 W (15 min)*. After cooling, the digests were transferred to a 10 mL volumetric flask and the volume was completed with deionised water.

All solutions were stored in Nalgene™ high-density polypropylene flasks (Nalge Nunc International, Rochester, NY, USA). Plastic bottles, autosampler cups, and glassware were cleaned by soaking overnight in a 10% (v/v) HNO_3 solution and rinsing abundantly in deionised water before use.

2.4. Instrumentation

A Perkin–Elmer SIMAA® 6000 simultaneous multielement atomic absorption spectrometer with longitudinal Zeeman-effect background correction, equipped with a Ti ultrasound probe USS-100 (Perkin–Elmer, USA) and AS-72 auto sampler were used. The standard Perkin–Elmer THGA® transversely heated graphite atomiser with integrated platform was used. Graphite tubes pre-treatment with Rh or W (referred to as the W-, Rh-coated platform)

were also used. A Perkin–Elmer Lumina® hollow cathode lamp (HCL) was used for the determination of V at the analytical wavelength recommended by the manufacturer ($\lambda = 318.4$ nm) and was operated at 40 mA current. Argon (White Martins, São Paulo, Brazil) with 99.999% purity was used as purge gas throughout at a flow rate of 250 mL min^{-1}. Experiments were carried out using the STPF-concept (Slavin, Manning, & Carnrick, 1981). Tungsten and Rh-coated platforms were prepared automatically by using the facilities provided by the original software of the autosampler and graphite furnace, according to a heating programme adapted from the literature (Freschi, Freschi, & Neto, 2006; Lima, Krug, & Jackson, 1998). A volume of 50 μL of 1.00 g L^{-1} W or Rh stock solution was delivered onto the integrated platform and the heating programme for deposition shown in Table 1 was run. This programme was repeated 5 or 10 times to produce W-coated or Rh-coated platforms, respectively. The optimised temperature programme used for the determination of V in plants is shown in Table 2. The pyrolysis and atomisation temperatures were optimised using all selected modifiers in slurry medium. All measurements were made with at least three replicates and based on integrated absorbance.

2.5. Procedure

The electrothermal behaviour of 500 pg V in the absence and presence of BaF$_2$, W and Rh as modifiers was studied by means of pyrolysis and atomisation temperature curves built up in 0.2% (v/v) HNO$_3$ solution and 0.5% (m/v) parsley slurry + 0.2% (v/v) HNO$_3$ + 0.05% v/v of Triton X-100. In all situations, a volume of 20 μL of sample was dispensed into the graphite tube and all measurements of integrated absorbance were made at least in triplicate. For the BaF$_2$ modifier, aliquots of 6 μL of the 1000 mg L^{-1} BaF$_2$ solution were co-injected with blanks, standards and samples.

Matrix effects were evaluated by comparing the slopes of the analytical curves (5.0–50.0 μg L^{-1} V) built up in 0.2% (v/v) HNO$_3$ and 0.5% (m/v) of parsley + 0.2% (v/v) HNO$_3$ + 0.05% (v/v) Triton X-100.

For analysis of samples, calibration was done by matrix-matching method. For this, a parsley sample containing V at concentration lower than the limit of quantification was employed.

After optimisation of main parameters, the proposed procedure was applied to V determination in parsley samples in order to assess the accuracy and precision of the method. In addition, recovery tests were carried out in eight parsley samples spiked with 20 μg L^{-1} V. The integrated absorbance corresponding to each original sample was adopted as the blank. In addition to the analyses

of samples without pre-treatment, samples were also analysed after microwave-assisted digestion for comparison purposes.

3. Results and discussion

3.1. Thermal behaviour of vanadium using different chemical modifiers

Pyrolysis and atomisation curves are useful to define the optimum pyrolysis and atomisation temperatures of the heating programme of the atomiser. Hence, these curves were built up in the absence and presence of BaF$_2$, W and Rh as chemical modifiers in order to study the thermal behaviour of vanadium in aqueous solution and slurries of plant. Pyrolysis and atomisation temperatures, matrix effects, characteristic mass, repeatability, atomic signal profile and background level were elected as the main characteristics to evaluate the performance of each modification type. Vanadium presents tendency to form compound refractory that exhibit high thermal stability (Jackson, 1999). In the GF AAS technique, the carbon structure of the atomiser is favourable to produce vanadium carbide (Welz & Sperling, 1999). In this work, the platform of the graphite tube was coated with the Rh or W permanent modifiers to minimise the formation of vanadium carbide. These metals were selected because they present different affinity to carbon: the tendency to form metallic carbide is greatly higher to W than Rh. The modifier barium fluoride has been tested to increase the volatility and atomisation of vanadium (Fernandes et al., 2004). The optimum pyrolysis and atomisation temperatures, characteristic masses, relative standard deviation and background absorbance obtained in the absence and presence of BaF$_2$, W and Rh are shown in Table 3.

The pyrolysis and atomisation temperatures for 500 pg V in absence of modifier were respectively 1600 and 2600 °C for 0.2% (v/v) HNO$_3$ and 1700 and 2600 °C for 0.5% (m/v) parsley slurry (Table 3). In these conditions, the characteristic mass (m_0) calculated for the parsley slurry was 17 pg V, close to that obtained with the modifier BaF$_2$ (16 pg). The repeatability calculated as the relative standard deviation was 0.6% and the background level (0.0094 s^{-1}) was close to those obtained with W (0.0160 s^{-1}) and Rh (0.0091 s^{-1}) permanent modifiers. Shown in Fig. 1 is the atomic absorption (AA) and background (BG) signals for 500 pg V in 0.5% (m/v) parsley slurry plus 0.2% (v/v) HNO$_3$. Analysis of this figure reveals that the transient profile is typical for refractory elements: broad peak with tendency for no baseline restoration.

When the platform was coated with W, broader atomic peaks were observed (Fig. 1B), suggesting that this modifier inhibits the kinetic of atomisation. This effect is attributed to the competition

Table 1
Heating programme for the deposition of Rh and W as permanent modifiers.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow (mL min^{-1})
1	110	5	25	250
2	150	10	25	250
3	600	10	20	250
4	1200	10	20	250
5	2000	3	10	250
6	2200	1	5	0

Table 2
Optimised heating programme of atomiser for vanadium determination in parsley slurries without modifier.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow (mL min^{-1})
1	110	5	10	250
2	140	5	20	250
3	1700	10	40	250
4	2600	0	6	0
5	2650	1	5	250

Table 3
Pyrolysis (T_p) and atomisation (T_a) temperatures, characteristic mass (m_0), relative standard deviation (RSD) and background (BG) obtained for V in aqueous and slurry medium in the absence and presence of W, Rh and BaF$_2$ as modifiers.

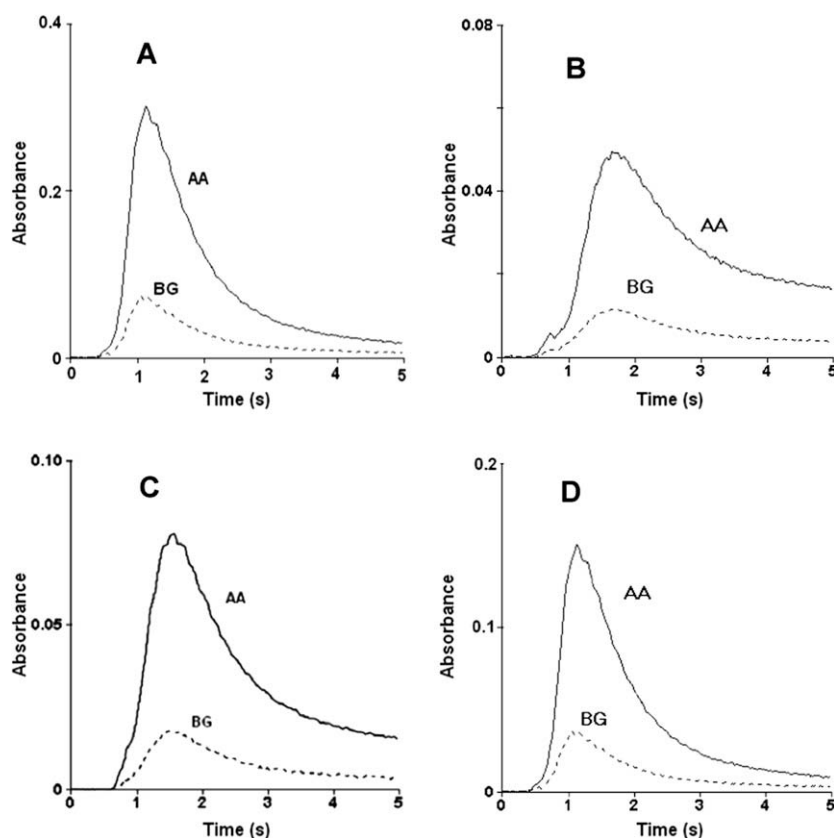| Modifier	T_p (°C)	T_a (°C)	m_0 (pg)	RSD (%)	BG (s^{-1})
Absence					
Aqueous	1600	2600	21	4.4	0.0094
Slurry	1700	2600	17	0.6	0.1026
W					
Aqueous	2000	2600	104	10.7	0.0160
Slurry	1700	2600	58	9.8	0.0285
Rh					
Aqueous	1800	2600	52	11.2	0.0091
Slurry	1600	2600	37	10.8	0.0302
BaF$_2$					
Aqueous	1600	2600	20	1.9	0.0371
Slurry	1600	2600	16	1.3	0.0808

Fig. 1. Atomic absorption (AA) and background (BG) transient signal profiles for 500 pg vanadium in 0.5% (m/v) slurry + 0.2% (v/v) HNO$_3$ medium recorded in the absence of modifier (A) and in presence of W (B), Rh (C) and BaF$_2$ (D) as modifiers.

between W and V by carbon of the tube, or the formation of stable mixed carbides which difficult the vanadium releasing during atomisation step. For the W-coating platform, the pyrolysis and atomisation temperatures were respectively 2000 and 2600 °C for aqueous medium and 1700 and 2600 °C for parsley slurries (Table 3). This modifier depreciate both the characteristic mass (m_0 = 58 pg) and precision (RSD = 9.8%). Indeed, hard memory effects were observed even after 10 firings of the graphite tube.

For the Rh-coated platform, the pyrolysis and atomisation temperatures were, respectively, 1800 and 2600 °C for aqueous medium and 1600 and 2600 °C for slurries. Rhodium did not improve the thermal stabilisation of V in slurries and favored the retention of V on the platform and consequently formation of broader peaks (Fig. 1C). Memory effects were also observed even after 10 firings. The performance of this modifier was poorer than that found without modifier: the characteristic mass and the RSD were 37 pg and 10.8%, respectively.

Barium fluoride was chosen because among several modifiers investigated, it was selected as optimum to determine vanadium in milk and urine samples (Bermejo-Barrera et al., 2000; Fernandes et al., 2004). The effectiveness of BaF$_2$ was attributed to probable formation of volatile compounds among vanadium and fluoride, as for example, the vanadium(IV) fluoride, which decompounds in temperatures lower than 325 °C, except the vanadium(III) fluoride that it possess melting point 1406 °C, while the vanadium trihidrate(II) fluoride decompounds in low temperature. In the present work, the pyrolysis and atomisation temperatures in presence of BaF$_2$ were 1600 and 2600 °C for both aqueous and slurries medium (Table 3). Shown in Fig. 1D is the atomic absorption (AA) and background (BG) signals for 500 pg V in 0.5% (m/v) parsley slurry plus 0.2% (v/v) HNO$_3$. Analysis of figure reveals the profile of the transient peak is similar to that obtained without modifier.

It should be commented that the characteristic mass (16 pg) and RSD (1.3%) calculated for V in parsley slurries in presence of BaF$_2$ were close to those obtained without modifier (17 pg; 0.6%). Analysis of Table 3 reveals that the performance of BaF$_2$ was equivalent to the situation without modifier. Lower characteristic mass and % RSD, besides a more defined AA peak profile were obtained in these conditions. So, these two modes of modification were evaluated for further studies dealing with matrix effects and analyses of real samples.

The matrix effects were evaluated in the absence and presence of BaF$_2$ by comparing the slopes of the analytical calibration curves built up from aqueous and matrix-matched solutions. As the slopes varied depending on the medium, the matrix-matching procedure was used in the direct determination of V in parsley slurries. Accuracy was checked for the determination of V in 16 parsley samples and spinach and tomato leaves standard reference materials (NIST, 2009) in the absence and presence of BaF$_2$ as modifier. For 20 µL of sample, analytical curves in the 5.0–50.0 µg L^{-1} concentration range were always attained with good linearity (r = 0.9980 without modifier and r = 0.9988 in presence of BaF$_2$ as modifier). For comparative purposes, vanadium was also determined in microwave oven digested samples (Table 4). A paired t-test showed that the results obtained with the proposed procedure were in agreement with the certified values and digests at the 95% confidence level. It should be emphasised that parsley samples were cultivated by hydroponics – with only water and nutrients, without soil. Samples 1–4 and 5–8 were cultivated in mixed nutrient solution containing 1.5 and 3.0 mg L^{-1} V, respectively. Samples 9–16 are the corresponding parsley roots of samples 1–8. The recoveries of V added to eight samples varied from 93% to 108% (without modifier) and from 88% to 102% (using BaF$_2$ as modifier). Relative standard deviations for slurries of V obtained in the absence and presence of

Table 4
Mean ± standard deviation ($n = 4$) obtained for Vanadium determination in slurries and digests of parsley samples and two standard reference materials (SRM) using the proposed procedure without modifier and in presence of BaF_2 as modifier.

Samples	V, $\mu g\,g^{-1}$			
	No modifier		BaF_2	
	Slurry sampling	Acid digestion	Slurry sampling	Acid digestion
1[a]	0.70 ± 0.02	0.67 ± 0.03	0.69 ± 0.02	0.66 ± 0.03
2[a]	0.90 ± 0.01	0.88 ± 0.02	0.89 ± 0.02	0.85 ± 0.03
3[a]	1.09 ± 0.01	1.11 ± 0.03	1.07 ± 0.02	1.04 ± 0.01
4[a]	1.53 ± 0.05	1.55 ± 0.03	1.52 ± 0.03	1.46 ± 0.04
5[a]	2.23 ± 0.07	2.25 ± 0.06	2.21 ± 0.05	2.16 ± 0.03
6[a]	1.87 ± 0.02	1.84 ± 0.03	1.86 ± 0.05	1.73 ± 0.06
7[a]	1.72 ± 0.02	1.67 ± 0.04	1.71 ± 0.04	1.67 ± 0.05
8[a]	2.05 ± 0.06	2.01 ± 0.05	2.04 ± 0.03	1.96 ± 0.04
9[b]	3.20 ± 0.20	2.90 ± 0.18	3.19 ± 0.42	3.23 ± 0.11
10[b]	3.29 ± 0.19	3.17 ± 0.12	3.28 ± 0.19	3.35 ± 0.16
11[b]	3.38 ± 0.14	3.29 ± 0.27	3.37 ± 0.17	3.38 ± 0.15
12[b]	3.44 ± 0.13	3.56 ± 0.10	3.43 ± 0.15	3.46 ± 0.35
13[b]	2.93 ± 0.25	3.01 ± 0.17	2.92 ± 0.15	2.93 ± 0.25
14[b]	2.98 ± 0.14	3.16 ± 0.12	2.97 ± 0.16	3.09 ± 0.11
15[b]	3.18 ± 0.17	3.24 ± 0.16	3.17 ± 0.20	3.19 ± 0.16
16[b]	3.14 ± 0.27	3.12 ± 0.14	3.13 ± 0.25	3.18 ± 0.19
SRM 1	0.66 ± 0.09	0.65 ± 0.08	0.65 ± 0.09	0.64 ± 0.08
SRM 2	0.90 ± 0.06	0.88 ± 0.05	0.89 ± 0.06	0.88 ± 0.07

SRM 1: Trace elements in spinach leaves 1570a ($0.57 ± 0.03\ \mu g\,g^{-1}$).
SRM 2: Tomato leaves 1573a ($0.83 ± 0.01\ \mu g\,g^{-1}$).
[a] Parsley leaves.
[b] Parsley roots.

BaF_2 were, respectively, 0.6% and 1.3% ($n = 10$), and the corresponding limits of detection were 0.94 and 0.74 $\mu g\,L^{-1}$ (Currie, 2004). The lifetime of the graphite tube was around 250 firings, with or without injection of BaF_2.

4. Conclusion

This work describes a simple, fast, and accurate method for the direct determination of vanadium in plants by graphite furnace AAS. Tungsten and Rh-coated platform impaired the performance of the THGA® atomiser due to the significant memory effects and highest characteristic mass. The efficiency of the BaF_2 practically was equivalent to that not including modifier, but both required matrix-matching calibration. Calibration curve without modifier furnished good linear correlation coefficient ($r = 0.9980$), good recoveries (93–108%), and limit of detection (LOD = 0.94 $\mu g\,L^{-1}$) suitable to determine V in enriched plants. The study confirmed the advantages of solid sampling-based procedures over conventional methods for the analysis of plant digests, since no sample pre-treatment was necessary. Taking into consideration the importance of V to humans, further studies on parsley enrichment should be done, mainly those dealing with the nature and concentration of vanadium.

References

Ahmad, S., Isab, A. A., Ali, S., & Al-Arfaj, A. R. (2006). Perspectives in bioinorganic chemistry of some metal based therapeutic agents. *Polyhedron, 25*(7), 1633–1645.
Aloway, B. J. (1990). *Heavy metal in soil*. London: Blackie Academic and Professional.

Baran, E. J. (2003). Model studies related to vanadium biochemistry: Recent advances and perspectives (review). *Journal of the Brazilian Chemical Society, 14*(6), 878–888.
Bermejo-Barrera, P., Pardiñãs-Alvite, T., Barciela-Alonso, M. C., Mermejo-Barrera, A., Cocho de Juan, J. A., & Fraga-Bermúdez, J. M. (2000). Vanadium determination in milk by atomic absorption spectrometry with electrothermal atomization using hot injection and preconcentration on the graphite tube. *Journal Analytical Atomic Spectrometry, 15*(4), 435–439.
Currie, L. A. (2004). Detection and quantification limits: Basic concepts, international harmonization, and outstanding (low-levels) issues. *Applied Radiation and Isotopes, 61*(2–3), 145–149.
Fernandes, K. G., Nogueira, A. R. A., Neto, J. A. G., & Nóbrega, J. A. (2004). Determination of vanadium in urine by electrothermal atomic absorption spectrometry using hot injection and preconcentration into the graphite tube. *Journal of the Brazilian Chemical Society, 15*(5), 676–681.
Flores, A. V., Perez, C. A., & Arruda, M. A. Z. (2005). Evaluation of a synergetic effect between Rh as permanent chemical modifier and acetylacetone as complexing agent in Sc determination in sediment slurry samples by ETAAS. *Analytica Chimica Acta, 530*(2), 299–305.
Freschi, G. P. G., Freschi, C. D., & Neto, J. A. G. (2006). Evaluation of Ir, Ru, and W as permanent modifiers for the simultaneous determination of As, Bi, Pb, Sb, and Se in natural water by electrothermal atomic absorption spectrometry. *Atomic Spectroscopy, 27*(1), 1–5.
Hoagland, D. R., & Arnon, D. I. (1950). *The water culture method of growing plants without soil*. Berkeley: California Agriculture Experiment Station.
Jackson, K. W. (1999). *Electrothermal atomization for analytical atomic spectrometry*. Weinheim: Wiley.
Lesniewicz, A., Jaworska, K., & Zyrnicki, W. (2006). Macro and micro-nutrients and their bioavailability in polish herbal medicaments. *Food Chemistry, 99*(4), 670–679.
Lima, E. C., Krug, F. J., & Jackson, K. W. (1998). Evaluation of tungsten rhodium coating on an integrated platform as a permanent chemical modifier for cadmium, lead, and selenium determination by electrothermal atomic absorption spectrometry. *Spectrochimica Acta Part B, 53*(13), 1791–1804.
Meeravali, N. N., & Kumar, S. J. (2001). The utility of a W–Ir permanent chemical modifier for the determination of Ni and V in emulsified fuel oils and naphtha by transverse heated electrothermal atomic absorption spectrometer. *Journal Analytical Atomic Spectrometry, 16*(5), 527–532.
Mertz, W. (1987). *Trace elements in human and animal nutrition*. New York: Academic Press.
Miller-Ihli, N. J. (1998). Slurry sample preparation for simultaneous multi-element graphite furnace atomic absorption spectrometry. *Journal of Analytical Atomic Spectrometry, 3*(1), 73–81.
Myron, D. R., Givand, S. H., & Nielsen, F. H. (1977). Vanadium content of selected foods as determined by flameless atomic absorption spectroscopy. *Journal of Agricultural and Food Chemistry, 25*(2), 297–300.
Nakamoto, Y., Ishimaru, T., Endo, N., & Matsusaki, K. (2004). Determination of vanadium in heavy oils by atomic absorption spectrometry using a graphite furnace coated with tungsten. *Analytical Sciences, 20*(4), 739–741.
National Institute of Standards and Technology (2009). <https://www-s.nist.gov/srmors/detail.cfm> Accessed on January 26, 2009.
Oliveira, S. R., Oliveira, A. P., & Neto, J. A. G. (2007). Tungsten permanent chemical modifier with co-injection of $Pd(NO_3)_2$ + Mg ($NO_3)_2$ for direct determination of Pb in vinegar by graphite furnace atomic absorption spectrometry. *Food Chemistry, 105*(1), 236–241.
Roberfroid, M. B. (1999). What is beneficial for health? The concept of functional food. *Food and Chemical Toxicology, 37*(9–10), 1039–1041.
Roberfroid, M. B. (2002). Functional food concept and its application to prebiotics. *Digestive and Liver Disease, 34*(2), 105–110.
Rosa, C. R., Moraes, M., Neto, J. A. G., Nóbrega, J. A., & Nogueira, A. R. A. (2002). Effect of modifiers on thermal behaviour of Se in acid digestates and slurries of vegetables by graphite furnace atomic absorption spectrometry. *Food Chemistry, 79*(4), 517–523.
Saavedra, Y., Fernández, P., & González, A. (2004). Determination of vanadium in mussels by electrothermal atomic absorption spectrometry without chemical modifiers. *Analytical and Bioanalytical Chemistry, 379*(1), 72–76.
Sabbioni, E., Kuéera, J., Pietra, R., & Vesterberg, O. (1996). A critical review on normal concentrations of vanadium in human blood, serum, and urine. *Science of the Total Environment, 188*(1), 49–58.
Sigel, H., & Sigel, A. (1995). *Vanadium and its role in life*. New York: Marcel Dekker.
Slavin, W., Manning, D. C., & Carnrick, G. R. (1981). The stabilized temperature platform furnace. *Atomic Spectroscopy, 2/5*, 137–145.
Teissèdre, P. L., Krosniak, M., Portet, K., Gasc, F., Waterhouse, A. L., Serrano, J. J., et al. (1998). Vanadium levels in French and Californian wines: Influence on vanadium in dietary intake. *Food Additives and Contaminates, 15*(5), 585–591.
Thomaidis, N. S., & Piperaki, E. A. (1996). Comparison of chemical modifiers for the determination of vanadium in water and oil samples by electrothermal atomization atomic absorption spectrometry. *Analyst, 121*(2), 111–117.
Wang, J., Yuen, V. G., & McNeill, J. H. (2001). Effect of vanadium on insulin sensitivity and appetite. *Metabolism: Clinical and Experimental, 50*(6), 667–673.
Welz, B., & Sperling, M. (1999). *Atomic absorption spectrometry*. Weinheim: Wiley.
Willsky, G. R., Goldfine, A. B., Kostyniak, P. J., McNeill, J. H., Yang, L. Q., Khan, H. R., et al. (2001). Effect of vanadium (IV) compounds in the treatment of diabetes: in vivo and in vitro studies with vanadyl sulfate and bis(maltolato)oxovanadium (IV). *Journal of Inorganic Biochemistry, 85*(1), 33–42.