Talanta 113 (2013) 19–25

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of vanadium in soils and sediments by the slurry sampling graphite furnace atomic absorption spectrometry using permanent modifiers

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ARTICLE INFO

Article history:
Received 20 January 2013
Received in revised form
27 March 2013
Accepted 29 March 2013
Available online 6 April 2013

Keywords:
Vanadium determination
Slurry sampling atomic absorption spectrometry
Soils
Sediments
SEM-EDX
XRD

ABSTRACT

A new analytical procedure for vanadium (V) determination in soils and sediments by the slurry sampling graphite furnace atomic absorption spectrometry (slurry sampling GFAAS) using the mixed permanent modifiers is described. Moreover, the comparison of action of the modifiers based on the iridium (Ir) and carbide-forming elements: tungsten (W) and niobium (Nb) deposited on the graphite tubes is studied, especially in terms of their analytical utility and determination sensitivity. The mechanism of their action was investigated using an X-ray diffraction technique (XRD) and scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector (EDX). Finally, the mixture of 0.3 μg of Ir and 0.04 μg of Nb was used for the graphite tube permanent modification. The analytical procedure was optimized on the basis of the data from pyrolysis and atomization temperature curves studies. The results obtained for the four certified reference materials (marine sediments: PACS-1 and MESS-1, lake sediment: SL-1, soil: San Joaquin Soil SRM 2709), using the slurry sampling GFAAS and the standard calibration method, were in good agreement with the certified values. The detection and quantification limits and characteristic mass calculated for the proposed procedure were 0.04 μg/g, 0.16 μg/g and 11.9 pg, respectively. The precision (RSD% less than 8%) and the accuracy of vanadium determination in the soil and sediment samples were acceptable.

1. Introduction

Vanadium is widely used in industrial processes including the production of special steels, temperature-resistant alloys, in glass industry, in the manufacture of pigments and paints, for lining arc welding electrodes and as a catalyst. Vanadium compounds released in large quantities, mainly by burning fossil fuels and also from various industrial processes, are precipitated on the soil drained by rain and groundwater and may be directly adsorbed by plants and then by animals and humans [1]. Therefore, there is an increasing interest from the public health, environmental and analytical points of view to develop high sensitivity, simple and economical methodologies for determination of trace amounts of vanadium in soils and sediments.

Graphite furnace atomic absorption spectrometry (GFAAS) is still the method of choice for a wide variety of applications, especially when only one or a few trace metals are determined. However, some problems, mainly concerned with tailing of the V signal and carbide formation, have been encountered [2–6]. In the pre-atomization stage, thermal decomposition of vanadium compounds leads to formation inter alia of vanadium carbides, which results in reduction of sensitivity and reproducibility. For this reason, total pyrolytic graphite tubes have been recommended. Classical procedures for the V determination in solid samples by GFAAS often involve acid digestion step, which is time-consuming and prone to contamination and analyte loss, especially when dealing with complex matrices such as soil and sediment samples. Those inconveniences can be overcome when the slurry sampling graphite furnace atomic absorption spectrometry is used [7]. Since the topic is of practical interest, it has been the subject of study of several authors [7–11]. Mierzwa et al. [8] determined V in sediments and soils by the ultrasonic slurry sampling electrothermal atomic absorption spectrometry with the Zeeman effect background correction using 4% nitric acid as a slurry liquid medium and two steps of thermal pretreatment (at 400 °C and 1350 °C). However, the authors did not indicate how many measurement cycles could be carried out with respect to vanadium carbide formation. The ultrasonic slurry sampling GFAAS was also applied for V determination in complex matrices (such as coal fly ash, soils and sediments) without any other modifier than 0.5% nitric acid [9]. The graphite surface was not protected and the formation of refractory carbides limited long term application of the graphite tube. Unfortunately the authors did not describe the variation of the slope of the calibration curve with the firing numbers for vanadium determination. Barałkiewicz et al. [10] described the ultrasonic slurry sampling electrothermal atomic absorption

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http://dx.doi.org/10.1016/j.talanta.2013.03.085

spectrometry for V determination in soils using the surfactant, KO300G, as the stabilizing agent and a 6% suspension of polytetrafluoroethylene (PTFE) as a chemical modifier. Campillo et al. [11] used a fast program methodology for vanadium determination in soil, sediment and sludge samples by electrothermal atomic absorption spectrometry and slurry sample introduction. In the case of high silica/silicate content samples, concentrated hydrofluoric acid (HF) was used as a chemical modifier. However, HF or PTFE forms volatile fluoride compounds with V such as VF_5 (boiling point 111.2 °C), VF_4 (decomposition point at 325 °C) or VF_3 (sublimation point at 800 °C) and lower pyrolysis temperature should be applied. Additionally, hydrofluoric acid is aggressive for graphite tube and considerably decreases the tube lifetime. Some limitations of the slurry sampling GFAAS, e.g. high background and problems with the adequate calibration [12], can be partly eliminated by an application of appropriate modifiers. Apart from using conventional modifiers, carbide forming elements, such as W, Zr, and Nb alone or combined with noble metals (Rh, Ru, and Ir), have been used as permanent modifiers [13]. The most important advantages of permanent modifiers over conventional modifiers application include extended tube lifetime, lower reagent blank and detection limit [14]. However, the high melting carbides coated tubes not only gave poor sensitivity but also increased the memory effect, so their masses should be properly optimized [15]. According to the best knowledge of the authors, there are no previous works specifically dealing with application of mixed permanent modifiers in the slurry sampling GFAAS for V determination in soil and sediment samples.

In this paper two kinds of modifiers: Ir/W and Ir/Nb have been compared as a preferable permanent modifier for V determination in soil and sediment samples by the slurry sampling GFAAS technique. Valuable information about the distribution of iridium and tungsten on the pyrolytic graphite tubes and interactions between the components of modifier and graphite were obtained by means of SEM-EDX. Model experiment of niobium and vanadium carbides formation in respect to temperature by XRD was also elaborated. The effects of mass and mass ratio of permanent modifiers on V absorbance values, pyrolysis and atomization temperature curves of V in solutions and slurries were studied in detail. Based on the experimental data a preferable modifier was chosen and finally the analytical procedure for V determination in the soil and sediment samples by the slurry sampling GFAAS technique was proposed. An evaluation of the accuracy of this methodology was carried out by using the certified reference materials. The proposed method was applied for various samples with acceptable precision for V determination.

2. Experimental

2.1. Instrumentation

The scanning electron microscope Carl Zeiss Ultra Plus (Germany) equipped with an energy dispersive X-ray detector Bruker AXS (Germany) was used for the topochemical inspection of graphite samples. The microscope was also equipped with secondary electron (SE) and backscattered electron (BSE) detectors. All experiments were carried out under the required conditions (20-kV acceleration voltage and 5-nA probe current). The X-ray diffractograms of the modified graphite were recorded using the diffractometer Empyrean (PANalytical, Holland).

Measurements were carried out using the AAS-3 (Carl Zeiss Jena, Germany) atomic absorption spectrometer equipped with a deuterium-lamp background corrector, an EA-3 electrothermal atomizer and an MPE autosampler. Pyrolytically coated graphite tubes were obtained from PerkinElmer. Measurements were performed using the V hollow cathode lamp (PerkinElmer). Argon with 99.999% purity was used as the purge gas with the flow rate of 280 mL/min except in the atomization stage. Background-corrected integrated absorbance was used as the analytical signal. Instrumental parameters and operational conditions for the determination of V in soil and sediment slurries by GFAAS are given in Table 1. The temperature program for the determination of V in soil and sediment slurry samples using permanent modifiers is presented in Table 2.

Standard solutions and slurries were prepared using Transferpette micropipettes (Brand, Wertheim, Germany), a Sartorius R-200D balance (Gottingen, Germany), a Vortex agitator and an MPW-50 separator (Mechanika Precyzyjna, Warsaw, Poland). Eppendorf's polyethylene vessels were used for the solutions and slurries preparation and storage. They were filled with nitric acid for 24 hours and flushed with doubly distilled water before use.

2.2. Reagents and certified reference materials

Spectral purity nitric acid (Merck, Darmstadt, Germany) was used for the preparation of standard solutions and slurries. Iridium (SCP Science, Quebec, Canada) and niobium (CPI International, Santa Rosa, USA) standard solutions diluted in an appropriate way with 5% (v/v) HNO_3 and tungsten standard solution (Fluka, Buchs SG, Switzerland) diluted with doubly distilled water with a resistivity of 18.2 MΩ cm were used for modification of the graphite tube. The calibration standards were obtained from the standard solution of V (Merck, Darmstadt, Germany) by dilution with 5% (v/v) nitric acid. Marine sediments certified reference materials (PACS-1 and MESS-1) were obtained from the National Research Council of Canada (Ottawa, Canada). SL-1 obtained from the International Atomic Energy Agency (Vienna, Austria) was used as the lake sediment certified reference material. San Joaquin Soil SRM 2709 was obtained from the National Institute of Standards and Technology (Gaithersburg, USA) and was used as soils certified reference material. The samples of estuarine sediment from Ume (Ümea, Sweden) were also studied. The three Polish soils were collected from the Polish agriculture areas: Felin (Loess Soil), Parczew (Lithic Rendolls) and Bezek (Entic Rendolls).

Table 1
Instrumental parameters and operational conditions.

	V
Wavelength (nm)	318.6
Lamp current (mA)	7
Spectral band pass (nm)	0.2
Injection volume (μL)	20
Integration time (s)	5
L'vov platform	No
Injection volume (μL)	20

Table 2
Temperature program for the determination of V in soil and sediment samples using Ir/Nb permanent modifier.

Step	Temperature (°C)	Ramp (°C/s)	Hold (s)	Ar flow (mL/min)
Drying I	80	20	3	280
Drying II	105	2	40	280
Ashing	1200	100	5	280
Atomization	2600	FP*	5	0
Cleaning	2650	1000	3	280

* FP—"full power"—maximum of ramp.

Niobium pentoxide (Nb_2O_5) and ammonium metavanadate (NH_4VO_3) were obtained from Merck (Darmstadt, Germany).

2.3. Procedure of graphite tube modification

20 μL of 0.05–1 g/L standard solution of Ir, Nb, and 20 μL of 0.05–5 g/L standard solution of W were injected into the graphite tube and heated according to the temperature program based on the previous work [16]. This procedure was repeated a few times resulting in an optimal mass of the modifier for which the maximum of the integrated absorbance signal of V was obtained. After modification the graphite tubes were ready for direct V measurements in the soil and sediment samples.

2.4. Procedure of modified graphite tube preparation for the SEM-EDX studies

The graphite tube modified with Ir/W was prepared as described in Section 2.2 and cut with EM UC7 ultramicrotome (Leica Microsystems (Schweiz) AG, Heerbrugg, Switzerland). The properly cut pieces were cleaned by blowing dry air onto the surface. Finally, the tubes prepared in this way were broken, which was necessary since the analytical information might have got lost by the cutting procedure of a soft material like graphite. The broken tubes were fastened to the sample holder by carbon taps, which are sticky on both sides. Since the samples showed good electrical conduction, coating with gold or carbon was not necessary. In this way, there was no interference of the coating with elemental spot analyses carried out with the energy dispersive X-ray EDX detector. All EDX-point analyses were carried out under the following conditions: primary electron beam: accelerating voltage −20 kV; beam focused to a magnification of ×10,000. Images were derived from the secondary electrons (SE) and the backscattered electrons (BSE).

2.5. Procedure of modified graphite preparation for the XRD studies

The optimal conditions of tube modification by niobium carbide in respect to V determination in soil and sediment slurries were studied by application of XRD. The crystals formed on the graphite surface were studied by simulation of this process in the ring chamber tube specially designed for the solid sampling used for the AAS-3 spectrometer. This methodology was described earlier by Dobrowolski [16]. The tube allows the introduction of a relatively large amount of solid into the separate chamber around the middle part of the tube. The powdered graphite (Ringsdorff-Werke GMBH, Bonn, Germany) used for the tube manufacturing was mixed in the molar ratio 1:1 with ammonium metavanadate (NH_4VO_3), introduced into the ring chamber tube and subjected to a heating process in the AAS-3 spectrometer up to 1600 °C. After the modification procedure, the graphite was removed from the tube and its composition was examined using XRD. In the second step, NH_4VO_3 was added to the graphite earlier coated with NbC in the molar ratio 1:1 and introduced into the ring chamber tube. The graphite prepared in this way was subjected to a heating process in the AAS-3 spectrometer up to 1600 °C in order to evaluate its composition by XRD.

2.6. Sediment and soil slurries preparation

For slurry preparation the soil and sediment samples were ground using the MM-2 vibrational mill (K. Retsch, Haan, Germany), equipped with the chambers and balls made of tungsten carbide. The effectiveness of grinding was examined by monitoring slurries prepared in alcohol by means of scanning electron microscopy. It was experimentally stated that after 15 min of grinding, about 80–85% of the particles had sizes below 25 μm. Then the soil and sediment samples were dried at 105 °C in the laboratory oven to constant weight. The slurries were prepared by the weighing of 0.4–2 mg of powdered soil samples into clean polyethylene vessels. After weighing 1 mL of 5% nitric acid was added. Then the slurries were homogenized using the Vortex agitator before each measurement, which reduced drastically the errors caused by the lack of slurry stability.

3. Results and discussion

3.1. Selection of modifier (composition, mass and thermal pretreatment)

The conditions of permanent modifiers deposition were optimized in order to achieve the best analytical performance of atomic absorption measurements. In this way optimization of proper masses of permanent modifiers was carried out by studying their influence on the analytical signal of V, first for the increasing mass of Ir, then for the constant mass of Ir with respect to the highest signal of V with the increasing mass of W. Similar studies were carried out for Ir/Nb modification. The influence of Ir, Ir/W and Ir/Nb as permanent modifiers on the analytical signal for V is shown in Fig. 1. The integrated absorbance for V increases with respect to the increasing Ir mass, reaches the maximum around 0.3 μg of Ir, and then slightly decreases. In the case of Ir/W as a mixed modifier, the integrated absorbance for V increases with respect to increasing W mass, reaches the maximum around 0.6 μg of W, and then slightly decreases. In the case of graphite modified with Ir/Nb, the integrated absorbance for V increases rapidly for very small masses of Nb and reaches the maximum around 0.04 μg of Nb, then approaches the value of 0.3. Quite surprisingly, in the case of the graphite surface modified with Ir/Nb, the integrated absorbance for V is almost 2 and 3 times higher than for the graphite surface modified with Ir/W and Ir alone, respectively. On the basis of the above consideration 0.3 μg of Ir mixed with 0.6 μg of W and 0.3 μg of Ir mixed with 0.04 μg of Nb have been found as efficient masses and proportion of modifiers for V determination. The dissimilarity in the behavior of Nb and W as permanent modifiers seems to be a difference in catalytic properties rather than carbides texture formation.

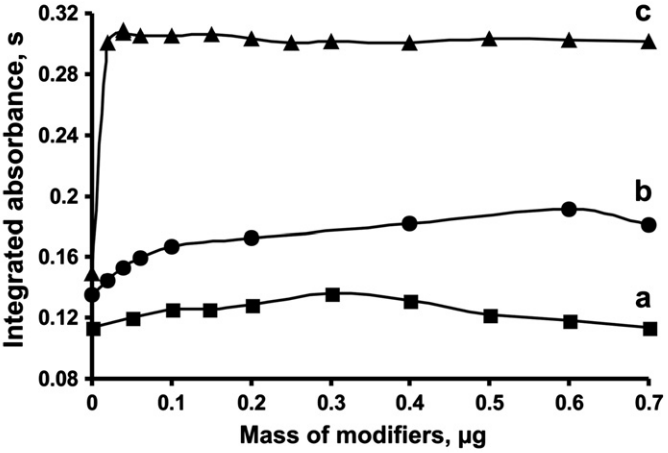

Fig. 1. Ir (a), 0.3 μg of Ir+W (b) and 0.3 μg of Ir+Nb (c) masses influence on V (1 ng) analytical signal. Pyrolysis temperature—1100 °C, atomization temperature—2600 °C.

3.2. SEM-EDX study

Particular study on morphology of the graphite tube modified with Ir/Nb was reported in our previous work [17]. To the best of the authors' knowledge, morphology of the graphite tube modified with Ir/W is not fully known. In the present work pyrolytically coated graphite tubes freshly modified with Ir/W and after about 120 firings were examined by SEM-EDX in order to find the changes of the graphite structure. The experiment included the scanning electron microscopy investigations with the secondary electron (SE) as well as the backscattered electron imaging (BSE) and the energy dispersive X-ray detection EDX.

Fig. 2 presents the exemplary SE images of the pyrolytically coated graphite tubes freshly modified with Ir/W and after about 120 firings at the magnification of 10,000. The micrograph 2A shows that Ir and W are distributed inhomogeneously along the pyrolytic graphite surface with the large surface area free of the modifiers. The clearer areas distributed on the graphite surface are mainly spherical and their sizes are differentiated in a diameter which ranges between 0.26 and 1.8 μm. The micrograph 2B shows that in the investigated graphite tube modified with Ir and W, originally smooth pyrographite surface becomes destroyed. Surprisingly, in Fig. 2B less clear islands of Ir and W are presented on the pyrolytic graphite surface contrary to those in Fig. 2A. Their sizes are between 0.2 and 1.0 μm as opposed to those of the Ir/Nb modifier. It can be assumed that tungsten carbide reacts with chloride compounds, presented in the analyzed samples with a quite high content, above 400 °C and forms the volatile compounds (melting points of WCl_6, WO_2Cl_2 and $WOCl_4$ equal 275 °C, 265 °C and 211 °C, respectively). It is worth noting that WC shows lower resistance against concentrated mineral acids in comparison to NbC.

On the basis of the EDX examination it was stated that the clearer areas contain the main quantity of the Ir/W modifier. Additionally, when the EDX point spectra were taken, strong Ir and W signals were detected all over the white areas on the surface and no signal was detected outside those areas. The EDX spectra and SEM images provide clear evidence for the composite character of the islands. Moreover, they are all formed from both Ir and W, despite the fact that stepwise deposition was carried out. The permanent modifiers: Ir and W are, therefore, deposited by the island formation [4–5,17–19].

Additionally, in Fig. 2 the areas on the micrographs, from which the exemplary SEM-EDX spectra were taken, are marked. In Fig. 3 the SEM-EDX spectra for the pyrolytically coated graphite tubes freshly modified with Ir/W and after about 120 firings of slurries are presented. For both profiles Ir N_α and Ir N_β ($E<0.5$ keV), W N_α and W N_β ($E<0.5$ keV), Ir M_α ($E=1.977$ keV) and Ir M_β ($E=2.053$ keV), W M_α and W M_β ($E=1.78$ keV), Ir L_α ($E=9.167$ keV), Ir L_{β_1} ($E=10.706$ keV) and Ir L_{β_2} ($E=10.907$ keV), W L_α ($E=8.398$ keV), W L_β ($E=9.672$ keV) and W L_β ($E=9.7$ keV) signals were registered. On the other hand, the EDX spectrum for the graphite tube modified with Ir/W after about 120 firings of slurries shows the evidence of Si K_{α_1} ($E=1.740$ keV) signal and Ti L_α and Ti L_β (about $E=0.9$ keV), Ti K_{α_1} ($E=4.509$) and Ti K_{β_1} ($E=4.932$) signals were also detected (Fig. 2B). These facts confirm the assumption, made previously by Cal-Prieto et al. [20] and Dobrowolski [17], that silicon and titanium are the factors responsible

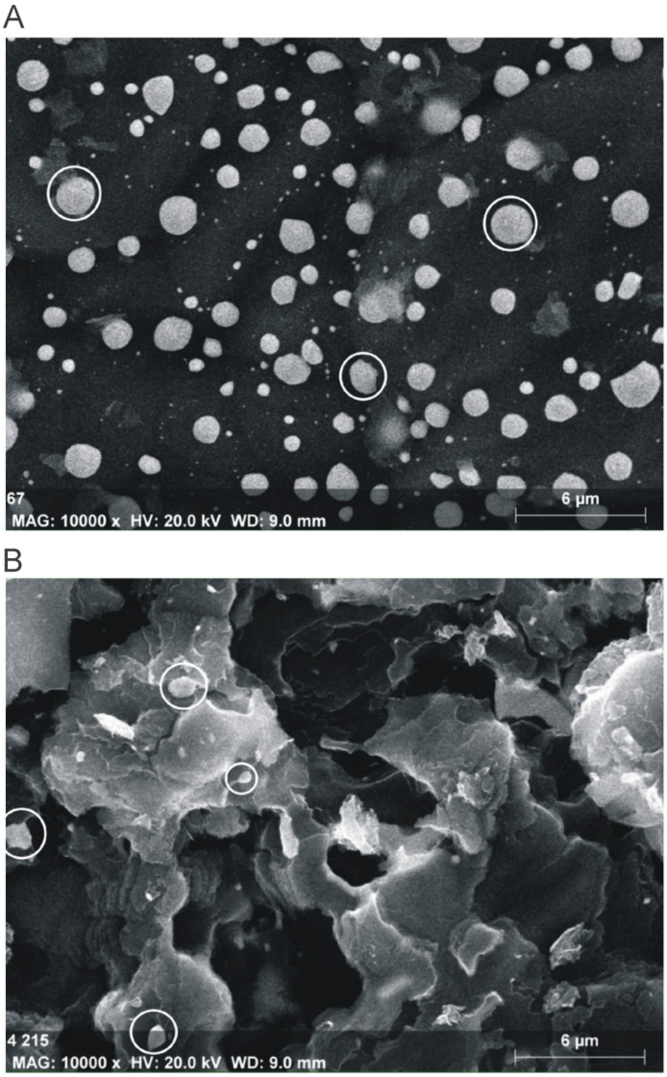

Fig. 2. SEM micrographs of pyrolytically coated graphite tubes freshly modified with Ir/W (A) and after about 120 firings of slurries (B) at a magnification of 10,000 using the SE detector.

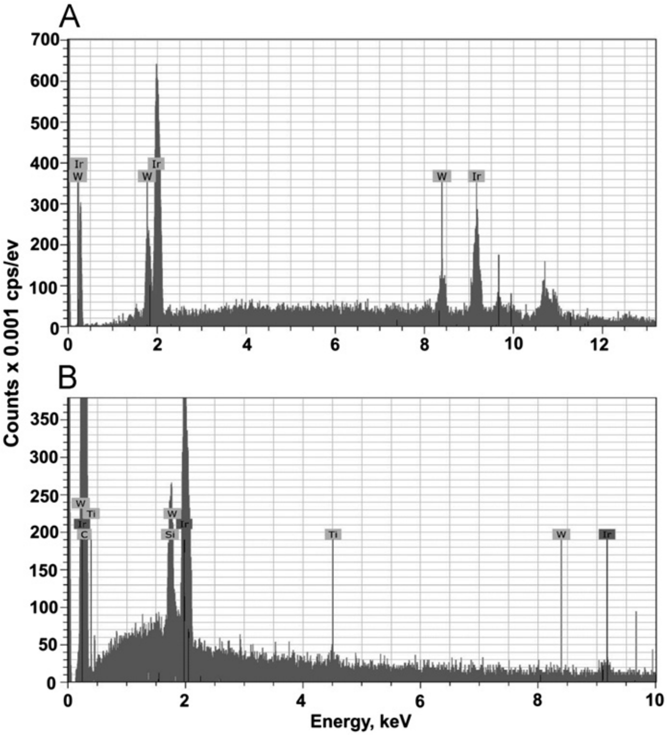

Fig. 3. SEM-EDX spectra for graphite tubes freshly modified with Ir/W (A) and after about 120 firings of slurries (B).

for graphite tubes ageing due to the formation of both SiC and TiC, which can lead to graphite structure deterioration.

To the best of the authors' knowledge, Nb forms the intercalation compounds with Ti, which are industrially used as a superconducting alloy, contrary to W [21].

3.3. *XRD studies of graphite surface modified with NbC*

Particular study on niobium carbide formation on the graphite surface was reported earlier [22]. The aim of the present XRD studies was to prove that in the presence of NbC coating, formation of vanadium carbides did not take place. In Fig. 4 part of the X-ray diffraction patterns of the graphite modified at a temperature of 1600 °C with ammonium metavanadate (A) and graphite coated with NbC and modified by ammonium metavanadate (B) is shown. It can be seen that at the temperature of 1600 °C the crystals of V_8C_7 are formed (Fig. 4A). However at the same temperature, in the case of graphite earlier coated with NbC the formation of V_2O_5 is observed (Fig. 4B). Additionally, the characteristic lines for V_8C_7 crystals are not detected. The mechanism of this phenomenon seems to be as follows: the most reactive sites on the graphite surface are occupied by formed NbC and in this way the formation of V_8C_7 is blocked. Moreover, the mass of Nb used for graphite modification should be optimized, because the excess of NbC can block the catalytic sites, responsible for V_2O_5 thermal decomposition. It means that in the presence of niobium carbide on the graphite surface the formation of vanadium carbide up to the temperature 1600 °C is impossible. It is worth noting that at the temperature higher than 1600 °C thermal decomposition of V_2O_5 takes place [23].

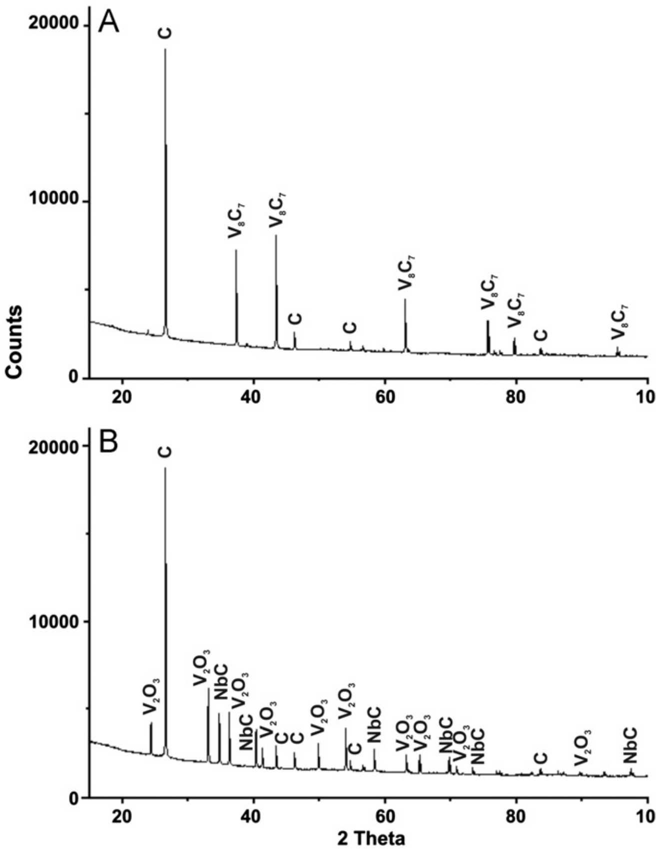

Fig. 4. Part of X-ray diffraction patterns of the graphite modified at a temperature of 1600 °C with ammonium metavanadate (A) and graphite earlier coated with NbC and modified by ammonium metavanadate (B).

3.4. *Optimization of the temperature program*

The furnace program was optimized using wall atomization because no significant advantages were obtained when the platform atomization was applied. The influence of the pyrolysis and atomization temperatures on the V analytical signals was studied for the aqueous solution of V as well as for slurries prepared from soil and sediment in the presence of 0.3 μg of Ir+0.6 μg of W and 0.3 μg of Ir+0.04 μg of Nb as mixed permanent modifiers. Fig. 5A presents the comparison of pyrolysis and atomization curves for 1 ng of V in the aqueous solution and V in the slurry prepared from NIST 2709 in both cases using 0.3 μg of Ir+0.04 μg of Nb as a permanent modifier. The shape of pyrolysis and atomization curves is similar for the slurry and the aqueous solution. The maximum pyrolysis and atomization temperatures for the slurry and the aqueous solution of V are 1200 °C and 2600 °C, respectively. Fig. 5B presents the comparison of pyrolysis and atomization curves for 1 ng of V in the aqueous solution and V in the slurry prepared from NIST 2709 in both cases using 0.3 μg of Ir+0.6 μg of W as permanent modifiers. In the case of the pyrolysis and atomization curves for Ir/W a similar pattern as for Ir/Nb modification is observed. The maximum pyrolysis and atomization temperatures for the slurry and the aqueous solution of V are 1200 °C and 2600 °C, respectively.

Comparing the integrated absorbance values for both modifications, it is obvious that the sensitivity of V determination in the case of Ir/Nb modification is almost 1.5 times higher than that for Ir/W modification. Moreover, it is worth noting that the chemical and thermal resistance of NbC formed on the graphite surface is

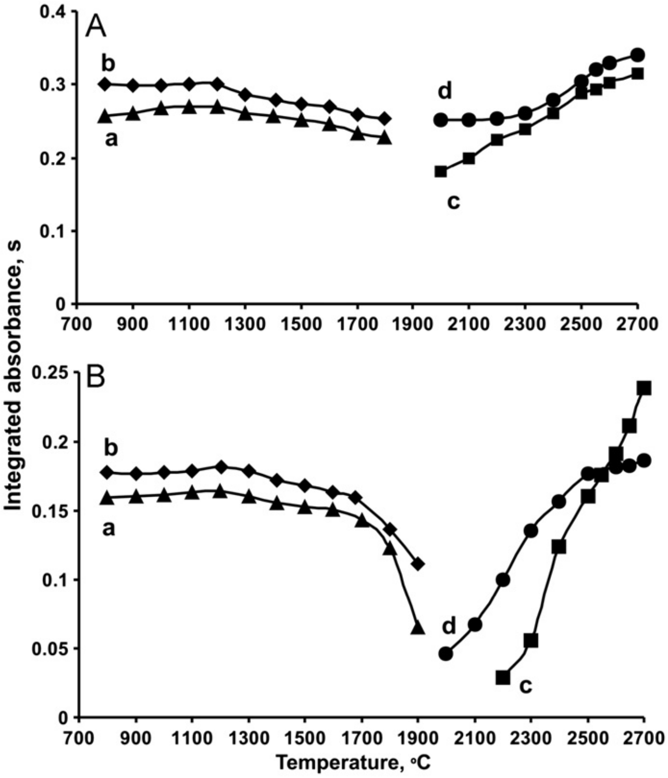

Fig. 5. Comparison of pyrolysis and atomization curves for 1 ng of V in aqueous solution and in NIST 2709 (0.45 mg/mL): (A) using Ir/Nb as permanent modifier (a, b—pyrolysis curves for the slurry of NIST 2709 (a) and 1 ng of V in aqueous solution (b), atomization temperature—2600 °C; c, d—atomization curves for 1 ng of V in aqueous solution (c) and the slurry of NIST 2709 (d), pyrolysis temperature—1200 °C); (B) using Ir/W as permanent modifier (a, b—pyrolysis curves for the slurry of NIST 2709 (a) and 1 ng of V in aqueous solution (b), atomization temperature—2600 °C; c, d—atomization curves for 1 ng of V in aqueous solution (c) and the slurry of NIST 2709 (d), pyrolysis temperature—1200 °C).

better than that of WC [17]. As follows from the above considerations, the tube modified with Ir/Nb seems to be preferable and the optimal pyrolysis and atomization temperatures for V determination are 1200 °C and 2600 °C, respectively.

3.5. *Long term performance investigation*

The role of mixed permanent modifiers in slurry sampling GFAAS technique has not been thoroughly recognized yet. Specific chemical interactions in the vanadium–niobium–carbide–iridium–soil matrix–graphite system may significantly influence the efficiency of the mixed modifiers. The exact mechanism of the above processes cannot be explained on the basis of current knowledge of the material science and thermodynamics. The lower volatility of iridium coated by the niobium carbide on the modified graphite surfaces often results in a significant increase in the lifetime of the tube [15]. Iridium as the permanent modifier additionally protects graphite surface against corrosion, especially in the case of soils and sediments analysis where a large amount of silica, calcium, and titanium is presented on the graphite surface during an atomization step. Additionally, niobium carbide may block the most active site on the graphite surface and in this way it may prevent vanadium carbides formation which are thermally stable. This hypothesis was verified practically by investigation of influence of proposed modifiers on tube lifetime with respect to slurry sampling GFAAS technique for vanadium determination. Fig. 6 shows the relationship of a number of firings and integrated absorbance of V in slurry of NIST 2709 (0.45 mg/mL) for nonmodified and modified by Ir/Nb graphite surface. In each series of measurements the slurry prepared from NIST 2709 was injected into the graphite tubes and signals of vanadium were measured up to exhaust possibilities of proper signal measurements because of vanadium carbides formation. Reproducibility of vanadium signal was acceptable for Ir/Nb graphite modification especially in the segments related to the fifty successive firings, where the RSD % for measured signals was below 4%. After 200 firings the reproducibility decreases significantly. In the range of 1–200 firings the integrated absorbance of V decreased up to 20% of the initial value. Hence the repeated recalibration is recommended after 50 runs of the samples. On the other hand, the integration of V signals was impossible for nonmodified graphite tube after 50 firings because the tail of vanadium signal did not reach the baseline even for very long integration time. Additionally, as it can be seen in Fig. 6, in the case of aqueous solution the vanadium signals for nonmodified graphite tube decreased dramatically even after a few injections.

It is noteworthy that a pyrolytic graphite tube coating by Ir/Nb had a particular effect on the analytical signals of vanadium for slurry sampling. For comparison in Fig. 7 the absorbance–time profiles for the atomization of 1 ng V in the aqueous solution and the slurry sampling of NIST 2709 with respect to the presence or absence of permanent modifier are shown. The shift of V signals for slurry, in relation to the aqueous solution, both for modified and nonmodified graphite tubes is observed. Moreover, a slurry introduction into nonmodified graphite tube causes strong tailing of vanadium signal with the evident difficulty of its integration. After a few injections of the slurry into a nonmodified graphite tube, V signals practically did not show a maximum and they became parallel to the baseline. This confirms strong interaction of soil matrix with a graphite surface, which leads to damage of a pyrolytic graphite layer. For a tube modified with Ir/Nb this effect takes place after more than 200 firings of the slurries.

3.6. *Analytical features*

The analytical features of the proposed method were established using the aqueous standards and the furnace program shown in Table 2. The calibration curves were established with a blank and five calibration solutions in the concentration range of 10–75 μg/L. The comparison of the calibration curves slopes for aqueous solutions and various slurries proved that in the case of the integrated absorbance measurements, it is possible to use the standard calibration method for quantitative determination of vanadium. The detection limit for V determination (LOD, based on the threefold standard deviation of the blank) and the quantification limit (LOQ, based on tenfold standard deviation of the blank) for a 5% slurry of sample were 0.04 and 0.16 μg/g, respectively. The characteristic mass, based on the integrated absorbance, was 11.9 pg.

3.7. *Determination of V in samples*

The proposed methodology was validated by the application of four certified reference materials. Additionally, this procedure was applied for determination of vanadium in the samples of the agriculture soils and the estuarine sediment. On the basis of preliminary studies, slurries and standards for the quantitative analysis were prepared in 5% acid. Table 3 shows the final results

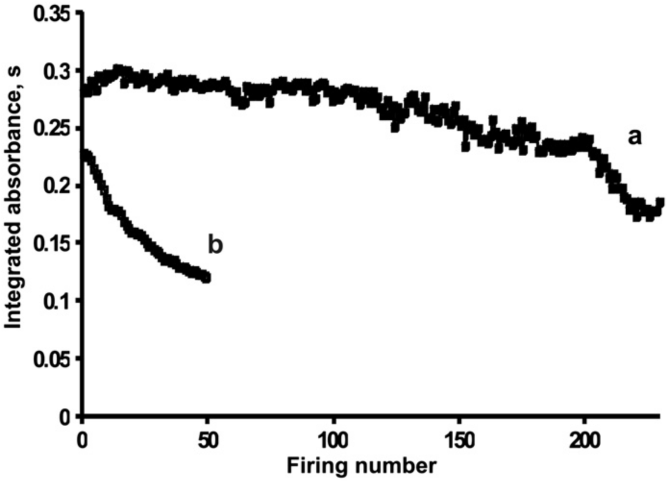

Fig. 6. The relationship of a number of firings and integrated absorbance of V in NIST 2709 (0.45 mg/mL) in the presence of Ir/Nb (a) and in the absence of the modifier (b). Pyrolysis temperature—1200 °C, atomization temperature—2600 °C.

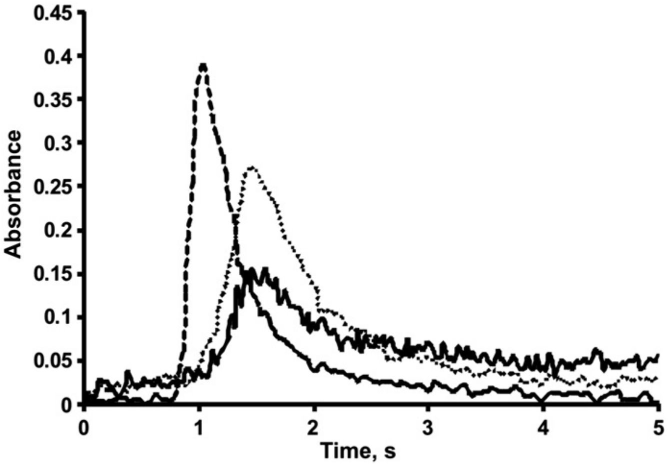

Fig. 7. Absorbance–time profiles for the atomization of 1 ng V in (—) aqueous solution, without modifier; (----) aqueous solution and the presence of Ir/Nb; (· · · ·) NIST 2709 slurry (0.45 mg/mL) and the presence of Ir/Nb. Pyrolysis temperature—1200 °C and atomization temperature—2600 °C.

Table 3
Certified and determined concentrations of V in CRMs and in 'real' samples obtained by slurry sampling GFAAS using graphite tube modified with Ir/Nb.

Element	Certified reference material	Certified value (μg/g)	Determined value (μg/g)	Sample	Determined value (μg/g)
V	San Joaquin Soil 2709	112 ± 5	109 ± 6*	Loess soil	40.5 ± 3.2*
	PACS-1	127 ± 5	124 ± 3*	Lithic soil	26.4 ± 2.1*
	MESS-1	72.45.3	68.0 ± 3.9*	Entic soil	35.4 ± 1.7*
	SL-1	170 ± 15	154 ± 10*	Umea sediment	108 ± 6*

* Standard deviation for seven replicate measurements.

of V determination in soils and sediments by the slurry sampling GFAAS technique using the graphite tubes coated with Ir/Nb. The obtained data are in good agreement with certified values, that was confirmed by the method which compares the difference between the certified and measured values with its uncertainty [24]. The precision of V determination by the presented method can be regarded as acceptable for the practical application. The relative standard deviations (RSD%) calculated for seven replicate measurements of slurries did not exceed 8%.

4. Conclusions

It was pointed out that the application of Ir/Nb modifier for V determination in soils and sediments by the slurry sampling GFAAS technique is preferable. The SEM-EDX studies proved that used mixed permanent modifiers, when deposited on the graphite surface, form islands, which have the composite character. The XRD studies conformed that the presence of NbC on the graphite surface prevents the V_8C_7 formation in the case of soil and sediment slurries introduction into the graphite tube. The masses of Ir and Nb as permanent modifiers should be carefully optimized. Application of Ir and Nb as permanent modifiers and the pyrolysis temperature of 1200 °C allow determination of V in soils and sediments without an interference effect. The analysis of CRMs confirmed the reliability of the proposed approach.

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