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

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## 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  $\mu\text{g}$  of Ir and 0.04  $\mu\text{g}$  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  $\mu\text{g/g}$ , 0.16  $\mu\text{g/g}$  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.

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## 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. Barańkiewicz et al. [10] described the ultrasonic slurry sampling electrothermal atomic absorption

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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<sub>5</sub> (boiling point 111.2 °C), VF<sub>4</sub> (decomposition point at 325 °C) or VF<sub>3</sub> (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<sub>3</sub> 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), Parzew (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.

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