



Chemical modification in atomic emission: Determination of V in lubricant oils by tungsten coil atomic emission spectrometry



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ABSTRACT

A procedure based on the use of chemical modifiers to determine V in lubricant oil samples by tungsten coil atomic emission spectrometry (WCAES) is described. Cobalt, Ni and Pd were evaluated as chemical modifiers, and the best sensitivity and limit of detection were obtained with the latter. As previously described for Cr, signal enhancements may be related to charge-transfer and electron recombination reactions in the gas phase. Using Pd as a modifier, calibration curves in the 0.25–10.0 mg L⁻¹ V range, with $R^2 > 0.999$ and relative standard deviations better than 5.6% were obtained. Accuracy was checked by determining V in a certified reference material of lubricating oil. Results were in agreement with reference values at a 95% confidence level (*t*-test). The procedure was also applied to two samples of unused, and five samples of used lubricant oil submitted to acid digestion. The V content found in these samples was between 20.5 and 67.4 mg kg⁻¹. Some of these concentrations were below the limit of detection for determinations without chemical modification (30 mg kg⁻¹). A 10-fold improvement of the limit of detection was obtained by employing Pd as the chemical modifier (3 mg kg⁻¹).

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1. Introduction

Lubricant oils are added to the metallic parts of machines and engines to reduce the wear by friction of their moving pieces and to prevent corrosion [1]. Several organometallic additives containing B, Ba, Bi, Ca, Cd, Co, Mo, P, Sb, Se, etc.; or wear and contaminant metals (Ag, Al, Ca, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Sn, Ti, V, and Zn) are present in the matrix of both used and unused lubricant oils. Some of these species can act either as performance enhancers or decomposition catalysts, depending on their concentrations [2]. Because of the complexity of this sample matrix and also because these metals are present in low concentrations, the use of sensitive analytical techniques is essential to ensure product quality and proper maintenance of machinery [3,4].

The application of electrothermal vaporization (ETV) in elemental analysis has been extensively described in the literature [5–7]. In fact, ETV coupled to spectroanalytical techniques can be considered a suitable choice for complex organic matrices such as oils due to its capability of performing sample pre-treatment by acting as a thermochemical reactor [8]. Although graphite tubes are the most common choice in atomic absorption spectrometry procedures (GFAAS), metallic atomizers present some inherent advantages such as low cost, low power requirements, potential portability, and no requirement for bulky cooling apparatus [9]. Spectrometric methods based on tungsten coil atomic absorption (WCAAS) [10–12] and emission (WCAES) [13–15]

present sensitivities comparable to GFAAS, and have been successfully applied to various elements and samples. However, severe matrix effects associated to a significant temperature gradient between the atomizer surface and the gas phase are still shortcomings for these methods [16,17].

One of the main features of GFAAS is the ability to perform *in situ* thermochemical separations of analyte and matrix components during the pyrolysis step. Chemical modifiers are generally used to promote the thermal stabilization of the analytes or to enable the formation of volatile matrix species. Incorporated in the stabilized temperature platform furnace concept (STPF) and widespread in atomic absorption spectrometry, chemical modifiers are generally employed to improve accuracy and precision by allowing higher temperatures during the pyrolysis step, which can contribute to minimizing background signals, matrix effects and potential interferences [18].

In WCAAS, several works have described the use of conventional modifiers such as Pd(NO₃)₂ [19–23], Mg(NO₃)₂ [21–23], phosphates [20,24,25], ascorbic acid [21,23,26], and permanent atomizer surface modification with Ir [11,23,27] and Rh [23,28,29]. Similar to GFAAS, the modifiers provide further analyte stabilization during the pyrolysis step and help with matrix removal in WCAAS. On the other hand, some of them are ineffective because of inadequate matrix decomposition and shortening of the atomizer lifetime due to the formation of carbides on the coil surface [30].

In spite of the extensive use of modifiers in AAS, recent works have demonstrated a novel and still underexplored use for chemical modifiers in atomic emission (AES) determinations [31,32]. In those

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cases, the modifiers were not used to favor matrix decomposition nor to stabilize the analytes as usual, but to improve sensitivity and precision by promoting gas-phase reactions between analyte and modifier species. Improvements in the limits of detection up to 29-fold for Sr and 10-fold for Cr were observed in determinations employing this strategy [31,32]. Silva et al. proposed that gas-phase reactions involving charge-transfer and electron recombination were responsible for such sensitivity improvements [32].

The present work describes the evaluation of chemical modifiers to improve sensitivity in V determinations by WCAES. Considering the mechanism proposed by Silva and co-workers, the modifiers were chosen according to their ionization energies (IE) and boiling points (BP) [32]. The procedure was then applied to V determination in used and unused lubricating oil samples submitted to acid digestion.

2. Experimental

2.1. Instrumentation

The WCAES schematic setup is presented in Fig. 1 [14]. The tungsten coil atomizers were extracted from 150 W, 15 V microscope light bulbs (Osram Xenophot 64633 HXL, Pullach, Germany) by removing the bulb's fused silica involucre. The connection base was kept intact and plugged into a standard two-pronged ceramic power socket. The filament is held in a T-shaped borosilicate glass cell (Ace Glass, product No. D131703, Vineland, NJ, USA) with fused silica windows in the horizontal plane. A gas mixture of 10% hydrogen and 90% argon flowing at 1.0 L min^{-1} is used as protective gas.

A 200 W constant current power supply (Vicor, VI-LU1-EU-BM, Andover, MA, USA) is employed to resistively heat the atomizer. A digital multimeter (RadioShack, Fort Worth, TX, USA) is used to monitor the potential across the coil, which contributes to minimizing analyte losses during the drying, pyrolysis and atomization processes [15]. The emitted radiation is focused using a 25 mm diameter fused silica lens with a 75 mm focal length, and then directed to the entrance slit of a crossed Czerny-Turner spectrograph (MonoSpec18, Scientific Measurement Systems Inc., Grand Junction, CO, USA) with a linear dispersion of about 2 nm/mm at 400 nm . A thermoelectrically-cooled charge-coupled device (CCD, Spec-10, Princeton Instruments, Roper Scientific,

Trenton, NJ, USA) is used as a detector. In order to minimize blackbody emissions and prevent the saturation of the detector, the focused light beam is positioned approximately 1 mm off of the vertical center of the spectrograph's entrance slit. Additional details on the instrumental setup and WCAES heating program can be found elsewhere [14,15].

2.2. Standard reference solutions, reagents and samples

Standard reference and chemical modifier solutions were prepared using single-element 1000 mg L^{-1} Co, Ni, V (High Purity, Charleston, SC, USA), and $20,000 \text{ mg L}^{-1}$ Pd (Spex, Edison, NJ, USA) aqueous stock solutions diluted with high-purity distilled-deionized water (Milli-Q, Millipore, Bedford, MA, USA). Trace metal grade HNO_3 and HCl (Fisher Scientific, Ottawa, ON, Canada), and H_2O_2 30% $v v^{-1}$ (GFS Chemicals, Columbus, OH, USA) were used in the digestions of the samples. Two unused and five used machine mineral lubricant oil samples were analyzed: canned WD-40 (WD-40 Company, San Diego, CA, USA) and Fisherbrand 19 (Fisher Scientific).

To evaluate the influence of modifier concentrations on the analyte emission signal, 10 mg L^{-1} V solutions were prepared in the absence or presence of $100\text{--}1000 \text{ mg L}^{-1}$ of Co, Ni and Pd. The blanks in each case were solutions containing $0\text{--}1000 \text{ mg L}^{-1}$ of each modifier without the analyte. In this case, the modifier concentration in the blank was the same as in the V reference solution. A certified reference material of Wear Metals in Oil from the National Institute of Standards and Technology (NIST SRM # 1085b, Gaithersburg, MD, USA) was used to check the procedure's accuracy.

2.3. Analytical procedure

Four V emission lines at 437.9, 438.4, 438.9 and 429.5 nm were evaluated in this work. In WCAES, most elements present maximum emission intensities between 1.5 and 2.0 s after the beginning of the atomization. Therefore, 6 subsequent spectra of integrated 500 ms each were recorded, totalizing 3 s of signal collection. To minimize sample residues on the atomizer from consecutive runs, a 2-s cleaning step was incorporated, and the atomization step was extended to 5 s. The optimized heating cycle used in this work is shown in Table 1.

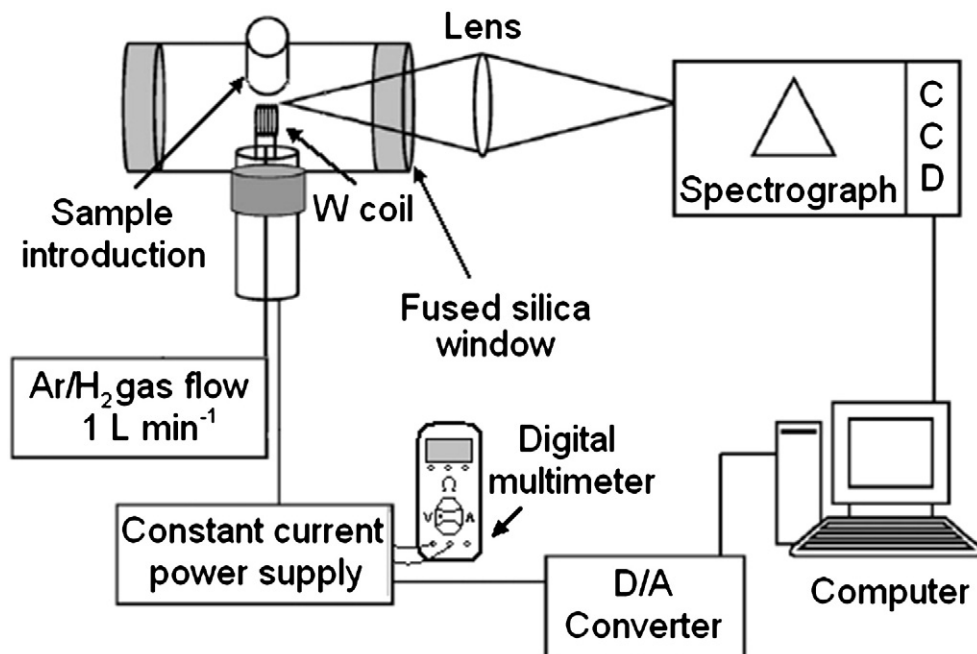


Fig. 1. Schematic diagram of the WCAES instrumental setup. Adapted from reference [14].

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