ELSEVIER

Spectrochimica Acta Part B 62 (2007) 273 – 282

SPECTROCHIMICA
ACTA
PART B

www.elsevier.com/locate/sab

Effect of chemical modification on behavior of various organic vanadium forms during analysis by electrothermal atomic absorption spectrometry☆

Zofia Kowalewska*

Research-Development Center for Refinery Industry, Chemików 5, 09-411 Płock, Poland

Received 1 September 2006; accepted 16 January 2007
Available online 23 January 2007

Abstract

The behavior of various organic V forms dissolved in xylene during analysis by electrothermal atomic absorption spectrometry (ETAAS) was compared. The investigated analyte forms included compounds with vanadium at the oxidation state III, IV or V, as well as N, O or S atoms in molecules. Another group consisted of petroleum products containing naturally-occurring V species. Although the characteristic mass determined under different analytical conditions was in the very wide range from 11 up to 55 pg, some rules of V behavior were found. In the case of porphyrins and petroleum products, the application of Pd as a chemical modifier (xylene solution of Pd(II) acetylacetonate) seemed to be crucial. It was shown that Pd must be introduced to a furnace together with a sample. Pd injected and thermally pretreated before the sample injection was less effective for porphyrins and the petroleum products, but it increased signals of V compounds containing O as donor atom. The iodine pretreatment followed by the methyltrioctylammonium chloride (MTOACl) pretreatment was advantageous for these V forms. The air ashing in a graphite tube appeared to be important to improve decomposition of the petroleum products. No significant influence of the V oxidation state on the analytical signal was observed. The behavior of V contained in two Conostan oil standards, the single-element and the S21 multielement standard, was different in many situations. Probably, the joint action of other elements is responsible for this effect. In general, chemical modification was applied in the work for two reasons: to reduce the V volatility (in some cases losses at about 300 °C were observed) and to enhance the atomization efficiency. For routine analysis air ashing, modification by Pd introduced into the furnace together with the sample solution and petroleum products with known V content as standard is recommended. Using this procedure the characteristic mass varied from 16 to 19 pg for porphyrins and all the investigated petroleum products of different character and origin. The detection limit of 1.8 $\mu g\ kg^{-1}$ obtained for xylene solutions of petroleum products is very beneficial. Additionally, the stability of V in petroleum products xylene solutions allows the use of an autosampler. A more general finding of this work is that the effect of the organic part of an analyte compound molecule in ETAAS analysis can be enormous which should be taken into account in routine analyses of various samples.

Keywords: Vanadium; Electrothermal atomic absorption spectrometry; Chemical modification; Palladium; Oil

1. Introduction

The different behavior of various analyte forms in an analytical procedure can be a basis of speciation analysis. On the other hand it can be a serious drawback and a reason of bias during the determination of the total analyte content. The powerful tool to overcome this problem in the case of electrothermal atomic absorption spectrometry (ETAAS) seems to be chemical modification [1]. According to some systematic studies it is more difficult to achieve complete unification of the various analyte forms behavior in the case of organometallic species [1–3].

The ETAAS analysis performed in organic solutions is very attractive for samples which can be completely dissolved in these solvents. This simple and short sample preparation gives low detection limits, like direct solid sampling. The direct introduction of organic solvents to a graphite furnace is little problematic in comparison with introduction to the inductively coupled plasma [4]. However, there is a discrepancy in accuracy

---

☆ This paper was presented at the VII European Furnace Symposium on Atomic Absorption Spectrometry, Electrothermal Vaporization and Atomization (VII EFS) and XII Solid Sampling Colloquium with Atomic Spectrometry (XII SSC), held in St. Petersburg, Russia, July 2–7, 2006 and was published in the special issue of Spectrochimica Acta Part B, dedicated to that conference.

* Tel.: +48 24 3653432; fax: +48 24 3653307.
E-mail address: zofia.kowalewska@obr.pl.

0584-8547/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.sab.2007.01.005

evaluation of ETAAS used for organic solution analysis. As early as in 1971 xylene solutions of mineral oil were analyzed by this technique [5]. Since that time ETAAS results comparable with the results of other analytical methods and/or sample preparation procedures have been reported [6]. On the contrary, strong dependence of the absorption signal on an analyte form was found in studies conducted using flame atomic absorption spectrometry (FAAS) [7,8]. It was expected that organic compounds do not influence ETAAS analysis results because the applied solvent is effectively evaporated and the organic matrix is pyrolyzed and removed before the measurement step. This expectation of simple analysis in an organic solution by ETAAS has not been fulfilled [9,10]. It was found that analysis in an organic solution can be influenced not only by the chemical form of analyte but also by the nature of solvent, the type of matrix, the type of atomizer surface, analytical conditions, and, the chemical modifier used [11,12].

The topic of this work is determination of V by ETAAS. The need of V determination at trace level appears due to its biological role and/or environmental pollution. However, in terms of the organic solution analysis, the most important application of the technique is petroleum products analysis. Vanadium, the most abundant metal in crude oil (below 0.1 up to 1500 mg kg^{-1}), causes detrimental technological effects at different steps of crude oil processing [13]. The determination of V in petroleum products at the level of a few mg kg^{-1} and more, can be reliably carried out by standard test methods widely used in the petroleum industry [14–18]. Direct analysis by wavelength dispersive X-ray fluorescence spectrometry (WDXRF) [14] or the mineralization with detection by inductively coupled plasma optical emission spectrometry (ICP-OES) [16], FAAS [17] and ETAAS [18,19] is applied. Problems arise if it is required to determine V at the level of about or below 0.1 mg kg^{-1}. For example, this situation occurs when petroleum products are the cracking unit feed (V compounds are severe poison to cracking catalysts). The approved methods are not sensitive enough for such analysis [14–16] or require mineralization of the large sample masses e.g. 2–4 g [18] or even 20 g [19]. The practical purpose of this work is to avoid the petroleum product mineralization by the implementation of organic solution ETAAS analysis. The selection of investigated organic compounds and test samples in this work is accordingly.

V is present in crude oil in the form of organometallic complexes [19,20]. The best recognized group is porphyrin with four N donor atoms and vanadyl cation as the central ion. The non-porphyrin group comprises modified or degraded porphyrins and complexes of tetradentate mixed ligands. In the case of the last group nitrogen, oxygen and sulfur can act as donor atoms in different combinations (e.g. structures analogous to β-diketones, β-ketoimines, β-dithions). The part of V occurring in crude oil as porphyrins is from 3 up to 50% [20,21].

In the determination of V by ETAAS different chemical modifiers were used: magnesium nitrate [1,22–25], nitric acid [25], ammonium nitrate [26] or phosphate [27], palladium [28] and palladium with citric acid [29]. Saavedra et al. concluded that no distinct improvement was achieved with the use of modifiers [30].

V in petroleum products was usually determined without any chemical modification in organic sample solution [5,6,31–36] or emulsion [37,38] analysis. The most often used solvent was xylene [5,6,32–35,39], which effectively dissolves high molecular weight petroleum fractions containing asphaltenes [41]. The other applied solvents were: a mixture of 50% xylene, 40% MIBK and 10% methyl alcohol [31], a mixture of 50% THF and 50% light oil [36], CH_2Cl_2 [38] and MIBK [40]. An inorganic compound [5], bis(1-phenyl-1,3-butanedione)oxovanadium [6,32,36], Conostan oil [33–35,39,41] and petroleum-derived products [33,35] were the standards used for the organic solution analysis. The usage of petroleum product emulsion enables introduction of an inorganic analyte compound to the system for standardization purpose [38,42,43].

It was found that V-containing porphyrins are lost at temperatures not considerably higher than 300 °C [44]. The significant decrease of the V signal at about 400 °C was observed for pyrolysis curves presented by Zamilowa et al. [33] and by Gonzales et al. [34]. Zamilowa et al. explained the fact as decrease of unspecific absorption with increase of pyrolysis temperature [33]. Gonzales et al. proposed using 400 °C pyrolysis for lighter petroleum products and 800 °C for others [34].

Thomaidis and Peperaki were probably the first who tried to use chemical modification for V determination in the petroleum industry [40]. However, they did not investigate real petroleum products, but only multielement Conostan standard oil dissolved in MIBK. The modifiers were Pt and $Mg(NO_3)_2$. $Mg(NO_3)_2$ caused Conostan standard signal decrease at the pyrolysis temperature up to 1300 °C. Pt did not influence V integrated absorbance, but enhanced peak absorbance and increased stability during pyrolysis (up to 1400 °C). In comparison with aqueous solutions higher characteristic mass and lower thermal stability were obtained for Conostan standard in MIBK.

The organic Pd form (Pd(II) acetylacetonate) was used as a modifier in the V determination in the case of xylene solutions of various petroleum products analysis [39]. It was found that Pd can increase the V signal for low and medium boiling oils up to several times. Mg acetylacetonate added to the Pd modifier did not cause any additional improvements but the omission of the pyrolysis step produced additional V signal increase. The results confirmed the volatility problem of V compounds contained in petroleum.

The aforementioned problem was also observed by Damin et al. [42] and Lepri et al. [43]. Damin et al. analyzed petroleum emulsions using also Pd modifier but in the inorganic form [42]. In the work by Lepri et al. [43] a prototype of ETAAS with high-resolution continuum source was applied. Due to high background correction capability of that equipment, low temperature pyrolysis (300 °C) was possible. The results obtained in both works and given as the total V content were similar. If the measurements were repeated at 800 °C without the modifier, volatile V compounds evaporated from a furnace and only “thermally stable” compounds were detected. A kind of speciation analysis can be carried out using the described method.

In the present study the application of xylene as a solvent was expected to prevent any troubles with asphaltene