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Structural and spectrophotometric characterization of 2-[4-(dimethylamino)styryl]-1-ethylquinolinium iodide as a reagent for sequential injection determination of tungsten

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ABSTRACT

Structure, spectrophotometric and protolytic properties of the styryl dye 2-[4-(dimethylamino)styryl]-1-ethylquinolinium iodide (R) as well as its complex with tungsten were studied. The selective protonation of dimethylamino group was confirmed by density functional theory investigation through the computation of Fukui function, NPA partial atomic charges, and NICS(0) aromaticity indexes. The TD-DFT study explains the experimental change of color by excluding the dimethylamino group from HOMO orbital upon protonation. The acid dissociation constant, the optimum wavelength and the molar absorptivity of R were found to be: 3.02, 501 nm and $4.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. The protolytic properties of the reagent were found to change significantly in the presence of tungsten(VI). Analysis of bond critical points between the anions and Quinaldine Red cation gives the selectivity raw $\text{HWO}_4^- > \text{MoO}_4^- > \text{H}_2\text{VO}_4^- > \text{ReO}_4^- > \text{ClO}_4^-$, that perfectly match with the experimental data. Based on this observation, a non-extractive sequential-injection spectrophotometric method for the determination of tungsten was developed. The absorbance of the colored extracts obeys Beer's law up to 55.2 mg L^{-1} of W at 520 nm wavelength. The limit of detection calculated from a blank test ($n = 10$) based on 3 s was 0.96 mg L^{-1} . The developed method was applied for the determination of tungsten in model samples.

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1. Introduction

Tungsten is a rare element. Its compounds are generally inert and the effects of tungsten on the environment are limited [1]. Tungsten is the heaviest element known to be biologically functional [2,3]. Its density is similar to that of gold, and this allows it to be used in jewelry as an alternative to gold or platinum [4,5]. Due to its excellent physical properties (the highest melting point among metals and the lowest vapor pressure), tungsten has a very wide range of uses in electrotechnics; hard alloys formed on the basis of tungsten carbide are particularly important. A great many analytical methods have been developed for tungsten determination, mainly spectroscopic methods such as UV–Vis spectrophotometry, atomic absorption spectrometry and techniques that employ inductively coupled plasma [6–11]. It needs to be noted that atomic absorption determination of tungsten is strongly complicated by the complexity of atomization, the occurrence of heat-resistant carbides and significant matrix effects.

Several organic dyes and reagents for determination of tungsten can be used, such as toluene 3,4-dithiol [12], 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline, 5,7-dibromo-8-hydroxyquinoline and 8-mercaptoquinoline [13], malachite green [7], [5,7-dibromo-1,3,3-trimethyl-3H-indolium-2]-[1',3',3'-trimethyl-3'H-indolium-2']-trimethinecyanine chloride [9].

Among the most frequently used methods for tungsten determination are spectrophotometric methods which, however, suffer from several limitations and/or problems. Thus, in the most commonly used thiocyanate method the formation of the W(V)-SCN complex requires acidic mediums and the presence of SnCl_2 . Furthermore, in order to increase the sensitivity of determination, most of the above methods require preconcentration of tungsten by using preliminary extraction [14] or sorption [15].

In the light of the above facts, one must conclude that the methods commonly used for determination of tungsten often require a relatively complicated procedure of separation/preconcentration by extraction, which is associated with many problems such as, for example, the use of large volumes of toxic extraction solvents, difficulties in their regeneration and subsequent contamination of the environment with the

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