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A Novel Optode for Vanadium Speciation: Sol–Gel Based Optical Sensor for Vanadium Determination

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Abstract

A highly selective optical sensor for V(IV) ions was established depended on entrapment of a sensitive reagent, 5-(2`,4`-dimethylphenylazo)-6-hydroxy-pyrimidine-2,4-dione (DMPAHPD), in a silica sol–gel thin film coated on a glass substrate. The thin films fabricated depended on tetraethoxysilane (TEOS) as precursor, sol–gel of pH = 2.5, water: alkoxyde ratio of 4: 1 and DMPAHPD concentration of 2.5×10^{-4} M. The effect of sol–gel parameters on sensing behavior of the fabricated sensor was also illustrated. The fabricated sensor can be used to detect V(IV) ion with an outstanding high selectivity over a wider dynamic range of 5.0–145 ng mL^{-1} and a detection limit of 1.35 ng mL^{-1}. It also recorded reproducible results with relative standard deviation of 1.75% and 1.02% for 20 and 70 ng mL^{-1} of V(IV), respectively, along with a fast response time of two min. Total vanadium was determined after reduction of V(V) to V(IV) using ascorbic acid as reducing agent. The V(V) amounts were estimated by subtracting the concentration of V(IV) from the total vanadium concentration. Interference studies reported a good selectivity for V(IV) with trapping DMPAHPD into sol–gel matrix and appropriately adjusting the structure of doped sol–gel. The proposed sensor was compared with others and was applied to define vanadium in different environmental samples with good results.

Keywords

Optical Sensor Membrane; Vanadium Determination; Spectrophotometry; Environmental Analysis.

1. INTRODUCTION

In the recent years. an element chemical form plays a significant role involving the bioavailability, toxicity and transport properties was accepted. In the past, total detection of an element was used to find out potential health harmfulness or benefits, whereas, a researcher knows that total elemental quantification alone is deficient [1]. For understanding the biochemical influence of elements on living organisms mechanism, it is essential to not only detecte the species formed inside specific environmental or biological matrix but also quantify those species with high accuracy [2].

The exposure of trace elements to the environment has increased and activated the science community to introduce new analytical techniques and instrumentation, capable of detecting concentration levels at ultra trace amount [3]. Vanadium is known as an essential trace element for animals and plants, which performs in helps young animals to grow and the preparation of chlorophyll. The studied daily intake of vanadium ranges from 6.0 to 18 µg [4].

Compounds containing vanadium are toxic after long periods of exposure or in high levels [5]. They exhibit chemotherapeutic influences in the treatment of leukemia and recent studies showed promising application in management of diabetes [6].

Vanadium in air is released in large amounts from the combustion of fuel oil, especially residual oil, which is known to be rich with vanadium and is precipitated on the soil that was drained by rain and groundwater and can be directly adsorbed by plants [7]. Vanadium is applied as a developer in photography a depolarizer, a catalyst (e.g., in polymer synthesis), and in the manufacture of yellow glass [8]. Dissolved vanadium is generally noticed as the index element in natural water and environmental pollution. It can be toxic in high concentration levels (µg mL^{-1}) [9].

Vanadium can exist in various oxidation states from −1 to +5, but it is most commonly found in the +4 and +5 states. Speciation analysis of trace amounts of V(V) known as vanadate ion and V(IV) presents as vanadyl ion, has become important. Vanadium(V) is more toxic than vanadium(IV) therefore, it is nesseccary to monitor the concentration of individual oxidation form vanadium in the environment for detecting both the potential risk and benefits [10].

Vanadium concentration in water ranges from 0.5 to 2.5 mg L^{-1} in natural water [11], from 0.2 to 29 ng mL^{-1} in sea water [13], from 0.2 to > 100 ng mL^{-1} in fresh and drinking water [12], and typical values being between 1.0 and 6.0 ng mL^{-1} [14]. The permitted vanadium level is 50 µg mL^{-1} according to the Environmental Protection Agency (EPA) [3].

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Various analytical techniques have been applied to detect vanadium and they include gamma-ray spectrometry [15], fluorescence spectrometry [16], electro-analytical methods [17], liquid chromatography [18], atomic absorption spectrometry [19], Inductively coupled plasma-atomic emission spectrometry [20], inductively coupled plasma optical emission spectrometry [21], laser-induced breakdown spectroscopy [22] and inductively coupled plasma-mass spectrometry [23]. However, spectrophotometric methods are most frequently applied to determine vanadium due to their simplicity, reliability, relatively low-cost instrumentation, sensitivity, and selectivity [24]. Spectrophotometric methods employ optical sensors [25], the catalytic effect of vanadium on chemical reactions [26,27] or in most cases various colorimetric reagents {e.g., leucocrystal violet [28], desferrioxamine B [29], 2-pyrrolealdehyde phenylsemi-carbazone [30], rhodamine B [31], variamine blue [32], salicylaldehyde acetoacetic acid hydrazone [33], and xylenol orange [34]. Most of these colorimetric reagents, and in particular xylenol orange, form coloured complexes with different metal ions and therefore an appropriate separation step could be done in the analytical procedure to complete reliable determination of vanadium.

Comparison with other analytical methods [35–39], sensors depended on optical signal measurements and fabricated with ionospheres, have been accepted as fast and economical sample monitoring device with an excellent detection limit and sensitivity, which should minimize the effect of other captions and anions present in real sample matrixes especially to heavy metal analysis in a real time. Optical sensors need simple instrumentation and are suitable for multi-sensor array fabrication [40,41]. Type of polymer matrix has a significant influence on the performance of the sensors. Different supporting materials, as polydimethyl-siloxanes (PDMS), cellulose derivatives, polyvinyl chloride (PVC) and sol–gel can be used to prepare the sensor membranes [42,43].

The sol–gel technology has recently attracted considerable attention for the development of the biosensors and sensors, largely due to its versatility and simplicity [44–46]. In this technique, a porous silica matrix is formed from hydrolysis and condensation of alkoxyde precursors under acidic or basic conditions, followed by the densification process at low temperature while entrapping the analyte sensitive species within it. The structure and properties of doped sol–gels heavily based on some operational parameters involved in the preparation as water : silica molar ratio, catalyst, pH, solvent, and temperature. These factors are highly affected on the hydrolysis and condensation while allowing to the pore size control of the final product [47]. Such a control is essential for obtaining a proper balance between nonleaching characteristic of the entrapped dye molecules and its accessibility to the analyte. The advantage of applying doped sol–gel thin film as sensing material is that they are inert, tough, more resistant in aggressive environments and exhibit fast response times [48,49]

To the best of our knowledge, most of the illustrated sol–gel based optical sensors were hitherto related to the measurement of pH and a few reports were published concerning the metal ions detection [42]. In this work, a durable optical chemical sensor was syntheses using sol–gel procedure to determine trace Vanadium. To construct the sensor 5-(2`,4`-dimethylphenylazo)-6-hydroxypyri-midine-2,4-dione (DMPAHPD) is incorporated into a sol–gel matrix onto the glass substrate. The sensor response is easily monitored by means of spectral and color changes. The main objective is to design a highly selective, sensitive, and stable V(IV) sensor that can be applied to the analysis of the real samples.

2. EXPERIMENTAL

2.1. Apparatus

A pH-meter of type Jenway 3505 pH meters 9V-AC Power was applied to measure the pH values. The spectroscopic measurements were made applying a JASCO 530V UV–Vis spectrophotometer. A Perkin Elmer model 5300 DV; ICP-AES (Waltham, MA, USA) was used for all ICP-AES measurements. The thin films were placed in a quartz cuvette and all absorption experiments were carried out in a batch mode at room temperature.

2.2. Reagents and solutions

All chemicals used were of analytical grade and bidistilled water was used throughout the experiments. Tetraethoxysilane (TEOS), absolute ethanol (EtOH), methanol (MeOH) hydrochloric acid (HCl) were purchased from Merck. 5-(2`,4`-dimethylphenylazo)-6-hydroxypyrimidine-2,4-dione (DMPAHPD) applied in the present investigation was prepared according to the method described previously [50,51]. A stock solution 2.5 × 10^{-4} M of DMPAHPD was prepared by dissolving an appropriate weight of the reagent in a minimum amount of pure MeOH and brought to 100 mL in measuring flask with pure MeOH.

Stock solutions (1000 mg L^{-1}) of vanadium(IV) and vanadium(V) were prepared by dissolving NH_4VO_3 (Merck) and $VOSO_4.5H_2O$ (Merck) in bidistilled water, respectively and were standardized [52]. Working standard solutions were prepared by diluting stock solution. To investigate the interferences, the metal cations tested were of their nitrate salts. All glassware used for handling solutions were cleaned with detergent solution, soaked in aqueous HNO_3 (10% v/v) then rinsed thoroughly with bidistilled water several times.

2.3. Preparation of sol–gel coated slides

According to the procedure described in the literature [48], the sol–gel thin film was prepared. The sol–gel silica thin films containing DMPAHPD were synthesized by spin-coating on soda-lime glass microscope slides as substrates. Prior to coating, the silanol groups on the surface of the glass were activated via treatment with concentrated nitric acid for one day and then washed with copious amounts of bidistilled water and methanol, followed by drying at 100 ºC for 45 min. Several types of sol–gel thin films were prepared to achieve the most suitable sensor with high sensing parameters. The sol–gel process characters such as H_2O : TEOS and pH were illustrated. The acid-catalyzed procedure and water : TEOS ratios of 2, 4, 6 and 8 were used.

The coating mixture was synthized by mixing equal volumes (2.0 mL) of methanol and TEOS in closed vial. After stirring the solution for 15 min, several amounts of water, HCl (to adjust pH of the solution to ≈ 1.0, 2.0 and 3.0), 2.0 mL dopant (DMPAHPD) in the range of 2.5×10^{-4} M in methanol and few drops of Triton X-100 were added while continuing to stir at 25 ± 1.0 ºC. The prepared sols containing the DMPAHPD were left to age in absence of light for various times to give more viscous solutions, before coating on glass slide,. This aging time should be < the gelation time. The coatings were performed by a handmade spinning device in a duration time of 1.0 min on both sides of glass slides. All films were dried in air at 25 ± 1.0 ºC for ten days which led to obtain crack-free thin films. The thin films were stored in desiccators before their applied.

2.4. Analytical procedure

An aliquot of V(IV) solution and a suitable amount of phosphoric acid were added to a 5.0 mL measuring flask so that the final concentration of phosphoric acid reached to 0.1 M and was diluted to mark with water. A certain amount of this solution was transferred to a spectrophotometer cell in which a glass slide was presented. Then, the absorbance was measured at λ_{max}= 624 nm after 3.0 min.

2.5. Preparation of samples

2.5.1. Determination of V(IV) in water and dietary supplements samples

Tap water samples were collected from the water tap in laboratory of Benha University, Egypt. River water which supplies water to Benha River Rashid, Egypt and rain water was achieved in Benha. All bottles and filtration apparatus were previously washed with 10% (v/v) HNO_3 [53] and then rinsed thoroughly with distilled water. Dissolved and particulate matters in the river water were commonly separated by filtration via a cellulose membrane filter having 0.45 μm pore size. Filtered aliquots of sample were stored in polyethylene bottles and stored in a refrigerator when not used. The water samples were spiked with different levels of V(V) and V(IV) before analysis. The analysis was recorded out at λ_{max} 624 nm using a calibration curve.

The vanadium concentration was also determined in three dietary supplements samples. The sample preparation followed the method reported in the literature [54,55] which involved the addition of concentrated HNO_3 (10 mL) to a measured mass of ground tablets or capsule powder and heating the mixture to reduce the volume followed by the addition of 5.0 mL of 30% hydrogen peroxide with further heating. Deionized water was added and the solution was filtered. The pH of the solution was checked to be in the range 1.5–4.0, and, if required, was adjusted by the addition of sodium hydroxide solution. Finally, the sample volume was transferred to 100 mL with deionized water. Depending on its V(IV) concentration, between 2.5 and 5.0 mL of the sample solution were further diluted to 10 mL prior to the analytical measurement. V(IV) was detected in three replicate samples by both developed sensor and by ICP-OES methods.

2.5.2. Soils

The samples were dried and grounded into fine powder applying a glass mortar, then an accurately weight of 1.00 g of a powdered soil sample was brought into a 25 mL platinum crucible and digestion method was carried out in accordance to the protocol of Molathegi [56]. The sample was treated firstly with 10 mL of HF and 2.0 ml of $HClO_4$ and then evaporated till near dryness. Subsequently a 2.0 mL HF and 1.0 mL of $HClO_4$ were added and the mixture again evaporated to near dryness. Finally, $HClO_4$ (1.0 mL) was added and the sample was evaporated until white fumes appeared. The residue was dissolved in 5.0 mL of 6.0 M HCl and diluted to 50 mL with deionized water. Extraction and determination of vanadium species were performed by the proposed and ICP-OES methods.

2.5.3. Rice

The rice sample was treated according to the method adopted [57] by taking 1.0 g of dried rice at 110 ºC and digested with 10 mL of 5.0 M HNO_3 followed by addition of 5.0 mL of $HClO_4$ (70% w/w). The solution was evaporated to near dryness and the residue was dissolved in 10 mL of 0.1 M HCl. Then heated to boiling, cooled and filtered. The filtrate was brought into a 50 mL measuring flask and completed to the mark with deionized water. An appropriate amount (i.e. 2.0 mL) of this solution was transferred and subjected to the sensor described above to determine vanadium species by the proposed and ICP-OES methods.

2.5.4. Vegetables

Three vegetables samples (potato, spinach, carrot) were supplied from local markets and subjected to the method described by [58] with little modification. Dried vegetables were first air-dried in an oven at 105 ºC for three days under uncontaminated conditions. A 1.0 g of each grounded powder sample were brought into glass beaker and digested with 10 mL of HNO_3 and 2.5 mL of HCl (4 : 1 v/v) on a hot plate at low temperature till complete digestion. After cooling at at 25 ± 1ºC, the solution was completed 50 mL with deionized water in a 50 mL measuring flask. An aliquot (2.0 mL) of the sample solution was transferred, followed the proposed sensor procedure and the amount of the two species was detected using the proposed and ICP-OES methods.

3. RESULT AND DISCUSSION

The pH and the water : TEOS molar ratio (R) are the most significant process parameters which have strong influences on porosity and pore size of sensor and performance of key factors as stability, response time and reagent leaching. Concentration of reagent, the R-value of the sol and the HCl acid concentration were the most important factors that can greatly affected on incorporation of reagent rhodamine B in their case into silica sol–gel films and optical, leaching and light fastness properties of a silica layer [59]. By careful tailoring of these factors a proper balance between non-leaching characteristic of the entrapped reagent molecules and its accessibility to the analyte can be obtained. Preparation of sol at pH = 1.0 is the most frequently applied pH in the production of sol–gel optical sensors due to its typically produces structures with higher durability, small pore size and less prone to leaching and so it was the strategy firstly adopted for the preparation of the sensor. The spectroscopic information of the given films depended on polymerization of tetraethoxysilane with a H_2O : TEOS of 4 : 1 at pH = 1.0 reported no interaction with vanadium on any of the pH values examined. The same results were obtained for other water : alkoxyde ratios (R) (2, 6 and 8). This may be attributed to the fact that the pore sizes were not optimized for V(IV) ions to penetrate into porous gel–silica matrix and react with the reagent studied.

In most of the reports, in order to both increase porosity and maintain excellent optical characteristics, base-catalyzed sol–gel procedures have been employed. Using the basic mechanism, a highly porous matrix with more open structure is introduced, whereas, the base-catalyzed sol–gel films are more susceptible to degradation and leaching of reagents than acid-catalyzed films. Increasing sol–gel pH gave an increase in porosity and pore size; therefore, the performances of the sensor were examined through controlling various pHs of the sol–gel by means of acid-catalyzed process [33, 42–44]. The films achieved at pH 1.5 showed no reaction with vanadium, however, at pH about 2.5 good optical response was achieved when immersing into V(IV) solution. In the next step, the effect of water : alkoxyde ratio (2, 4, 6 and 8) on the response time and reagent leaching of the sensor was investigated. When immersed into V(IV) solution, reagent leaching of films produced with R = 4 was visible to the naked eye but such a phenomenon was not obtained for sensors produced with R = 2, 6 and 8 even after long immersion time (120 min) in V(IV) solution. So they were adopted for further investigates. In the next step, response time for films with R = 2, 6 and 8 was illustrated. For the films with R = 6 and 8 no acceptable signal was observed in the first two min while for R = 2 only after half min absorbance of 0.06 and 0.156 was recommended for V(IV) concentration of 45 and 90 ng mL^{-1}, respectively.

Reagent leaching behavior of film with R = 4 was also investigated. For this purpose, the reagent leaching was reported by soaking the sol– gel glass slide doped with DMPAHPD in the acidified water with H_3PO_4 and then the absorbance of the solution measured as a function of soaking time at the wavelength of 423 nm (wavelength of maximum absorbance for

DMPAHPD in the solution). As demonstrated in Fig. 1, no reagent leaching was reported for sensor even in long soaking time. As a result, the optimum H_2O : TEOS ratio and sol–gel pH were fixed at 4 : 1 and 2.5, respectively for the preparation of the sol–gel standard solution.

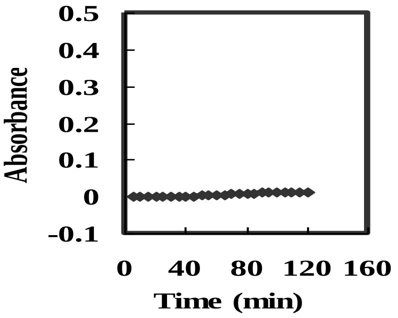

Fig. 1. Leaching profile of the sol-gel film based on R=4 in the acidifield water with H_3PO_4.

3.2. Optical properties of DMPAHPD entrapped in sol–gel-derived matrix

DMPAHPD is often applied as a chromogenic reagent for the detection of Y(III) [50], Pt(IV) [51], Th(IV) [59] and Hg(II) [60]. V(IV) form a complex with DMPAHPD in acidic media. DMPAHPD is examined as extremely sensitive and selective reagent for spectrophotometric detection of trace amount of vanadium which can form an intensely violet colored complex with tetravalent vanadium with a molar absorptivity of 9,750 L mol^{-1} cm^{-1}.

After incorporating DMPAHPD in the sol–gel thin film, the optical characterization of the sensor was recommended against blank thin film. Fig. 2 represents the absorbance spectra of the glass slide before and after reaction with various levels of V(IV).

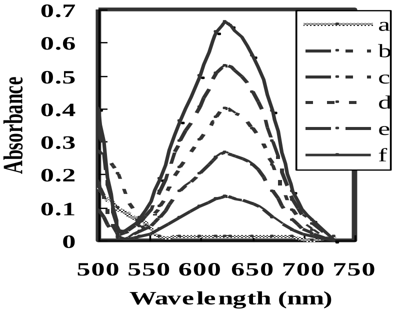

Fig. 2. Absorption spectra of DMPAHPD immobilized in sol-gel film after reaction with different amount of V(IV) in 0.1 M phosphoric acid (a)0, (b) 20, (c) 40, (d) 60, 80 and 100 ng mL^{-1}.

Formation of the complex caused an obvious change in color of the sensor from orange to violet with a strong absorption maxima at 624 nm which was the wavelength adopted for all analytical studies. These noticeable color and spectral changes can be associated with diffusion of V(IV) into sol–gel film and the effective interaction between the V(IV) ion and the DMPAHPD in the film.

3.3. Optimization of the experimental variable parameters

3.3.1. Effect of pH of solution on the response of the sensor

The influence of pH on the response of sensor was investigated when it was introduced into a solution 70 ng mL^{-1} V(IV) at variable pH values for a fixed time of 2.0 min. The pH of solutions was adjusted using H_3PO_4 and NaOH. Fig. 3 shows the effect of different pHs on the complete color development of the sensor formed. It can be reported that the optimum pH value for complex formation between immobilized DMPAHPD and V(IV) is from 2.0 to 2.5. Since pH = 2.0–2.5 was selected as optimum, in another experiment the influence of acidity on the sensitivity of sensor (A) was studied using phosphoric acid in the range of 0.00–0.25 M. As demonstrated in Fig. 4, the optimum H_3PO_4 concentration was observed in range of 0.03–0.25 M for the complex formation between immobilized DMPAHPD and V(IV). The absorbance was enhanced by increasing H_3PO_4 concentrations up to 0.12 M while in higher concentration a slight decrease was observed. Therefore, 0.1 M of phosphoric acid concentration was selected as optimum pH value.

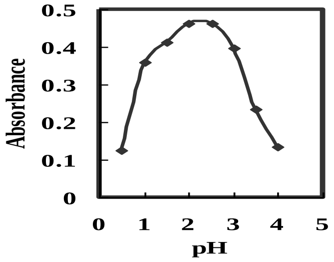

Fig. 3. Effect of acidity on the optode response.

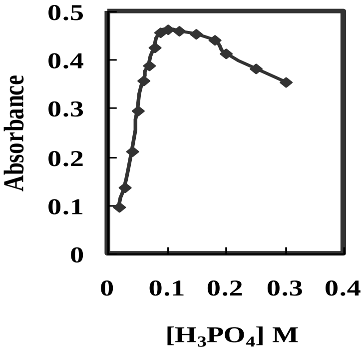

Fig. 4. Effect of phosphoric on the optode response.

3.3.2. Response time and regeneration

The response time is an important analytical feature for any sensor. The absorbance responses of the optical film versus time in chosen experimental conditions for 40 and 120 ng mL^{-1} of V(IV) were established. As represented in Fig. 5, the response times of the prepared sensor ($t_{95\%}$) were calculated to be three and two min for 40 and 120 ng mL^{-1} of V(IV), respectively. Thus, a sensor response time of three min was selected for the subsequent experiments. A good sensor could completely regenerate at short time for repeated usages. The sensor can be regenerated and reused by exposure to an EDTA solution in pH = 9.0. A short regeneration time of lower than one min obtained using a 0.25 M solution of EDTA.

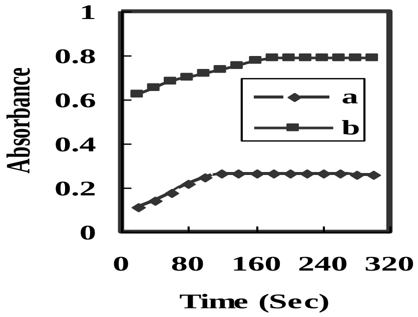

Fig. 5. Response curve of the sensor as a function of time when the [V(IV)] were (a) 40 and (b) 120 ng mL^{-1}.

3.4. Determination of V(V)

Since V(V) does not react with DMPAHPD, total vanadium could be measured after the reduction of V(V) to V(IV) by 2.5 × 10^{-3} M ascorbic acid as reducing reagent. The V(V) concentration should be calculated by subtracting the concentration of V(IV) from the total vanadium concentration. In the next step, to check the reliability of sensor, various solutions containing mixtures of both oxidation states (IV and V) were prepared and vanadium concentration was determined by applying the procedure. The results recorded sin Table 1 indicates that this procedure is perfectly capable of vanadium speciation.

Table 1. Results for the determination of V(IV, V).

Added (ng mL^{-1})		Found (ng mL^{-1})^{a}		Calculated (ng mL^{-1})
V(IV)	V(V)	V(IV)	V(IV) + V(V)	V(V)
100	0	99.70 ± 0.78	99.75 ± 0.87	ND^{b}
75	25	74.30 ± 1.05	99.50 ± 1.27	25.20 ± 1.46
50	50	50.75 ± 0.85	100.30 ± 1.15	49.55 ± 1.55
25	75	24.80 ± 0.94	101.20 ± 0.69	76.40 ± 1.73
0	100	ND^{b}	101.25 ± 0.86	101.25 ± 0.90

[a] $\bar{x} \pm t_s/\sqrt{n}$, $n = 3$; [b] Not detected

3.5. Effect of interfering ions

The influence of various species on the absorbance of a mixture containing V(IV) was established. An ion was considered as interference when its presence produced a variation in the absorbance of the sample greater than 5.0 %. This increment of absorbance was evaluated at 624 nm (corresponding to the maximum absorption of V(IV) complexes), in order to establish the different influences of the interfering ions on the analyte. As it is well-known, various metal ions are ubiquitous in real samples. Hence, it is essential to carry out an interference study to evaluate the performance of sol–gel membrane doped with DMPAHPD as a selective colorimetric sensor. The selectivity of the glass slide was examined for 70 ng mL^{-1} of vanadium in the presence of various levels of foreign ions using the reported method. The results of the interference investigation were recorded in Table 2. Result specified that most of the common cations and anions have no obvious influence on the determination of vanadium even at high concentrations.

Table 2. Effect of interfering ions on the determination of 70 ng mL^{-1} of V(IV)

Foreign ion	Tolerance limit molar ratio ([interference]/[V(IV)])
Na^+, K^+, PO_4^{3-}	1500
Cs^+, Li^+, Ti^{4+}	1200
$C_2O_4^{2-}$, SO_4^{2-}, Cl^-	1000
NO_3^-, IO_3^-, Br^-	800
Ca^{2+}, Mg^{2+}, Al^{3+},	650
Ag^+, Fe^{3+}, Pb^{2+},	500
Be^{2+}, Ba^{2+}, Cd^{2+},	400
Hg^{2+}, Ni^{2+}, Zn^{2+},	350
Mn^{2+}, Cr^{3+}, Cr^{6+},	300
Co^{2+}, Cu^{2+}	250
Pt^{2+}, Pd^{2+}	200
La^{3+}, Y^{3+}, Sc^{3+}	160
Th^{4+}, UO_2^{2+}	140
V^{5+}, Mo^{6+}, W^{6+}	125

3.6. Analytical figure of merit

All optimized parameters mentioned above are applied in order to make an V(IV) calibration curve. The calibration graph depended on absorbance of the thin film versus V(IV) concentration was linear in the range of 5.0–145 ng mL^{-1} with equation of $A = 0.0066C + 0.07$ and correlation coefficient (R^2) of 0.9992, where C is concentration of V(IV) in ng mL^{-1} and A is absorbance of sensor at 624 nm. The limit of detection and of quantification based on three and ten times the standard deviation of blank [65] were 1.35 and 4.95 ng mL^{-1}. When the detection limits of several detection methods for the determination of vanadium are compared, it can be said that the detection limit of the proposed method is comparable or lower than most of those reported in the literature (Table 3).

Table 3. Comparison of detection limits of some methods for vanadium speciation

Complexing reagent	λ_{max} / nm	Detection limit $\mu g\ mL^{-1}$	Matrix	Ref.
Variamine blue (VB) as a chromogenic reagent for V(V)	570	0.1	Steel	[32]
Pyrogallol red as chelating agent for V(IV) and V(V)	---	0.6 (IV) 0.3 V(V)	Real samples	[61]
3-hydroxy-2-(2-thienyl)-4H-chromen-4-one (HTC) as chromogenic reagent for V(V) and in 0.04-0.30 M CH_3COOH	420	1.3	Synthetic and technical samples	[62]
Calmagite	490	0.12 0.18	Tap, rain and river water	[63].
1-(2-hydroxy-4-methoxybenzo-phenone)-4-phenylthiosemi- carbazone (HMBPT) as chromogenic reagent for V(IV)	560	0.16	Natural water	[64]
5-(2`,4`-dimethylphenylazo)-6-hydroxypyrimidine-2,4-dione	624	0.0135	Environmental samples	This work

Additionally, in the analytical characteristics, this optode in comparison with other literature procedures for V(V) detection, it can be seen that the proposed method is applied for tap, rain and river water but others only worked on natural water, synthetic and technical samples. It is simpler and this method does not require any pretreatments.

The analytical characteristics of this optode compared with other literature methods for V(V) determination can be seen that the proposed method is more superior in terms of sensitivity and simplicity. The analysis of water samples revealed the reliability, selectivity and robustness of the proposed method (with total relative standard error less than 4.0%). These findings might open up new opportunities in the speciative spectroscopy of cations.

3.7. Reproducibility and lifetime of the sensor

The reproducibility and repeatability are two of the crucial properties of the chemical sensor for knowing its working activity. Reproducibility was investigated through the results obtained from the V(IV) solution 70 ng mL^{-1} using five sol–gel coated glass slides which were constructed independently in similar conditions. The relative standard deviation of response among sol–gel thin films found to be 1.75%. In addition, the repeatability using a single membrane was tested by performing eight replicate measurements on 20 and 70 ng mL^{-1} of V(IV) solutions. The relative standard deviation (RSD) was 1.75% and 1.02%, respectively.

The useful lifetime of the sensor was estimated by subsequent dipping of film in solution containing 70 ng mL^{-1} V(IV). After 35 determinations, a reduction of 5.0 % was observed in the sensor response. In another experiment, the change in the absorbance was measured after keeping the sol–gel coated glass slides in desiccators for 45 days (maximum time tested). The absorbance values of the thin film at 624 nm were decreased only about 1.5 % over a period of one month. This result indicates that the sensor is very stable; therefore, it can be stored for at least 45 days without losing its characteristics.

3.8. Analytical application to real samples

The proposed sensor methodology was applied for the analysis of V(IV) in various real samples such as two spiked water samples (tap and reservoir water) and in three dietary supplements samples was carried out using the optimized sensor system and the results are presented in Table 4 together with those obtained using ICP-AES [20]. The results obtained by the two methods were statistically indistinguishable by using the t-test at the 95% confidence level.

According to the considerable analytical features that have been achieved in the proposed method, such as low detection limit, high recoveries and interference-free, the method was employed for the detection of both species in water, soil, rice and vegetables samples after the digestion procedures that described in experimental work and measured in triplicate. At the same time, the sample solutions were also determined by electrothermal atomic absorption spectrometric method (ICP-AES) to test the significance of the proposed method. The findings are presented in Tables 5. The statistical computations using t-paired test for all tested sample reveals that the proposed method has no significant difference compared with ICP-AES method at 95% confidence level.

The performance of the proposed method was assessed by calculation of the t- value (for accuracy) and F- test (for precision) compared with ICP-AES method. The mean values were obtained in a Student's t- and F- tests at 95% confidence limits for five degrees of freedom [66]. The results showed that the calculated values (Table 4 and 5) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability and less time consuming, shows the advantage of the proposed method over other method.

Table 4. Determination of vanadium in water and dietary supplements samples.

Sample	Added actual	Concentration – found* Sensor	ICP-AES*[20]*	t_{exp}**
Spiked tap water (ng mL^{-1})	50	49.2 ± 0.06	50.7 ± 0.02	0.89
	100	98.5 ± 0.07	103.0 ± 0.02	1.13
Spiked reservoir water (ng mL^{-1})	60	60.4 ± 0.08	58.8 ± 0.03	1.34
	120	118.7 ± 0.07	122.2 ± 0.01	1.39
Dietary supplement 1 (µg/tablet)	30	29.6 ± 0.08	29.5 ± 0.10	1.65
	60	60.8 ± 0.07	59.1 ± 0.12	1.87
Dietary supplement 2 (µg/tablet)	40	40.5 ± 0.10		
	80	80.7 ± 0.07	83.0 ± 0.05	1.19
Dietary supplement 3 (µg/tablet)	60	59.2 ± 0.09		
	120	118.5 ± 0.06	123.2 ± 0.04	1.42

* The results with their ± standard deviations are calculated based on six replicate measurements.

** t- value at 95% confidence level and for four degrees of freedom is 2.57.

Table 5. Results of the estimation of V(IV) and V(V) ions in different real samples with statistical paired t-test at 95% confidence level

Sample	Added ng mL^{-1}	V(IV) (ng mL^{-1}) Proposed^a	ICP-AES^a [20]	Paired t_{test}^{b}	F-value^b
Rice					
Egypt	---	0.35 ± 0.28	0.25 ± 0.72		3.94
	10	10.50 ± 0.47	10.15 ± 1.07	1.64	
	20	20.25 ± 0.28	20.40 ± 0.89		3.56
Iraqi	---	0.28 ± 0.14	0.20 ± 0.048	1.81	
	15	15.20 ± 0.52	15.40 ± 0.76		2.98
	30	30.35 ± 0.33	30.10 ± 0.82	1.37	
Indian	---	0.17 ± 0.19	0.16 ± 1.22		3.27
	20	20.30 ± 0.34	20.35 ± 0.76	1.84	
	40	40.10 ± 0.63	40.45 ± 0.93		3.76
Soil					
1	---	<0.120	<0.120		
	7.5	7.60 ± 0.47	7.80 ± 0.78	1.26	
	15	15.10 ± 0.51	15.30 ± 0.65		2.78
2	---	<0.120	<0.120		
	5.0	4.97 ± 0.67	5.10 ± 1.07		3.35
	10	10.10 ± 0.48	9.80 ± 0.79	1.69	
3	---	<0.120	<0.120		
	10	9.95 ± 0.19	10.15 ± 0.93		2.77
	20	20.25 ± 0.45	20.35 ± 0.78	1.43	
Vietnamese	---	0.60 ± 0.15	0.57 ± 0.83		
	6.0	6.55 ± 0.36	6.75 ± 0.64		3.27
	12	12.70 ±0.53	12.40 ± 1.05	1.16	
Potato	---	<0.12	<0.12		
	15	15.05 ± 0.54	15.10 ± 0.71		2.59
	30	29.95 ± 0.72	30.20 ± 0.54	1.49	
Spinach	---	0.15 ± 0.09	0.14 ± 0.83		2.24
	12.5	12.70 ± 0.22	12.75 ± 0.58	1.08	
	25	25.05 ± 0.39	25.25 ± 0.73		
Carrot	---	0.63 ± 0.23	0.72 ± 0.67		
	17.5	18.10 ± 0.56	18.40 ± 0.82		3.04
	35	36.50 ± 0.38	35.95 ± 1.11	1.53	

^{a} The mean value and its standard deviation for six replicate measurements at 95% confidence level (x± t.s/√n);

^{b}: Theoretical values for *t* and *F* at 95% confidence limit are 2.57 and 5.05, respectively.

4. CONCLUSION

The use of sol–gel as support material for optical sensing applications seems to be very promising. To fabricate a sensitive and selective sensor for determination of vanadium species depended on encapsulation of DMPAHPD in sol–gel matrix was described. These results allow us to conclude that entrapment of a sensitive reagent into the sol–gel matrix and control of the variables of the preparation procedure to tailor the network structure and pore size could improve the selectivity. The proposed sensor is able to determine V(IV) even in the presence of other metal ions that can exist in environmental samples with an excellent limit of detection. The fabricated glass slides elucidate high performance in all key parameters such as reproducibility, reversibility, stability, response time and leaching characteristics. Moreover, this sol–gel sensor offers low limit of detection, fast response time and long-term stability in comparison to the sensors which were previously reported.

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یک حسگر نوری جدید برای تعیین وانادیم: حسگر نوری بر پایه سل-ژل برای تعیین وانادیم

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چکیده

یک حسگر نوری کاملاً انتخابی، با استفاده از واکنشگر حساس ۵-(۲و۴دی متیل فنیل آزو)-۶- پیریمیدین-۲و ۴- دی ان (DMPAHPD) در یک فیلم نازک سل-ژلی سیلیسی بر روی شیشه، برای تعیین یون V(IV) تهیه شد. فیلم نازک با استفاده از تترااتوکسی سیلان به عنوان پیش ماده، سل ژل با pH=۲,۵، آب:آلکوکسید به نسبت ۴:۱ و DMPAHPD با غلظت $۲,۵\times۱۰^{-۴}$ M طراحی گردید. اثر پارامترهای سل-ژل بر روی رفتار حسگر بررسی شد. حسگر طراحی شده برای شناسایی یون های V(IV) با انتخاب پذیری بالا در رنج خطی ۵,۰–۱۴۵ (ng mL^{-1}) و حد تشخیص ۱,۳۵ (ng mL^{-1}) مورد استفاده قرار گرفت. تکرار پذیری روش با انحراف استاندارد نسبی ٪ ۱,۷۵ و ٪ ۱,۰۲ برای غلظت های ۲۰ و ۷۰ نانو گرم بر میلی لیتر V(IV) با زمان پاسخ دهی ۲ دقیقه بدست آمد. کل وانادیم بعد از کاهش V(V) به V(IV) توسط آسکوربیک اسید تعیین گردید. مقدار V(V) بعد از کم کردن غلظت V(IV) از غلظت کل وانادیم تخمین زده شد. بررسی تداخلات، انتخاب پذیری خوبی را برای V(IV) با استفاده از DMPAHPD فرورفته در ماتریس سل-ژل نشان داد. حسگر پیشنهادی در مقایسه با سایر حسگرها نتایج خوبی را در تعیین وانادیم در نمونه های محیطی مختلف از خود نشان داد.

واژه‌های کلیدی

غشای حسگر نوری؛ تعیین وانادیم؛ اسپکتروفتومتری.