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Nafion-based optical sensor for the determination of selenium in water samples

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Abstract

An optical chemical sensor responsive to selenium ($SeO_3{}^{2-}$) in water samples was developed. Its matrix was nafion membrane suffused with an organic ligand *p*-amino-*p*'-methoxydiphenylamine or variamine blue (VB). The method of analysis was flow injection (FI) where in the membrane was fixed in a flow-through demountable measuring cell and connected to a computer-controlled simple spectrophotometer.

Variamine blue was previously established to determine amounts of selenium in water and other media by means of a spectrophotometer. The method involved reacting selenite with potassium iodide to generate iodine gas, which reacts with variamine blue to form a colored species.

Experimental results showed the optrode to be an effective tool in analyzing the selenium content of water samples particularly for remote or in situ applications. Interference studies proved that the method is free of intervention from tested ions.

Keywords: Optrode; Selenium; Nafion

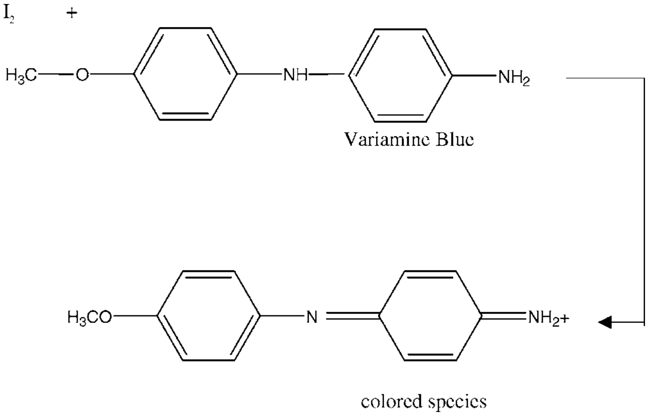
1. Introduction

Selenium is a naturally occurring metal that coexists with other metals as ores. It is used in so many ways and it is very much a part of our daily existence. Selenium in its various forms is used as component in photoelectric cells, xerography and in insecticides. It is also used in the treatment of skin diseases like dandruff and seborrheic dermatitis [1]. The release of selenium into the environment through its usage and through the production of selenium-containing by-products from industrial processes, like roasting of copper or sulfuric acid manufacturing can lead to the accumulation of selenium in exposed living systems. Studies showed that selenium if present in excess amounts could lead to cancer and birth defects [2,3].

Evidently, there is a need to monitor amounts of selenium in the environment particularly in water, a basic commodity among living systems. It is therefore essential to develop an analytical method, which is economical and at the same time resilient for purposes of in situ or remote applications. The designed optrode-FIA technique, which satisfies both requirements for an effective and suitable selenium sensor is appropriate for this purpose.

Studies done by Revanasiddappa and Kiran Kumar in 2001, proved variamine blue (VB) to be a suitable chromophore for the spectrophotometric analysis of selenium in various media like water, soil, cosmetic products, plant material and human hair [4]. The reaction as written in literature is:

$$SeO_3{}^{2-} + 4I^- + 6H^+ \rightarrow Se^0 + 2I_2 + 3H_2O \qquad (1)$$



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The iodine gas, which is generated from the oxidation of iodide by selenite, oxidizes the VB to a violet colored species.

Based on this established reaction, an optrode was developed for the indirect determination of selenium in water. The ligand variamine blue was immobilized in a nafion membrane, which served as the matrix for the reaction to take place. Flow injection (FI) technique was employed in the optimization of the developed optrode system and in the analysis of water samples.

2. Experimental

2.1. Validation experiment

20 μl of 1000 ppm selenium standard was placed in a 10 ml volumetric flask. To the flask, 1 ml of 2% KI and 1 ml of 2 M HCl were added, respectively. The appearance of a yellowish color in the solution indicated the liberation of iodine gas. 0.5 ml of 3.5×10^{-3} M of VB was then added immediately, followed by the addition of 2 ml 1 M sodium acetate to keep the pH around 4. The mixture was diluted to the 10 ml mark by deionized water and their absorbance determined using a UV-3101 PC Shimadzu spectrophotometer. Appearance of a dark violet solution with $\lambda_{max} = 555$ nm, signaled a positive result.

2.2. Qualitative experiment of nafion-VB

2.2.1. Preparation of the active membrane

Pieces of nafion membrane (1 cm × 2 cm) were cleaned and converted to their H^+-form by soaking in 5 M HNO_3 for 24 h. The membranes were then rinsed several times with boiled ultra pure water, vacuum dried at 70 °C for 4 h and stored in a desiccator.

The immobilization of VB into the nafion membrane is carried out by first soaking the clean membrane in 40% ethanol, the same solvent used for the preparation of the ligand to be immobilized. Initial soaking in 40% ethanol is done for 30 min to prevent structural changes of the membrane due to the solvent and to prepare the membrane for the actual immobilization process [5]. The membrane is then soaked in 10 ml 3.5×10^{-3} M VB solution for another 40 min. Prolonging the soaking time in the VB solution increases the amount of VB immobilized into the membrane.

2.2.2. Feasibilty study of the reaction to occur in the membrane

As the soaking period of the membrane in the VB solution approached the ideal, 40 min, a solution composed of 20 μl selenite standard, 1 ml 2% KI, 1 ml 2 M HCl and 2 ml 1 M sodium acetate was prepared. The VB-infused membrane was then soaked immediately into the prepared solution to allow the reaction to occur.

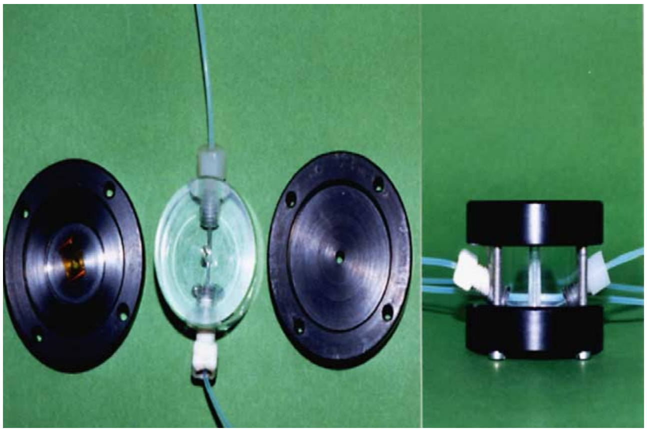

Fig. 1. Flow cell.

2.2.3. Spectrochemical characterization of the active membrane

The absorbance spectra of the different states of the nafion membrane from the preparation to the immobilization and finally to the reaction process (i.e. clean nafion membrane, VB-infused nafion/active membrane and the reacted nafion membrane) were determined by attaching a 1 cm × 2 cm of each of the forms of the membrane to a cuvette and by scanning these attached membranes within the visible region using a UV-3101 PC Shimadzu spectrophotometer.

2.3. Optrode-FIA system

The optrode-FIA used was identical to the set-up described in Talanta 58 (2002) 1063-69 [6]. The active membrane was mounted to a flow-through measuring cell (Fig. 1) and then connected to a flow injection system for solution delivery. The miniaturized spectrophotometer is coupled to the system via an optical fiber. The light source used in the spectrophotometer was an orange light emitting diode (LED) with an optimum emission of approximately 655 nm where the oxidized form of VB immobilized in nafion membrane absorbs. The optrode-FIA system was linked to a computer with software designed for system control and data collection. The complete optrode system set-up is shown in Fig. 2.

Reaction in the membrane was accomplished through the sequential introduction of solutions via flow injection system. These solutions, which were freshly prepared and degassed prior to analysis, were passed into the system by injecting each solution through each individual input channel into the carrier stream. 1 ml of the standard solution was injected first at the main injection plug followed immediately by the KI–HCl solution. Both solutions collected at a T-junction tubing, then flowed into a mixing coil to generate iodine gas. Sodium acetate was injected next, which went straight to the active membrane to set the pH at 4 before the iodine gas in solution, indicated by a yellow color, reached the membrane. The I_2 reduces the VB immobilized in the membrane signaled by a color change from clear blue to

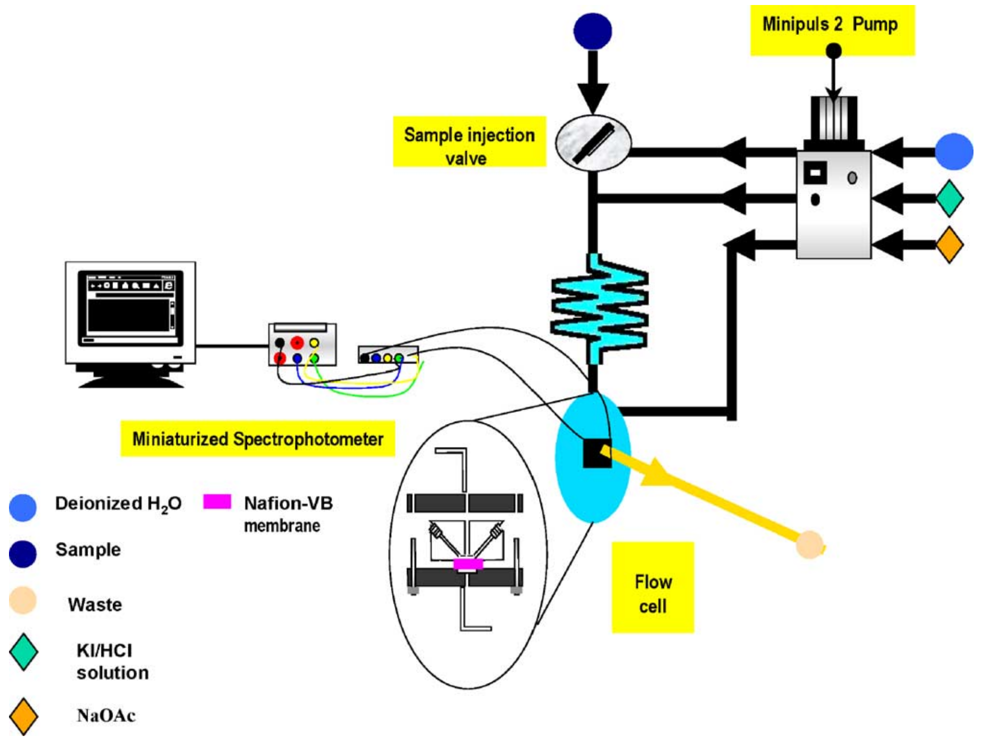

Fig. 2. Se-optrode-FI system.

dark violet. Degassed ultra pure water served as the carrier liquid and at the same time was used to convert the oxidized VB to its original form, regenerating the membrane.

2.4. Optimization experiments

2.4.1. Soaking period of membrane in variamine blue

Pretreated nafion membranes were soaked in 3.5×10^{-3} M of VB in 40% alcohol for varying periods of time. The amount of VB absorbed into the membranes was determined by the difference in the initial and final concentrations of the soak solutions. The difference in concentration was determined using a UV-visible spectrophotometer at 760 nm.

2.4.2. Amount of HCl in the KI–HCl mixture

The effective generation of I_2 is affected by the pH of the KI solution. Optimum pH was obtained by varying the amount of 2 M HCl added to the KI solution.

2.4.3. Contact time of 1 M sodium acetate

The flow rate of 1 M sodium acetate was varied to establish the effect of contact time of 1 M sodium acetate on the sensitivity of the nafion-VB membrane.

2.5. Interference studies

Different oxidants that may be present in the water system that will possibly interfere in the oxidation of variamine blue were tested. These were CrO_4^{2-}, Cu^{2+}, Fe^{3+}, MnO_4^-, IO_3^-, Sn^{4+}, and SO_3^{2-} [4]. 1 ml of 1 ppm of each was added to 1 ppm of the selenium standard to determine individually their effects on the absorbance readings [4].

2.6. Precision experiment

The absorbance of six identical 4 ppm Se standards was determined using the developed optrode and flow injection set-up. Deviation of the results was then calculated.

2.7. Linear range of the optrode-FI system

The absorbance of selenium standards ranging from 0.05 to 20 ppm was determined using the developed optrode and flow injection system.

2.8. Environmental water samples

Water samples were collected along the Marikina river system at two points: (i) Tumana bridge; (ii) Riverbank area (Fig. 3). The acquired water samples were immediately bottled and kept in an icebox. Upon arrival in the lab, the samples were filtered through a 0.45 μM Whatman cellulose nitrate filter paper. Se content was determined using the developed optrode system and the method used by Revanasiddappa and Kiran Kumar [4] by means of a UV–vis spectrophotometer.

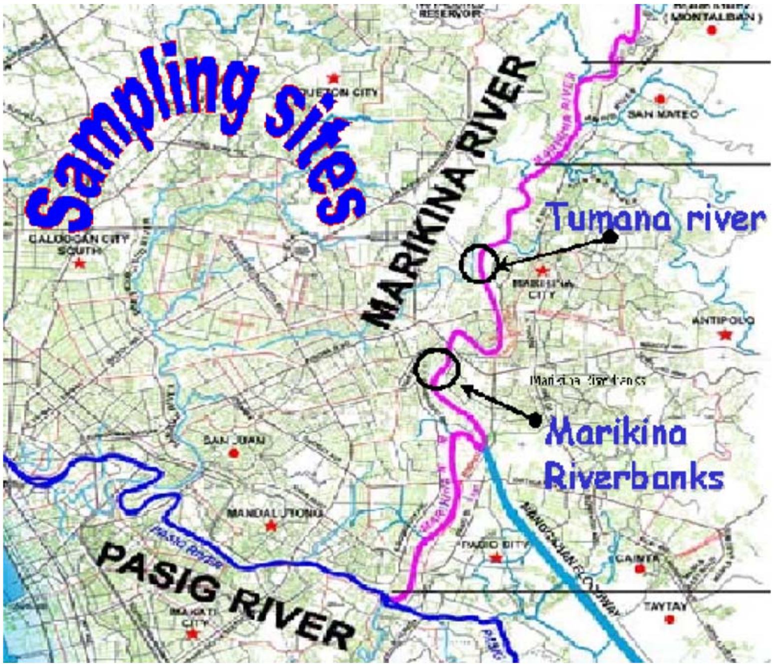

Fig. 3. Marikina river sampling sites.

3. Results and discussion

Selenium exists as an anion (selenite) in water. Ideally, an anionic polymer membrane would be an appropriate matrix for selenite for optical sensing purposes [7]. Commercially available anionic membranes today, however, are not suited for this function. The option of crafting an anionic membrane just for selenium is moreover impractical as it is expensive.

In this application, nafion which is a cationic polymer membrane is tried as the support matrix due to its ease in handling and to its chemical and thermal inertness [5,6]. Selenite being anionic cannot go through nafion, and is prevented from reacting with the immobilized ligand in the matrix. In answer to this, the method used for the optrode is an indirect method for the determination of Se which was obtained from literature where instead of directly reacting selenite with the ligand VB, selenite is reacted with KI [4]. The iodine gas oxidizes variamine blue from a light blue colored species ($\lambda_{max} = 760$ nm) to a dark blue–violet species ($\lambda_{max} = 555$ nm) (Fig. 1). This method is employed initially in solution for validation. Calibration curve obtained show good linearity as can be seen in Fig. 4.

With these results, nafion was tested as the support matrix for the VB reagent. The qualitative experiment proved to be encouraging since the blue activated nafion-VB membrane turned dark violet as soon as it was immersed in a selenium solution. This is indicative of the release of iodine gas, an uncharged species that apparently went through the support matrix. An orange light emitting diode which emits visible radiation in the range of 645–665 nm is selected as the light source for the miniaturized spectrophotometer.

The flow injection system is basically a closed set-up composed of inlets or injection plugs for the needed solutions and carrier liquid and outlet for the wastewater. Unwanted gases from the environment, which form bubbles inside the set up are kept from entering the system. These bubbles can essentially affect the stability of the base line, which in turn can affect the dignity of the results. On this basis, the solutions used were freshly prepared and properly degassed and the system is kept sealed.

Parameters that directly affect the sensitivity of the optrode are the amount of VB absorbed into the membrane, the amount of 1 M HCl in the KI solution and the contact time of sodium acetate in the nafion-VB membrane.

Varying the soaking time of the membrane in the VB solution (3.5×10^{-3} M) controlled the amount of VB immobilized into the membrane. At 40 min saturation time, the nafion membrane showed good sensitivity to selenium.

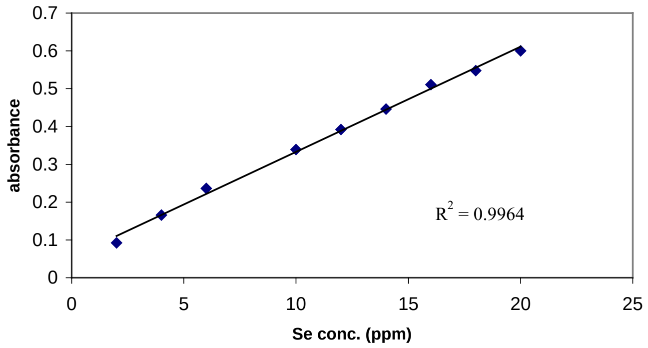

Fig. 4. Calibration curve of Se using UV–vis spectrophotometer set at $\lambda_{max} = 555$ nm.

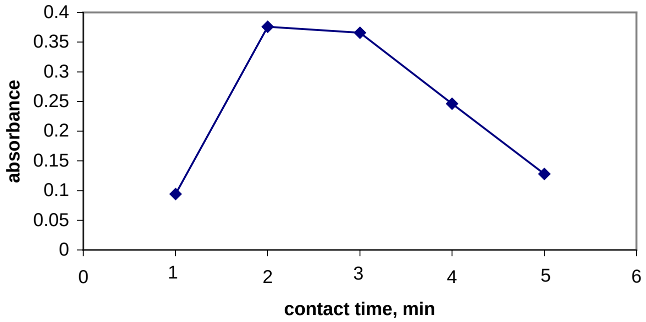

Fig. 5. Optimization of the contact time of 1 M sodium acetate in the nafion-VB membrane, flow rate = 1.0 ml min^{-1}.

Subsequent runs with different concentrations of selenium showed very good linearity with respect to absorbance.

At pH 1.5, generated I_2 is found to react instantaneously with VB and this is achieved by the addition of 1 ml of 1 M HCl per 1.0 ml of 2% KI solution.

Fig. 5 shows that the contact time of 2 min at flow rate of 1.0 ml min^{-1} of 1 M sodium acetate registered the highest absorbance reading.

At the optimum conditions, (i) 40 min-soaking time of nafion in 3.5×10^{-3} M VB; (ii) KI solution at pH 1.5; and (iii) contact time of 2.0 min for sodium acetate, the limit of detection was found to be 4.00 ppm of Se with a linear range of 4.0–20 ppm (Fig. 6). The reaction of selenium with KI was proven to be the exclusive source of iodine gas for the absorbance readings because without injecting selenium into the system, no light absorption is observed. This construes that the amount of iodine gas generated from other sources, like the oxidation of KI by oxygen is negligible or not enough to exhibit an absorbance signal.

Water, which is the carrier fluid in the flow injection set-up is also the reagent used to regenerate the oxidized nafion-VB membrane. The electrons of water interact with the oxidized, electron deficient VB and convert it back to its neutral original form. The nafion-VB membrane is found to be regenerated up to a maximum of 30 injections. Moreover, injections of six identical 4 ppm selenium standards into the optrode-FI sytem showed very good precision, 1.8% RSD.

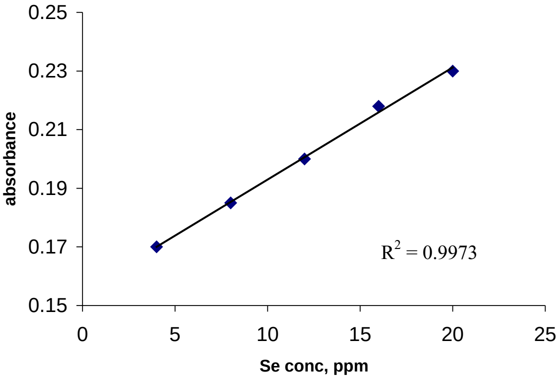

Fig. 6. Calibration curve of Se showing linear range, 4.0–20 ppm using the developed Se-optrode-FI system.

Very good results and observations from these runs show that the immobilized VB is stable and is not leached out by the flowing solutions. Under normal conditions, sample throughput of 10 injections per hour is easily achievable.

Interference studies show that the optrode is not sensitive to the tested interfering ions. The absorbance reading of 0.01000 due to the standard 1 ppm Se is not affected by the addition of 1 ppm of each of the interfering ions as can be seen in Fig. 7. The only deviants were the manganese cation and tin cation, but their difference from the standard is only 1×10^{-5}, which is negligible. Other ions expected to interfere like Ce^{4+} and $VO_4{}^{3-}$, were no longer tested as these ions occur in very minute amounts in water.

River water samples were collected from the Marikina river, one of the most important river systems in Metro Manila. The river water condition is deteriorating fast, as it is subjected to various activities like tanning of leather as it traverses long stretches of towns and communities. It is actually used as an unauthorized catch basin for residential, recreational and industrial waste waters. The Riverbank point, which is a recreational and industrial area registered high levels of selenium of 60–74 ppm. On the other hand, the Tumana point, which is near residential areas, registered higher levels of 85–90 ppm selenium. A comparative run

Table 1
Results of comparative analysis of Se content using the developed Se optrode and UV-visible spectrophotometer

Site	Method FIA (ppm)	UV–vis (ppm)	Tests for significance (95% confidence level) *t*-test	*f*-test
Marikina river				
1	69.12	71.55	0.0843 < 3.18 no significant difference	0.0264 < 9.28 no significant difference
2	74.13	73.31		
3	63.06	74.21		
4	60.24	74.43		
Tumana river				
1	86.73	88.94	0.429 < 3.18 no significant difference	0.236 < 9.28 no significant difference
2	85.33	89.09		
3	86.33	88.50		
4	90.23	79.71		

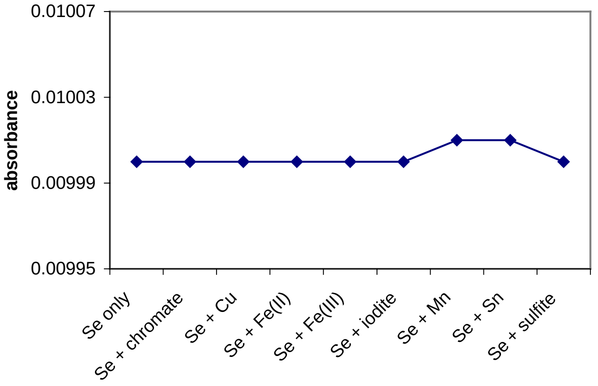

Fig. 7. Effect of the added interfering ions on the absorbance reading of the selenium standard solution.

using the UV–vis spectrophotometer and the developed optrode on the analysis of water samples reveals no significant difference in values obtained from the performed *t*-test and *f*-test (Table 1).

4. Conclusion

The developed optrode is sensitive to selenium in the form of selenite in water. The good correlation and interference results proved the optrode to be useful in determining concentrations of selenium of water from 4.0 to 20.0 ppm. This method is advantageous as it is affordable, light and easy to handle making it ideal for in situ studies.

References

[1] R.D. Brown, Jr., Selenium and Tellurium, U.S. Geological Survey Minerals Yearbook, 1999.
[2] Environmental Health Criteria 58, International Programme on Chemical Safety, 1986.
[3] Selenium: Nutrition, Health and Supplement Review.
[4] H. Revanasiddappa, T.L. Kiran Kumar, Anal. Sci. 17 (2001) 1309.
[5] L.dlC. Coo, T.J. Cardwell, R.W. Cattrall, S.D. Kolev, Anal. Chim. Acta 392 (1999) 201.
[6] L.dlC. Coo, C.J. Belmonte, Talanta 58 (2002) 1063.
[7] R.W.Cattrall, Chemical Sensors, Oxford Science Publications, Oxford, 1997.