A New Spectrophotometric Method for the Determination of Selenium (IV) by Using Ferrous Ammonium Sulphate as a Reluctant.

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Abstract -A new, simple, rapid and inexpensive wet chemical approach has been developed to spectrophotometric determination of selenium (IV) using iron (II) as a reducing agent in acid medium[pure phosphoric acid 80%] at room temperature. The method is capable of producing the results of selenium particles in a range ʎ maximum 440nm under ambient conditions. The spectral results of selenium particles when the reaction completion time and the selenium solutions have been observed and confirmed by UV-Visible Spectrophotometry. The absorption spectra of these ground state selenium solution explained by the ranging of wavelength from UV initial 200µ to final

end of the filter range 800µ. Through the absorption spectra the stable values are observed, the concurrent readings observation of the time variation in between each five minutes the reaction completion time decided based on peak value in absorption spectra.

Keywords: Selenium (IV), Iron(II) as reductant, phosphoric acid medium, Spectrophotometric determination, absorption spectra

INTRODUCTION

Selenium is well known for its photoelectrical & semiconductor[1] properties and high reactivity towards a wealth of chemicals[2] therefore, it finds numerous applications in several photoelectrical devices, solar cells, xerography[3] and in the production of functional materials[2] such as Ag_2Se, ZnSe , CdSe etc. The selenium particles or fabricates are found to be associate with a large number of properties such as relatively low melting point, a high photoconductivity, high catalytic activity (towards hydration and oxidation reactions) , high refraction coefficient in devices and relatively large piezoelectric, thermoelectronic and linear optical responses[4,5] compared to its bulk material. Colloidal solutions of selenium has been employed in the preparation of nutritional suppliments[6] and developed for applications in medical diagnostics[7], and in some biological activities[8].

A survey of literature reveals that the main nanofabrication methodologies adopted in preparing selenium are based on the chemical reduction of higher valent selenium to zero valent selenium using a suitable reductant based on 'bottom up approach' of spectrophotometric determination. In most of these methods selenium (IV) in the form of sodium selenite, selenic acid, or selenium dioxide (as a precursor) is reduced to elemental selenium. Some of the various reducing agents such as dextrose[9], sodium ascorbate[10], ascorbic acid[11,12], hydrazine[13,14], hydrazine hydrate (in the presence of polyvinyl pyrrolidine)[15], sodium metabisulfite (in presence of sodium dodecylsulfate)[16], sodium thiosulphate (in presence of surfactant stabilizer)[16],glutathione[17], polyvinyl alcohol[18] etc.

A careful delves into these methods reveals that most of them suffer from one disadvantage or the other. For example, the methods involving dextrose[9], hydrazine[13,14], glutathione[17] as reductants are tedious and time consuming while those with hydrazine hydrate[15], sodium metabisulphite[16] and sodium thiosulphate[16] need the presence of some reagents to stabilize the selenium particles obtained. The reduction of selenium(IV) by sodium ascorbate[10] or ascorbic acid[11,12] is extremely slow and requires about 5hrs. to realize the formation of a red colored selenium. The reaction with polyvinyl alcohol[18] must be carried out at elevated temperatures (140^{0}C for 48hrs.). The other types of methods cited above[19-23], besides being tedious, necessitate use of the expensive state of the art technologies imperative and to provide appropriate culture medium for the growth of bacteria is a difficult task in the fermentation procedure[24].

In the present paper, we mentioned the use of iron (II) as a reducing agent to generate selenium zero from selenium (IV) and the procedure is free from the drawbacks of the earlier ones mentioned above. This new method consists in treating aqueous solution of sodium selenate [selenium (IV)] taken as a precursor in 8M phosphoric acid and IM hydrochloric acid medium with iron (II) solution [as a reductant] at room temperature. The method is simple, inexpensive, the reduction reaction is rapid and selenium solutions are technologically useful range can be observed. Moreover, the authors proposed the nature of iron (II) as a reducing agent for the spectrophotometric determination of selenium from high state [Se (IV)] to their next low state (Se (0)) by using iron (II) as a reducing agent.

EXPERIMENTAL

Preparation of solutions

Selenium (IV) solution

An approximately 0.05M solution of selenium(IV) solution has been prepared from an AR grade sodium selenite (anhydrous) by dissolving the required amount of the salt in distilled water and the solution standardized using a standard solution of permanganate as described by Shrenk and Browning[R]. In the method selenium(IV) solution in 2M sulphuric acid medium also containing 8% disodium hydrogen phosphate are needed to about 90^{o}c in presence of a no excess of permanganate solution and titrated the excess permanganate with iron(II) solution visually or potentiometrically in the normal way. From the solution a 0.02M and a 0.0025M solutions been prepared by suitable dilution to be utilized in the preparation of synthetic mixture [consisting of Se(IV) and Se(VI)] and in the spectrophotometric determinations respectively.

Iron (II) solution

An approximately 0.60M solution of iron (II) has been prepared from an AR grade ammonium iron(II)sulphate hexahydrate in1M sulphuric acid medium plus the solution standardized by titrating against a standard solution of dichromate. In this method iron(II) solution in 1M sulphuric acid and 1M phosphoric acid medium is titrated against a standard dichromate solution using barium salt of diphenyl amine sulphonatre as a redox indicator. From the solution iron(II) solutions of required strengths have been prepared by suitable dilution.

Starch solution

An approximately 20% w/v solution of starch has been prepared and utilized it as a protective colloid in the determination to keep the selenium colloidal particles under suspension in the solution.

AR grade syrupy phosphoric and hydrochloric acids have been utilized in this investigation.

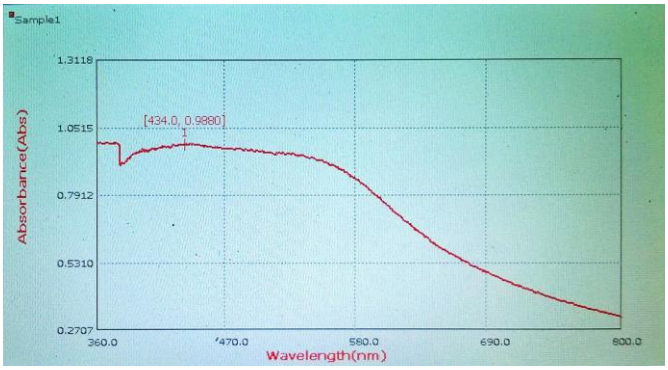
Absorption spectra of colloidal selenium particles obtained from

Selenium (IV) with iron (II) in 10.5 M phosphoric acid medium.

In order to select an appropriate wavelength for spectrophotometric determination of selenium (IV) with iron (II) in phosphoric acid medium. The author has recorded the absorption spectra of the selenium(IV), iron(II), iron(III) and the colloidal selenium particles in 70% phosphoric acid medium, in the visible region of the spectrum i.e., from 360-800 nm. From the spectra it was found that except the colored colloidal selenium particles all the other solutions are found to have negligible absorbance in the visible region. Therefore, only the absorption spectra of colloidal selenium particles [overall concentration 0.0045M] obtained in 10.5M phosphoric acid medium have been recorded. The spectral properties of colloidal selenium particles observed in phosphoric acid medium or phosphoric-hydrochloric acid medium are a typical and interesting. The absorbance at ʎ maximum and the shape of the absorbance are found to change with progress of time. Therefore the author has measured the spectrum at every fifteen minutes interval of time and shows the results.

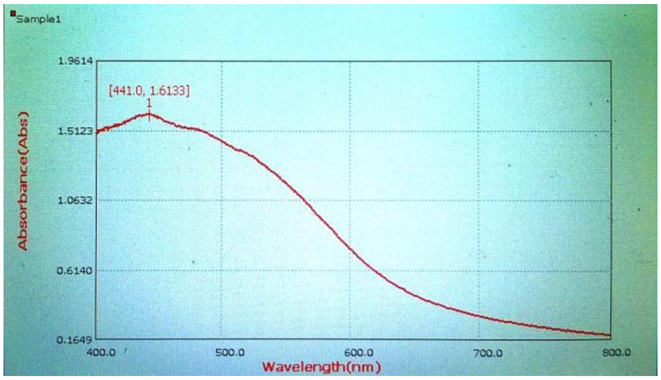
Earlier authors who studied the absorption properties of colloidal selenium particles in the acid medium or in other reaction conditions reported that the shape of the absorbance spectra including ʎ maximum and its absorbance change continuously from the onset of the reaction, until the colloids reached a stable state of equilibrium and the process of crystalline is stable. These changes are attributed to different energy factors involved in reaching the colloids to a stable state of equilibrium.

The absorbance spectrum of colloidal selenium particles obtained by reduction of selenium (IV) [overall concentration 0.00045M] with an excess [30 folds] of iron(II) in 10.5M phosphoric acid medium at the onset of the reaction [zero interval of time] has been shown in figure-2.1.



Absorption spectrum of colloidal selenium particles obtained from Se (IV) in [overall concentration 0.00045M] in 10.5M H_3PO_4 medium at the onset of reaction

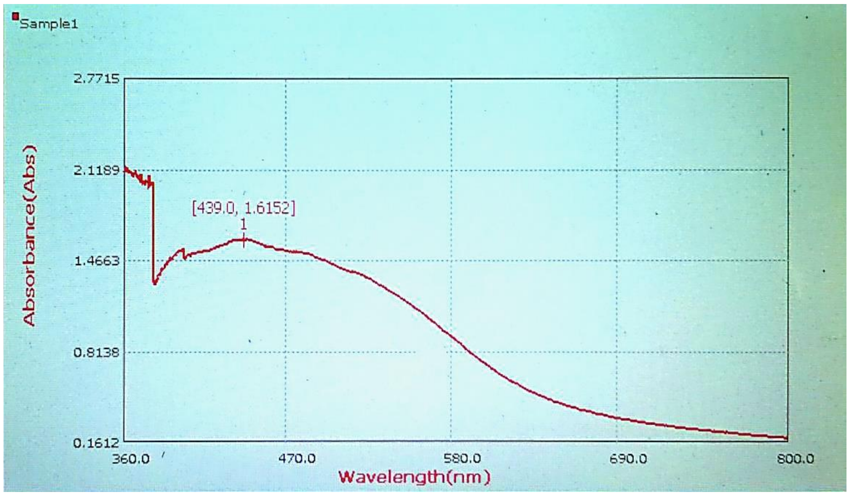
This spectrum shows a broad absorption band with a small peak [λ_{max}] at 434nm with an absorbance value of 0.980. The formation of broad band indicates the presence of selenium colloids of broad size distribution [may be in the range 100nm to 1µg] in the medium in the beginning of the redox process.. The authors believe that in highly viscous phosphoric acid medium [10.5M or 70%(v/v)], it is likely that the added iron(II) ions for reduction of selenium(IV) are unevenly distributed because of the poor transportation of the ions in the highly viscous phosphoric acid medium; consequently selenium particles of broad size distribution or varying sizes are expected to be obtained. Thereafter, with increase in time, the spectrum shows gradual change in shape, size , λ_{max}, absorbance value at the λ_{max} , etc



Absorption spectrum of colloidal selenium particles obtained from Se(IV) in 10.5M H_3PO_4 medium

after 45minutes

Thus, typically up to 45 minutes, the spectrum has gradually become less broad [figure 1.2] followed by a red shift from 434nm to 441nm and with an increase in absorbance from 0.989 to 1.613. Based on the explanation provided by the earlier authors, with respect to the behavior of colloidal selenium particles, we contemplate that among the different sizes of colloids formed in the reaction medium, the smaller and unstable ones may combine or aggregate into a stable optimum size particles. The decrease in the number particles of different sizes accounts for the decrease in the broadness of the spectrum, while increase in size of some of the particles due to aggregation accounts for the red shift observed. Since it has already been noticed from our laboratories and stated above that the redox process between selenium(IV) and iron(II) in phosphoric acid medium is a slow one, so, the increase in absorbance at the peak [from 0.989 to 1.613] is mainly due to more number of red colored colloidal selenium particles formed with the progress of time



Absorption spectrum of colloidal selenium particles obtained from Se(IV) in 10.5M H_3PO_4 medium
after 1.15 minutes

Thereafter, up to another 30 minutes, the spectrum shows a small or negligible blue shift from 441nm to 439nm with a small increase in absorbance from 1.613 to 1.615, as shown in figure 1.3. The broadness of the spectrum almost remained the same. Thereafter, no significant changes in the spectrum [such as in λ_{max}, or the value of maximum absorbance etc.] have been noticed even after waiting for a period of two hours . Since the shift in the spectrum [in this case it is blue] is small, we assume that there is no change in the broadness of the spectrum. Though the blue shift is mall, based on the explanation offered by the earlier authors to such a blue shift observed in selenium colloids, the authors contemplate that the small aqueous environment (only 30% , because the other 70% is phosphoric acid) of the medium may favor the formation of a few spherical colloids of mono size distribution which aggregate and then split into smaller colloids due to Releygh instability. Thus the formation of smaller units from the bigger ones accounts for the blue shift observed in the spectrum.

No significant changes in the spectrum after a period of about 1.15hours, indicate that the reduction of selenium(IV) by iron(II) has been completed in a total period of about 1.15 hours and selenium colloids reach a stable state of equilibrium. Therefore, the spectrophotometric determination of selenium(IV) with iron(II) in phosphoric acid medium [10.5M] was carried out at 440 nm [which is very close to the observed ʎ max,439 in the spectrum] as per the recommended procedure.

Recommended procedure for the spectrophotometric determination of Selenium(IV) with iron(II) in phosphoric acid medium:

To an aliquot (3-12 ml) of 0.0025M selenium(IV) solution taken in a 100ml standard flask, about 70 ml of syrupy phosphoric acid[over all concentration of the acid when the solution is diluted to 100ml is about 10.5M] and 4 ml of starch(20% W/V) solution [which acts as a protective colloid] are added and shaken well. The solution is now treated with required volume of about 0.6M iron(II) solution such that its concentration is about 30 fold in excess to that required for complete reduction of selenium(IV) [se(IV)reduced to se(0)] taken as per the stoichiometric equation . The solution is diluted to the mark. The reaction mixture is occasionally shaken for about 1.15 hours and the absorbance of the solution measured against its corresponding blank at 440 nm. It is compared with the absorbance of the standard calibration curve drawn [between concentration and absorbance] previously using solutions of known concentrations of selenium(IV) in the Beer's law limitations and the amount of selenium(IV) present in the solution is computed.

It is contemplated that the highly viscous medium, such as phosphoric acid where there is poor transport of the ions, is in general not conducive for the process of crystallization of the selenium colloids. This view is strengthened by the fact that the electron diffraction [shown in figure 2.10] taken from the colloidal particles obtained in 10.5M H_3PO_4 the medium indicate that they were all in the amorphous phase.

Spectrophotometric determination of Se (IV) with Fe(II) in H_3PO_4 medium

	Selenium(IV) found,			95%Confidence

S.No	mg.		Pooled Standard Deviation(sg)	$\frac{(1.96Xsg)}{\sqrt{n}}$	Limits $\bar{x} \pm \frac{(1.96Xsg)}{\sqrt{n}}$
	Reference Method.	Author's Method.			
1	0.5922	0.5963	0.001	0.0008	0.5955-0.5971
2	0.8883	0.8829			0.8821-0.8837
3	1.1844	1.1903			1.1895-1.1911
4	1.4805	1.4745			1.4737-1.4753
5	1.7766	1.7737			1.7829-1.7845
6	2.0727	2.0664			2.0656-2.0672
7	2.2306	2.2373			2.2365 -2.2381

The accuracy of the method is found to be ± 0.7%. The precession of the method is expressed in the form of pooled standard deviation and 95% confidence limits to the mean X bar and including in the table 2.1. From these statistical results it may be seen that the new method now developed is accurate and resize.

CONCLUSIONS

In summary, we have provided a convenient and fast approach for the determination of selenium (IV) by reducing sodium selenite using Iron (II) as a reducing agent in pure phosphoric acid medium. According to the previous method was done by prof. vijayaraju and co workers[1995] when for the reaction completion time is more than 68hrs, but in case of the same author prof.kvr and coworkers[2017] done the reaction within 1.15hrs that is the best advantage compared to previous method through variable of time. This method is simple and inexpensive for determination of selenium (IV) for various applications.

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