Spectrophotometric determination of selenium (IV) with Titanium (III)

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Abstract: The author has demonstrated the use of titanium(III) Chloride as a reducing agent to generate selenium nanoparticles using sodium selenite as precursors and titanium(III) chloride as a reducing agent in 2M hydrochloric acid medium with out using any stabilizers and at room temperature. 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 the stable values are observed and the concurrent readings of the reaction and time variation in between each five minutes the reaction completion time decided based on peak value in absorption spectra.

Keywords: Selenium (IV), Titanium (III) Chloride as reductant, Spectrophotometric determination, absorption spectra.

Introduction:

The author has carried out some preliminary investigations to find out the optimum conditions for the determination of selenium (IV) by using titanium (III) chloride as a reducing agent in 2M hydrochloric acid medium.

A careful delve into these methods reveals that most of them suffer from one disadvantage or the other. For example, the methods involving dextros¹, hydrazine^{4,5}, glutathione¹¹ as reductants are tedious and time consuming while those with hydrazine hydrate¹², sodium metabisulphite⁷ and sodium thiosulphate⁸ need the presence of some reagents to stabilize the selenium particles obtained. The reduction of selenium (IV) by sodium ascorbate¹⁰ 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 alcohol¹⁴ must be carried out at elevated temperatures The other types of methods cited above⁻¹⁷, 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 procedure¹⁸.

In the present paper, we develop a method generate selenium zero from selenium (IV) by using titanium (III) chloride as a reducing agent. The procedure is free from the drawbacks of the earlier ones mentioned above. This new method consists in treating aqueous solution of sodium selenite (IV)] taken as a precursor in 2M hydrochloric acid medium with titanium (III) chlotide solution 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 titanium (III) as a reducing agent for the spectrophotometric determination of selenium from high state [Se (IV)] to (Se (0)) by using titanium (III) as a reducing agent. In this method the aqueous nature of the solution when the reaction time is very less compared to pure phosphoric acid medium. The absorption spectra of that solution involved in the determination, such as titanium (III) and titanium (IV) chloride, selenium(IV) solution, the solution containing colloidal selenium are needed. But it has been found that except the solution containing titanium (III) and colloidal selenium solution all the other solutions have negligible absorbance in the visible region of the spectrum (350-800nm). Inorder to avoid the interfearence due to the color of titanium(III) in the spectrophotometric determination the author has added a saturation solution of potassium persulphate dropwise to the solution containing colloidal selenium particles until the color of titanium(III) in the solution is completely disappeared.

the absorption spectra of colloidal selenium solutions obtained in 2M hydrochloric acid medium has been recorded and show results it may be seen that the most appropriate wave length for the spectrophotometric determination of selenium(IV) with titanium(III) chloride is 532nm (Λ maximum). Hence, the spectrophotometric determination of selenium(IV) with titanium(III) chloride has been carried out spectrophotometrically at 532nm. The author has reported the absorption spectra of the same solution at every ten minutes interval of time [up to one hour] and found that there is no change in the spectrum with respect to Λ maximum, size, shape and the absorbance at the peak.

Reaction between sodium selenite (Na₂SeO₃) and titanium (III) chloride as a reducing agent.

In this method sodium selenite[Selenium(IV)] is reduced to selenium(0) by titanium(III) which act as a reducing agent in 2M hydrochloric acid medium. A 20-30% excess of titanium(III) chloride is added as in all other methods to ensure complete reduction of selenium(IV) to selenium(0). The redox reaction taken places in the medium may be represented as follows.

$$4 \operatorname{Ti}(\operatorname{III}) \to 4 \operatorname{Ti}(\operatorname{IV}) + 4 e^{-}$$
$$\operatorname{SeO}_{3}^{2^{-}} + 6\mathrm{H}^{+} + 4e^{-} \to \operatorname{Se}(0) + 3\mathrm{H}_{2}\mathrm{O}$$

4 Ti(III) + SeO₃²⁻ + 6H⁺
$$\rightarrow$$
 4 Ti(IV) + Se(0) + 3H₂O

Preparation of solutions:

Selenium (IV) solution [sodium selenite (Na₂SeO₃)].

An approximately 0.05M selenium(IV) solution has prepared from sodium selenite(Na₂SeO₃) and the solution standardized as described earlier [pg no] from this a 0.0025M solution has been prepared by suitable dilutions.

Titanium(III) chloride solution: [TiCl₃]

A 0.1M solution of titanium(III) chloride in 2M hydrochloric acid medium has been prepared by dissolving required volume of 15% AR grade titanium(III) chloride solution in distilled water containing about 2M hydrochloric acid. The solution was standardize with standard solution of potassium dichromate as described in literature.

Starch solution:

A 20% w/v solution of starch has been prepared as described earlier [pg no]

Hydrochloric acid:

An AR grade concentrated hydrochloric acid has been utilized in this investigation. The same spectrophotometer mentioned in chapter (II) has been made use of in this investigation. An optical glass cell of 1cm path length has been utilized for absorption measurements.

Absorption spectra:

To determine appropriate wave length for the spectrophotometric determination of selenium(IV) with titanium(III) chloride . The absorption spectra of that solution involved in the determination, such as titanium(III) and titanium (IV) chloride , selenium(IV) solution, the solution containing colloidal selenium are needed. But it has been found that except the solution containing titanium(III) and colloidal selenium solution all the other solutions have negligible absorbance in the visible region of the spectrum (350-800nm). In order to avoid the interfearence due to the color of titanium(III) in the spectrophotometric determination the author has added a saturation solution(0.06M) of potassium persulphate drop wise to the solution containing colloidal selenium particles until the color of titanium(III) in the solution is completely disappeared. To ensure complete oxidation of titanium(III) a few more drops (10-15) have also been added and the solution shaken thoroughly well. Therefore, the absorption spectra of colloidal selenium solutions obtained[as described in the procedure 4.7] in 2M hydrochloric acid medium has been recorded and shown in figure 4.1. From the figure it may be seen that

the most appropriate wave length for the spectrophotometric determination of selenium (IV) with titanium (III) chloride is 532nm (λ maximum). Hence, the spectrophotometric determination of selenium (IV) with titanium(III) chloride has been carried out spectrophotometrically at 532nm. The author has reported the absorption spectra of the same solution at every ten minutes interval of time [up to one hour] and found that there is no change in the spectrum with respect to λ maximum, size, shape and the absorbance at the peak etc..



Figure 1: Absorption spectra of reaction mixture.

Adherence to Beer's law:

Adherence to the Beer's law of the colloidal selenium solution has been tested in the following way. Known aliquots of selenium (IV) solution[0.0025M] have been taken into different 50ml standard volumetric flasks. To each of the flask about 10ml of concentrated hydrochloric acid [overall concentration about 2.3M] followed by twofold excess of titanium (III) chloride solution [(0.025M) as per the stoichiometric equation,(p no)] and 4ml of 20% starch solution are added. The solution is diluted to the mark shaken thoroughly well for about 3 minutes. The absorbance of each of solution is now measured against its corresponding blank. As usual the concentration of selenium (x-axis) versus the absorbance (y-axis) is depicted graphically and found that the beers law is obeyed when the concentration of elemental selenium is the range 0.6mg to 2.0mg per 50ml of the solution in this redox process selenium (IV) reduced to elemental selenium in a four electron duration step, while titanium (III) chloride is oxidized titanium (IV) in a one electron exchange process.

Recommended procedure for the Spectrophotometric determination of selenium (IV) with titanium (III) chloride in hydrochloric acid medium (2M):

Procedure;

An aliquot (2-10ml) of selenium (IV) solution (0.0025M) is taken into a 50ml standard volumetric flask. To this solution required volume of concentrated hydrochloric acid is added such that its concentration is 2-3M in a total volume of 50ml. To the reaction mixture twofold excess of titanium (III) chloride is added and the solution shaken thoroughly well. The excess titanium (III) chloride is removed by treating with persulphate solution as described earlier. (pg). A four ml of 20% starch solution is added and the absorbance of the solution is diluted to the mark. The solution is shaken thoroughly 2-3 minutes and the absorbance of the solution is measured against its corresponding blank at 520, using a glass cell of 1cm path length. The absorbance so obtained is compared with the standard calibration curve drawn under similar conditions for selenium content verses absorbance earlier. The selenium content thus computed for the sample solution. Some of the tipical results obtained by the procedure have been shown in following table.

	Selenium(IV) found, mg.				95%
			Pooled Standard	(1.96Xsg)	Confidence Limits
S.No	Reference	Author's	Deviation(sg)	\sqrt{n}	(1.96Xsg)
	Method.	Method.			$\bar{x} \pm \frac{1}{\sqrt{n}}$
1	0.6122	0.6079			0.6066 to 0.6092
2	0.8295	0.8344			0.8331 to 0.8352
3	1.0467	1.0414	0.0016	0.0013	1.0401 to 1.0427
4	1.2245	1.2293			1.2280 to 1.2306
5	1.4412	1.4368			1.4355 to 1.4381
6	1.6787	1.6837			1.6824 to 1.6850
7	1.9552	1.9512			1.9499 to 1.9525

 Table 1: Spectrophotometric determination of selenium (IV) with titanium (III) chloride in 2M

 hydrochloric acid medium

The accuracy of the method is found to be $\pm 0.7\%$. The precession of the method is found by computing the pooled standard deviation and 95% confidence limits to the mean bar and including in the same table. From these statistical results it may be seen that the new method now developed is accurate and precise.

Conclusions

In this method authors provided a convenient and speed approach for the determination of selenium (IV) by reducing sodium selenite using titanium (III) chloride as a reducing agent in 2M hydrochloric acid medium. This method is simple and inexpensive for determination of selenium (IV) for new analytical applications.

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