



O-ANISIDINE AS INDICATOR IN TITRIMETRIC DETERMINATION OF IRON (II) IN PHARMACEUTICAL FORMULATIONS AND WATER SAMPLES

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ABSTRACT

In spite of the beautiful red coloured oxidized product of O-anisidine, the studies on its application in analytical techniques are scanty. So, authors have taken up the investigation on the utility of O-anisidine as a new Analytical reagent in the bromatometric-Indicator reaction. The detailed reaction on the potassium bromate and O-Anisidine has enabled the authors to utilize O-Anisidine in titration of Iron (II). Suitable conditions have been established with different acids viz., hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid to give sharp colour change at the equivalence point. This method could be used successfully for determination of the Iron (II) content of Spiked water and Pharmaceutical samples. Results obtained are in good agreement with the values obtained by standard methods.

Keywords: O-Anisidine, Bromatometric, Iron (II), Water.

INTRODUCTION

O-Anisidine is used as a reagent for the spectrophotometric determination of gold in biological samples and also in some salts such as silver nitrate in Acid media. Smith and Bliss¹ were the first to report the bromatometric titration of Iron (II) using basic Mercuric bromate as the titrant and fuchsine, chrysoidine R, bordeaux and naphthol blue black as indicators. Szebelledy and Madis² proposed potassium bromate as reagent for the titrimetric determination of Iron(II) at 60°-70°C using gold chloride as indicator. Kolthoff³ found that naphthol blue black can be employed as indicator in the Iron (II) - potassium bromate titration and that the titration can be conducted satisfactorily without any interference by tartaric, citric and Succinic acids. According to the critical studies the effects of oxygen and the presumptive catalysts and found that the role of copper (II) are reported was not to catalyse the Iron(II) - Bromate reaction but only to bring about rapid attainment of the equilibrium potentials of the indicator electrode. The potentiometric titration of iron (II) with potassium bromate in 9.0-10.0M phosphoric acid medium. Proposed cacotheline as an indicator in the same titration in phosphoric acid medium is reported. In these titrations methylene blue, thionine, azures A, B and C, toluidine blue, new methylene blue, p-ethoxychrysoidine and brilliant ponceau 5R can be used as indicators in the Iron (II) - bromate titration in a medium of 9-10M phosphoric acid and prescribed the addition of the indicators, except p-ethoxychrysoidine, towards the close of the titration. Recent results proposed three azine dyes neutral violet, neutral red and wool fast blue GL as indicators in the titration of iron (II) with bromate in phosphoric acid medium. They have observed that wool fast blue GL can be satisfactorily

employed as an indicator in the reverse titration also i.e., titration of bromate with Iron (II), in phosphoric acid medium. Several kinetic methods were reported for the determination of Iron (II)⁴⁻⁸. The authors would like to develop a selective, accurate, and simple titrimetric method for the determination of iron (II)⁹⁻¹⁸ based on the catalytic oxidation of crystal violet with bromate in real matrixes such as pharmaceutical products and water samples. Even though O-dianisidine is used as indicator in bromatometric titrations, the survey of literature revealed, no attempts have been made in the application of O-anisidine as indicator in the titrations with bromated. So, the present investigation has taken up the study of o-anisidine as indicator in titrations of Iron (II) with potassium bromate and the results obtained are incorporated.

MATERIALS AND METHODS

Titration of Iron (II)

The present author has investigated the use of O-anisidine as indicator in the titration of Iron (II) with potassium bromate in hydrochloric, sulphuric, phosphoric and acetic acid media and established suitable conditions for satisfactory titrations.

Reagents

Potassium bromate solution: Potassium bromate solution of 0.1N concentration is prepared by dissolving 2.784 g of the recrystallised and dried (at 180°C for 2 hours) potassium bromate (E. Merck) in water and diluting the solution to one liter with triply distilled water.

All other reagents, hydrochloric acid, sulphuric acid, acetic acid and phosphoric acid used are of analytical reagent grade quality.



Method

In order to ascertain the effect of different acids studied viz., hydrochloric, sulphuric, phosphoric and acetic acid on the reaction between the indicator, O-anisidine and potassium bromate, the author has carried out the following experiments. 0.1 ml of 1% solution of o-anisidine is treated with sufficient quantity of hydrochloric, sulphuric, phosphoric and acetic acid and water to make up to 50 ml. To this solution, one drop of 0.1M potassium bromate solution is added and the observations are recorded in table 1.

Table 1: Treatment observations

Acidity, N	Colour Change
Hydrochloric acid	
0.5	Colourless to red in 25 seconds
1.0	Same as above
2.0	Colourless to red in 10 seconds
3.0	Same as above
4.0	Same as above
5.0	Colourless to red in 5 seconds
6.0	Same as above
Sulphuric acid	
0.5	Pale yellow to orange red in 20 seconds
1.0	Same as above
2.0	Same as above
4.0	Pale yellow to red in 15 seconds
6.0	Same as above
8.0	Pale yellow to red in 2 seconds
10.0	Same as above
Acetic acid	
0.5	Nil
1.0	Nil
2.0	Pale green to red Turbidity
4.0	Pale green to red colour
6.0	Same as above
8.0	Same as above
10.0	Same as above
Phosphoric acid	
1.0	Nil
2.0	Nil
4.0	Light pink to red colour Turbidity
6.0	Light pink red colour in 5 seconds
8.0	Same as above
10.0	Same as above
12.0	Light pink to bright red colour immediately
14.0	Same as above
16.0	Same as above
20.0	Same as above

RESULTS AND DISCUSSION

In order to establish the optimum conditions for the visual determination of iron (II), the author has earned out the following experiments in different acid media.

5.0 ml of 0.1036N iron (II) is taken in the titration vessel, required amount of acetic, hydrochloric, sulphuric or phosphoric acid are added to give desired concentration and 0.1 ml of 1% o-anisidine indicator and distilled water added to a total volume of 50 ml. The titration is carried out in an inert atmosphere of carbondioxide with 0.1072N bromate to a colour transition from light yellow to red colour. The results are tabulated in table 2.

From the experimental observations it is found that the indicator is not functioning well at any hydrochloric and acetic acid concentrations. Turbid solutions are obtained

with hydrochloric acid. In case of sulphuric acid medium between 2.0-8.0N the colour change is observed from colourless to red and waiting for about 15 seconds was necessary near the end point. The colour change is sharp in case of 6.0-12.0N phosphoric acid medium i.e., from light yellow to red colour in the titration of Iron (II) with bromate. So, the author has chosen 3N sulphuric acid and 10N phosphoric acid to carry out the titrations to get satisfactory end points.

Table 2: Titration observations
(5.0 ml 0.1036N Iron (II) = 4.83 ml of 0.1072N bromate.)

Overall strength of acid, N	Volume of bromate consumed, ml	Observations
Hydrochloric acid		
0.5	4.70	The indicator colour titration is not sharp
2.0	4.50	Same as above
4.0	4.50	Orange colour turbidity is formed
6.0	4.50	Same as above
Sulphuric acid		
0.5	4.70	Colour titration is not sharp
2.0	4.83	Colourless to red, sharp and waiting for about 15 seconds necessary near the end point.
3.0	4.83	Sharp colour transition
4.0	4.83	Same as above
6.0	4.83	Same as above
8.0	4.83	Same as above
Acetic acid		
0.5	4.70	Turbid, colour change not sharp
2.0	4.70	Same as above
4.0	4.80	Light yellow to reddish yellow and not sharp and is at lower value.
6.0	4.80	Same as above
8.0	4.80	Same as above
10.0	4.80	Same as above
Phosphoric acid		
2.0	4.70	Turbid, no colour transition observed.
4.0	4.70	Same as above
6.0	4.83	Light yellow to red colour and is sharp.
8.0	4.83	Same as above
10.0	4.83	Colour change is very sharp
12.0	4.83	Same as above

Effect of indicator concentration

The effect of concentrations of o-anisidine is also studied using different volumes at 3N sulphuric acid and 10.0N phosphoric acid concentration in the titrations of Iron (II) with bromate (table 3). The colour change of the indicator is sharp in 0.1-0.5 ml of 1% o-anisidine. So the author prescribes 0.2 ml of indicator to be added in titrations of iron (II) with bromate.

Table 3: Effect of indicator concentration
(5.0ml 0.1036N Iron (II) = 4.83 ml 0.1072N bromate)

Volume of indicator, ml	Volume of bromate, ml	
	Sulphuric acid, 3 N	Phosphoric acid, 10N
0.05	4.70	4.69
0.10	4.83	4.83
0.20	4.83	4.83
0.30	4.83	4.83
0.40	4.83	4.83
0.50	4.83	4.83



Recommended Procedure

An aliquot of 0.1036N Iron(II) is taken in the titration vessel, an overall acidity of 3N sulphuric or 10N phosphoric acid is maintained in a total volume of 50 ml, 0.2 ml of indicator is added and the titration is carried out with 0.1072N bromate to a colour change from light yellow to red colour. Some typical results of the estimation of Iron(II) are given in table 4.

Table 4: Estimation of Iron(II) with Bromate

Amount of Iron (II), mg		
Taken	Found	Relative error (%)
Sulphuric acid, 3 N		
5.8080	5.8160	-0.1372
14.5202	14.5202	Nil
23.2323	23.2332	0.0381
29.0404	29.0506	-0.0350
34.8485	34.8532	-0.0132
43.5606	43.5606	Nil
Phosphoric acid, 10 N		
5.8080	5.8175	-0.1631
14.5202	14.5015	0.1286
23.2323	23.2323	Nil
29.0404	29.0404	Nil
34.8485	34.8521	Nil
43.5606	43.5790	- 1.8402

Reverse Titrations

Reverse titrations i.e., the estimation of bromate with iron (II) is earned out by the author adopting the same procedure as above in different acid concentrations.

It is found that the indicator is not functioning well at any of the hydrochloric, sulphuric and acetic acid concentrations. But in 6.0-12.0N phosphoric acid concentrations the indicator functioned well and the colour change of the indicator is from red to light yellow colour. Hence an optimum concentrations of 10.0N phosphoric acid for the estimation of bromate with Iron (II) is recommended. Some typical results obtained are given in table 5 and 6.

Application of the Developed Method

To confirm the usefulness of the proposed method, Fe (II) was determined in pharmaceutical samples and spiked water samples.

In Pharmaceutical Formulations

The Indicator method developed can be applied successfully for determination of Iron content in pharmaceutical tablets as per recommended procedure, One tablet is ground to a free powder and dissolved in double distilled water and the solution filtered through G-4 sintered glass funnel and diluted to a known volume. An aliquot of this solution is titrated with 0.10N bromate solution in 2.0 N sulfuric acid medium using O-anisidine as indicator. A similar aliquot is titrated with potassium bromate using Thiocyanate as indicator. The samples of pharmaceutical tablets and typical results obtained while employing both the methods are present in the table 7. It

is observed that these results are in good agreement with standard methods.

Table 5: Reverse titrations
(5.0 ml 0.1072N bromate = 5.17 ml 0.1036N Iron (II))

Overall strength of acid, N	Volume of bromate consumed, ml	Observations
Hydrochloric acid		
0.5	5.20	The indicator colour change is at Higher value
1.0	5.20	Same as above
2.0	5.20	Same as above
4.0	5.20	Red coloured turbidity is obtained
5.0	5.20	Same as above
Sulphuric acid		
1.0	5.00	Colour titrations of indicator is not sharp due to turbidity
2.0	5.10	Same as above
4.0	5.10	Same as above
6.0	5.10	Indicator transition is not sharp.
Acetic acid		
2.0	5.20	Colour change is not sharp
4.0	5.20	Same as above
6.0	5.20	Indicator transition is not sharp
8.0	5.20	Same as above
Phosphoric acid		
2.0	5.20	Colour transition is not found
4.0	5.20	Turbid colour change not sharp
6.0	5.17	Colour changed from red to Light yellow
8.0	5.17	The colour transition of indicator is not sharp
10.0	5.17	Very sharp colour change
12.0	5.17	Very sharp colour change

Table 6: Estimation of Bromate with Iron (II)

Amount of bromate, mg		
Taken	Found	Relative error (%)
Phosphoric acid, 10 N		
10.1883	10.1765	0.1158
25.4707	25.4806	-0.0388
40.7532	40.7532	Nil
50.9415	50.9506	-0.0178
76.4122	76.4220	-0.0128

In Water Samples

Treatment of samples

River water and wastewater samples were collected at different points from the polluted regions of Coastal Andhra. Prior to analysis, river water samples were treated as follows. 50ml of sample was evaporated to about 5ml in a 1000ml beaker on a hot plate at about 90°C, the 1 ml of concentrated nitric acid and 0.5ml of H₂O₂ (30%) was added and the contents were heated to dryness at 90°C. After cooling, the digest was diluted to 25ml with water and adjusted to P^H = 5 with saturated ammonium carbonate. It was boiled for 5 min to expel the dissolved CO₂. After cooling, the solution was transferred to a 50ml volumetric flask and diluted to the mark with water, which was ready for analysis. Bottled mineral water samples were obtained from a local convenient store and analyzed directly without pretreatment. Results are tabulated in table 8.



Table 7: Analysis of pharmaceutical products by the proposed method

Name of the pharmaceutical sample	Citified amount of iron present (mg/mL)	By thiocyanate method (mg/mL)	By present method *(µg/mL)	Recovery (%)
Fer-In-Sol	2.0	1.98	1.97	99.4
Slow-Fe	1.33	1.32	1.32	100
Safron – Z	1.452	1.453	1.454	100

Table 8: Recovery values for iron (II) determination in water samples

Sample	Iron / µg/L		Recovery ± s, ^a %	Recovery ± s, ^b %
	Added	Found		
Tap water	0	1.5		
	100	101.5	99.9±0.2	0.21
	500	502.0	100±0.1	0.25
Well water	0	2.5		
	100	102.0	99.5±0.1	0.29
	500	505.0	100.3±0.2	0.15
Lake water	0	130.0		
	100	228.0	98.7±0.3	0.25
	500	635	100.5±0.5	0.27
River water (Sarada River)	0	5.0		
	100	103.0	99±0.2	0.13
	500	505.0	100±0	0.00
Sea water (Bay of Bengal)	0	3.5		
	100	104.0	100.5±0.5	0.08
	500	505.0	100.3±0.4	0.10

a) Average of five replicate determinations

b) The measure precision is the relative standard deviation

CONCLUSION

A new reaction system was suggested for the Titrimetric Determination of iron(II) in Pharmaceutical and Spiked water samples. This method offers several advantages, as follows: high selectivity and sensitivity ease of operation and rapidity, and cheaper reagents. The reliability and simplicity of this method permit the analysis of pharmaceutical samples with satisfactory results. Results obtained are in good agreement with the values obtained by standard methods.

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