

**A New Method for the Determination of Iodide  
via Andrew's Reaction Study with Hexamminecobalt (III)  
Tricarbonatocobaltate (III)  
as Volumetric Oxidimetric Titrant**

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**Summary:** Andrew's reaction for the determination of iodide through the use of hexamminecobalt(III) tricarbonatocobaltate (III) as redox analytical volumetric titrant, has been studied. The reaction between iodide and  $\text{Co}^{3+}$  proceeds quantitatively in 0.5N  $\text{H}_2\text{SO}_4$  and 5N HCl. Effects of chloride, bromide and nitrate as interfering radicals have also been studied separately and collectively on this determination. In either of the cases, the tolerance of foreign ions is quite high. Therefore, the method standardized is recommended for routine use in the determination of iodide.

## Introduction

The high redox potential (1.84V) exhibited by hexamminecobalt(III) tricarbonatocobaltate(III) in acidic media has been successfully utilized for the standardization of methods for the determination of a variety of organic and inorganic substances [1-8]. The solution of the reagent is highly stable when kept at about pH 8.4 and there is no need of its repeated standardization before use, rather the solution does not exhibit any appreciable change in its factor even after a week [1]. It has also been reported that when it is kept in saturated bicarbonate medium it does not show marked decrease in its concentration even up to 2 months [1]. The reagent is very weak oxidant in bicarbonate medium, but when added to acidic solution, the cobalt(III) thus generated is very strong oxidant and could be easily compared with potassium permanganate, potassium dichromate, cobalt(III)

acetate and lead tetraacetate with respect to their high redox potential. Therefore, keeping in view its high redox potential, longer shelf-life and easy to prepare, like in our previous studies [1-8], we have tried to use hexamminecobalt(III) tricarbonatocobaltate(III) as analytical oxidimetric titrant for standardizing a suitable method for the determination of iodide and some of the results of this investigation are reported in this communication.

## Experimental

### *Reagents*

#### *Ferrous sulphate*

Ferrous sulphate A.R. Grade (BDH) 7g was dissolved in 200 ml distilled water which contained 5 ml of concentrated  $\text{H}_2\text{SO}_4$  and after making the

volume to 250 ml its exact normality was determined with standardized potassium permanganate [9].

#### *Potassium dichromate*

Potassium dichromate A.R. Grade (Merck) 4.904g was dissolved in distilled water and the volume was made upto 1l and was used as such [9].

#### *Sodium thiosulphate*

About 25g of A.R. Grade (Merck) was dissolved in 1l of distilled water and its exact factor was determined against potassium iodate [9].

#### *Potassium iodate 0.1N (0.025 M)*

Potassium iodate about 10g A.R. Grade (Merck) was dried at 120°C for one hour and cooled to normal temperature in a desiccator. Weighed out exactly 5.305g of the finely powdered potassium iodate and transferred it quantitatively in 1L volumetric flask and the solution was made to 1l with distilled water [9].

#### *Starch solution*

A 0.5% solution of starch (BDH) was prepared to be used as indicator [9].

#### *Iodine solution (0.1N)*

The solution of iodine was prepared and standardized against  $As_2O_3$  according to the known method [9].

#### *Ferrouin*

Ferrouin 1/40 M solution (Fluka) was used as indicator in the process of standardizing the method for the determination of iodide.

All other reagents used in the course of this work were also A.R. Grade or of equivalent purity.

#### *Apparatus*

The glass-ware used throughout the course of this work was of A Grade calibration.

#### *Procedure*

#### Preparation of Hexamminecobalt (III) Tricarbonatocobaltate (III).

This preparation consists of two parts:

(a) Preparation of Hexamminecobalt (III) Chloride and

(b) the preparation of the final solution of hexamminecobalt(III) tricarbonatocobaltate(III) from the above solution are already described in detail in another communication [1].

#### *Standardization of hexamminecobalt (III)-Tricarbonatocobaltate (III) [1].*

Ferrous sulphate solution was standardized with standard  $K_2Cr_2O_7$  solution [9]. The known volume of standard ferrous sulphate solution was taken in titration flask acidified with  $2N H_2SO_4$  and then was titrated against  $Co^{3+}$  solution using two drops of ferroin indicator, change of red colour to pale blue was end point. The volume of cobalt(III) solution used in the standardization was corrected for the amount of the oxidant used for the oxidation of ferroin as indicator. From the volume of cobalt(III) solution used for the known volume of ferrous sulphate, the normality of cobalt(III) was calculated.

#### *Determination of Iodide*

To a definite volume of the acid of a definite concentration, an aliquot of the iodide solution alongwith 3 to 4 drops of ferroin indicator were added to this mixture. which was shaken

Table-1: Determination of iodide

S.No.	Medium	Iodide		Error %
		Taken mg	Found* mg	
1.	0.5N H <sub>2</sub> SO <sub>4</sub>	1.27	1.29	+ 1.58
2.		3.05	3.06	+ 0.33
3.		6.35	6.33	+ 0.32
4.		12.69	12.66	-0.32
5.		15.25	15.23	+0.13
1.	5N HCl	1.50	1.51	+0.66
2.		4.50	4.47	-0.44
3.		7.50	7.45	-0.66
4.		12.00	11.98	-0.17
5.		13.00	13.02	+0.15
6.		15.00	15.04	+0.26
7.		17.00	17.25	+1.47
8.		20.00	20.85	+4.25

\* Result of 7 titrations.

thoroughly and the hexamminecobalt (III) tricarbonatocobaltate(III) solution from the burette was run which was constantly shaken in the titration flask. The end point was reached when the colour from red to persistent pale blue was reached. For testing the effects of interferences, a definite aliquot of interfering ion was added to the above mixture, the procedure of titration was repeated, and the end results were calculated. The end point can also be found potentiometrically using platinum as indicating and saturated calomel as reference electrodes.

### Results and Discussion

In order to find some suitable media in which the reaction between cobalt (III) and iodide could go stoichiometrically a number of acids including H<sub>2</sub>SO<sub>4</sub> from 0.1 to 10N, HCl from 1 to 10N acetic acid from 30% to glacial and perchloric acid from 5 to 20% were explored for this purpose. With the exception of 0.5N H<sub>2</sub>SO<sub>4</sub>, and 5N HCl in all the other tested media, the results obtained were highly erroneous and therefore, they did not carry any

Table-2: Effect of chloride, bromide and nitrate on the determination of iodide

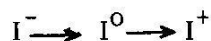
S.No.	Medium	Iodide taken mg	Foreign ion added mg		Iodide found* mg	Error
1.	5.0N HCl	2.14	0.50		2.15	+ 0.46
2.		2.14	3.05		2.15	+ 0.46
3.		2.14	9.25		2.15	+ 0.46
4.		2.24	15.75	Chloride	2.15	+ 0.46
5.		2.14	20.20		2.15	+ 0.46
6.		2.14	30.00		2.15	+ 0.46
1.	0.5N H <sub>2</sub> SO <sub>4</sub>	2.14	0.50		2.17	+ 1.40
2.		2.14	3.25		2.18	+ 1.86
				Bromide		
3.		2.14	5.21		2.22	+ 3.73
4.		2.14	8.33		2.26	+ 5.60
				Nitrate		
1.	0.5N H <sub>2</sub> SO <sub>4</sub>	2.07	0.50		2.06	- 0.48
2.		2.07	5.00		2.09	+ 0.96
3.		2.07	7.20		2.12	+ 2.41
4.		2.07	15.00		2.18	+ 5.31
5.		2.07	20.00		2.32	+ 12.07
1.		0.5N H <sub>2</sub> SO <sub>4</sub>	1.27	0.30		1.25
	1.27		3.30		1.26	-0.78
3.	1.27		9.27	Chloride	1.26	-0.78
4.	1.27		12.75		1.24	-2.36

Table-2: Continued

S.No.	Medium	Iodide taken mg	Foreign ion added mg	Iodide found * mg	Error %
5.		1.27	15.35	1.25	-1.57
6.		1.27	25.90	1.26	-0.78
1.		1.27	0.30	1.25	-1.57
2.		1.27	3.50	1.24	- 2.36
Bromide					
3.		1.27	8.75	1.23	- 3.14
4.		1.27	15.35	1.21	-4.72
1.		1.27	0.30	1.28	+ 0.78
2.		1.27	5.25	1.27	± 0.00
Nitrate					
3.		1.27	8.45	1.26	- 0.78
4.		1.27	15.25	1.25	+ 1.57
5.		1.27	20.95	1.24	- 2.36

\* Results of 7 titrations.

analytical significance. Consequently these results were discarded with the exception of those obtained in 0.5N H<sub>2</sub>SO and 5N HCl, where the reaction proceeded quantitatively. According to Andrew's reaction [10].



iodide is oxidised to iodine which in turn is further oxidised to I<sup>+</sup>. We also observed that iodide is first oxidised to iodine which in turn is oxidized to I<sup>+</sup> in case of 5N HCl. In this way

during the reaction a total of 2 electrons change takes place. The stoichiometry of the reaction also shows that iodide is oxidized to iodine quantitatively which in turn is further oxidized to I<sup>+</sup> also quantitatively. In this way this oxidation is exactly according to Andrew's reaction. On the other hand the oxidation of iodide proceeds quantitatively only to I<sup>0</sup> in 0.5N H<sub>2</sub>SO<sub>4</sub> medium. Therefore, in either of the cases the determination of iodide is quite easy.

Table-3: Combined effect of chloride, bromide and nitrate on the determination of iodide.

S.No.	Medium	Iodide	Chloride	Bromide	Nitrate	Iodide	Error
		taken	added	added	added	added*	
		mg	mg	mg	mg	mg	%
1.	5.0N HCl	3.04	0.50	0.50	0.50	3.06	+ 0.05
2.		3.04	2.25	0.32	5.00	3.09	+ 1.64
3.		3.04	9.75	2.75	7.20	3.14	+ 3.28
4.		3.04	30.00	5.50	10.00	3.17	+ 4.27
1.	0.5N H <sub>2</sub> SO <sub>4</sub>	2.95	3.30	0.30	5.25	3.06	+ 0.33
2.		3.05	9.27	3.50	7.35	3.05	± 0.00
3.		3.05	15.35	9.85	15.25	3.01	- 1.31
4.		3.05	25.90	15.35	20.95	3.06	+ 0.33

\* Result of 7 titrations.

It has been observed that reaction between iodide and cobalt(III) in either of the two media is fast, one titration is completed within 2 to 3 minutes and the end point is very sharp and distinct which is persistent to the extent that there is no misleading observation as to its detection.

According to the Table-1, iodide in 0.5N H<sub>2</sub>SO<sub>4</sub> medium can be determined within the range from 1.27 to 15.25 mg with a maximum error of + 1.58% in the former case. Similarly as reported in the Table 1 iodide can also be determined with great accuracy within the range from 1.5 to 17.0 mg of iodide taken with the maximum of + 1.47% error in the later case.

During the investigations on the effect of foreign ions on the determination of iodide it was found that chloride upto about 14 folds excess

of iodide, bromide upto 4 folds excess of iodide and nitrate upto about 4.7 folds excess of iodide do not interfere on the determination of iodide in 5.0N HCl as medium. The rate of reaction also remains the same and the end point discernibility is not hindered. Similarly when 0.5N H<sub>2</sub>SO<sub>4</sub> was used

as medium for the determination of iodide in the presence of chloride, bromide and nitrate the tolerance limits of these ions on the determination of iodide are quite reasonable. The results of these studies are exhibited in Table-2.

During the course of study of combined effect of chloride, bromide and nitrate on the determination of iodide in 5N HCl and 0.5N H<sub>2</sub>SO<sub>4</sub> as media it is observed (Table-3) that these ions to a great extent when present together do not effect the determina-

tion of iodide or the rate of reaction is effected and the end point remains sharp, distinct and stable for a pretty long time.

According to our experience, the method reported here is quite rapid, accurate, sensitive, convenient and practical. Therefore, it is recommended for the routine use in the determination of iodide.

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