

Determination of Microgram Amounts of Phenol, p-Bromophenol, Aniline, p-Bromoaniline, Thioacetamide, Tartaric Acid, Arsenic (III) and Titanium (III) Using Hexamine Cobalt (III) As Redox Titrant

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Summary: Hexamine cobalt (III) tricarbonato cobaltate (III) has been used for quantitative determination of phenol p-bromophenol, p-bromo aniline, thioacetamide arsenic and titanium (III). Procedures and conditions of titration were given, and interferences of tartrates and oxalates were studied. Reactions based on results were suggested.

Introduction

Previously the solution of hexamine cobalt (III) tricarbonato (III) has been successfully used for the quantitative determination of some organic and inorganic compounds 1-3. When $\text{Co}(\text{NH}_3)_6\text{Co}(\text{CO}_3)_3$ is added to any medium having a pH less than 7, the tricarbonato complex decomposes to yield free cobalt (III) has possible utility as a redox titrant in volumetric Analysis 5. The present work is an extension of the same work and a method for the determination of microgram amounts of phenol, p-bromophenol, aniline, p-bromoaniline, thioacetamide, tartaric acid, arsenic and titanium. Survey reveals that there are only few references available 1-4.

Experimental

All reagents used were analar grade obtained from Riedel-de-Hain, Ag Wunstorfer Strabe 44, 3016 Seelze and BDH.

Preparation and Standardisation of the hexamine complex:

The hexamine cobalt (III) chloride was prepared as follows:

The method comprises of mixing in 10 ml of water 173 g of cobalt (III) nitrate hexahydrate along with 80 g. of ammonium nitrate, 2 g of activated charcoal

and 180 g of concentrated ammonia. The resulting mixture can be oxidized with hydrogen peroxide. Alternatively, it can also be oxidized by passing air through it until the brown precipitate ceases to form. The contents are filtered through filter paper, the precipitate is washed with water and dissolved in 1300 ml of hot water containing suitable quantity, of hydrochloric acid to give acid reaction. Charcoal is removed by filtering the hot solution. To the filtrate are added 400 ml of concentrated hydrochloric acid. The solution is allowed to cool and solid $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ is separated by filtration, washed successively with 95% ethyl alcohol and then dried in a vacuum desiccator.

Hexamine cobalt (III) tricarbonato cobaltate (III) was prepared according to the method of Bricker et al (1); to 50 ml 1 M cobalt (II) chloride were added 100 ml of water and suitable quantity of sodium bicarbonate to saturate this solution, which was cooled with ice and while constantly stirring 100 ml of 30% hydrogen peroxide was added in small portions. Stirring was continued further for about 10 minutes to allow any excess hydrogen peroxide to decompose, the resulting mixture was filtered through "RPP SELECTA" Nr 489 filter paper, to obtain a clear dark green filtrate (A), to the solution (A) was added solid hexamine cobalt (III) chloride until the supernatant liquid developed an orange tinge and the resulting solution was once again

filtered. The solid material was washed several times with water until the washings were colourless and was kept in a vacuum desiccator until dry. The dry solid was stored in a bottle at room temperature (25°C). Solution of $[\text{Co}(\text{NH}_3)_6 \text{Co}(\text{CO}_3)_3]^{3+}$ was prepared according to Baur et al⁽¹⁾ by addition of 3 g of the salt to 1 liter of water previously saturated with sodium-bicarbonate. Stirring was applied for 2-3 hours, after which it was filtered through fritted glass crucible and the resulting green solution was ready for use after standardization.

The above prepared redox titrant solution was standardised as mentioned below against ferrous ethylene-diammonium sulphate tetrahydrate, used as primary standard, standardised ferrous sulphate solution also gave correct result.

To an accurately measured aliquot of the standard iron (III) solution is added 125 ml of 1.8 M sulphuric acid. After the addition of 2 drops of ferroin indicator (prepared) by mixing 0.594 g 1, 10 Phenanthroline with 0.278 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml of distilled water, titration is done while pouring in Co (III) solution from a 10 ml micro-burette, graduated at 0.02 ml intervals.

The contents in the reaction vessel are stirred constantly with magnetic stirrer the end point is reached with the first sharp change of the colour of the indicator. The volume of Co (III) solution used in the standardization should be corrected for the volume of the titrant used for the indicator.

Solutions of concentration of 100 PPM were prepared of analytical grade, aniline hydrochloride, p-bromoaniline, phenol, p-bromophenol, thioacetamide tartoric acid, oxalic acid, citric acid, ascorbic acid, arsenic trioxide and titanous chloride.

Aniline HCl, p-bromoaniline, phenol and p-bromophenol solutions were standardised bormometrically (5). Thioacetamide solution was standardized by 0.1 N KBrO_3 . Tartaric acid solution was standardized by previously standardized solution of 0.1 N NaOH. Concentration of ascorbic acid solution was checked by 0.1 N KBrO_3 . Concentration of oxalic acid was checked by previously standardized. 0.1 N KMnO_4 . Concentration of citric acid was checked iodometrically (6). Solution of As_2O_3 prepared from pure As_2O_3 obtained from the national bureau of standard (Sample 83 a)

was used as standard solution (5). Titanium chloride solution was standardized according to Kolthoff and Belcher (5).

A definite aliquot (1-10 ml) of the solutions of any of the substances under test was taken in a 100 ml. conical flask to which water and H_2SO_4 were added in such a quantity as to make total volume of about 20 ml, 4 N with reference to H_2SO_4 for aniline hydrochloride, p-bromoaniline, phenol, p-bromophenol, tartaric acid, arsenic and titanium, while for thioacetamide the solution was acidified to 0.5 N, about 1 drop of ferroin indicator was added to the contents of the flask and the titration was carried out by adding the titrant solution in small portions, from a 10 ml microburette graduated at 0.02 ml intervals. During titration contents of flask were stirred well and warmed up to 60°C for aniline hydrochloride p-bormoaniline, phenol, p-bromophenol and tartaric acid, while for thioacetamide, titanium and arsenic were carried out at room temperature (25°C) and were shaken slowly. The end point was reached by a sharp change of the colour of indicator the end point colours for various substances are discussed at their respective places. The exact volume of $[\text{Co}(\text{NH}_3)_6] \text{Co}(\text{CO}_3)_3^{3+}$ used for the exact oxidation of any substances was determined by subtracting the volume consumption of titrant for blank from that the results are given in table 1 to VI.

The calculations were carried out according to the following equation.

$$\text{Amount of X in mg} = (N) (V) (E)$$

Where.

X= aniline hydrochloride, p-bromoaniline, phenol, p-bromophenol, thioacetamide, tartaric acid, arsenic and titanium.

N= normality of $\text{Co}(\text{NH}_3)_6 \text{Co}(\text{CO}_3)_3$

V= Volume of $\text{Co}(\text{NH}_3)_6 \text{Co}(\text{CO}_3)_3$

E= equivalent weight of X

The results are shown in table 1 to IV. They are based on oxidation reaction processes given in literature (7). The results indicate the possibility of measuring

Results and Discussion

(Table 1 continued)

Table 1. Determination of Phenol, p-bromophenol, aniline, p-bromoaniline, thioacetamide, tartaric acid, arsenic and titanium.

Substance	Substance taken μg	Substance found μg	Relative standard deviation %
Phenol	20.00	20.00	1.10
	40.00	40.01	1.30
	60.00	60.02	1.16
	80.00	80.60	0.43
	100.00	101.00	0.34
p-bromophenol	20.00	20.24	0.14
	40.00	40.50	0.14
	60.00	61.10	0.13
	80.00	80.97	0.10
	100.00	101.21	0.09
Aniline	20.00	20.09	0.38
	40.00	40.30	0.55
	60.00	60.58	0.01
	80.00	80.37	0.01
	100.00	100.70	0.01
p-bromoaniline	20.00	20.12	0.15
	40.00	40.26	0.15
	60.00	61.00	0.13
	80.00	81.13	0.12
	100.00	100.64	0.10
Thioacetamide	20.00	20.25	0.90
	40.00	41.00	0.85
	60.00	61.15	0.85
	80.00	81.00	0.72
	100.00	100.00	0.58
Tartaric acid	20.00	20.02	0.95
	40.00	40.05	0.75
	60.00	60.30	0.61
	80.00	80.55	0.50
	100.00	100.80	0.50

Arsenic (III)	20.00	20.02	0.03
	40.00	40.70	0.70
	60.00	60.08	0.60
	80.00	80.80	0.50
	100.00	101.40	0.76
Titanium (III)	50.00	50.05	0.37
	100.00	100.10	0.86
	200.00	200.80	0.93
	300.00	300.35	0.93
	400.00	400.40	0.35
	500.00	500.80	0.80

Result of 7-titrations

(20-100) $\mu\text{g/ml}$ of phenol and bromophenol with RSD values of 1.3 and 0.14 respectively.

Bromophenol was more quickly oxidised compared to phenol similarly aniline and bromoaniline can be precisely and accurately determined in the range 20-10 μg with max. RSD of 0.25 and 0.15 respectively.

The simplicity of the reaction and the condition required to conduct the analysis make the method useful compared to other possible procedures. In the four cases of determination of the four organic solutions only acidification with 4N H_2SO_4 and one titration, is required to finish the analysis within 10 minutes. The time of titration could be reduced by warming the content of titration flask up to 60°C. At higher concentration some yellowish tinge appeared which could be due to the formation of a quinonoid product.

Determination of thioacetamide was carried out from 20 μg to 100 μg in 0.5 N H_2SO_4 with maximum RSD (0.9). The reaction goes very smoothly and very fast at room temperature (25°C) and one titration could be completed within 5 minutes. End point was reached by very sharp change in colour which was pale blue or colourless.

Tartaric acid was determined (20-100 μg) with maximum RSD of 0.95, 4N H_2SO_4 was found suitable medium for its oxidation. Titration was completed within 15 minutes. During titration warming to 60°C with strong stirring in necessary. End point was colourless

Table 2. Effect of oxalic acid on tartaric acid determination

Tartaric acid taken μg	Oxalic acid added μg	Tartaric acid found μg	Standard deviation %
100.00	100.00	134.55	0.34
100.00	200.00	164.70	0.27
100.00	300.00	197.10	0.22
100.00	400.00	229.05	0.19
100.00	500.00	267.78	0.20

Result of 7 titrations

Table 3. Effect of citric acid on tartaric acid determination

Tartaric acid taken μg	Citric acid added μg	Tartaric acid found μg	Standard deviation %
100.00	100.00	100.80	0.40
100.00	200.00	100.80	0.45
100.00	300.00	100.80	0.40
100.00	400.00	100.80	0.30
100.00	500.00	100.80	0.40

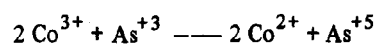
Result of 7-titration

Table 4. Effect of ascorbic acid on tartaric acid determination

Tartaric acid taken μg	Ascorbic acid added μg	Tartaric acid found μg	Standard deviation %
100.00	100.00	121.50	0.27
100.00	200.00	138.10	0.24
100.00	300.00	155.52	0.20
100.00	400.00	178.15	0.20
100.00	500.00	190.35	0.20

Result of 7-titrations

or pale blue. In all these oxidations; end points were stable for reasonable period. The effect of oxalic acid, citric acid and ascorbic acid on quantitative determination of tartaric acid is given in table II, III and IV respectively. From the results shown in these tables conclusions were drawn that it is not possible to do accurate determination of tartaric acid in the presence of these interfering acids; however, citric acid has no significant effect on tartaric acid determination; most probably due to its resistance to oxidation in the medium of titration. Results shown in table II and IV; indicate that constant increase in tartaric acid is found. This result predicts that oxalic acid and ascorbic acid are also oxidised by cobalt (III). The determination of ascorbic acid and its application will be reported in future paper. It is concluded that due to precision and accuracy of the obtained result and reasonable stability of $[\text{Co}(\text{NH}_3)_6] \text{Co}(\text{CO}_3)_3^{3+}$ solution. this redox titrant can be utilised for quantitative determination of phenol, p-bromophenol, aniline, p-bromoaniline, thioacetamide and tartaric acid. The hexamine cobalt (III) tricarbonatocobaltate (III) is not limited to oxidation of organic solution. Any inorganic species that has oxidation potential lower than that of (Co^{+3}) can be determined. The oxidation potential of As (III) and Ti (III) are + 0.56 V and + 0.05 V. Therefore a direct titration of the two cations according to the following reactions is possible.



(20-100) μg of arsenic and titanium (III) can be easily and quantitatively determined-with (0.03 - 0.7) % and (0.37-0.93) % RSD values respectively.

Conclusion

It has been demonstrated that (Co (III) is still useful for determination of variety of inorganic and organic compounds. The rapidity, convenience and less requirement of chemicals special working conditions

make the present reagent very useful. The stability of solution of titrant (up to one month at least) is another advantage of its use for routine analysis.

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