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VOLUMETRIC DETERMINATION OF URANIUM AND VANADIUM WITH HEXAMINECOBALT (III) TRICARBONATOCOBALTATE(III)

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Hexaminecobalt (III) tricarbonatocobaltate(III) has been successfully used as redox titrant for the volumetric determination of uranium from 59.5 μg to 35.7 mg with maximum error of –0.73% in 0.1 to 0.5N H_2SO_4 and vanadium from 0.54 to 31.74 mg with a maximum error of +5.55%. The method is quick, precise and rapid. There is no interference by Ag(I), Pb(II), Zn(II), and Ni(II) and chromium for uranium and vanadium determination respectively within the given limits whereas Fe(II) interferes seriously in both the cases.

INTRODUCTION

The strong oxidizing behaviour of various trivalent cobalt compounds has been used for the determination of a variety of substances [1]. Similarly hexaminecobalt (III) tricarbonatocobaltate(III) has been successfully employed as a strong redox titrant for the determination of a number of inorganic as well as organic compounds [2]. Its solution, at pH 7.5–8.0, is fairly stable over longer period but when acidic its tricarbonatocobaltate (III) part splits up to yield Co^{3+} which exhibits redox potential round about 1.8 V[3]. In order, therefore, to extend its usefulness, the present studies on the standardisation of suitable methods for the determination of uranium and vanadium were carried out and the results have been reported.

EXPERIMENTAL

Reagents

Hexaminecobalt(III) Tricarbonatocobaltate (III). A stock solution of the reagent, in saturated solution of sodium bicarbonate, was prepared according to the method described earlier [3] and standardized volumetrically against iron (II) in 2N H_2SO_4 using ferroin as indicator [2].

Uranyl Acetate. Approximately 0.1N solution was prepared by dissolving 21.212g of the salt (BDH) in conductivity water and diluted to one litre. The solution was passed through zinc/mercury amalgam in Jone's Reductor, any uranium(III) formed during the reduction process was oxidized to Uranium (IV) by passing air for 1–2 min and determining its factor with standard potassium dichromate solution [4]. This was used as test stock solution.

Ferrous Sulphate. A 0.025N solution of ferrous sulphate (Merck) was prepared by dissolving the substance in distilled water and checking its factor against standardized potassium dichromate solution [5].

Nickel Chloride. A 0.05N solution was prepared from $NiCl_2\ 6H_2O$ (Hopkins and Williams Ltd., England) and its exact strength was determined gravimetrically with dimethylglyoxime [6].

Vanadium Pentoxide. Solution of vanadium pentoxide was prepared by dissolving 1.698g of the salt (BDH) in 1000.0 ml of double distilled water. This solution of vanadium(V) was reduced to divalent stage by passing it through Jone's Reducter containing zinc/mercury amalgam. The factor of this stock solution was determined against potassium permanganate according to the usual method [6].

Chromium Chloride. A 0.05N solution of the substance was prepared by dissolving 6.65g $CrCl_3\ 6H_2O$ (Hopkins and Williams) in distilled water and was standardised against potassium permangnate according to the usual method [6].

The solutions of zinc, cobalt, lead and silver were also prepared by dissolving appropriate amounts of their salts in conductivity water and standardising according to the conventional methods [6].

Apparatus. Offically calibrated glassware was used for all volumetric measurements.

Procedure

(i) To an aliquot (1.0 ml to 10.0 ml of U(IV)

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solution in a 250 ml titration flask, 20.0 ml of 0.5N H_2SO_4 was added and titrated against standard hexaminecobalt(III) tricarbonatocobaltate(III) solution using ferroin as indicator. Formation of pale blue colour was taken as the end point. A blank titration was also run and the titrant used was substracted from the volume used in the previous one with U(IV) and, thus, the exact volume of the titrant consumed was obtained.

(ii) An aliquot (15.0 – 30.0 ml) of vanadium(II) solution containing 0.54 to 32.0 mg V (V) was taken in a 250.0 ml titration flask. The solution was made 4.0N with respect to hydrochloric acid and titration was run using standard hexaminecobalt(III) tricarbonatocobaltate(III) as titrant and ferroin as indicator. The end point was reached with the appearance of blue colour.

In order to investigate interferences from foreign ions, exact amount of each one of these were added to a constant amount of U(IV) and the above procedures were repeated.

Calculation

Amount of uranium in mg = NxVxE
Where N = Normality of the titrant
V = Volume of the titrant used for one titration
E = Equivalent weight of uranium/vanadium.

RESULTS AND DISCUSSION

Hydrochloric acid from 1.0 to 4.0 N and sulphuric acid from 0.1 to 10.0N were tried as media to oxidise U(IV) to U(VI) quantitatively. Hydrochloric acid did not prove useful in the studies, whereas sulphuric acid from 0.1 to 0.5N turned out quite conducive to the quantitative oxidation of U(IV) to U(VI). The reaction proceeds according to the following equation in which two molecules of cobalt(III) gain two electrons to be reduced to cobalt(II), on the other hand one molecule of uranium(IV) loses two electrons to be oxidised to uranium(VI).

$$U^{+4} + 2Co^{+3} \longrightarrow U^{+6} + 2Co^{2+}$$

The rate of reaction is so fast that one titration can be completed in about 2 min and the end point is quite sharp. As is apparent from the Table 1, U(IV) can be easily determined within the range from 59.5 μg to 35.70 mg with a maximum error of –0.73%.

Studies regarding possible interferences by the foreign ions on the determination of U(IV) showed that Ag(I), Pb(II), Zn(II) and Ni(II) upto 1:4.4, 1:2.9, 1:2.9, and 1:3.0 ratio of U(IV) to the respective ions did not interfere with the accurate determination of U(IV). Whereas iron interferes seriously. Hence as shown in the Table 2, U(IV) can be conveniently determined in the presence of these elements within the limits shown therein.

Sulphuric acid, hydrochloric acid, acetic acid and perchloric acid in various concentrations were tried for the oxidation of vanadium from divalent to pentavalent state, with the titrant. The reaction proceeded quantitatively in 4.0N hydochloric acid only. The rate of reaction in this medium was so fast that one titration was completed in about 2 mints. The end point was sharp. The reaction followed the following course:

$$V^{2+} + 3Co^{+3} \longrightarrow V^{+5} + 3Co^{+2}$$

According to the above equation one molecule of vanadium(II) loses 3 electrons to be oxidised to pentava-

Table 1. Determination of uranium (IV) in 0.5N sulphuric acid.

Uranium(IV) taken mg	Uranium(IV) found mg*	Error %	Uranium(IV) taken μg	Uranium(IV) found μg*	Error %
4.94	4.93	– 0.18	59.50	59.33	– 0.29
11.90	11.91	+ 0.05	178.50	177.66	– 0.47
17.85	17.82	– 0.15	297.50	297.06	– 0.15
23.80	23.69	– 0.46	595.00	594.10	– 0.15
29.75	29.56	– 0.65	987.00	989.00	+ 0.20
35.70	35.44	– 0.73			

*Average of 7 titrations.

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Table 2. Determination of uranium(IV) in the presence of foreign ions.

Uranium(IV) taken mg	Foreign ion added mg	Uranium(IV) found mg	Error %
11.90	6.55	11.89	– 0.08
11.90	13.10 Ag(I)	11.89	– 0.08
11.90	26.20	11.89	– 0.08
11.90	52.40	11.88	– 0.17
11.90	4.25	11.90	± 0.00
11.90	8.50 Pb(II)	11.91	+ 0.08
11.90	17.00	11.90	± 0.00
11.90	34.00	11.91	+ 0.08
11.90	4.52	11.90	± 0.00
11.90	9.04 Zn(II)	11.90	± 0.00
11.90	18.08	11.91	+ 0.08
11.90	36.16	11.91	+ 0.08
11.90	4.31	11.90	± 0.00
11.90	8.62 Ni(II)	11.89	– 0.08
11.90	17.24	11.88	– 0.17
11.90	34.48	11.88	– 0.17
11.90	1.5	12.50	– 5.04
11.90	3.00 Fe(II)	14.40	+21.0
11.90	6.00	16.80	+41.18
11.90	9.00	19.70	+65.55

Table 3. Determination of vanadium (II) in 4.0N hydrochloric acid.

Vanadium(II) taken mg	Vanadium(II) found mg*	Error %
0.54	0.57	+ 5.55
1.08	1.08	± 0.00
2.16	2.16	± 0.00
4.32	4.31	– 0.23
5.30	5.29	– 0.18
10.59	10.60	+ 0.09
15.89	15.90	+ 0.06
21.19	21.19	± 0.00
31.74	31.76	+ 0.06

*Average of 7 titrations.

Table 4. Effect of foreign ions on vanadium(II) determination.

Vanadium(II) taken mg	Foreign ion added mg	Vanadium(II) found mg*	Error %
10.59	4.50	10.59	± 0.00
10.59	9.00 Cr(III)	10.59	± 0.00
10.59	18.00	10.59	± 0.00
10.59	36.00	10.59	± 0.00
10.59	1.35	10.95	+ 3.39
10.59	2.70 Fe(II)	11.85	+ 2.45
10.59	5.40	14.52	+ 37.11
10.59	10.80	18.52	+ 74.96

*Average of 7 titrations.

lent form whereas three molecules of trivalent cobalt gain 3 electrons and are reduced to divalent state. As apparent from Table 3 vanadium can be conveniently determined from 0.54 to 31.74 mg with a maximum of +5.55% error. Iron(II) interfered with the determination of vanadium because it is easily oxidised by the titrant while chromium(III) did not affect the quantitative oxidation of vandaium to vanadium(V) as shown in Table 4.

The methods reported here are quite simple, accurate and sensitive and can be used for routine analysis of uranium and vanadium in the presence of silver, lead, zinc, nickel and chromium respectively within the prescribed limits.

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