

## Potentiometric Determination of Ruthenium with Cobalt(III) Acetate

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**Summary:** A simple, precise and quick potentiometric method for the determination of Ru(III) from 84.00  $\mu\text{g}$  to 3.35 mg in a total volume of 70.0 ml with a maximum relative standard deviation of 0.7% using Co(III) acetate as redox titrant has been devised. Interference effects of foreign ions on this determination have also been investigated.

### Introduction

The number of volumetric methods for the determination of platinum metals is rather limited when compared to the gravimetric methods, and of the recorded volumetric methods only a few are acceptable while the others require modification<sup>1-2</sup>. In some case the peculiarity of changing identity of the dissolved metal is also an important factor<sup>2</sup>. Much effort is still needed regarding the development of volumetric methods for the determination of platinum metals.

Similarly the available volumetric methods for the determination of ruthenium require special precautions<sup>1-2</sup>. These conditions increase the chance of error. A few among the cited methods make use of the reduction of ruthenium to lower state by another reagent, the excess of which is then back-titrated. Alternatively excess potassium iodide is added to ruthenium chloride and the liberated iodine is then titrated with sodium thiosulphate. The method by Zyka et al. for this determination is quite promising<sup>9</sup>:

In view of the need for a viable analytical method on the one hand and the need to extend the usefulness of Cobalt(III) acetate having a redox potential of about 1.8V in certain mineral acids<sup>4-8</sup>, on the other, we tried to devise a method for the determination of ruthenium. Some of the results of this study are reported here.

### Experimental

#### Reagents

1) *Cobalt(III) acetate solution.* The solution of Cobalt(III) acetate was prepared by the anodic oxidation of Cobalt(II) in glacial acetic acid and it was standardized using ferrous sulphate potentiometrically<sup>3</sup>.

*Ruthenium(III) chloride.* A 0.01 N solution of ruthenium(III) chloride was prepared by dissolving 0.2180g Ru Cl<sub>3</sub> 3H<sub>2</sub>O(BDH) in 250 ml water and its factor was checked against lead tetracetate<sup>9</sup>.

All other reagents used were either of analytical grade or equivalent purity.

### Apparatus

Potential measurements were made with a potentiometer (W.G. Pye and Co. Ltd. Cambridge, England) using platinum as indicating and saturated calomel as reference electrodes.

All officially calibrated glass-ware was used for various measurements.

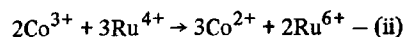
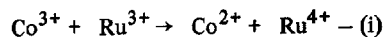
### Procedure

A definite aliquot (0.5 to 20.0 ml) of ruthenium(III) chloride solution, previously standardized with Pb(CH<sub>3</sub>COO)<sub>4</sub> was taken in a 250 ml pyrex glass beaker to which water and sulphuric acid were added to get a final volume of 70 ml, (0.1 N with respect to H<sub>2</sub>SO<sub>4</sub>). The titration was done by running in Co(III) acetate solution from a 5.0 ml burette, graduated at 0.02 ml intervals. Slow and constant stirring of the reactants was continued with an electromagnetic stirrer throughout the course of the titration. The potential measurements were recorded when the needle of the potentiometer showed stable reading after each addition. Just before and after equivalence point the addition of the titrant was made in 0.02 ml lots. The exact volume of the titrant was read from the graph, plotted between mV and volume of the titrant.

### Results and Discussion

Sulphuric acid from 0.1 to 10.0 N, HCl from 1.0 to 4.0 N, perchloric acid from 1.0 to 10.0% and acetic acid from 50% to glacial state were tried to find out the medium in which the reaction between Co(III) and Ru(III) could proceed stoichiometrically and with a reasonable rate.

The reaction went quantitatively in 0.1 N H<sub>2</sub>SO<sub>4</sub>. The total reaction could be represented by the following equation:



*Determination of Ru(III) in 0.1 N H<sub>2</sub>SO<sub>4</sub>*

Ru <sup>3+</sup> taken mg	Ru <sup>3+</sup> found mg	Inflection Potential mV	Relative standard deviation % *
0.084	0.85	350	0.09
0.174	0.170	565	0.06
0.345	0.341	550	0.02
0.502	0.511	750	0.02
0.859	0.852	715	0.01
1.230	1.200	750	0.70
1.660	1.700	750	0.40
2.500	2.550	835	0.30
3.350	3.400	865	0.20

\*Each result is based on seven titrations.

The oxidation of Ru(III) proceeded to Ru(VI) state via Ru(IV) according to the above equations. Accordingly two oxidation steps were exhibited on the potentiometric curve plotted for each titration. The first step corresponded to the oxidation of ruthenium(III) to ruthenium(IV) while the second represented the oxidation of ruthenium(IV) to ruthenium(VI). Evaluation of these two steps on the curve showed that the first one corresponded to the quantitative oxidation of Ru(III) to Ru(IV) while the second was due to further partial oxidation of Ru(IV) to Ru(VI). It was also observed that with increasing amounts of Ru(III), the height of the second step decreased to the extent that with 2.55 mg Ru(III) per 70 ml it was completely eliminated.

The reaction in 0.1 N sulphuric acid was quite fast, the potential was stable immediately after each addition of the titrant and one titration could be completed in 10 minutes. Accordingly Ru(III) was determined from 84.00 µg to 3.35 mg with a maximum relative standard deviation of 0.7%. The results of these studies are shown in the table. The effect of foreign ions on the determination of ruthenium(II) was studied by keeping its amount constant and after the addition of the interfering ion to it, the titration was carried out and error of determination with varying amounts of various ions was calculated. Uranium(IV), Pt(IV), V(II) and Fe(II) were found to interfere seriously at all levels while Ag(I)

(0.15 mg added to 0.083 mg) Ru(III) did not interfere.

The method reported here for Ru(III) determination is precise, quick and quite simple and does not require any special or elaborate conditions to be followed. Moreover the titrant does not need repeated standardization due to its long keeping quality.

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