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Amperometric methods for trace determination of Rhodium (III) and Ruthenium (III)

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ABSTRACT

Amperometric determination of Rh(III) and Ru(III) was successfully carried out with the help of tetrahydrofurfuryl xanthate at dropping mercury electrode (DME) 0.05M ammonium tartrate +0.1M potassium nitrate medium. The metal to ligand ratio was found to be 1:3. Determination of 0.617 mg of Rh(III) gave relative standard deviation of 0.49%. While 0.606 mg of Ru(III) gave relative standard deviation of 0.58%. The interference of various ions has been studied. The method is found to be fairly selective, sensitive, rapid, precise and accurate.

Keywords: Rh(III), Ru(III), Tetrahydrofurfuryl xanthate, Amperometry.

INTRODUCTION

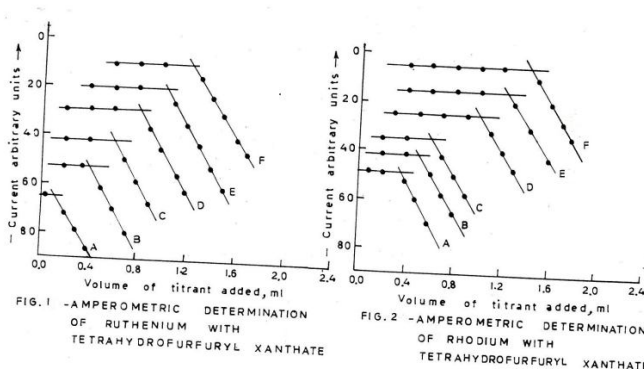
Rhodium together with ruthenium, palladium, platinum, osmium and iridium forms a group of elements referred as the platinum group metals. Rhodium and ruthenium are the best hardeners for palladium and platinum. They alloyed with these metals to make electrical contacts with extreme wear resistance. Rhodium is one of the most important metal and is indispensable for automotive catalytic converters. Rh(III) finds use in furnace windings and in anodes for electrical processes especially for thermocouples. Ru(III) is a hard metal. It does not transit at room temperature, but oxidizes explosively at high temperatures. The chief source of Ru(III) is osmiridium, in which it ranges from 0.25 to about 20%. Various reagents were used for the spectrophotometric determination of Rh (III) [1-3] and Ru (III) [4]. Whereas there is a scarcity of literature on the amperometric determination of Rh(III) and Ru(III). Amperometric titration has also been used in the past for trace determination of Rh(III) with different ligands like 2-mercapto,3-mercaptopropanoic acids[5-6], thiomalic acid [7] and thioglycolic acid [8]. 2-mercaptopropanoic acid [6, 9] has been used as analytical reagent for the amperometric determination of Ru(III).

MATERIALS AND METHODS

Instruments and Chemicals: All the titrations were performed at D.M.E. vs S.C.E. using a Toshniwal manual polarograph (Toshniwal India, model CLO2A). A stock solution of Rh(III) chloride and Ru(III) chloride was prepared by dissolving by 1 gm ampule in 10 mL of 1 M hydrochloric acid and was diluted

further up to the mark in 100 mL standard flask and standardized [10]. Solution of tetrahydrofurfuryl xanthate was prepared in double distilled water. Ammonium tartrate and Potassium nitrate solution were prepared from their A.R. samples. Dilute solution of ammonia and formic acid was used to adjust the pH. A simple form of an amperometric titration unit with a dropping mercury electrode in conjunction with saturated calomel electrode (S.C.E.) was connected to a polarographic cell via a potassium chloride agar-agar bridge.

Recommended method : An aliquot of Ru(III) solution and Rh(III) was taken in a beaker containing the requisite amounts of ammonium tartrate and potassium nitrate to keep their concentration at 0.05M and 0.1M respectively in 25 mL of the final solution. The pH of the medium was adjusted to 9. Nitrogen gas was passed slowly through the solution for 15 min. A potential of -0.2V was applied to the dropping mercury electrode. The current reading was recorded initially as well as after each small addition of standard xanthate solution. The volume of titrant added was plotted against current readings. Some typical titration curves are shown in Fig.1 and Fig.2 for Ru(III) and Rh(III) respectively.



RESULTS AND DISCUSSION

Effect of pH: The results for the determination of Ru(III) and Rh(III) with these reagents were found to be quantitative and reproducible over the pH range of 7.0-10.2 and 8.5-10.0 for Ru(III) and Rh(III) respectively.

Effect of base electrolyte concentration: Preliminary investigations showed that a solution of ammonium tartrate and potassium nitrate in the concentration range of 0.05-0.25M was found to be most suitable one for the determination of Ru(III) and Rh(III) by this method.

Stoichiometry of the reaction: Under the optimum condition as described above, varying amounts of Ru(III) and Rh(III) were titrated against tetrahydrofurfuryl xanthate according to the general procedure. The nature of the titration curves was found to be the same in all the cases (Fig.1 and Fig.2) indicating the formation of only one type of complex. The metal to ligand ratio was found to be 1:3.

Accuracy and precision: Determination of 0.606 mg of Ru(III) and 0.617 mg of Rh(III) gave relative standard deviation of 0.58% and 0.49% for Ru(III) and Rh(III) respectively. From the Table 1 and Table 2 it is obvious that the determination of Ru(III) and Rh(III) can be done accurately.

Table 1: Determination of Ru (III)

Curve	Amount of Ru taken (mg)	Amount of Ru found (mg)*	Relative Standard Deviation (%)
A	0.202	0.201	0.85
B	0.404	0.405	0.70
C	0.606	0.607	0.58
D	0.808	0.808	0.67
E	1.011	1.013	0.65
F	1.213	1.216	0.51

Average of six determinations. Base electrolyte=0.1M potassium nitrate, 0.05M ammonium tartrate, Tetrahydrofurfuryl xanthate = 3×10^{-2} M, pH = 9, Applied potential = -0.2V, Indicator electrode = D.M.E

Effect of diverse ions: Interference due to various ions in the determination of Ru(III) and Rh(III) was checked. It was found that Pd(II), Co(II), Ni(II) and Fe(II) interfered in the determination of Ru(III). The interference due to Co(II) and Ni(II) was eliminated by masking with sodium cyanide. Fe(II) was masked with sodium fluoride. It was found that Pd (II), Co (II), Ni (II) and Fe (II) interfered in the determination of Rh(III) also. All the interfering cations could be masked with the addition of 5 mL of 5% solution of EDTA.

Table 2: Determination of Rh (III)

Curve	Amount of Rh taken(mg)	Amount of Rh Found(mg)*	RelativeStandard Deviation (%)
A	0.360	0.360	0.72
B	0.515	0.514	0.67
C	0.617	0.618	0.49
D	1.029	1.030	0.37
E	1.235	1.237	0.17
F	1.441	1.440	0.19

Average of six determinations. Base electrolyte= 0.1M potassium nitrate, 0.05M ammonium tartrate, Tetrahydrofurfuryl xanthate = 3×10^{-2} M, pH = 9, Applied potential = -0.2V, Indicator electrode = D.M.E.

APPLICATION

Primary uses of rhodium and ruthenium are in alloys and catalysts for industrial processes. Ru(III) has highly effective ability to harden platinum and palladium and it is alloyed with these metals to make electrical contacts for severe wear resistance. Corrosion resistance of titanium is improved to a hundred fold by using 0.1% of Ru(III). This is also used as catalyst in some platinum alloys. Rh(III) is a rare platinum group metal that is chemically stable at high temperature, resistant to corrosion and mainly used in the production of automobile catalytic converters.

CONCLUSIONS

The present method developed for the micro determination of Ru(III) and Rh(III) using tetrahydrofurfuryl xanthate as an amperometric titrant. The method is found to be fairly selective, sensitive, rapid, precise and accurate.

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