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The Reduction of Divalent Copper and Tetravalent Tellurium by Ascorbic Acid—Application to Copper Telluride Analysis

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Synopsis. Quantitative reduction of Cu^{2+} to metal copper and Te^{4+} to metal tellurium by ascorbic acid in alkaline and acid medium respectively has been studied. Based on this a new method for easy and simultaneous determination of copper and tellurium as in copper-telluride has been developed with reproducible results.

In redox-gravimetry, ascorbic acid has been extensively employed as a metal precipitant for determining such elements as selenium,[1)] silver,[2)] mercury,[3)] and gold.[4)] In these methods, the metal ion in mineral acids is reduced to the metallic stage and weighed. Despite these applications and the versatility attained by ascorbic acid in diverse analytical methods,[5)] its "reducibility" in strongly alkaline medium appears to be much less studied. And although reduction of quadrivalent selenium to metal selenium has been reported, identical observations with tellurium find a meagre mention in available literature.

Preliminary experiments revealed that when ascorbic acid was introduced separately in solutions of copper sulphate and sodium tellurite, metals copper (in strongly alkaline medium) and tellurium (in strongly acid medium) were precipitated. In NaOH solutions Cu^{2+} was reduced preferentially to metal while Te^{4+} remained in solution and a reverse phenomenon was witnessed on making the solutions acidic. Quantitative aspects of these two redox-reactions and their extension to simultaneous determination of copper and tellurium in copper telluride have been reported in this paper.

Experimental

All reagents used in these investigations were of Analytical Grade purity.

Reduction of Cu^{2+} to Metallic Copper. 2.96 g of AR copper turnings were dissolved in minimum nitric acid in a 250 ml beaker and fumed with 5 ml of sulphuric acid. The residue was dissolved in distilled water and made up to one litre. Its copper content was checked iodometrically. An aliquot portion of this solution was taken in a round bottom flask fitted with a ground glass seal condenser. 20% aqueous sodium hydroxide solution was introduced into the flask till the pale-blue gelatinous precipitate of cupric hydroxide was formed. The contents were diluted to 60—70 ml and an adequate volume of the alkali was further added to maintain its overall normality at or above 1N (a minimum volume of 60—70 ml of the reaction mixture was found to be convenient for reflux, preventing formation of a paste and facilitate observance of supernatant liquid). Crystalline ascorbic acid (a minimum of 5 to 6 times the weight of copper present in aliquot) was then added when a colloidal reddish yellow precipitate appeared almost immediately. The condenser was fitted in and the system refluxed for about 10 to 15 min on a suitable heating mantle. The reddish yellow precipitate was reduced gradually to metallic copper which settled down leaving behind a clear supernatant liquid. The system was cooled, condenser detached and the copper filtered under suction through a weighed sintered glass crucible of porosity-4. It was washed 3 to 4 times with hot 1% sodium hydroxide solution, then with hot water till free from alkali and finally with a small quantity of absolute alcohol and ether. The precipitated copper was sucked dry, heated in an air oven at 110 °C for about one hour, cooled in a desiccator and weighed to a constant weight. It was later dissolved in 1: 1 nitric acid, diluted to about 100 ml, titrated iodometrically against 0.1 N thiosulphate solution. Results at serial nos. 1 to 7 in the table pertain to these studies. For quick routine analysis, the precipitated copper may be filtered through a Whatman 42 fitter pulp, dissolved in 1: 1 nitric acid, washed and titrated iodometrically.

Reduction of Te^{4+} to Metallic Tellurium. 7.4 g of AR tellurium metal was dissolved in 100 ml of concentrated hydrochloric acid in a 500 ml beaker. The solution was made up to 1 liter maintaining its overall HCl normality at about 2.5 N. Tellurium content in the solution was checked gravimetrically.

A measured volume of the Te^{4+} solution was taken in a round bottom flask fitted with a ground glass seal condenser followed by an adequate volume of concentrated HCl and distilled water to achieve an overall normality at or above 2.5 N and the total volume of the reactants at 60—70 ml. Crystalline ascorbic acid (4 to 5 times the weight of tellurium in aliquot) was now added to the flask when black colloidal precipitate of tellurium was seen almost instantaneously. The system was refluxed for abour 10 min when the precipitate settles down leaving behind a clear supernatant liquid. The contents were cooled and tellurium was filtered under suction through a weighed sintered glass crucible of porosity-4. The precipitate was washed thoroughly with hot water till free from chloride ions and then with a small quantity of absolute alcohol and ether. It was sucked dry, heated in an air oven at 105 °C for about an hour, desiccated and weighed to constant weight. Results at serial nos. 8 to 14 in the table correspond to these experiments.

Separation and Estimation of Copper and Tellurium when Present Together as in Copper Telluride. Synthetic copper telluride solutions were prepared by weighing accurately electrolytic copper and high purity tellurium in weight ratios 1: 1, 1: 2, 2: 1, and 2: 3 in a 250 ml beaker and dissolving in a minimum volume of 1: 1 nitric acid by careful heating. Excess nitric acid was removed by fuming with concentrated sulphuric acid. The residue when cooled was taken up with HCl and made up to 250 ml in a standard volumetric flask such that overall normality of HCl in the solution was maintained at about 2.5 N. In a 25 ml portion of each of these copper was first determined by ascorbic acid in alkaline medium by weighing and titration (*cf.* experimental for copper). The alkaline filtrate was transferred to a 500 ml Pyrex beaker, evaporated to 100 ml, concentrated HCl added to the prescribed normality and precipitated tellurium weighed gravimetrically (*cf.* experimental for tellurium).

Results of experiments at serial nos. 15 to 18 in the table refer to these investigations.

TABLE

Expt. No.	Copper (g)			Tellurium (g)	
	Present	Obtained gravimetrically	Obtained volumetrically	Present	Obtained gravimetrically
1	0.1773	—	0.1776	—	—
2	0.1478	0.1474	0.1474	—	—
3	0.1182	0.1180	0.1182	—	—
4	0.0739	—	0.0737	—	—
5	0.0591	0.0590	0.0591	—	—
6	0.0296	0.0294	0.0296	—	—
7	0.0148	0.0147	0.0148	—	—
8	—	—	—	0.2908	0.2895
9	—	—	—	0.1818	0.1815
10	—	—	—	0.1454	0.1452
11	—	—	—	0.0727	0.0726
12	—	—	—	0.0364	0.0363
13	—	—	—	0.0181	0.0179
14	—	—	—	0.0091	0.0092
15	0.0536	0.0535	—	0.0502	0.0501
16	0.0543	0.0542	—	0.0941	0.0939
17	0.1056	0.1055	—	0.0529	0.0528
18	0.0500	0.0497	—	0.0750	0.0746

Ratio of Cu^{2+} to Te^{4+} in experiments at serial nos. 15, 16, 17, and 18 was respectively 1: 1, 1: 2, 2: 1, and 2: 3.

Discussion

In order to study various reaction parameters, a series of experiments were carried out and it was established that the optimum conditions for a quantitative reduction of Cu^{2+} to metallic copper are, (1) 5 to 6 folds excess of ascorbic acid, (2) overall sodium hydroxide concentration at or above 1 N, (3) duration of reflux 15 to 20 min, and those for Te^{4+} to metal tellurium, (1) 4 to 5 folds excess of the acid reagent, (2) HCl concentration at or above 2.5 N and (3) time of reflux 10 to 15 min.

The close agreement between the amount of copper and tellurium taken for investigation and that obtained gravimetrically and volumetrically (for copper only) show that the accuracy is high for a fairly wide range of the metal ion concentrations, the errors being 0.2 to 0.7% for copper and 0.1 to 1.0% for tellurium. The deviations in most of the cases are on the negative side which may be attributed to the losses occuring during transfer and washing of the precipitated metals. A special feature of the present method is that both the metal ions are determined simultaneously by just altering the medium of reaction.

Studies on tellurides of silver and bismuth on identical lines and applications of the copper-ascorbic acid redox-reaction to direct determination and/or separation of copper in brasses, bronzes and aluminium alloys have shown encouraging results and will be communicated later.

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