Reduction of Cu(II), Ag(I), Au(III) & Mo(VI) on Tetrachlorohydroquinone Column & Oxidation of Mo(V) on Tetrachlorquinone Column

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Quantitative reduction of Cu(II), Ag(I), Au(III) and Mo(VI) in the form of molybdophosphate complex to Cu(I), Ag(0) Au(0) and Mo(V) respectively takes place on tetrachlorohydroquinone column at pH 4 (and 4N with respect to NaCl), in 5×10^{-4} N H_2SO_4, 3N HCl and at pH 2 respectively. The tetrachlorquinone formed has been estimated by the ascorbic acid method. Quantitative oxidation of Mo(V) to Mo(VI) takes place on tetrachloroquinone column in 5N HCl. The tetrachloroquinone formed has been estimated by the dichromate method.

Materials and Methods

Cupric sulphate, silver nitrate, chloroauric acid, sodium molybdate, disodium hydrogen phosphate, tetrachlorohydroquinone, celite, ascorbic acid, iodine, etc. were of AR grade. An approximately 0.1 N Cu(II) solution was prepared by dissolving cupric sulphate in distilled water. Cu(II) solutions containing different amounts of NaCl were prepared by appropriate dilution with NaCl solution. The pH was adjusted with 0.5% solution of sodium acetate. The solutions were standardized iodometrically with sodium thiosulphate using starch as the indicator. About 0.1 N Ag(I) solution was prepared by dissolving silver nitrate in distilled water. Ag(I) solutions containing different amounts of H_2SO_4 were prepared by appropriate dilution with dilute H_2SO_4 of known concentration. About 2 g of chloroauric acid was dissolved in 250 ml of distilled water. Lower concentrations of Au(III) solutions were prepared by appropriate dilution with dilute HCl of known concentration. Au(III) solution was standardised gravimetrically as elemental gold by the addition of hydroquinone. Sodium molybdate was dissolved in water to give a molybdenum concentration of 20 mg ml^{-1} and aliquots were suitably diluted for preparing dilute solutions. The solution was standardised by ceric sulphate after reduction to molybdenum(V) by mercury.

Disodium hydrogen phosphate was dissolved in 250 ml of water to give a phosphorus concentration of 2 mg ml^{-1}.

Sodium molybdate solution was reduced with mercury in presence of 3N HCl to give a Mo(V) solution containing 2–10 mg ml^{-1} of molybdenum. It was standardised by ceric sulphate solution in presence of ferroin indicator.

TCHQ and TCQ columns were prepared as mentioned earlier.

Procedure — The TCHQ and TCQ columns were conditioned initially by passing a solution of appropriate pH or acid. Each time an aliquot of the oxidising or reducing agent was passed at a flow-rate of 1-5 ml min^{-1} depending upon the oxidant or reductant. Sufficient time was allowed to enable all the effluents to come out. The column was then washed with 50–60 ml of solution of the same pH or acid solution and finally with 50–60 ml of distilled water at a flow-rate of 5–6 ml min^{-1}. The effluent and the wash solution were kept aside for any analysis that was required.

The TCHQ column was treated by passing ascorbic acid (25 ml of 0.1 N solution) through the column at
a flow-rate of 4-5 ml min\(^{-1}\). The column was washed with 50-60 ml of distilled water and the combined eluate was titrated with 0.1N iodine solution. The amount of oxidising agent reduced on the column is equivalent to the difference in the titre between the original quantity of dichromate added and the amount obtained finally. An ascorbic acid blank was run in the case of Ag(I) and Au(III). The columns (blank) were prepared by passing desired volume of aliquot through the TCHQ column followed by washing with a solution of the appropriate pH or acid solution. Finally, the column was washed with distilled water. An excess volume of ascorbic acid was passed through the column to reduce the oxidised band followed by washing with distilled water to remove the last traces of ascorbic acid. This is ready for column (blank) operation. The TCHQ column was treated by passing potassium dichromate (25 ml of 0.1 N solution) through the column at a flow-rate of 2-3 ml min\(^{-1}\). The column was washed with 50-60 ml of distilled water and the combined eluate was titrated with 0.1 N standard ferrous ammonium sulphate solution. The amount of reducing agent oxidised on the column is equivalent to the difference in the titre between the original quantity of dichromate added and that obtained finally.

**Copper (II)** — To determine Cu(II) in a solution, the TCHQ column was initially conditioned with 4N NaCl solution of pH 4. An aliquot of Cu(II) adjusted to pH 4 and 4N with respect to NaCl was allowed to pass through the TCHQ column at a flow-rate of 1-2 ml min\(^{-1}\) followed by 4N NaCl solution of pH 4. Finally, the column was washed with distilled water. The amount of Cu (II) was determined by the ascorbic acid method.

Copper in the copper ore concentrate was determined by heating in nitric acid an accurately weighed amount of the sample. When all the sample was dissolved, the solution was boiled after adding water to drive off nitrous fumes. Iron was removed by precipitation with ammonia. pH of the copper(II) solution was then adjusted to 4 and it was made 4N with respect to NaCl. An aliquot was passed through the TCHQ column and the analysis, carried out as described above.

**Silver (I)** — To determine silver an aliquot of Ag(I) was adjusted to pH 5.5 or 5 x 10\(^{-3}\)N with respect to H\(_2\)SO\(_4\) and passed through the TCHQ column previously conditioned with a 5 x 10\(^{-3}\)N H\(_2\)SO\(_4\) solution or pH 5.5 at a flow-rate of 4-5 ml min\(^{-1}\). The column was first washed with the same acid solution and finally with distilled water. The amount of silver was determined by the ascorbic acid method.

**Gold (III)** — Amount of Au(III) in a solution was determined by passing an aliquot volume of Au(III) in 1-3 N HCl through TCHQ column at a flow-rate of 1-2 ml min\(^{-1}\) previously conditioned with 1-3 N HCl. The column was first washed with the same acid and finally with distilled water. The amount of gold was ascertained by the ascorbic acid method.

**Molybdenum(V)** — To a solution containing 2-10 mg ml\(^{-1}\) molybdenum, a suitable amount of sodium phosphate solution was added\(^{16}\) to give Mo/P ratio in the range 20-37 (w/w). The mixture was acidified with the minimum quantity of 1 N H\(_2\)SO\(_4\) to pH 2; the total volume was 25-30 ml. It was passed through a TCHQ column previously conditioned with H\(_2\)SO\(_4\) solution of pH 2 at a flow-rate of 1-2 ml min\(^{-1}\). The column was first washed with 50-60 ml of H\(_2\)SO\(_4\) solution of pH 2 and finally with distilled water. The amount of molybdenum was determined by the ascorbic acid method.

**Results and Discussion**

Copper — The reduction of Cu(II) to Cu(I) on TCHQ column was carried out in different concentrations of NaCl. Fig. 1 shows that whereas no reduction of Cu(II) takes place in the absence of NaCl, the extent of reduction increases with progressive increase in NaCl concentration and reaches a value of 55% in 4 N NaCl at pH 3.5. The standard redox potential of the Cu(II)/Cu(I) system is +0.15 V\(^{17}\) which is less compared to the potential (+0.67 V)\(^{18}\) of the TCQ/TCHQ system. Therefore, Cu(II) is not expected to be reduced on the TCHQ column. However, the potential of the Cu(II)/Cu(I) system increases with increase in [chloride ion]. The redox potential of the system Cu\(^{2+}\)+Cl\(^-\) + e\(^-\)CuCl is +0.54 V\(^{17}\). It is known that increase in pH decreases redox potential of the TCHQ/TCQ system to a very low value\(^{18}\). Thus, at higher [chloride ion] and pH values it was expected that Cu(II) might be completely reduced to Cu(I). Attempts to reduce Cu(II) to copper metal by varying experimental conditions were unsuccessful since the redox potential of Cu(II)/Cu(0) is +0.337 V\(^{17}\).

Experimental results show that quantitative reduction of Cu(II) to Cu(I) on TCHQ column can be achieved by raising the pH of the solution to 4 and the [chloride ion] to 4 N or above by adding NaCl. Table 1 shows some typical results for the determination of Cu(II) on TCHQ column. Both the ascorbic acid reacted [as a measure of Cu(II) present] and the Cu(I) formed during reduction were measured. For the latter determination\(^{19}\), the effluent was collected...
in a solution of ferric ammonium sulphate and the ferrous iron formed was titrated with standard dichromate using barium diphenylamine sulphonate as the indicator. The two results are in close agreement and compare well with the amount of copper taken.

The method was applied to the determination of copper in copper concentrate (Chitradurga copper corporation, India). The experimental value of copper is 28.0% (value obtained from iodometry is 28.1%).

Silver — The extent of reduction of Ag(I) to metallic silver is shown in Fig. 2. In 5 $\times$ $10^{-3}N H_2SO_4$ or at pH 5.5 Ag(I) is quantitatively reduced to metallic silver. As the acid concentration is increased beyond 5 $\times$ $10^{-3}N$, the extent of reduction decreases and at 0.5 $N H_2SO_4$ Ag(I) is not reduced at all. The redox potential of Ag(I)/Ag(0) system is +0.799 V. It is therefore expected that Ag(I) will be reduced on TCHQ column.

Experimental results show that a quantitative reduction of Ag(I) to metallic silver can be achieved in 5 $\times$ $10^{-3} N H_2SO_4$ or at pH 5.5. Table 1 shows typical results for the determination of Ag(I) on TCHQ columns. Similar results were obtained by using HNO$_3$ in the place of H$_2$SO$_4$. Both, the ascorbic acid reacted as a measure of Ag(I) present and the metallic silver deposited on the column during reduction, were measured. For the latter determination the deposited silver was dissolved in 1N HNO$_3$ and the silver nitrate in the effluent was titrated with standard NaCl solution in the presence of potassium chromate indicator. The two results are in close agreement and compare well with the amount of silver taken.

Gold — The extent of reduction of Au(III) to gold metal in different HCl concentrations is shown in Fig. 3. The extent of reduction of Au(III) decreases with increase in HCl concentration. The reduction is quantitative in 1 to 3 $N$ HCl but at 7$N$ HCl no reduction takes place. The normal redox potentials of AuCl$_7^-$/AuCl$_6^-$, AuCl$_6^-$/Au and AuCl$_6^-$/Au systems are +0.93, +1.13 and +0.99 V respectively. The redox potential of AuCl$_7^-$/Au decreases with increase in chloride ion concentration. This explains the increase in the extent of reduction of Au(III) with decrease in HCl concentration. All quantitative studies on TCHQ were therefore carried out in 1 to 3 $N$ HCl. For every run metallic gold gets accumulated on the TCHQ column. After determining the extent of reduction of Au(III) by ascorbic acid method, 1-2 ml of cold aqua-regia solution were allowed to pass through the column. The effluents containing Au(III) were collected and estimated gravimetrically by the hydroquinone method. Experimental results for the determination of gold are presented in Table 1. Values obtained by the ascorbic acid method and by the analysis of deposited metallic gold on the column are in close agreement and compare well with the amount of gold taken.

Molybdenum — During the oxidation of TCHQ with molybdophosphate, an equivalent amount of TCQ is formed on the column. This TCQ was estimated by the ascorbic acid method. Table 1 gives a
summary of the results obtained for the reduction of molybdophosphate on TCHQ column both through the TCQ measurement and analysis of the Mo(V) in the eluate. There is good agreement between these results and the amount of molybdenum taken. The errors are within the range expected from the accuracy of the titrations. It may be emphasised that for a quantitative reduction the conditions of acidity and Mo/P ratio must be maintained properly. The procedure described here can also be used for the indirect estimation of phosphorus.

In the reduction of TCQ with Mo(V) an equivalent amount of TCHQ is formed on the column which is estimated by the dichromate method. Table 2 gives a summary of the results obtained for the oxidation of Mo(V) on TCQ column both through the TCQ measurement and analysis of Mo(VI) in the eluate. There is good agreement between these results and the amount of molybdenum taken. It is reported that increase in HCl concentration increases the redox potential of the Mo(VI)/Mo(V) system and the value in 2 N HCl is +0.53 V. It is also known that different coloured complex species of Mo(V) are formed in different HCl concentrations. The extent of oxidation of Mo(V) to Mo(VI) may also vary in different concentration of HCl. It was observed that extent of oxidation increases with increase in HCl concentration and Mo(V) is converted completely and quantitatively into Mo(VI) in 5 N HCl.

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