Chromic acid oxidation of oxalic acid catalysed by manganese(II) – Kinetic method of estimation of manganese(II) and water soluble and extractable manganese in soil

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Abstract : The catalytic effect of manganese(II) on the oxidation of oxalic acid by chromic acid has been pressed into use for its determination. A simple kinetic method has been developed using fixed time and iodometric procedures. The method is found to be suitable for the estimation of water soluble and exchangeable manganese in soil and the results have been compared with those of Atomic Absorption Spectrophotometer (AAS).

Keywords : Manganese(II), oxidation, chromic acid, soil.

Introduction

Many of the catalytic kinetic methods reviewed[1] so far for the determination of manganese(II) require the use of instrumentation and expensive reagents. However, a kinetic method has been developed utilising the catalytic effect of manganese(II) on the oxidation of oxalic acid by chromic acid[2], both the chemicals being quite inexpensive. The author has employed titrimetric method in which the unreacted chromic acid is titrated iodometrically and studied the influence of various other ions on the method of determination of manganese(II). Water soluble and exchangeable manganese is extracted from soil by 1 N ammonium acetate (pH = 7.0) and estimated by the same method. This is an alternative for the use of the costly instrument, Atomic Absorption Sprectrophotometer (AAS) which is not available in many rural areas.

In many homogeneous-catalysed reactions the rate of the reaction increases proportionally with the concentration of catalyst. In kinetic method, quantitative measurements are made during the course of the reaction before the system reaches equilibrium and the amounts of catalyst that can be found are small. In the present investigation, the catalyst concentration is determined by the initial rate method and by the general approach that the change in composition of the reactant or product over a fixed time interval at various initial concentrations of the catalyst is measured. The initial rate is given by the equation :

$$\frac{dx}{dt} = F[c]_0 + F^1 \tag{1}$$

where $F[c]_0$ and F^1 are rate of catalysed and rate of uncatalysed reactions respectively. $[c]_0$ is initial concentration of catalyst. For fixed time procedure, eq. (1) may be written as

$$\Delta x = \Delta t \, (F[c]_0 + F^1) \tag{2}$$

and a graph is drawn between Δx and $[c]_0$, which serves as calibration curve. In the present reaction, the change in composition, Δx, is measured i.e. the change in concentration of chromic acid is measured by arresting the reaction exactly at fixed time. Oxalic acid is taken in large excess compared to Cr^{VI}. The experimental conditions have been developed such that the concentration of Mn^{II} in equivalents is considerably smaller than that of Cr^{VI} (no. eq. of Cr^{VI}/no. eq. of Mn^{II} is equal to 5 at maximum concentration of manganese(II) employed).

Results and discussion

Part-A : Kinetic runs have been carried out under the conditions, $[OXH_2] >> [Cr^{VI}] > [Mn^{II}]$. The decrease in concentration of chromic acid at fixed period of time is measured with the difference in the volume of $Na_2S_2O_3$ used to titrate the liberated iodine from unreacted chromic acid of its aliquot from the 100 ml kinetic run and the titre value for the same aliquot volume of 5.0 × 10⁻⁴ mol dm⁻³ chromic acid in 5% acetic acid. It is denoted as ΔV,

which is proportional to the amount of chromic acid reacted in fixed time. The kinetic runs are repeated at different known manganese(II) concentrations and a plot of ΔV versus [Mn^{II}] is a good straight line in the range of manganese(II) concentration, 2.0 × 1 0^{-5} to 30 × 10^{-5} mol dm^{-3}, which serves as a calibration curve (Fig. 1(A)). Under the experimental conditions employed, there is also uncatalysed component of the reaction between chromic acid and oxalic acid as shown by the intercept of the above calibration curve. This is the value of ΔV determined in the absence of manganese(II) denoted by ΔV_0. Subtraction of ΔV_0 from ΔV did not improve the accuracy of the method. Hence, the author considers that the subtraction of uncatalysed component is not necessary. Thus kinetic runs have been repeated by taking five solutions containing different unknown amounts of manganese(II)

and ΔV values have been determined from which the molar concentrations of unknowns are read from calibration line (Fig. 1(A)). Manganese(II) taken and manganese(II) found have been included in Table 1. The amount (A) of manganese(II) present in 1 ml solution has been calculated by the formula :

$$A = \frac{\text{Molarity} \times 54.94}{1000} \text{ g.}$$

Each of above determinations has been repeated five times. The ΔV values are determined and [Mn^{II}] values are read from the calibration line. The average value of the amount of manganese(II) found is shown in Table 1. These results show that manganese(II) can be determined in microgram amounts with a maximum error of 3.5%.
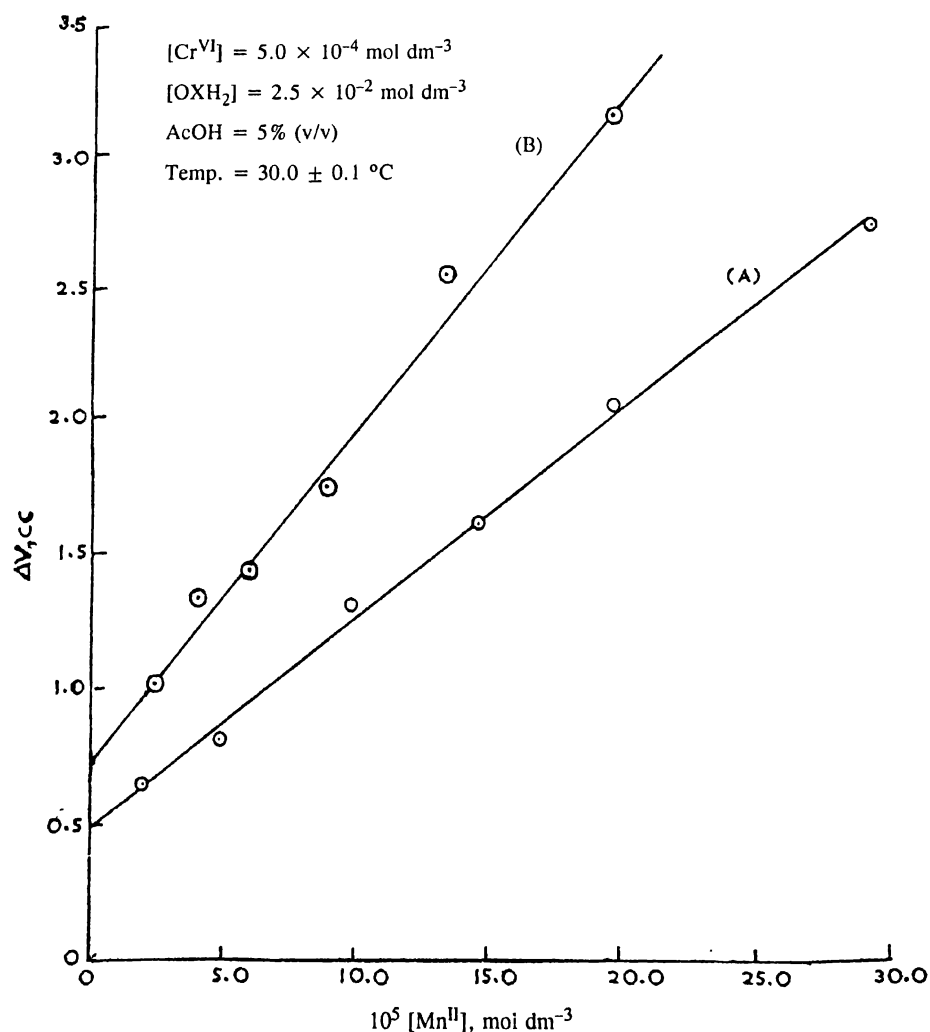

$[Cr^{VI}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$

$[OXH_2] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$

AcOH = 5% (v/v)

Temp. = 30.0 ± 0.1 °C

10^5 [Mn^{II}], mol dm^{-3}

Fig. 1. Calibration curve for the determination of manganese(II).

623

Table 1. Determination of manganese(II)

$[Cr^{VI}] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[OXH_2] = 2.5 \times 10^{-2}$ mol dm^{-3}, AcOH = % (v/v), Temp. = 30.0 ± 0.1 °C

10^5 [Mn^{II}] given (mol dm^{-3})	Mn^{II} given (μg/ml)	Mn^I found (μg/ml)	Error (%)
4.0	2.20	2.276	+3.45
7.5	4.12	4.136	+0.39
12.0	6.60	6.776	+2.66
17.0	9.62	9.57	-0.52
25.0	13.75	13.6	-1.12

The effect of various other ions on the kinetic method of estimation of manganese(II) at a fixed concentration of manganese(II) (25×10^{-5} mol dm^{-3}) under the established conditions has also been studied.

F$^-$: The presence of fluoride ion in the concentration range 1.0×10^{-6}-0.1 mol dm^{-3} causes no appreciable change in the amount of manganese(II) found.

PO$_4^{3-}$: The presence of phosphate ion upto 2.5×10^{-2} mol dm^{-3} causes no appreciable change in the amount of manganese(II) found.

Zn^{2+}, Ni^{2+} and Co^{2+} : When each of these ions is present in concentrations upto 1.0×10^{-3} mol dm^{-3} in the kinetic run, there is no change in the amount of manganese(II) found. Therefore, these ions do not interfere in the method in the concentration range 0-1.0 × 10^{-3} mol dm^{-3}. At higher concentrations of these ions, precipitation has been observed.

Mg^{2+} : Magnesium ion upto 7.5×10^{-3} mol dm^{-3} has no effect on the amount of manganese(II) found.

Pb^{2+} : At $[Pb^{2+}] > 1.0 \times 10^{-4}$ mol dm^{-3}, the amount of Mn^{II} found is lower than that found in the absence of lead ions.

Part-B : Solutions of three different soils collected from different agriculture lands have been prepared and used in kinetic runs for the estimation of soil manganese. To construct calibration line for soil analysis, six solutions of manganese(II) are prepared to give concentrations shown in Table 2 in the same way as the solution of soil is prepared i.e. by treating aliquots of MnSO$_4$ solution with NH$_4$OAc, HNO$_3$ and H$_2$O$_2$. With these, kinetic runs have been carried out under the same experimental conditions established. The values of ΔV are plotted against [Mn^{II}] and calibration line is obtained (Fig. 1(B)). These values are presented in Table 2. Similarly kinetic runs with the solutions of soils have been carried out and ΔV values are determined. From these values, the molar concentrations of manganese in soil samples have been obtained using the standard line (Fig. 1(B)). The amount of

Table 2. Data for calibration line (Fig. 1(B)) and the determined amounts of manganese in soils

$[Cr^{VI}] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[OXH_2] = 2.5 \times 10^{-2}$ mol dm^{-3}, [AcOH] = 5% (v/v), Temp. = 30.0 ± 0.1 °C

Sl. no./ Sample of soil	[Mn^{II}] × 10^5 taken (mol dm^{-3})	ΔV (cc)	[Mn^{II}] × 10^5 read from standard line (mol dm^{-3})	Amount of manganese (ppm) Found	Amount of manganese (ppm) AAS report
1.	2.5	1.00			
2.	4.0	1.30	–	–	–
3.	6.0	1.40	–	–	–
4.	9.0	1.70	–	–	–
5.	13.5	2.50	–	–	–
6.	20.0	3.10	–	–	–
Red gel (1092)	–	1.05	2.9	15.9	15.07
Clay (7826)	–	1.30	5.0	27.5	32.18
Clay (7833)	–	2.00	10.9	60.0	66.28

manganese in soil (A_s) in ppm is calculated using the formula :

$$A_s = \frac{\text{Molarity} \times 54.94}{\text{Weight of soil sample (g)}} \times 10^5.$$

The amounts of manganese found in the three soils viz. redgel (Sample no.1092) and two clays (Sample nos. 7826 and 7833) are shown in Table 2. These values are in good agreement with the amounts of manganese reported by AAS in the same three soil samples.

Fe^{3+} and Cu^{2+} ions interfere in the method of determining the value of ΔV by liberating excess iodine from KI. However, these ions are not expected in the solution of soil because the extraction is carried out with ammonium acetate[3a] at pH = 7. Further, Fe^{3+} ions form oxalate complex, $H_3[Fe(C_2O_4)_3]$, in the presence of excess oxalic acid which does not react with KI. The absence of Cu^{2+} ions in the soil solution is evidenced by the fact that the soil solution did not give any precipitate with potassium ferrocyanide. The possible precipitation of calcium oxalate is avoided by eliminating Ca^{2+} ions by the addition of sodium fluoride to the soil solution which also eliminates Pb^{2+}, Zn^{2+} and Cu^{2+} ions as insoluble precipitate[4].

Conclusion :

The range of manganese(II) concentration, 2.0×10^{-5} to 30×10^{-5} mol dm^{-3}, in which ΔV varies linearly with the concentration of manganese(II) corresponds to the amount of Mn from 1.1 to 16.5 µg/ml and facilitates the determination of unknown concentrations of Mn^{II} solutions containing manganese in microgram quantities. The same range of quantity corresponds to 6 to 91 ppm of Mn^{II} in soil determined by this method using 10 g of sample. Thus, water soluble and exchangeable manganese in surface layers of soil can be easily estimated as its amount generally ranges from 5 to 100 ppm[5].

Experimental

All the solutions were prepared using de-ionised distilled water.

Chromium(VI) :A $0.1/3$ mol dm^{-3} chromic acid solution has been prepared using chromium(VI) oxide ('pro analysi', E. Merck) and standardised by the improved iodometric procedure[6].

OXH_2 : A 0.25 mol dm^{-3} solution of oxalic acid has been prepared using oxalic acid (GR,

SM) and standardised with standard NaOH solution using phenolphthalein.

$Mn^{II}SO_4$: A 0.05 mol dm^{-3} solution has been prepared using manganese sulphate ('pro analysi', E. Merck) and standardised by the procedure described by Vogel[7a].

Glacial acetic acid, hydrochloric acid, nitric acid, KI and starch used were of analytical reagent grade.

$Na_2S_2O_3$: A 0.1 mol dm^{-3} solution has been prepared by dissolving sodium thiosulphate (AnalaR, B.D.H.) in water containing 5 mg of sodium carbonate stored in ambor coloured bottle and standardised iodometrically.

A 0.5 mol dm^{-3} solution of sodium fluoride[7b], 0.1 mol dm^{-3} solution of sodium dihydrogen phosphate[7c], 0.05 mol dm^{-3} solutions of lead acetate[7d], zinc sulphate[7d], cobalt nitrate[7d], nickel nitrate[7e] and magnesium nitrate[7a] have been prepared using Excela R, Glaxo grade reagents and standardised by the procedures described by Vogel.

NH_4OAc : A 1 M solution has been prepared using ammonium acetate suitable for soil testing (Qualigens) dissolving 78 g in 1 litre water. The pH of NH_4OAc solution has been checked using a digital pH meter and adjusted to 7 with few drops of concentrated ammonia.

H_2O_2 : 30% (100 volumes) hydrogen peroxide (SD fine chemicals) has been used.

Kinetic measurements : Calculated amount of oxalic acid and acetic acid to give over-all concentration of 2.5 $\times 10^{-2}$ mol dm^{-3} and 5% respectively are mixed with the solution of manganese ions in a clean pyrex bottle. The bottle is placed in a thermostat along with another pyrex bottle containing chromic acid. After the temperature equilibrium is attained, calculated quantity of chromic acid to give an over-all concentration of 5.0 $\times 10^{-4}$ mol dm^{-3} is added to the above mixture, simultaneously starting the stop watch. Exactly after 20 min, 10 ml of the reaction mixture is withdrawn and added to the solution of 10 ml of 10% KI followed by 5 ml of 6 mol dm^{-3} hydrochloric acid and 10 ml of water in a conical flask. Oxalic acid present in the reaction mixture helps the immediate liberation of iodine[6], which gives the concentration of unreacted chromic acid. The liberated iodine is titrated against 1.5×10^{-3} mol dm^{-3} sodium thiosulphate using 0.5 ml 1% starch solution as indicator.

Preparation of soil solution : For soil analysis, man-

ganese is extracted from soil as follows[3b]. 10 g of air-dried sample of soil and 100 ml of 1 N NH$_4$OAc (pH adjusted to 7.0) are transferred into a 250 ml Erlenmeyer flask. The flask is stoppered and shaked for 1 h and intermittently for 6 h. Now, the suspension is filtered through Whatman filter paper. The filtrate is again filtered and the clear filtrate is taken in a 250 ml beaker. The beaker is placed on a hot plate at low heat to evaporate the contents to dryness. Heating is continued until NH$_4$OAc ceased to fume. The beaker is removed from hot plate. After cooling to room temperature (R.T.), 5 ml of conc. HNO$_3$ and 2 ml of 30% H$_2$O$_2$ are added to the mass in beaker and evaporated again to dryness. After it is cooled to R.T., conc. HNO$_3$ and H$_2$O$_2$ are once again added and dried as before. The substance so obtained is cooled to R.T. and dissolved completely in 50 ml of distilled water. To this solution, 20 ml of 0.5 M NaF solution is added and the white precipitate formed is filtered off. This filtrate is used as the solution of manganese in the kinetic run.

Acknowledgement

References

1. V. A. Ramam and M. N. Sastri, *J. Chem. Sci.*, 1983, 9, 74.

2. D. N. Chakravarty and S. Ghosh, *Proc. Natl. Acad. Sci., India, Sect. A*, 1960, 29 (Part 2), 199.

3. P. C. Jaiswal, "Soil, Plant and Water Analysis", Kalyani Publishers, New Delhi, 2003, (a) p. 212 and (b) p. 213.

4. V. Alexeyev, "Qualitative Analysis", MIR Publishers, Moscow, 1967, p. 442.

5. Firman Bear, "Chemistry of the Soil", 2nd ed., Oxford & IBH Publishing Co., New Delhi, 1964, pp. 345 and 359.

6. G. Gopala Rao and C. R. Viswanadham, *Curr. Sci.*, 1942, 2, 102.

7. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", 3rd ed., Longman, London, 1961, (a) p. 434, (b) 570, (c) 448, (d) 443 and (e) 435.