

Mechanistic study and kinetic determination of vitamin C

SALAH M. SULTAN*‡ and EDMUND BISHOP†

* *Chemistry Department, College of Sciences, King Fahd University of Petroleum and Minerals, KFUPM Box No. 2026, Dhahran 31261, Saudi Arabia*

† *Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, UK*

Abstract: A simple specific method for the determination of vitamin C has been investigated by elucidating the reaction mechanism of its oxidation with cerium(IV) in sulphuric acid media. The reaction kinetics and rate measurements which form the basis of this method were determined by following the decrease of the intense yellow colour of cerium(IV) at 405 nm. The fixed-time and fixed-concentration methods were investigated. The former was found to be more precise and was consequently used for the determination. Advantages of this method over the B.P. and other methods are discussed.

Keywords: Mechanism; kinetics; fixed-time method; fixed-concentration method; vitamin C and cerium(IV).

Introduction

Vitamin C (ascorbic acid) has received the attention of various researchers in different fields and many analytical methods have been described. The kinetics and mechanism of its oxidation with different oxidizing agents has also been extensively investigated [1-7]. The mechanism suggested by Devenport *et al.* [8] in 1937 and verified by others, is a two-electron process accompanied by the release of two protons. However, there are different opinions regarding the actual reducing species. It has been suggested that either the ascorbate ion or the molecular ascorbic acid [7] is the reducing species while other investigators have suggested that attack by both the ascorbic acid and the ascorbate anion occurs [9].

Erdey [10] recommended the use of ascorbic acid as a reductometric titrant in 1950 and the term "ascorbinometric titrations" was established. Since then, numerous methods have been described for its determination involving the use of iodine [10], permanganate [10], titanium(III) [11], hexacyanoferrate(III) [10, 12], bromine cyanide [13], vanadium [14], iodate [15], 2-4-dinitrophenylhydrazine [16], dipyriddy [17, 18], and recently flow injection analysis [19]. Cerium(IV) has been employed for the titrimetric determination of ascorbic acid in phosphoric acid medium using ferroin

sulphate indicator [20]. One disadvantage of the method that was recognised by the authors was the possibility of the formation of cerium(IV) phosphate precipitate during the titration.

Cerium(IV) has also been employed for the titrimetric determination of ascorbic acid (in tablets) by the B.P. method [21] in which the titration is carried out in sulphuric acid medium using ferroin sulphate indicator. It is interesting that errors in its determination arising from the slowness of the reaction under the experimental conditions employed have not been reported and that no investigation of the rates of reaction with cerium(IV) has been made. The standard method for the determination of ascorbic acid in drug substance form, that is described by the B.P. monograph [22], is a titration with a standard iodine solution in sulphuric acid using starch indicator.

The present work investigates the kinetics and mechanism of the oxidation reaction of ascorbic acid with cerium(IV) in sulphuric acid solution to allow the proper validation of a newly introduced kinetic method for the determination of ascorbic acid.

Experimental

Apparatus

Cary 16, Unicam SP 1800 and Beckman 35

‡ Fifty per cent of this work has been accomplished by the main author (‡) to whom all correspondence should be addressed.

spectrophotometers were used. Matched sets of W 210/UU 10.00-mm cells were also used.

Reagents

Quartz-processed high purity distilled water was used throughout.

Ascorbic acid Analar (BDH) was dried at 50°C *in vacuo* over magnesium perchlorate, stored in the dark, and used only if white. It was 99.98% pure and complied with the B.P. specification [21]. Ascorbic acid (1 mg ml⁻¹) stock solution was prepared by dissolving an accurately weighed quantity about 1 g in warm water, stirring for 10 min and after cooling to room temperature diluting to volume with water.

Cerium(IV) solution (2.0 × 10⁻² M) was prepared from Analar cerium sulphate 4H₂O dried *in vacuo* at 40°C over magnesium perchlorate and dissolved in water containing sulphuric acid. This solution was standardized by titration with a standard solution of arsenic(III) by the method described by Gleu [23]. In this method, the arsenic(III) solution, containing three drops of 0.1 M osmium tetroxide solution as a catalyst, is acidified with sulphuric acid (such that the acid concentration at the end point is 0.5 M) and titrated with the cerium(IV) solution using ferroin sulphate as indicator.

Sulphuric acid (2.75 × 10⁻² M) was prepared by diluting Aristar grade sulphuric acid (98.0%) with water. A stock solution was titrated against a standard solution of sodium carbonate using methyl orange as indicator. A blank titration was carried out on an equimolar solution of sodium sulphate.

General procedure

Five millilitres of cerium(IV) stock solution were pipetted into a 50-ml standard flask. 5 ml of sulphuric acid solution and the appropriate amount of ascorbic acid solution were added and the mixture was diluted to the mark with distilled water. The contents were shaken and the reaction was allowed to proceed at 25°C. The absorbance at exactly 120 s was measured at 405 nm. The concentration of ascorbic acid in µg ml⁻¹ was calculated by using the appropriate calibration equation.

Results and Discussion

The rate of oxidation of ascorbic acid by cerium(IV) in sulphuric acid media was

measured by following the decrease of the absorbance of the intense yellow colour of cerium(IV) species at its wavelength of maximum absorbance, (λ_{max}) 405 nm.

Mechanism of the reaction

Stoichiometry. The reaction mixture, containing known amounts of cerium(IV) and a slight excess of ascorbic acid in the presence of sulphuric acid (1–3 M), was allowed to stand for 4 h to allow the reaction to proceed to completion. The excess of ascorbic acid was determined by titration against a standard solution of iodine using starch as indicator, as described by Erdey and Svehla [10]. The results obtained indicate that ascorbic acid reacts with cerium(IV) in the ratio 1:2.

The stoichiometry of the reaction in which there was an excess of cerium(IV) was investigated in different concentrations of sulphuric acid between 0.5–3.5 M. The absorbance of cerium(IV) remaining unreacted after each addition of ascorbic acid and hence the concentration of reacted cerium(IV) was determined by reference to a standard calibration equation of absorbance versus various concentration of cerium(IV) in sulphuric acid at the same concentration. Typical results in 3 M sulphuric acid are presented in Table 1. In sulphuric acid the reaction rate is slow and, therefore, the reactants were left for 20 min to ensure complete reaction. The results obtained clearly show that the reaction of ascorbic acid in the presence of an excess of cerium(IV) under the conditions of the kinetic method is not stoichiometric and gives a reacting ratio of >2:1 cerium(IV)–ascorbic acid.

Conditions. Prior to the full investigation, the reaction kinetics were studied and found to involve a two-step process. The first step with a half-life of only a few seconds, was found to be too fast to allow it to be followed spectrophotometrically at all sulphuric acid concentrations up to 6 M. The reaction rate for the second step decreases as the sulphuric acid concentration increases and above 3 M the reaction does not proceed. It was easy therefore to isolate the first-step process.

The reaction rate increases at higher concentration of ascorbic acid and decreases at low concentrations. It is too slow to be measured at very low concentrations that are present in the determination of the reaction order for ascorbic acid and in the procedure for the

Table 1

Molar ratios of reactants calculated from absorbances of solutions containing different volumes of equimolar solutions of 1.5×10^{-3} M cerium(IV) and ascorbic acid in 3 M H_2SO_4 in a 25-ml flask and measured at 405 nm after 20 min

Volume of ascorbic acid (ml)	Concentration of ascorbic acid ($\times 10^{-4}$ M)	Volume of Ce(IV) (ml)	$A_0 - A^*$	Concentration of Ce(IV) $\times 10^{-4}$ M†	Mole ratio Ce(IV):ascorbic acid
0.00	0.00	25.00	0.00	—	—
1.00	0.60	24.00	0.109	1.89	3.2
2.00	1.20	23.00	0.239	3.96	3.3
3.00	1.8	22.00	0.364	5.95	3.3
4.00	2.4	21.00	0.476	7.73	3.22
5.00	3.0	20.00	0.586	9.48	3.2
6.00	3.6	19.00	0.686	11.1	3.1
7.00	4.2	18.00	0.761	12.3	2.9
8.00	4.8	17.00	0.808	13.0	2.7
9.00	5.4	16.00	0.816	13.1	2.4

* Difference of the absorbance of unreacted cerium(IV) from that of initial cerium(IV) solution.

† As calculated from the calibration equation of $A = -0.01 + 628.48 C$.

kinetic determination. The rate was therefore accelerated by decreasing the concentration of sulphuric acid to 2.7578×10^{-3} M.

Reaction order for cerium(IV). The reaction order determined by the integral method [25] by measuring the absorbance at 405 nm was found to be first-order. The log absorbance decreased linearly with time, the regression of which gave a straight line with a correlation coefficient (r) = 0.99 and a constant slope of k' $8.571 \times 10^{-4} \text{ s}^{-1}$ (Table 2) for different cerium(IV) concentrations in the range 1.0×10^{-4} to 6.0×10^{-4} M. In these experiments the concentrations of sulphuric acid and ascorbic acid were high and constant (2.8956 M and 4.0123×10^{-3} M, respectively) thus confirming that the reaction is first-order with respect to cerium(IV).

Reaction order for ascorbic acid. Experiments were carried at 25°C by varying the ascorbic acid concentration and keeping the

other reactants at higher constant concentrations (at least 10 times the concentration of ascorbic acid). The absorbance versus time curves were plotted as illustrated in Fig. 1. In this case, as cerium(IV) and sulphuric acid concentrations were in excess and did not change appreciably during the course of the reaction, the rate was dependent upon the ascorbic acid concentration as follows:

$$\text{Rate} = k' [\text{ascorbic acid}]^n, \quad (1)$$

where k' is the pseudo-first-order rate constant and n is the order of the reaction with respect to ascorbate.

Hence, rates were measured by the variable time method [25] as $(\Delta A/\Delta t)$ and introduced into equation (1) as follows:

$$\frac{\Delta A}{\Delta t} = k' [\text{ascorbic acid}]^n. \quad (2)$$

The ascorbate concentration in equation (2) was calculated at the time interval (Δt) from the initial concentration of ascorbic acid after being half-oxidized.

$$\therefore \log_{10} \frac{\Delta A}{\Delta t} = \log_{10} k' + n \log [\text{ascorbic acid}].$$

A computer plot of values of $\log_{10} (\Delta A/\Delta t)$ versus \log ascorbic acid concentration (Table 3) gave a straight line with $r = 0.99$ and a slope equal to 0.916 indicating a first-order reaction with respect to ascorbic acid or ascorbate anion.

Table 2

Values of pseudo-first-order rate constants (k') for reaction rates conducted at 25°C with different cerium(IV) concentrations and concentrations of ascorbic acid and sulphuric acid of 4.0123×10^{-3} and 2.8956 M, respectively

Concentration of cerium(IV) (M)	k' (s^{-1})
1.1021×10^{-4}	8.58×10^{-4}
1.6532×10^{-4}	8.55×10^{-4}
2.2042×10^{-4}	8.56×10^{-4}
2.7553×10^{-4}	8.56×10^{-4}
3.3063×10^{-4}	8.60×10^{-4}
3.8574×10^{-4}	8.57×10^{-4}
4.4084×10^{-4}	8.59×10^{-4}
4.9595×10^{-4}	8.53×10^{-4}
5.5105×10^{-4}	8.64×10^{-4}

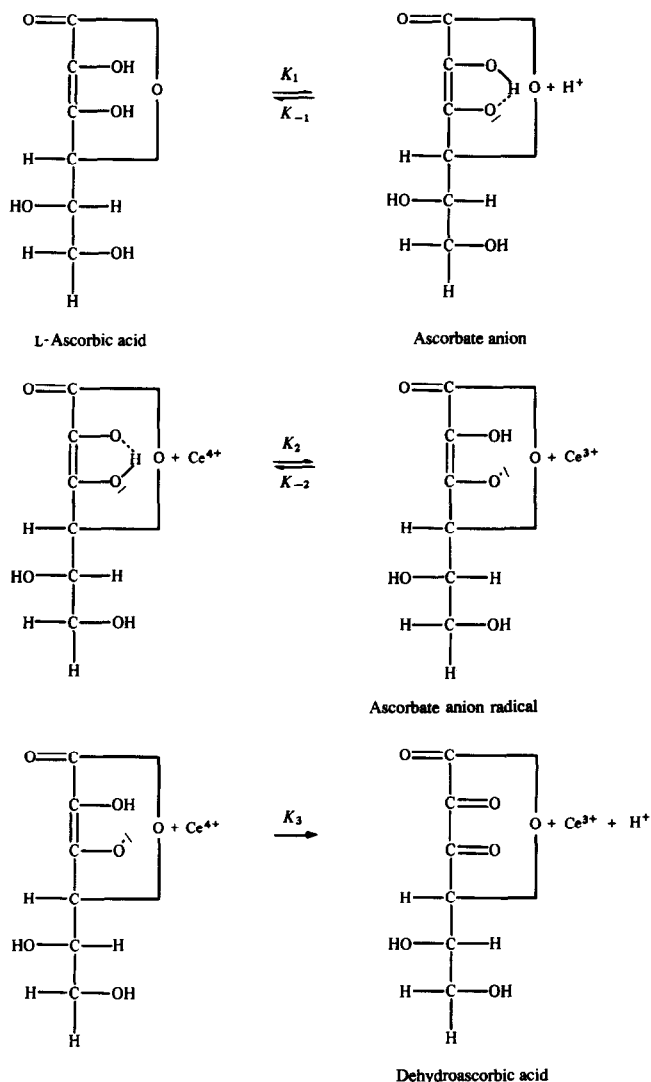


Figure 1
Reaction mechanism.

Table 3
Calculated rates of the reaction at 25°C as $\Delta A/\Delta t$ for different concentrations of ascorbic acid at constant concentrations of 2.0338×10^{-3} M cerium(IV) and 2.7578×10^{-3} M sulphuric acid

No.	$[\text{H}_2\text{A}] 10^{-5}$ M at Δt	$\log [\text{H}_2\text{A}]$	Δt (s)	$\frac{\Delta A}{\Delta t} \times 10^{-4}$	$\log \frac{\Delta A}{\Delta t}$
1	2.2358	-4.6506	17.5	11.4286	-2.9420
2	1.7304	-4.7619	25.0	8.000	-3.0969
3	1.2249	-4.9119	40.0	5.000	-3.3010
4	0.7196	-5.1429	60.0	3.3733	-3.4719
5	0.2142	-5.6692	160.0	1.250	-3.9031

Reaction order for hydrogen ion. A series of experiments was conducted at room temperature in which the concentration of the hydrogen ion was varied and in which those of cerium(IV) and ascorbic acid were constant

throughout. In Table 4, the rates calculated as $(\Delta A/\Delta t)$ from absorbance versus time curves seemed to decrease as the concentration of sulphuric acid increased. They were introduced into the equation for the differential method,

Table 4

Calculated rates of the reaction at 25°C for different sulphuric acid concentrations at constant concentrations cerium(IV) (2.024×10^{-3} M) and ascorbic acid (1.016×10^{-3} M)

No.	[H ⁺] (M)	log [H ⁺]	Δt (s)	$\frac{\Delta A}{\Delta t}$ (10^{-4})	log $\frac{\Delta A}{\Delta t}$
1	2.2981	0.3614	45.00	2.2222	-3.6532
2	2.5279	0.4028	50.00	2.000	-3.6989
3	2.7578	0.4406	55.0	1.8182	-3.7404
4	2.8727	0.4583	57.50	1.7391	-3.7597
5	2.9876	0.4753	60.00	1.6667	-3.7782
6	3.4159	0.5335	68.75	1.4545	-3.8373

$$\frac{\Delta A}{\Delta t} = k' [H^+]^n, \quad (3)$$

$$\therefore \log_{10} \frac{\Delta A}{\Delta t} = \log_{10} k' + n \log_{10} [H^+]. \quad (4)$$

The regression of the values of log ($\Delta A/\Delta t$) versus log [H⁺], as shown in Table 4, gave a slope of $n = -1.073$ which suggests that the reaction order is inversely dependent on the hydrogen ion concentration.

Activation energy. Experiments were carried out at temperatures varying between 20–40°C, in which all the reactants were constant as shown in Table 5. The pseudo-first-order rate constant (k') was calculated from the slope of a computer plot of log A (absorbance at 405 nm) versus time from the following equation:

$$-\log_{10} A = \frac{k't}{2.303} + C, \quad (5)$$

where $k' = 2.303 \times \text{slope}$ and C is a constant.

Regression of the values obtained for log k' versus T^{-1} (see Table 5) by the following Arrhenius equation:

$$\log_{10} k' = \frac{-E_a}{2.303R} \times \frac{1}{T} + \log_{10} A \quad (6)$$

Table 5

Calculated values of rate constants for the reaction mixture containing 2.137 M sulphuric acid, 2.032×10^{-3} M ascorbic acid and 4.046×10^{-5} M cerium(IV) at variable temperatures

No.	T (°C)	$1/T \times 10^3$ (K)	k' (10^{-3})	log k'
1	24.0	3.367	0.5245	-3.2803
2	28.5	3.3167	1.1901	-2.9244
3	30.0	3.3003	1.7743	-2.7510
4	31.5	3.28241	1.9195	-2.7168
5	37.0	3.2258	6.5565	-2.1883

(where E_a is the Arrhenius activation energy and equals $(-2.303 \times R \times \text{slope})$; R is the gas constant; T is the temperature in °Kelvin and A is the pre-exponential factor) gives the value of 146.8 kJ mol⁻¹ as the activation energy for the oxidation reaction of ascorbic acid by cerium(IV).

Proposed mechanism. On the basis of the results obtained above and the observation that the reaction slows down as sulphuric acid concentration increases and even stops at a concentration of 3 M, it appears that ascorbate anion is the active reductant for cerium(IV) and not molecular ascorbic acid. That the reaction is directly dependent on the oxidant and reductant, and inversely dependent on hydrogen ion, would lead to the following rate equation:

$$\text{Rate} = k_1 k_2 k_3 [\text{Ce(IV)}] [\text{ascorbate}] [H^+]^{-1}. \quad (7)$$

From the stoichiometry and the facts that ascorbic acid is a two-electron donor and cerium(IV) is a one-electron acceptor, it is thought that the ascorbate anion produced as the result of ascorbic acid ionization in solution attacks one mole of cerium(IV) producing ascorbate anion radical in a reversible fast reaction as a first step. In the second step, the ascorbate anion radical intermediate that is generated reacts irreversibly with another mole of cerium(IV) in a slow rate-determining step. Thus the inverse dependence on hydrogen ion is due to a proton being produced as a result of this reaction as shown in Fig. 1.

As the reaction stoichiometry in the particular case of excess cerium(IV) is not quantitative and is in a ratio >2:1 Ce(IV)–ascorbic acid, the reaction does not stop at the dehydro-ascorbic acid stage and oxidization proceeds further to carbon dioxide. This is in agreement

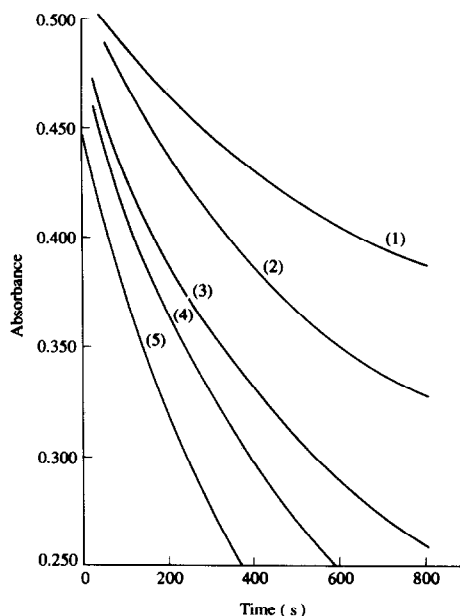


Figure 2

Absorbance versus time graphs showing the effect of different concentrations of ascorbic acid (1) 213, (2) 285, (3) 356, (4) 427 and (5) 498 $\mu\text{g ml}^{-1}$ on the reaction rate at 25°C of cerium(IV) (2.034×10^{-3} M) and sulphuric acid 2.758×10^{-3} M.

with the conclusions of Strohecker and Matt [24].

Kinetic determination of ascorbic acid

The results of the investigation above form the basis of a new method for ascorbic acid determination in which there is a full understanding of the optimum conditions of the reaction. Determination by kinetic methods of analysis is based on the use of excess concentrations of cerium(IV) and sulphuric acid. Consequently, rate equation (2) is the most applicable. Initial concentrations of 2.034×10^{-3} M cerium(IV) and 2.758×10^{-3} M sulphuric acid were chosen on the basis of their giving a measurable and moderate reaction rate. The fixed-time and the fixed-concentration methods [26, 27], were considered to be the most suitable methods for the determination of ascorbic acid by its oxidation reaction with cerium(IV).

Fixed-time method. As the reaction rate is dependent on the ascorbic acid concentration, an experiment was designed which involved constant concentrations of cerium(IV) and sulphuric acid at 2.034×10^{-3} and 2.758×10^{-3} M, respectively and different concentrations of ascorbic acid. At a preselected,

fixed time, the absorbance was accurately measured. Calibration graphs of absorbance versus initial concentrations of ascorbic acid were constructed at fixed times of 60, 120, 180, 240, 300 and 360 s and the corresponding calibration equations were calculated (Table 6). From this table it is clear that the negative slope increases with time and there appears to be a decrease in the intercept and correlation coefficient (r), indicating lower linearity at later times probably due to the consumption of ascorbic acid. At a fixed time of 120 s the results were satisfactory and this time was chosen as the most appropriate for the measurement.

Table 6

Calibration equations obtained at different fixed times for reaction rates measured at 25°C for variable concentrations of ascorbic acid in the range 200–500 $\mu\text{g ml}^{-1}$ and constant initial concentrations of 2.034×10^{-3} M cerium(IV) and 2.758×10^{-3} M sulphuric acid

Time(s)	Calibration equation	Correlation coefficient (r)
60	$A = 0.5689 - 0.000336 C$	0.99
120	$A = 0.5695 - 0.0004178 C$	0.99
180	$A = 0.5675 - 0.0004776 C$	0.98
240	$A = 0.5709 - 0.0005485 C$	1.0
300	$A = 0.5685 - 0.000589 C$	0.98
360	$A = 0.5776 - 0.000631 C$	0.96

Fixed-concentration method. An experiment was designed in which different concentrations of ascorbic acid, in the range 20–500 $\mu\text{g ml}^{-1}$, and constant concentrations of cerium(IV) and sulphuric acid (2.034×10^{-3} and 2.758×10^{-3} M, respectively) were used throughout. The various reaction rates obtained were recorded. A preselected value of absorbance, at a wavelength at which the absorbance of the reactants change by <2% was selected and the time to reach this value was measured in seconds. Examples of the reciprocal of time in seconds versus initial concentrations of ascorbic acid are given in Table 7. The regression equation was:

$$1/t = -0.05158 + 0.000206 C,$$

and a low correlation coefficient (r) of 0.84 was obtained due to the difficulty of determining the exact time in seconds.

Application. From the results above it was considered that the fixed-time method is the more suitable for the assay. It was, therefore,

applied to the determination of ascorbic acid in different concentrations and the results obtained were compared statistically with those obtained by the official B.P. method [22] (Table 8). The calculated Student's *t*-test values did not exceed the theoretical *t*-value at the 95% confidence limit, indicating that there was no significant difference between the mean values obtained by this method and those obtained by the official method.

The reaction rate measurements are specific and this is an advantage of the present method

Table 7

Calculated values of reciprocal of time in seconds measured at fixed absorbance for reaction rates of mixtures containing different concentrations of ascorbic acid and constant concentrations of cerium(IV) (2.034×10^{-3} M) and sulphuric acid (2.758×10^{-3} M) at 25°C

$1/t$ (s^{-1})	[ascorbic acid] ($\mu\text{g ml}^{-1}$)
0.07	498
0.018	427
0.013	356
0.005	285
0.003	213

Table 8

Statistical comparison of the results obtained by the fixed-time method (using the equation $A = 0.5695 - 0.0004178 C$) with the results obtained by the official B.P. method [22] for different concentrations of ascorbic acid

Concentration of ascorbic acid taken ($\mu\text{g m}^{-1}$)	% Recovery \pm standard deviation		<i>t</i> †
	Proposed method	Official method	
200	99.88 \pm 0.71	99.43 \pm 0.29	0.28
250	99.11 \pm 0.62	98.79 \pm 0.88	0.35
280	99.09 \pm 0.77	99.23 \pm 0.79	0.13
300	100.41 \pm 0.93	100.12 \pm 0.66	0.35
320	100.81 \pm 0.78	100.29 \pm 0.71	0.89
350	99.69 \pm 0.59	99.44 \pm 0.91	0.76
400	98.98 \pm 0.84	99.23 \pm 0.33	0.67
450	99.61 \pm 0.71	99.49 \pm 0.52	0.45
500	100.21 \pm 0.84	99.95 \pm 0.64	0.97

* Average of five determinations.

† Theoretical value 2.78 ($P = 0.05$).

over other methods. Moreover, this method is simple, and does not require tedious procedures or the use of catalytic agents or any of the indicators that are used in most of the other methods. It is also suitable for routine and trace analysis and in this respect is more favourable than the official B.P. method.

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