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Kinetic determination of manganese by its catalytic effect on the oxidation of Alizarin S by hydrogen peroxide

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Abstract

The manganese-catalysed oxidation of Alizarin S by hydrogen peroxide was monitored thermometrically in order to determine its rate graphically from a temperature–time curve. The rate of the reaction was found to be proportional to the Mn(II) concentration over the range 10–100 ng ml^{-1} The relative standard deviation for 50 ng ml^{-1} manganese was 4.0%. The method for determination of manganese thus developed is subject to few interferences, the most serious of which is posed by Ba(II), which is tolerated at an interferent-to-analyte ratio of 8·1. The proposed method was applied to the determination of manganese in brass, and performed with high accuracy and precision.

INTRODUCTION

Manganese(II) ion is known to be a catalyst for a number of oxidation reactions involving organic compounds. This has fostered the development of a number of methods – 18 in the last two years alone – for its determination on the basis of its catalytic action, most of which rely on spectrophotometric or fluorimetric detection because of the high sensitivity of these techniques. Such is the case with the stopped-flow injection photometric method reported by Kolotyrna et al. [1], which is based on the oxidation of *N,N'*-diethylaniline by KIO_4 and features a linear determination range between 0.01 and 1.0 ng ml^{-1}, and with various procedures based on the reaction between Malachite green and KIO_4 [2–8] and used for the determination of manganese in such samples as chemicals, water, bronze, foodstuffs, etc.

One of the research lines of our department is concerned with the development of new thermometric procedures for the determination of various species; some of the procedures surpass others based on commoner

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detection techniques by virtue of the higher selectivity arising from the absence of any interferences caused by coloured complexes or precipitates formed by foreign ions [9–11]. In addition, they require comparatively modest equipment for implementation. On the other hand, they involve longer start-up times because of the need for the temperature to stabilize before any measurements can be made and require the use of powerful enough solvents to obtain sufficiently high concentrations and hence measurable heats of reaction.

The method developed in this work is based on one previously reported by Janjic et al. [12] which allows the photometric determination of manganese over the concentration range 0.3–56.1 ng ml^{-1}. It relies on the catalytic effect of Mn(II) ion on the oxidation of Alizarin S by hydrogen peroxide in $(NH_4)_2CO_3$ medium. The method is subject to little interference.

EXPERIMENTAL

Apparatus

The set-up used to monitor temperature changes consisted of a rapid response thermometer-type thermistor with a nominal resistance of 100 kΩ (25°C), a Wheatstone bridge fed with 8.93 V from a stabilized source, and a recorder. The equipment was calibrated for maximum sensitivity (0.0055°C mV^{-1}) at the chosen working temperature (22°C), with full-scale deflection on the recorder of 20 mV (25 cm). This temperature monitoring system was set to be operated automatically under control of a PC-compatible microcomputer fitted with 640K RAM and an RS232C interface. Other elements making up the experimental assembly used included a Crison 2031 autoburette furnished with an RS232C interface, the volume and reagent addition speed of which were programmed via the computer, and DT2811-PGL data transducing, A/D converting board fitted in one of the computer expansion slots and featuring computer-programmable amplifications of 1, 10, 100 and 500 [11].

Reagents

A stock standard solution containing 1 mg ml^{-1} of Mn(II) was prepared from $MnCl_2$ (Titrisol Merck Art. 9988). This solution was diluted with distilled water and renewed daily in order to make working-standard solutions. A 1 M $(NH_4)_2CO_3$ buffer of pH 9.35 was used as reaction medium. A 1.01×10^{-2} M Alizarin S solution was prepared from its monosodium salt (Fluka Chemie AG). Finally, 0.6% H_2O_2 was made from a 30% solution that had been standardized tritrimetrically with $KMnO_4$.

All solutions were stored in the thermostated room (22 ± 1°C) where the experiments were carried out.

Procedure

A volume of 5 ml of 1.01×10^{-2} M Alizarin S, 10 ml of 1 M buffer of pH 9.35, an appropriate amount of the Mn(II) solution to obtain a final manganese concentration between 10 and 100 ng ml^{-1} and the volume of distilled water required to make up to 49 ml were placed in a 75-ml polystyrene cell. After the temperature had stabilized, 1 ml of 0.6% H_2O_2 was injected. The slope of the curve obtained by recording temperature changes was used to calculate the initial reaction rate (tan α). If the automated version of the procedure (the program THERKIN [13]) is used, the operator is prompted to select such settings as the maximum baseline slope, the reagent volume to be added, the minimum time between readings, experiment duration, etc. Once the requested values have been input, the experiment is started by opening the computer's communication channel according to a preset protocol and the burette is filled with the reagent to be added. After 10 experimental readings have been taken as 3 s intervals, the baseline slope is calculated. If this is smaller than the preset value, injection is effected. Otherwise, thermal stability has not been reached and a further experimental reading is made. The last 10 points are used to calculate a new baseline. The procedure is repeated until the baseline slope falls below the preset value. The maximum slope chosen was 1×10^{-5} mV s^{-1} (corresponding to 3.3×10^{-6}°C min^{-1} in our system), as the ideal zero value could not be reached at any time owing to small oscillations in the experimental readings arising from the apparatus background noise. In order to diminish such oscillations as far as possible, each point of the curve was obtained as the average of 10 experimental readings. This was feasible, even with very fast kinetics, thanks to the fact that each A/D conversion took only 30 μs and this did not distort the experimental curve. Once the system had reached thermal stability, the reagent was added, the internal clock was reset and the kinetic curve was experimentally recorded over the interval set by the analyst. In the event of small temperature differences between the solution in the cell and the external reagent to be injected, its injection caused the baseline to shift and required recalculation for reference in applying the kinetic methods of analysis.

Once data acquisition was finished, the equation of the best tangent to the thermometric curve (correlation coefficient $r \geqq 0.998$) was obtained for the interval set by the analyst by moving two graphical cursors. Optionally, data can be stored on disk, listed on screen or printed.

After the experimental kinetic curves are acquired, Option 2 on the main menu of THERKIN provides access to a data processing submenu

including such options as plotting up to eight files simultaneously and slope refitting or the quantitative determination of the analyte by one of the four classical kinetic methods of analysis, namely (a) tangent, (b) fixed-time, (c) fixed-temperature and (d) induction-period. Only the tangent method was used for the determination of manganese.

Procedure for the determination of manganese in brass

An amount of 0.5 g of brass sample was weighed accurately and transferred into a 200 ml beaker to which 25 ml of 1:3 HNO_3 was then added. The solution was boiled until the sample was completely dissolved and nitrogen oxide fumes were expelled, after which it was filtered if required and then diluted to a final volume of 250 ml.

The working solution was prepared by appropriate dilution with distilled water.

Because the sample matrix was found to interfere, the determination was carried out by the standard-addition method.

RESULTS AND DISCUSSION

Determination of the optimal pH

The optimal pH for the determination was found by keeping the concentrations of Alizarin S and manganese constant at 1.01×10^{-3} M and 50 ng ml^{-1}, respectively, within the cell. To each cell were added 10 ml of $(NH_4)_2CO_3$ buffer at a pH between 7.6 and 10.0, and distilled water to a final volume of 49 ml (final pH between 8.14 and 9.97). Once thermal equilibrium had been reached, 1 ml of 0.3% H_2O_2 was injected, which resulted in a 0.006% content in the cell.

As can be seen in Fig. 1, the rate of oxidation of Alizarin S (Ali S) decreased sharply below pH 9.2, which is consistent with the kinetic equation reported by Janjic et al. [12]

$$-dx/dt = K[\text{AliS}][Mn^{2+}][H_2O_2]^{-1}[H^+]^{1/2}[HCO_3^-]$$

insofar as CO_2 will be released at sufficiently low pH values, which will in turn bring about changes in the solution composition. Ammonium carbonate was found to be the optimal buffer because other potentially appropriate buffers of the same pH (e.g. Na_2HPO_4, $NaBO_2$,/HBO_2, NH_4Cl/NH_3, NH_4NO_3/NH_3, $NaHCO_3/Na_2CO_3$) do not favour the oxidation of Alizarin S (tan $\alpha = 0$).

The above findings led us to choose a 1 M $(NH_4)_2CO_3$ buffer to adjust the pH to 9.35.

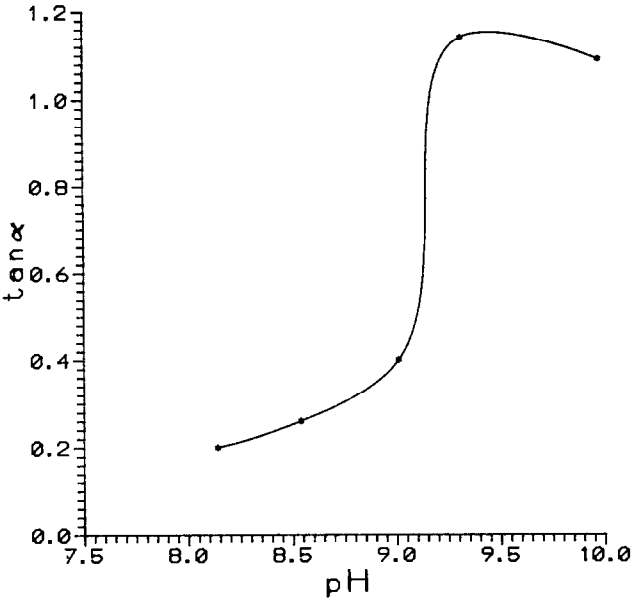

Fig. 1 Effect of pH on the initial rate of reaction: [Ali S] = 1.01×10^{-3} M; [H_2O_2] = 0.006%; [Mn(II)] = 50 ng ml^{-1}.

Determination of the optimal reactant concentrations

The influence of the concentration of Alizarin S on the reaction rate was investigated by varying it between 2.02×10^{-4} and 3.02×10^{-3} M while keeping that of Mn(II) and the pH constant at 50 ng ml^{-1} and 9.35, respectively. Once thermal equilibrium had been reached, 1 ml of 0.3% H_2O_2 was injected.

The optimal H_2O_2 concentration was determined at pH 9.35 and constant concentrations of Alizarin S and Mn(II) of 1.01×10^{-3} M and 50 ng ml^{-1}, respectively, and injecting 1 ml of hydrogen peroxide solutions with contents between 0.06 and 1.5%. Inasmuch as the oxidation of Alizarin S also takes place in the absence of Mn(II), albeit at a much lower rate, the slope of the kinetic curves of the blanks, which contained all reactants except Mn(II), were also determined.

Figures 2 and 3 show the variation of the slope as a function of the substrate and oxidant concentrations, respectively. The former shows a maximum corresponding to an Alizarin S concentration of ca. 4×10^{-4} M; however, the maximum is rather sharp, so small changes in the reactant concentration would have resulted in significantly altered thermometric curves. For this reason, later experiments were performed with an Alizarin S concentration of 1.01×10^{-3} M, which decreased the sensitivity by roughly one-half but resulted in better reproducibility. As far as the oxidant concentration is concerned (Fig. 3), the slopes of the thermometric curves

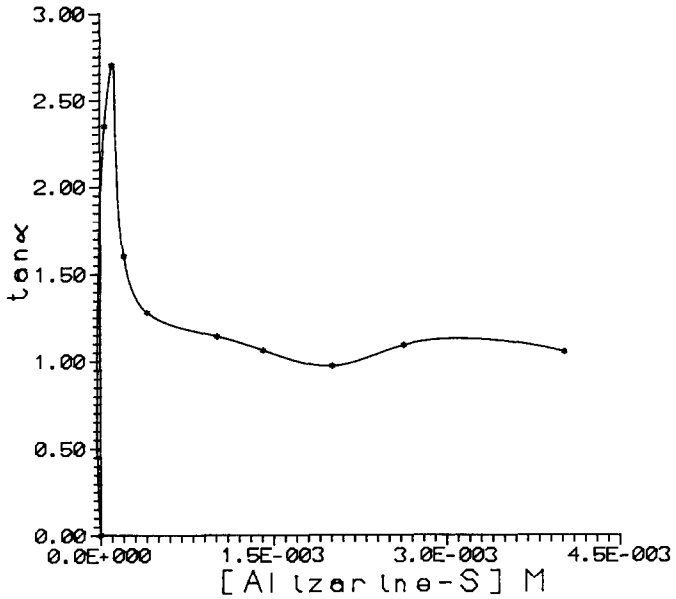

Fig. 2 Effect of the Alizarin S concentration on the initial rate of reaction. $[H_2O_2] = 0.006\%$; $[Mn(II)] = 50$ ng ml^{-1}, pH 9.35

increased with increasing concentration, both in the presence and in the absence of Mn(II) (blanks). An injection of 0.6% H_2O_2 was chosen as a compromise between good sensitivity and reasonably low blank values.

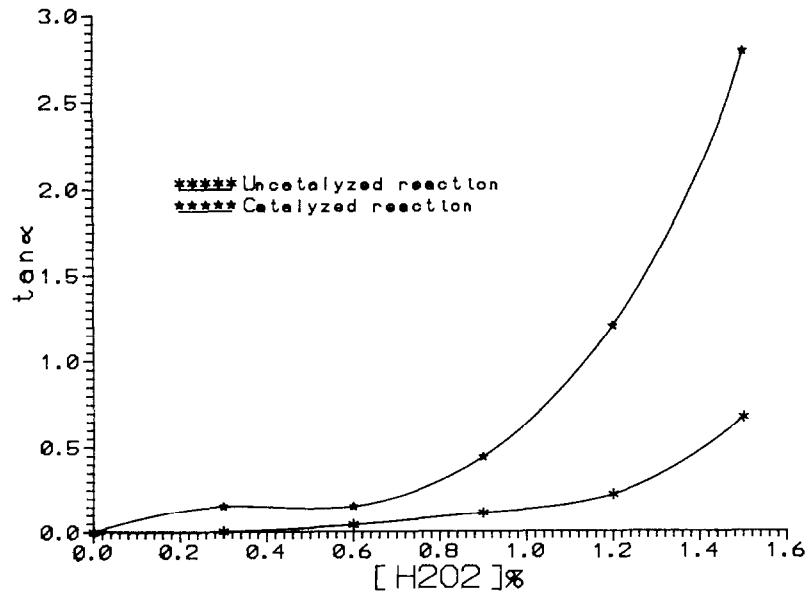

Fig. 3 Effect of the hydrogen peroxide concentration on the initial rate of reaction [Alizarin S] $= 1.01 \times 10^{-3}$ M, $[Mn(II)] = 50$ ng ml^{-1}, pH 9.35

Calibration graph and reproducibility

The calibration curve obtained was linear between 10 and 100 ng ml^{-1} of Mn(II) and conformed to the following equation

$$\tan \alpha = 0.241 + 0.0268\,[\mathrm{Mn(II)}] \quad (r = 0.997)$$

where the Mn(II) concentration is expressed in ng ml^{-1}.

The reproducibility of the proposed method under the optimal working conditions was determined on the basis of the relative standard deviation for a solution containing 50 ng ml^{-1} of Mn(II) (seven injections). The mean r.s.d. value obtained with manual chart recording was 4.0%.

Interferences

The effects of potential interferents were studied by using a series of solutions containing 25 ng ml^{-1} Mn(II) plus other ions at different concentrations and 1.01×10^{-3} M Alizarin S in an $(NH_4)_2CO_3$ buffer of pH 9.35. The solutions were added to the thermometric cell and made to 49 ml with distilled water, after which 1 ml of 0.6% H_2O_2 was added and the corresponding thermometric curve was recorded. The tolerated interferent-to-analyte ratios obtained (namely those resulting in $\pm 2\sigma$ of the tan α value) are listed in Table 1.

As can be seen, the proposed method is highly tolerant to the presence of other ions. In fact, the most serious interference was posed by Ba(II), which perturbed the determination of Mn(II) at a ratio of 8:1.

APPLICATIONS

The proposed method was applied to the determination of manganese in a brass (Reference 10e of the Bureau of Analyzed Samples) with the composition 61.1% Cu, 31.5% Zn, 0.15% Sn, 0.15% Pb, 1.38% Fe, 1.91% Mn, 0.11% Ni and 3.70% Al.

TABLE 1

Tolerated interferent-to-Mn(II) ratios

Foreign ion	Tolerated ratio
Mg^{2+}, Ag^{+}, Cd^{2+}, MoO_4^{2-}, Fe^{3+}, Cr^{3+}, Tl^{4+}, Pb^{2+}, Sn^{2+}, As^{3+}, NO_3^{-}, SO_4^{2-}, Cl^{-}, Na^{+}, K^{+}	400 1 [a]
Cu^{2+}, Al^{3+}, Zn^{2+}	80·1
Ni^{2+}, Co^{2+}, Ca^{2+}	40.1
Ba^{2+}	8:1

[a] Maximum assayed ratio

Conditions [Ali S] = 1.01×10^{-3} M, [H_2O_2] = 0.012%; [Mn(II)] = 25 ng ml^{-1}; pH 9.35 Maximum tolerated level, $\pm 2\sigma$.

The Mn content obtained by duplicate analysis ($1.92 \pm 0.3\%$) was quite consistent with the certified value.

CONCLUSIONS

The proposed method for the determination of Mn(II) traces is highly sensitive and selective, which allows application to real samples. In addition, it uses ordinary commercial reagents and inexpensive, handy instrumentation, which makes it a worthy alternative to methods based on other detection techniques.

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