Determination of Trace Manganese (II) by Its Catalytic De-colourizing Reaction On the Aerial Oxidation of 1.5-bis (2-hydroxy-5-chlorophenyl)-3-cyanoformazan and Its Kinetic Reaction Mechanism

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Abstract: A kinetic method is described for the determination of trace amounts of manganese (II) based on its catalytic effect on the aerial oxidation of 1.5-bis (2-hydroxy-5-chlorophenyl)-3-cyanoformazan.The reaction is followed spectrophotometrically by measuring the rate of change in absorbance at 580nm.The calibration curve (rate constant vs. manganese concentration) is linear in the range of 10~200ng in 25ml solutions. Kinetic parameters of the reaction are reported. There are few interferences.

Keyword: Catalytic-spectrophotometry, manganese, 1.5-bis (2-hydroxy-5-chlorophenyl)-3-cyano-formazan.

Introduction

Manganese (II) has well-known catalytic activity in oxidation reaction of organic compounds. Many procedures have been described to determine this ion by using its catalytic action.[1-8] All procedures described require an oxidizing agent (except two [7,8]) and an activator, and all require heating. Thus simple methods are needed for the determination of trace amounts of manganese (II) based on its catalytic effect.

1.5-bis (2-hydroxy-5-chlorophenyl)-3-cyanoformazan (HCPCF) is a reagent for determination of metal ions[9] based on equilibrium method. The authors found that traces of manganese (II) can catalyze the aerial oxidation of de-colourizing reaction of the reagent in alkaline medium, and the reaction can be stopped by the addition of inorganic acid. In this paper, a new catalytic spectrophotometric method for the determination of trace amounts of manganese (II) is presented based on this phenomenon. The proposed method offers the advantages of simplicity, sensitivity and without need for heating. Most ions do not exhibit this catalytic effect under the recommended conditions. The method was successfully applied to the determination of manganese in tobacco.

Experimental

Stock solution of Mn (II) (1.0 mg/ml) was prepared by dissolving manganese sulphate in hot dilute sulphuric acid and standardized by titration with EDTA. A 0.02% HCPCF solution was prepared by dissolving 50 mg of the compound in 250 ml of 95% alcohol. UNICO-2100 spectrophotometer with 1.0-cm cells was used.
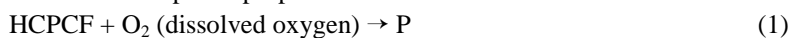
To a solution containing not more than 200 ng of Mn (II) in a 25 ml calibrated flask, add 4.0 ml of 0.1 mol/L sodium hydroxide solution, 2.0 ml of 5% Triton X-100 solution and 1.5 ml of 0.02% HCPCF solution and dilute to 25 ml with distilled water, mix well, and follow the reaction by recording the absorbance at 580 nm at various reaction times against water. Begin the measurements 5 min after preparation of the samples .Calculate the reaction rate from the slope of the absorbance-time curve.

Results and Discusion

The reagent HCPCF in alkaline medium gives a violet color, and the absorption spectrum shows maxima at 580 nm. The solution in acid medium turn red with λ_{max} at 488 nm.It is stable in acid media.

The aerial oxidation of the reagent in alkaline medium is very slow. In the presence of Mn (II), the oxidation rate is increased. Manganese (II) catalyzes the de-colouring oxidation, and the absorbance is inversely proportional to the manganese concentration. This reaction does not proceed in an inert atmosphere, and when other oxidants, *e.g.* persulphate, Ce (IV), periodate, *etc*., are used, the reagent is oxidized immediately, so that Mn (II) does not have a catalytic effect.

The mechanism of this catalytic reaction has not been elucidated completely.   The catalytic reaction probably involves the oxidation of manganese (II) to Mn (III) and/or Mn (IV) by dissolved oxygen in the alkaline medium. However, the main species of oxidized manganese seems to be Mn (IV) under the present experimental conditions. Thus the reaction steps are proposed as follows:

$$HCPCF + O_2 \text{ (dissolved oxygen)} \rightarrow P \qquad\qquad (1)$$
$$HCPCF + Mn \text{ (IV)} \rightarrow P + Mn \text{ (II)} \qquad\qquad (2)$$
$$Mn \text{ (II)} + O_2 \text{ (dissolved oxygen)} \rightarrow Mn \text{ (IV)} \qquad\qquad (3)$$

Reaction (2) is much faster than reaction (1). Mn (II) produced by reaction (2) is oxidized to Mn (IV) by reaction (3) and it accelerates the formation of P. The cycle can be stopped by the addition of sulphuric acid, probably because the Mn (III)/Mn (II) or Mn (IV)/Mn (II) redox potential is decreased. P is a colorless product, so the color of HCPCF can be decolorized completely by this catalytic reaction.

The oxidation of the reagent depends on the concentration of sodium hydroxide and manganese (II). In weakly alkaline medium the reaction rate was slowed down, the reaction proceeded faster with increasing pH, therefore dilute sodium hydroxide solution was used.

The influence of temperature on the de-colorizing reaction was examined in the range of 20~40°c. The reaction proceeded faster with increasing temperature. However, an increase in temperature and/or time also decreased the blank absorbance. For practical

purposes, 5 min and room temperature are selected for the reaction conditions.

The effect of the reagent concentration on the reaction rate was studied in the range of $1.35\times10^{-5}\sim1.08\times10^{-5}$ mol/L at a constant concentration of Mn (II). The rate of the catalytic reaction remained almost constant over the range of $4.10\times10^{-5}\sim8.10\times10^{-5}$ mol/L HCPCF. Thus a 5.40×10^{-5} mol/L HCPCF concentration (2.0 ml of 0.02% solution) was selected.

The effects of sodium hydroxide and Triton X-100 concentrations were examined. A final alkali concentration of 0.016 mol/L and surfactant concentration of 6.2×10^{-3} mol/L were chosen for the determination at 580 nm.

The absorbance-time curves for solution containing different amounts of manganese (II) were recorded against water. The tangent method was applied to the data in the absorbance-time curves, and the rate of the catalyzed reaction was plotted as a function of Mn (II) concentration. The calibration graph is linear in the concentration range of 0.4~8.0 ng/ml. The relative standard deviation for 4 ng/ml was 3.5% (n=11). The fixed time method was also applied. For this method, the fixed time 5min was selected. The relative standard deviation for 4 ng Mn/ml was 4.2% (n=11). In general, the tangent method is recommended.

To assess the selectivity of the method, the effect of several foreign ions on the determination of 4 ng Mn (II)/ml was examined by the proposed procedure. The tolerance limits for foreign ions are summarized in **Table 1** (a 5% error was considered to be tolerable). **Table 1** shows that 7.0 mg of pyrophosphate are tolerated, which can be used to mask Ca (II), Fe (III), Mg (II), and raise the limits to which they can be tolerated.

Application

The present method was applied to the determination of trace manganese in tobacco. Weigh 50~100mg powdered sample in a dried crucible. Prepare the sample solution as described previously[10], transfer 1.0~2.0 ml of the resultant solution in to a 25 ml calibrated flask, add 1.0 ml of 0.5% pyrophosphate solution and follow the general procedure for the determination of manganese. The results are summarized in **Table 2.**

Table 1 Tolerance limits for foreign ions on the kinetic determination of 4.0ng Mn (II)/ml by the tangent method

Foreign ions	Tolerance limit [Ion/Mn (II)]	Foreign ions	Tolerance limit [Ion/Mn (II)]
K (I)	200000	Zn (II)	350
Na (I)	200000	Cu (II)	100
Ba (II)	5000	Cr (III)	400
PO_4^{3-}	85000	Ce (IV)	15
Ni (II)	120	Mo (VI)	400
W (VI)	600	Bi (III)	800
La (III)	120	Cl^-	4000
V (V)	50	EDTA	30000
CH_3COO^-	15000	citrate	10000
Mg (II)	1500	Co (II)	60
tartrate	15000	pyrophosphate	70000

Fe (III)	80		Ca (II)	200	

Table 2. Analytical results of samples

Sample	Sample taken (ml)	Found (ng) (n=5)	RSD (%)	Added (ng)	Total found (ng)	Recovery (%)
Tobacco from Anhui	1.5	64	6.3	100	158	94
Tobacco from Yunnan	1.0	71	5.8	100	169	97

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