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KINETIC THERMOMETRIC DETERMINATION OF TRACES OF MANGANESE BY ITS CATALYTIC EFFECT ON THE REACTION BETWEEN TIRON AND HYDROGEN PEROXIDE

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We have developed a highly sensitive kinetic thermometric method for the determination of traces of Mn(II) by its catalytic effect on the oxidation of Tiron by hydrogen peroxide. The reaction is monitored by the initial-rate method, which is applied to temperature-time curves. Under the optimum conditions established in preliminary experiments, manganese can determined over the range 1-120 ng/mL, with an rsd of 5.8% and 1.3% for 5 ng/mL and 40 ng/mL Mn(II), respectively. The proposed method is subjected to few interferences, the most serious of which is posed by Pb(II), with a tolerated ratio of 20:1. The method was satisfactorily applied to the determination of Mn(II) in various types of sample (water, beer and wine).

Kinetic catalytic methods have been widely used in the last few decades for the determination of various metals at the trace level on account of their high sensitivity. A number of studies [1-3] on the different techniques with which these methods have been applied have been reported, as have periodical reviews [4].

Among the different methods proposed for the determination of manganese in different types of sample based on the catalytic action of the Mn(II) ion on the oxidation of various organic compounds, fluorimetric and spectrophotometric are worth special emphasis on account of their high sensitivity–normally higher than that of their conventional counterparts. In this context, Rubio *et al.* [5] developed a sensitive [0.2-3.0 ng/mL Mn(II)] fluorimetric method based on the oxidation of pyridoxal 2-pyridylhydrazone by hydrogen peroxide. Spectrophotometric methods usually afford even lower detection limits; such is the case with the method reported by Grases *et al.* [6], which relies on the autoxidation of succinimidedioxime and allows

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manganese to be determined over the range 0.2-12 ng/mL. The reaction between hydroxynaphthol blue and hydrogen peroxide has also been applied to the determination of Mn(II) [7], with a determination range of 0.01-10 ng/mL. Otto *et al.* studied the metal-catalyzed reaction between Tiron and hydrogen peroxide [8], which they later optimized by the simplex and the surface-response method to the determination of cobalt and manganese traces [9]. By using 1,10-phenanthroline as activator, they succeeded in determining Mn(II) over the range $2\cdot10^{-8}$-$6\cdot10^{-7}$ M.

In addition to their well-known simplicity, thermometric methods have the advantage that determinations can be carried out in a direct fashion and are not interfered by the sample colour or turbidity, so they are normally more selective and at least as sensitive as the above techniques.

On the basis of the oxidation reaction described elsewhere [9], we developed a thermometric method for manganese that features similar sensitivity and a wider determination range and is subject to rather few interferences which are less serious than those of the conventional spectrophotometric procedure in any case.

Experimental

Apparatus

The thermometric set-up used was described in detail elsewhere [10]. Basically, it consists of an adiabatic cell, a 100-kohm thermistor (25°), a Wheatstone bridge, a helical stirrer actuated by a synchronous motor, a stabilized power supply and an x-t recorder.

Reagents

- 0.1 *M* Tiron (3,5-pyrocatecholdisulphonic acid disodium salt), prepared from its monohydrated salt (Merck).
- 0.05 *M* 1,10-phenanthroline, prepared from its hydrochloride (BDH Chemicals Ltd).
- 0.1 *M* borax buffer of pH 10.5, prepared from sodium tetraborate decahydrate (Merck) and adjusted with NaOH.
- 1000 mg/L Mn(II) standard made from $MnSO_4\cdot H_2O$.
- 4.5 *M* hydrogen peroxide, prepared from a 30% solution standardized with $KMnO_4$.

All reagents used were PA grade, and distilled water was used throughout.

Procedure

In a thermometric cell place (37– x) mL of distilled water, 10 mL of the borax buffer of pH 10.5, 1 mL of 0.1 *M* Tiron, 1 mL of 0.05 *M* 1,10-phenanthroline and x mL of sample, in this order, so as to obtain a final Mn(II) concentration between 1 and 120 ng/mL. Once thermal equilibrium has been reached, inject 1 mL of 4.5 *M* hydrogen peroxide into the cell and record the pertinent thermometric curve.

Results and discussions

Optimization of experimental variables

The influence of the different variables influencing the reaction was studied in order to determine the most suitable conditions for achieving the highest sensitivity and widest determination range possible.

Figure 1 reflects the influence of the pH on the reaction between Tiron and hydrogen peroxide. The curve was obtained by plotting the values yielded by 0.1 *M* borax buffers whose pH was adjusted with HCl or NaOH as required. Other buffers (phosphate, ammonia/ammonium) inhibited the catalytic effect of manganese, which was probably masked in these media. The reaction was also studied by adjusting the pH with NaOH only, which resulted in a substantial decrease in the catalytic effect of the metal ion. This clearly reveals the activating effect of the tetraborate ion.

As can be seen in Fig. 1, the slope of the thermometric curve increases sharply above pH 9, and reaches a maximum at 10.5. More basic buffers resulted in decreasing reaction rates with increasing pH values.

Figure 2 shows the effect of the 1,10-phenanthroline concentration on the reaction kinetics. The maximum slope of the curve lies between $0.8\cdot10^{-3}$ and $1.2\cdot10^{-3}$ *M*, so we chose 10^{-3} *M* as the optimum working concentration.

Figure 3 reflects the influence of the Tiron concentration. As can be seen, the slope of the curve remains constant above $2\cdot10^{-3}$ *M*, which was thus chosen as the working concentration.

As can be seen in Fig. 4, the hydrogen peroxide concentration had virtually no effect on the reaction rate between 0.09 and 0.18 *M*. We chose the former concentration as optimum in order to avoid the occurrence of dilution heats.

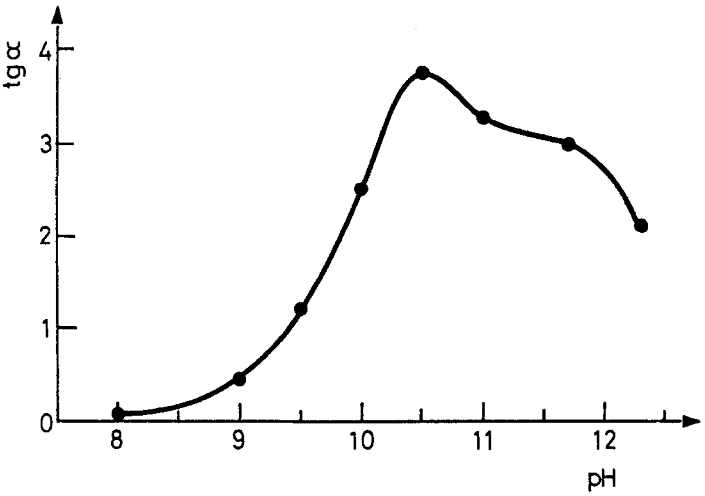

Fig. 1 Influence of the pH on the reaction rate. [Mn(II)] = 10 ng/mL; [Tiron] = $2 \cdot 10^{-3}$ M; [1,10-phen] = $4 \cdot 10^{-4}$ M; [H_2O_2] = 0.09 M

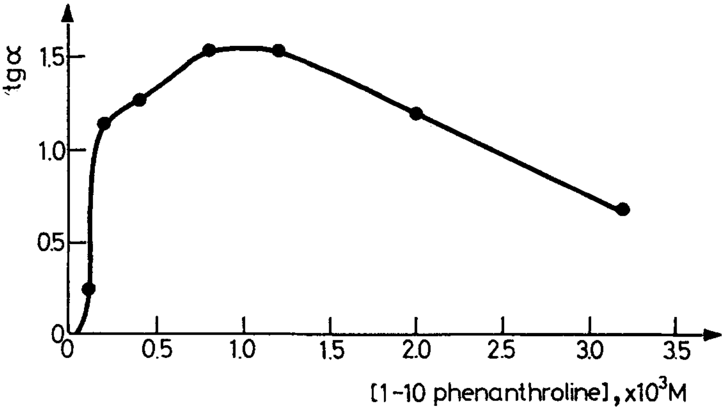

Fig. 2 Influence of the 1,10-phenanthroline concentration on the reaction rate. [Mn(II)] = 5 ng/mL; [Tiron] = $2 \cdot 10^{-3}$ M; [H_2O_2] = 0.09 M; pH 10.5

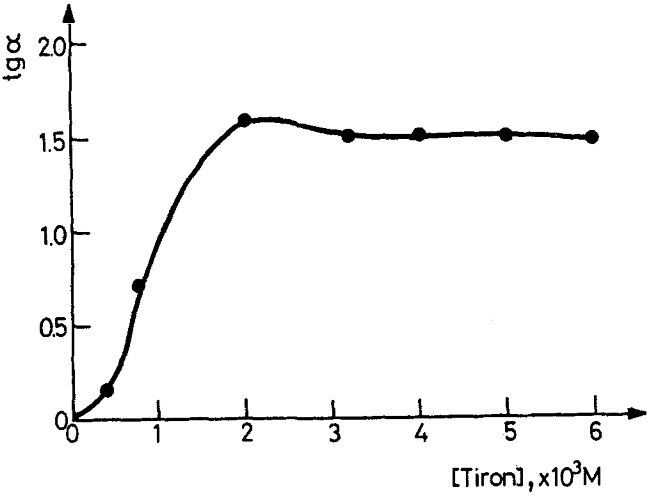

Fig. 3 Influence of the Tiron concentration on the reaction rate. [Mn(II)] = 5 ng/mL; [1,10-phen] = 0.001 M; [H_2O_2] = 0.09 M; pH 10.5

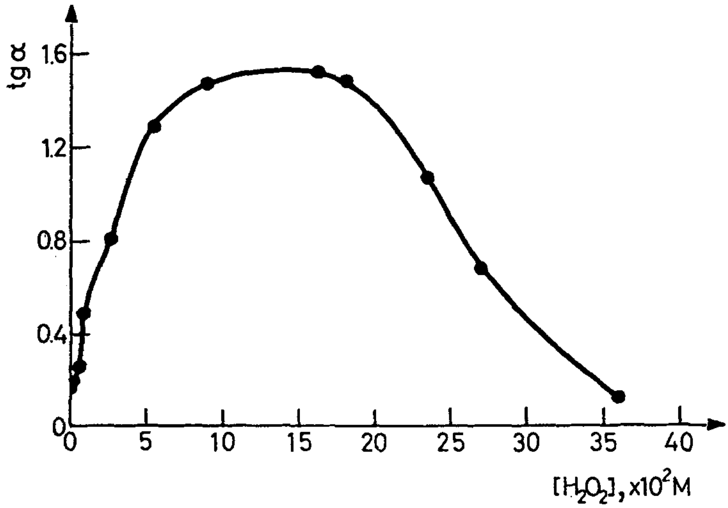

Fig. 4 Influence of the hydrogen peroxide concentration on the reaction rate. [Mn(II)] = 5 ng/mL; [Tiron] = $2\cdot10^{-3}$ M; [1,10-phen] = 0.001 M; pH 10.5

Calibration curve

Under the above-described optimum reaction conditions we ran a calibration curve in order to determine the application range of the proposed method, which was found to be 1-120 ng/mL, depending on the recorder sensitivity (Table 1). The rsd was 5.8% and 1.3% for 5 ng/mL (n = 8) and 40 ng/mL (n = 8) Mn(II) respectively.

Table 1 Applicability range of the proposed method

S, mV	Equation	r	Range, ng/mL
10	$\tan\alpha = -0.311 + 0.402[\text{Mn(II)}]$	0.9996	1- 10
50	$\tan\alpha = 0.009 + 0.027[\text{Mn(II)}]$	0.9996	5-120

Effect of foreign ions

We investigated the potential interference of a series of ions on the kinetic determination of 5 ng/mL of Mn(II). The tolerated limits found ($\pm 2\sigma$ the $\tan\alpha$ value) are listed in Table 2. The most serious interference was posed by Pb(II) and Fe(II), which were tolerated in ratios of 20:1 and 40:1, respectively. These interferences could not be avoided with any of the masking agents assayed, namely EDTA, NTA, acetate, citrate, oxalate, tartrate, fluoride and thiosulphate, the first two of which even masked Mn(II) itself. However, these interference levels should pose no problem in the analysis for Mn(II) in water and other beverages as they amply exceed the typical concentration rations found in most cases.

Table 2 Effect of foreign ions on the determination of 5 ng/mL of Mn(II)

Foreign ion	Tolerated [Ion]/[Mn(II)]ratio
Chloride, nitrate, sulphate, carbonate, phosphate, sodium(I), potassium(I), ammonium, calcium(II), barium(II)	10 000*
Nickel(II), copper(II)	2 000
Cadmium(II), aluminium(III), chorium(III)	1 000
Cobalt(II), zinc(II), magnesium(II), iron(III)	400
Iron(II)	40
Lead(II)	20

*Maximum assayed ratio

Applications

The proposed kinetic catalytic method was applied to the determination of Mn(II) in various types of sample by using the standard-addition technique.

Table 3 lists the analyte volumes used and the results obtained, both by the proposed thermometric method and by the graphite-chamber atomic absorption spectrometric procedure used for reference.

Table 3 Application of the proposed method to various types of sample

Sample	V_{sample}, mL	[Mn(II)], mg/L	
		Thermometry	GC-AAS
Tap water	25	$3.7\cdot10^{-3}$	$4.0\cdot10^{-3}$
Waste water	35	$1.4\cdot10^{-3}$	$1.0\cdot10^{-3}$
Beer (Lager)	1	0.16	0.10
Red wine (Majorca)	1	0.37	0.45
Rosé Wine (Rioja)	0.5	0.68	0.67
White wine (Navarra)	0.5	0.60	0.54

All determinations were performed in a direct fashion, thereby avoiding the mineralization processes usually required by spectrophotometric techniques and the solvent extraction steps included in flame atomic absorption methods.

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Zusammenfassung — Es wurde eine hochempfindliche kinetische thermometrische Methode zur Bestimmung von Spuren an Mn(II) anhand dessen katalytischen Effektes auf die Oxidation von Tiron mit Wasserstoffperoxid entwickelt. Der Verlauf der Reaktion wurde über die Anfangsgeschwindigkeiten bei den Temperatur-Zeit-Kurven verfolgt. Unter in Vorexperimenten ermittelten optimalen Bedingungen kann Mangan im Bereich 1-120 ng/ml mit einer relativen Standardabweichnung von 5.8% bzw. 1.3% für 5 ng/ml bzw. 40 ng/ml Mn(II) bestimmt werden. Das Verfahren wird von einigen Kreuzwirkungen beeinflußt, von denen die intensivste der Einfluß von Pb(II) mit einem zulässigen Verhältnis von 20:1 ist. Diese Technik konnte zur Bestimmung von Mn(II) in den verschiedenartigsten Proben (Wasser, Bier, Wein) zufriedenstellend angewendet werden.