



DETERMINATION OF NANOGRAMME Mn(II) AMOUNTS BY CATALYTIC OXIDATION OF CARMINE ACID WITH H₂O₂ IN THE PRESENCE OF ACTIVATORS

Todor G. Pecev
Rangel P. Igov
Sofija M. Rančić

Faculty of Science, Department of Chemistry, Ćirila i Metodija 2, 18000 Niš

Abstract: In one of previous works[1], the new catalytic reaction was suggested and the new kinetic method was prepared for ultra-micro amounts of Mn(II) ions on the carmine acid oxidation by hydrogen-peroxide in ammonium-buffer. Under the optimal initial conditions sensitivity of $1 \cdot 10^{-8}$ g/cm³ Mn(II) in the solution was reached.

In this labour, effect of electron-acceptor ligands: 1.10-phenantroline and 2.2'-dipyridile, was studied. Their effect on the indicatory reaction rate and the sensitivity of Mn(II) determination, was investigated. On the basis of the indicatory reaction kinetic examinations, the mechanism of activatory effect of phenantroline and dipyridile, was suggested.

In the presence of phenantroline, sensitivity of 5-10-10 g/cm³ was reached, while in the presence of dipyridile, it was 1-10-10 g/cm³ Mn(II). That means that indicatory reaction sensitivity in the presence of activators, was about 100 times greater than without them. Kinetic results were worked out by tangent method [2].

1. Introduction

There are few indicatory reactions for Mn(II) kinetic determination in pure solution, as well as, in the samples of natural or synthetic origin [3+9]. But, there is a small number of homogenous-catalytic indicatory reactions in the presence of activators, which are used for development of new kinetic methods for Mn(II) traces determination [10]. Dependence between the indicatory reaction rate ($tg\alpha$) and the concentration of activator (A), could give the precious information about activating mechanism, and also about the character of the limiting stadium of reaction.

So, in this work, the kinetic of carmine acid oxidation by H₂O₂, in the presence of Mn(II) as a catalyst and phenantroline and dipyridile as activators, was examined. Reaction rate was followed photometrically, the optimal conditions were found, and the maximal sensitivity of Mn(II) determination was reached. Results were statistically treated and the calibration curves were constructed by smallest squares method.

2. Experimental

Measurement of absorbtion (A) as a function of reaction time (t) was performed on Lange's photoelectric colourimeter, model J, with annexed thermostating system, with thickness of absorbtion layer of 25 mm, and with filter of $\lambda_{max} = 555$ nm. pH measurements were arranged by pH-meter 29, Radiometer. Solutions were thermostated in thermostate "Sutjeska" with water covering. Solutions in working kvete of colourimeter were thermostated by universale thermostate, type U 10. Absorbtion curves of indicatory substances were snapshotted on spectrophotometer "Specord UV-VIS", "Karl Zeiss", Jena. Specific

conductivity of redistilled water, which was used for all solutions preparing, was controlled on conductometer, model MA 5960 IEV. Solid substances were measured on analytical scales "Mettler", type B5. Redistilled water was prepared by distilling of distilled water on adequate glass apparatus for distillation. Reaction time was followed by chronometer. All solutions were prepared of p.a. substances, product of "Merck".

In the standard vessel of 50 cm³, adequate volumes of solutions were pipetted by this sequence: carmine acid (CA), ammon-buffer, activator (phenantroline, dypiridile), and Mn(II) ions solution. Mixture was diluted by thermostated redistilled water always to the same volume. Then the hydrogen-peroxide solution was added and the chronometer was started. The volume was then filled to 50 cm³ by redistilled water and well mixed. The solution was poured in the working kyvete and changes of absorbtion in the function of time, were measured each 30 seconds during 10 minutes of reaction.

So, insted the magnitude dc/dt , the magnitude $d(\log A)/dt$, as a proportional one, was measured, and it was equal to the reaction rate $tg\alpha$:

$$k \cdot (dc/dt) = d(\log A)/dt = tg\alpha, \quad (1)$$

where is: c - concentration of the indicatory substance (CA),

k - constant proportionality and

α - angle between the cinetic curve and abscisa in coordinates $\log A - t$.

Optimal conditions for kinetic determination of ultra-micro Mn(II) concentrations in solution, were determined by following the rate of reaction as a function of concentration change of one of the reactans, while the concentrations of the other reactants were constant.

3. Results and discussion

All dependences were received from the ratio: $tg\alpha = f(c)$. As it could be seen from Fig. 1, noncatalytic reaction rate ($tg\alpha$) is in linear dependence on the concentration of activator (curve 1), while catalytic reaction rate (curve 2) shows nonlinear flow with maximu on the phenantroline concentration of $15 \cdot 10^{-5}$ mol/dm³. So that concentration of phenantroline was used in following work.

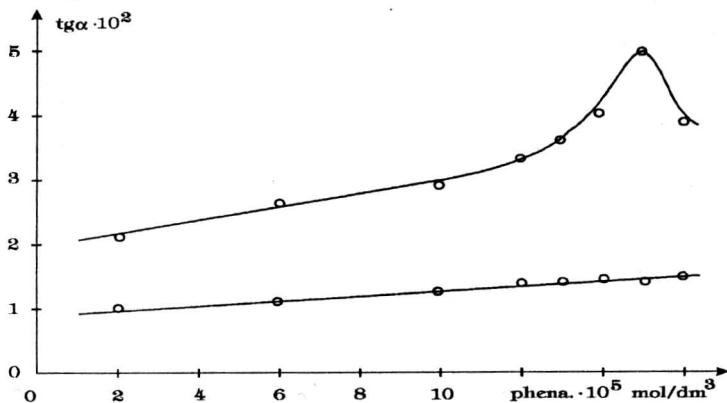


Figure 1: Dependence of $tg\alpha$ on the 1.10-phenantroline concentration for noncatalytic (curve 1) and catalytic (curve 2) reaction. Initial conditions: CA - $4 \cdot 10^{-5}$ mol/dm³; H₂O₂ - $4.8 \cdot 10^{-2}$ mol/dm³; Mn(II) - $4 \cdot 10^{-9}$ g/cm³; pH - 9.75; NH₄⁺/NH₃ buffer - $1.2 \cdot 10^{-1}$ mol/dm³; T = 296K.

Catalytic reactions activation is, in the majority of cases, connected with processes of activator complexing with catalyst or substrate (indicatory substance), no matter of activating mechanism. Building of complex catalyst-activator could make the process faster only if in

coordinative sphere of catalyst exist enough free places. That means places which could be occupied with molecules of solvent or with the other labile connected ligands which could be fast enough substituted with substrate molecules or with intermediate molecules which react with catalyst during the process.

So, if, under the reaction conditions, activator (A) build stable complexes with catalyst (M) and exists in system in great concentration, it could lead to forming the coordinative saturated complexes MA_n , and to the reaction rate diminution. Because of that, $\lg v$ dependence on the activator concentration in the similar cases passes through maximum. How much would the reaction rate be reduced during the blocking the coordinative sphere of catalyst by activator, depends of nature of formed complexes (labile or inert), what means in what measure the substitute reaction with substrate (S), is possible:

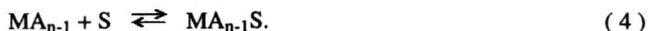


If the reaction (2) rate is less than the reaction rate between M and S, total fusion of M in the complex MA_n could lead to complete inhibition of catalytic reaction. But, if reaction (2) flows by measurable rate which is smaller than the reaction rate between M and S, it doesn't come to the complete inhibition of reaction. Under those conditions, summary catalytic reaction rate is, in fact, rate of reaction (2).

If the reaction (2) flows under the S_N1 mechanism, after complete connecting of catalyst in the nonactive complex MA_n , the diminution of the reaction rate could also be expected (maybe even very slowly) in the same time with the activator concentration growing. In this case, the limiting stadium of the reaction rate is the dissociation of complex MA_n , what isn't case in this work.



When the activator is not in excess, the reaction (2) rate doesn't depend on substrate concentration, because the reaction (4):



goes on much faster than complex dissociation according the reaction (3).

But, if activator is present in excess, the competition exists between the activator and substrate about the free place in the coordinative sphere of catalyst. Possibility for their coordination with catalyst, when the other conditions are the same, depends of their concentration in reacting system. So, with activator concentration growing, catalytic activity gradually declines, what is not case in this work. This diminution of catalytic activity is proportional to the molar share of activator (N_A) in system:

$$N_A = n_A / (n_A + n_S + n_{Solv}), \quad (5)$$

where n_A , n_S and n_{Solv} represent the moles of activator, substrate and solvent.

If the substitution of solvent in complex $M(Solv)_n$ with A or S, goes on very fast, n_{Solv} in the expression (5) could be neglected, and the catalytic activity will depend of ratio:

$$N_A = n_A / (n_A + n_S). \quad (6)$$

When the activator concentration highly increases, then $n_A \gg n_S$, and catalytic reaction rate doesn't depend on activator concentration. Under those conditions, total catalytic reaction rate reaches some limiting value under such activator concentration, that catalyst is completely connected in MA_n complex and then there are no changes with activator concentration increasing. Fig. 1 shows that when $c(A) > 4 \cdot c(S)$, catalytic reaction rate highly decreases, and it is supposed that activating mechanism flows according the reaction (2) which is, in fact, limiting stadium of reaction.

Fig. 2 shows the calibration curve which is used for unknown Mn(II) concentration determination in solution in the range from $5 \cdot 10^{-10}$ to $6 \cdot 10^{-9}$ g/cm³, or $9 \cdot 10^{-9}$ to $1 \cdot 10^{-8}$ mol/dm³.

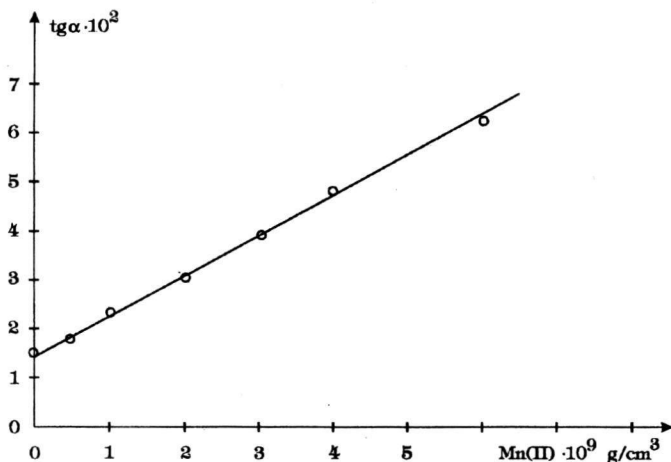


Figure 2: Dependence of $\text{tg}\alpha$ on the Mn(II) concentration in presence of activator 1.10-phenantroline. Initial conditions: CA - $4 \cdot 10^{-5}$ mol/dm³; pH - 9.75; H₂O₂ - $4.8 \cdot 10^{-2}$ mol/dm³; NH₄⁺/NH₃ buffer - $1.2 \cdot 10^{-1}$ mol/dm³; T = 296 K; phenantroline - $15 \cdot 10^{-5}$ mol/dm³;

Analytical expression of the calibration curve, got by smallest squares method, is:

$$\text{tg}\alpha = 8.48 \cdot c_{\text{Mn(II)}} + 0.0132, \quad (7)$$

where $c_{\text{Mn(II)}}$ is concentration of catalyst in $\mu\text{g}/\text{cm}^3$.

Results are statistically treated, and accuracy and precision of method are shown in Table I.

Table I: Accuracy and precision of Mn(II) determination in the presence of activator 1.10-phenantroline

Measured Mn(II) · 10 ⁹ g/cm ³	Found (x_{sr}) Mn(II) · 10 ⁹ g/cm ³	n	S · 10 ¹⁰	W, %	E _r , %
0.50	0.48	5	0.32	6.0	4.0
2.00	1.97	5	0.62	3.0	1.5
4.00	4.06	5	0.69	1.7	1.5

As it could be seen, under the statistics security of 95 %, exact value of manganese concentration is placed in interval from $(0.48 + 0.032) \cdot 10^{-9}$ to $(0.48 - 0.032) \cdot 10^{-9}$ g/cm³ for the smallest concentration, and from $(4.06 + 0.069) \cdot 10^{-9}$ to $(4.06 - 0.069) \cdot 10^{-9}$ g/cm³ for the greatest concentration. Relative error of Mn(II) determination by this method is from 4 to 1.5 %.

Kinetic investigation of catalytical and noncatalytical reaction as function of 2.2'-dipyridile concentration, is shown in Fig. 3. It could be seen that $\text{tg}\alpha$ of noncatalytical

reaction (curve 1) depends very little of dypyridile concentration. In the same time, $\text{tg}\alpha$ of catalytic reaction increases a great deal with dypyridile concentration increasing (curve 2), what means that dypyridile shows activating effect on catalytic reaction. In following work, dypyridile concentration of $9 \cdot 10^{-3} \text{ mol/dm}^3$ was used.

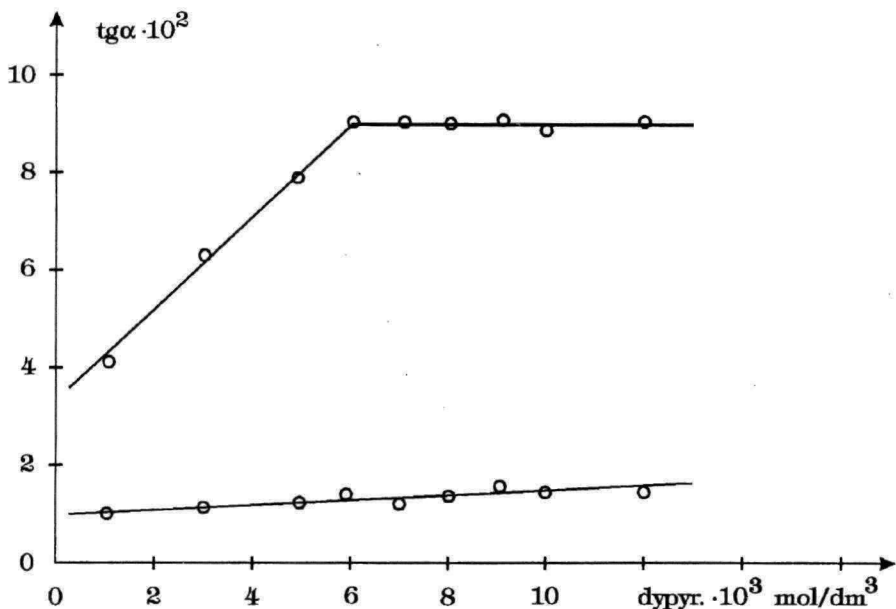


Figure 3: Dependence of $\text{tg}\alpha$ on the 2,2-dypyridile concentration for noncatalytic (curve 1) and catalytic (curve 2) reaction. Initial conditions: CA - $4 \cdot 10^{-5} \text{ mol/dm}^3$; H_2O_2 - $4.8 \cdot 10^{-2} \text{ mol/dm}^3$; Mn(II) - $4 \cdot 10^{-9} \text{ g/cm}^3$; pH - 9.75; $\text{NH}_4^+/\text{NH}_3$ buffer - $1.2 \cdot 10^{-1} \text{ mol/dm}^3$; T = 296 K.

Appearance of maximum, when dependence of reaction rate on activator concentration is investigated, is not the obligate condition for all activated catalytic reactions [11]. So, in the cases when activator accelerates reaction because displacing of some balancing process with catalyst including, different type of dependence would be expected. In the balance displacement in the limiting stadium of reaction comes from connecting of M (catalyst) in complex with A (activator):



it should be expected that reaction rate would be proportional to the MA complex concentration. From expression for MA complex constant of stability, [MA] would be:

$$[\text{MA}] = \beta \cdot [\text{M}] \cdot [\text{A}] \quad (9)$$

Total catalyst concentration (c_M) in the system, would be:

$$c_M = [\text{MA}] + [\text{M}] \quad (10)$$

By combination expressions (9) and (10), we have:

$$[\text{MA}]/(c_M - [\text{MA}]) = \beta \cdot [\text{A}] \quad (11)$$

It could be easily transformed to:

$$[MA] = \beta \cdot c_M \cdot [A] / (1 + \beta \cdot [A]). \quad (12)$$

For very low activator concentrations, when $\beta \cdot [A] \ll 1$, expression (12) has a form:

$$[MA] = \beta \cdot c_M \cdot [A]. \quad (13)$$

Now, it could be expected that in this concentration area, increasing of $[A]$, increases $[MA]$, and so the total catalytic reaction rate increases, too. If $[A]$ continues to increase, $[MA]$ concentration increases very slowly. Under the very high activator concentrations, when $\beta \cdot [A] \gg 1$, expression (12) gets to form:

$$[MA] = c_M. \quad (14)$$

This means that catalyst is completely complexed with activator. Increasing of activator concentration above this frontier, doesn't change the catalytic activity. On this way, the mechanism of activating effect of 2,2'-dipyridile is explained (Fig. 3, curve 2). So, limiting stadium of reaction of CA oxidation with H_2O_2 , catalyzed by Mn(II) ions and in the presence of 2,2'-dipyridile as activator, is in fact, reaction (8). Effect of activator on the catalytic reaction rate, would appear under the lower concentrations, and catalytic activity will reach the saturation as faster as the MA complex constant of stability is greater.

Figure 4, shows the calibration curve which could be applied for Mn(II) concentration determination in the range from $1 \cdot 10^{-10}$ to $10 \cdot 10^{-10}$ g/cm³, or $1.8 \cdot 10^{-9}$ to $1.8 \cdot 10^{-8}$ mol/dm³. Its analytical expression, received by the smallest squares method, is:

$$\text{tg} \alpha = 21.45 \cdot c_{\text{Mn(II)}} + 0.0229. \quad (15)$$

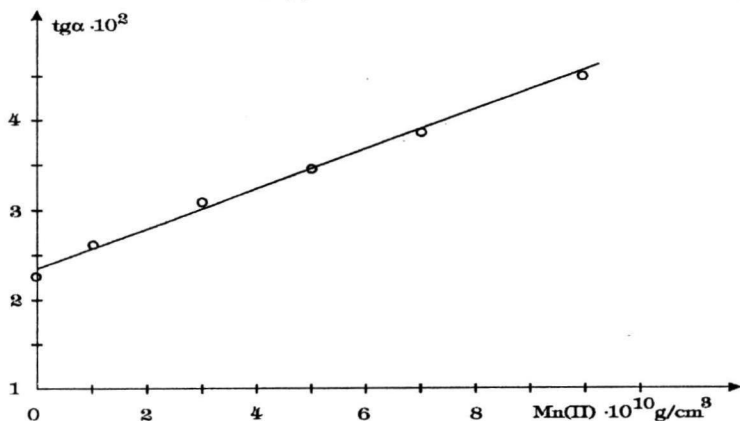


Figure 4: Dependence of $\text{tg} \alpha$ on the Mn(II) concentration in presence of activator 2,2'-dipyridile. Initial conditions: CA - $4 \cdot 10^{-5}$ mol/dm³; pH - 9.75; H_2O_2 - $4.8 \cdot 10^{-2}$ mol/dm³; NH_4^+/NH_3 buffer - $1.2 \cdot 10^{-1}$ mol/dm³; T = 296 K; dipyridile - $9 \cdot 10^{-3}$ mol/dm³;

Accuracy and precision of elaborated kinetic method for Mn(II) determination in solution are received by statistical treatment of results, and are shown in Table II.

Table II: Accuracy and precision of Mn(II) determination in the presence of activator 2.2'-dipyridile

Measured Mn(II)·10 ¹⁰ g/cm ³	Found (\bar{x}_{sr}) Mn(II)·10 ¹⁰ g/cm ³	n	S· 10 ¹¹	W, %	E _r , %
1.00	1.13	5	2.20	19.0	13.0
5.00	5.02	5	0.97	2.0	0.4
10.00	9.98	5	0.86	0.9	0.2

Under statistics security of 95 %, exact value of Mn(II) concentration is in the range from $(1.13 + 0.22) \cdot 10^{-10}$ to $(1.13 - 0.22) \cdot 10^{-10}$ g/cm³ for the lowest concentration, and in the range from $(5.02 + 0.097) \cdot 10^{-10}$ to $(5.02 - 0.097) \cdot 10^{-10}$ g/cm³ for the mean concentration. Mean relative error of manganese determination by this method is from 13 to 0.2 % for investigated interval of concentrations.

4. Conclusions

The new indicatory reaction was suggested and the new kinetic method was elaborated for Mn(II) ultra-micro amounts determination in solution, by applying 1.10-phenantroline and 2.2'-dipyridile as activators. On the basis of experimentally received dependences, a mechanism of activating effect of those activators on the catalytic process, was supposed. Reached sensitivity in the presence of 1.10-phenantroline is $5 \cdot 10^{-10}$ g/cm³ Mn(II), and in the presence of 2.2'-dipyridile - $1 \cdot 10^{-10}$ g/cm³ Mn(II). The determined accuracy of elaborated method, in the presence of phenantroline, is from 4 to 1.5 % for concentration interval of Mn(II) from $5 \cdot 10^{-10}$ to $4 \cdot 10^{-9}$ g/cm³, while, for the manganese interval concentration from $1 \cdot 10^{-10}$ to $10 \cdot 10^{-10}$ g/cm³ in the presence of dipyridile, error amounts from 13 to 0.2 %.

References

- [1] Igov R., Pecev T., Miletić G., Abstract of papers, 3rd. Yugoslav symposium on analytical chemistry, Novi Sad, (1982), p. VI-4, (in Serbian).
- [2] Yacimirski K.B., Kinetic method of analyse, Himia, Moskva, (1967), (in Russian).
- [3] Tiginjanu D.J., Oprja J.V., Journal of anal. chem, 28, (1973), 2206, (in Russian).
- [4] Nikolelis D.P., Hadjiioannou T.P., Anal. Chim. Acta, 97, (1978), 111, (in English).
- [5] Sičev A.J., Isak V.G., Pfainmeller U., Jour. of anal. shem., 33, (1978), 1351, (in Russian).
- [6] Sekheta M.A., Milovanović G.A., i dr., Microchimica acta, 1, (1978), 297. (in English).
- [7] Weisz H., Rotheimer K., Anal. Chim. Acta, 1, (1975), 119, (in English).
- [8] Zheng Z., Yaogang W., Liping H., Anal. Chem., 17, (1989), 160, (in English).
- [9] Wakil A.M., Farag A.B., Shahawi M.S., Talanta, 36, (1989), 738, (in English).
- [10] Sičev A.J., Tiginjanu D.J., Journal anal. chem., 24, (1969), (in Russian).
- [11] Bončev P.R., *Complex-forming and catalytical activity*, Nauka i izkustvo, Sofija, (1972), in Bulgarian.

ODREĐIVANJE NANOGRAMSKIH KOLIČINA MN(II) KATALITIČKOM OKSIDACIJOM KARMINSKE KISELINE VODONIK-PEROKSIDOM U PRISUSTVU AKTIVATORA

Pecev G. Todor, Rangel P. Igov, Rančić M. Sofija

U jednom od prethodnih radova, [1], predložena je nova katalitička reakcija i razrađena kinetička metoda za određivanje ultra-mikro količina Mn(II), na bazi njegovog katalitičkog dejstva na reakciju oksidacije karminske kiseline vodonik-peroksidom u amonijačnom puferu. Pri određenim optimalnim uslovima odvijanja reakcije postignuta je osetljivost od $1 \cdot 10^{-8}$ g/cm³ Mn(II) u rastvoru.

U ovom radu, proučavan je uticaj liganada sa elektron-akceptorskim osobinama, kao što su: 1.10-fenantrolin i 2.2'-dipiridil, na brzinu pomenute indikatorske reakcije u cilju razrade što osetljivije kinetičke metode za određivanje katalizatora - mangana. Na osnovu ispitivanja kinetike katalizovane indikatorske reakcije, predložen je mehanizam aktivatorskog dejstva fenantrolina i dipiridila.

U prisustvu fenantrolina postignuta je osetljivost od $5 \cdot 10^{-10}$ g/cm³, a u prisustvu dipiridila - $1 \cdot 10^{-10}$ g/cm³, odnosno, osetljivost je povećana za dva reda veličine u odnosu na postignutu osetljivost bez aktivatora. Kinetički podaci su obrađeni tangensnom

[2].