

KINETIC DETERMINATION OF Mn(II) TRACES IN FeCl<sub>2</sub> AND MgCl<sub>2</sub>

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**Abstract:** Kinetic method for Mn(II) trace determination in the solution, which is based on the catalytic effect of Mn(II) ions on the carmine acid (KA) oxidation by oxygene-peroxide in ammon-buffer, was applied for Mn(II) trace analyse in FeCl<sub>2</sub> · 4H<sub>2</sub>O (p.a.) and MgCl<sub>2</sub> · 6H<sub>2</sub>O (p.a.).

As 2,2'-dipyridile shows activating effect on this reaction and K-Na tartarate betters its selectivity, Mn(II) determinations in FeCl<sub>2</sub> · 4H<sub>2</sub>O were performed in the presence of 2,2'-dipyridile, and in MgCl<sub>2</sub> · 6H<sub>2</sub>O in the presence of K-Na tartarate. It is found that mean value of Mn(II) concentration in FeCl<sub>2</sub> · 4H<sub>2</sub>O was 5 · 10<sup>-3</sup> % (with relative error of ± 10%), and in MgCl<sub>2</sub> · 6H<sub>2</sub>O was 5 · 10<sup>-4</sup> % (with relative error of ± 4.7%).

## 1. Introduction

There are know few indicatory reactions which were basis for Mn(II) trace determinations in nature waters [1-5] and some salts [6-8] by kinetic methods of analyse.

It was found that small amounts of manganesse are present in all plants and animal organisms. In man's blood, for example, Mn(II) content is about 0.02 mg/dm<sup>3</sup>. In plants, it catalyses chlorophile formation and enlarges the possibility of plants to synthesize vitamine C. Its deficiency retards the animal,s growth and, also, their possibility to multiply. Besides, manganesse catalyses formation of substances which neutralize the harmful effect of strange proteins. The meaning of manganesse in high-quality steel production is also well known.

For these reasons, in this work is worked out the manganesse determination method in Fe(II)-chloride and Mg(II)-chloride. It is based on catalitic effect of Mn(II) ions on carmine acid oxidation by hydrogen-peroxide in the ammon-buffer solution. In the presence of 2,2'-dipyridile and K-Na tartarate, the selectivity of this method is so bettered that it was possible to determinate the manganesse in those salts without the preliminary separation.

## 2. Experimental

As during the inhibitory reaction initial red-violet colour of solution disappears because colourless oxidation product is forming, its rate was followed photometrically. The absorbance

changes were measured as function of reaction time. Because the linear dependence existed between logarithm of solution absorbance and reaction time in the first 10 minutes, kinetic results were treated by integral variant of tangent method [9].

Measurements were done on Lange's photocolourimeter with annexed thermostatic system on working temperature of  $25 \pm 0.1^\circ\text{C}$  and with  $\lambda_{\text{min}} = 555 \text{ nm}$ .

All used solutions were worked out by redistilled water and were kept in polyethylene vessels.

All used substances were of p.a. purity, product of "Merck".

Carmine acid solution ( $1 \cdot 10^{-3} \text{ mol/dm}^3$ ) was arranged by measuring and dissolving a solid substance in water.  $\text{H}_2\text{O}_2$  solutions were prepared of 30% reagent, and their concentration was verified by  $\text{KMnO}_4$ . Ammon - buffer was made by mixing  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3$  solution according the rule [10]. Basis Mn(II) solution ( $1 \cdot 10^{-3} \text{ g/cm}^3$ ) was prepared of solid  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$  and then it was used for working solutions ( $1 \cdot 10^{-7}$  and  $1 \cdot 10^{-8} \text{ g/cm}^3$ ) arranging. 2,2'-dipyridile solution was arranged from exactly measured solid substance dissolved in ethanol. K-Na tartarate solution was prepared by solid substance dissolving in water. On the same way, the  $\text{FeCl}_2$  (solid substance was  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and  $\text{MgCl}_2$  (solid substance was  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) were arranged.

The following photometric procedure was applied. In standard flask of  $50 \text{ cm}^3$ , adequate volumes of solutions were measured: carmine acid, ammon-buffer, Mn(II), 2,2'-dipyridile and K-Na tartarate. Then, Mixture was diluted by thermostated redistilled water,  $\text{H}_2\text{O}_2$  solutions was added and the reaction time was followed from that moment. This solution was used for working kyvete washing and then the absorbance of solution was measured each 30 sec., in the first 10 minutes of reaction.

On such a way, instead  $(dc/dt)$ , magnitude  $[d(\log A)/dt]$ , which was equal to the reaction rate, was determined.

### 3. Results and discussion

It was found that presence of 2,2'-dipyridile in the reaction mixture, betters the sensitivity of indicatory reaction for 100 times, what could be seen from the calibration curves showed in Figure 1 and Figure 2.

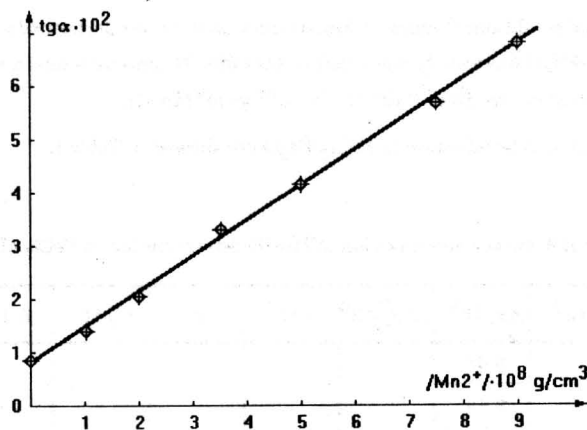


Fig. 1: Dependence of  $\text{tg}\alpha$  on Mn(II) concentration without presence of 2,2'-dipyridile. Initial conditions:  $\text{H}_2\text{O}_2$  -  $4.8 \cdot 10^{-2}$  mol/dm<sup>3</sup>; KA -  $4 \cdot 10^{-5}$  mol/dm<sup>3</sup>; buffer -  $1.2 \cdot 10^{-1}$  mol/dm<sup>3</sup>; pH - 9.75;  $t = 23 \pm 0.1^\circ\text{C}$ .

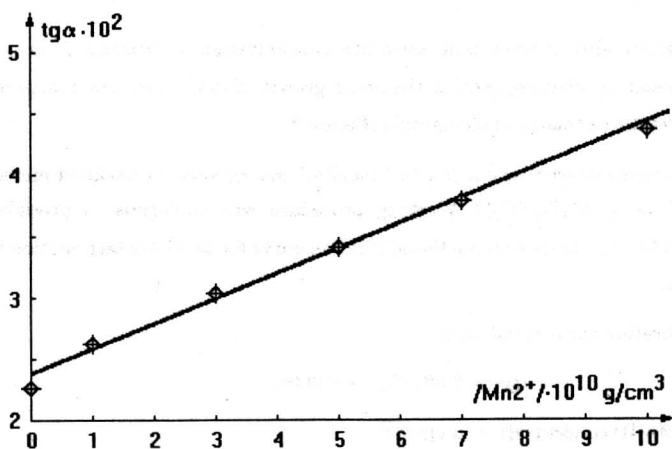


Fig. 2: Dependence of  $\text{tg}\alpha$  on Mn(II) concentration in the presence of 2,2'-dipyridile. Initial conditions:  $\text{H}_2\text{O}_2$  -  $4.8 \cdot 10^{-2}$  mol/dm<sup>3</sup>; KA -  $4 \cdot 10^{-5}$  mol/dm<sup>3</sup>; buffer -  $1.2 \cdot 10^{-1}$  mol/dm<sup>3</sup>; pH - 9.75;  $t = 23 \pm 0.1^\circ\text{C}$ ; 2,2'-dipyridile -  $9 \cdot 10^{-3}$  mol/dm<sup>3</sup>.

The calibration curve equation is:

$$\text{tg}\alpha = 21.45 \cdot C_{\text{Mn}} + 0.0229, \quad (1)$$

where is:  $C_{\text{Mn}}$  - Mn(II) concentration in  $\mu\text{g}/\text{cm}^3$ .

Under optimal conditions (Figure 2), Mn(II) trace analyse was performed on this way: for each determination  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  was exactly measured, so that Mn(II) concentration in solution was always in the area of calibration curve - from  $1 \cdot 10^{-10}$  to  $10 \cdot 10^{-10}$   $\text{g/cm}^3$  Mn(II).

Results of Mn(II) determination in  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  are showed in Table I.

Table I: Accuracy and precision of Mn(II) determination in  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ .

$x_i$ %Mn $\cdot 10^3$	$\bar{x} \cdot 10^3$	$\Delta x_i \cdot 10^3$	$\Sigma \Delta x_i^2 \cdot 10^6$	$S \cdot 10^3$	W	$S_{\bar{x}} \cdot 10^3$	$E \cdot 10^3$	G %
4.94	4.96	0.02	0.6766	0.41	8.30	0.51	$4.96 \pm 0.51$	$\pm 10$
5.60		0.64						
4.45		0.51						
4.90		0.06						
4.90		0.06						

Examination also showed that tartarate concentration increasing from  $1 \cdot 10^{-3}$  to  $6 \cdot 10^{-3}$   $\text{mol/dm}^3$  in the reacting solution, leads to the linear growth of  $\text{tg}\alpha$  of catalytic reaction, while the  $\text{tg}\alpha$  of noncatalytic reaction remains unchangeable (Figure 3).

K-Na tartarate concentration of  $4 \cdot 10^{-3}$   $\text{mol/dm}^3$  was choosed so modified method was applied for Mn(II) analyse in  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Working procedure was analogous to procedure for Mn(II) determination in  $\text{FeCl}_2$ . Figure 4 shows the calibration curve for Mn(II) determination in the presence of K-Na tartarate.

The calibration curve equation is:

$$\text{tg}\alpha = 0.891 \cdot C_{\text{Mn}} + 0.0095, \quad (2)$$

where is:  $C_{\text{Mn}}$  - Mn(II) concentration in  $\mu\text{g/cm}^3$ .

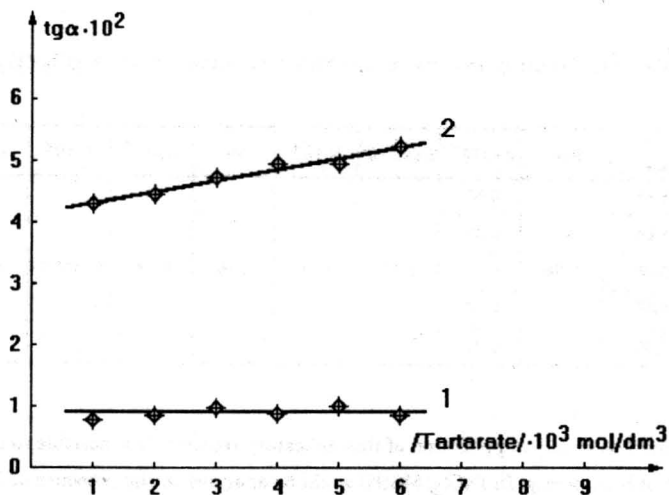


Fig. 3: Dependence of  $\text{tg}\alpha$  on K-Na tartarate concentration for noncatalytic (1) and catalytic (2) reaction. Initial conditions:  $\text{H}_2\text{O}_2$  -  $4.8 \cdot 10^{-2}$  mol/dm<sup>3</sup>; KA -  $4 \cdot 10^{-5}$  mol/dm<sup>3</sup>; buffer -  $1.2 \cdot 10^{-1}$  mol/dm<sup>3</sup>; pH - 9.75;  $t = 23 \pm 0.1^\circ\text{C}$ ;  $g/\text{cm}^3$  Mn(II) -  $4 \cdot 10^{-4}$

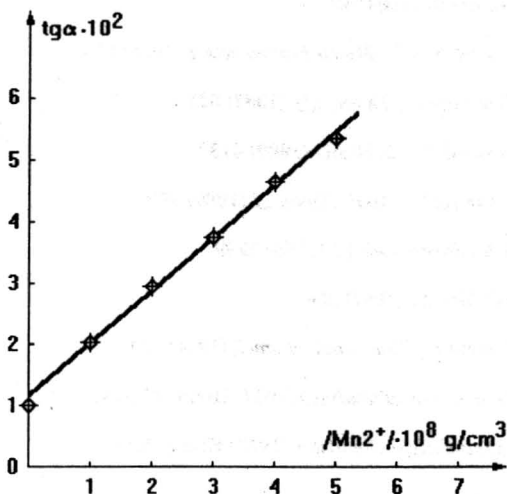


Fig. 4: Dependence of  $\text{tg}\alpha$  on Mn(II) concentration in the presence of K-Na tartarate. Initial conditions: KA -  $4 \cdot 10^{-5}$  mol/dm<sup>3</sup>;  $\text{H}_2\text{O}_2$  -  $4.8 \cdot 10^{-2}$  mol/dm<sup>3</sup>; buffer -  $1.2 \cdot 10^{-1}$  mol/dm<sup>3</sup>; pH - 9.75;  $t = 23 \pm 0.1^\circ\text{C}$ ;  $\text{C}_4\text{H}_4\text{O}_6$  -  $9 \cdot 10^{-3}$  mol/dm<sup>3</sup>.

Results of Mn(II) concentration determination in MgCl<sub>2</sub> are showed in Table II.

Table II: Accuracy and precision of Mn(II) determination in  $MgCl_2 \cdot 6H_2O$ .

$x_i$ %Mn·10 <sup>4</sup>	$\bar{x} \cdot 10^4$	$\Delta x_i \cdot 10^4$	$\Sigma \Delta x_i^2 \cdot 10^8$	$S \cdot 10^4$	W	$S_{\bar{x}} \cdot 10^4$	$E \cdot 10^4$	G %
5.15	5.09	0.06	0.15	0.19	3.70	0.24	$5.09 \pm 0.24$	$\pm 4.7$
5.00		0.09						
5.40		0.31						
4.90		0.19						
5.00		0.09						

As it could be seen, by application of this indicatory reaction, it is possible to determine Mn(II) in the samples of high purity. In  $FeCl_2$ , Mn(II) could be analysed in the presence of 2,2'-dipyridine, in the concentration range from  $1 \cdot 10^{-10}$  to  $10 \cdot 10^{-10}$  g/cm<sup>3</sup> with the error of  $\pm 10\%$ . In  $MgCl_2 \cdot 6H_2O$  in the presence of K-Na tartarate, analyse is possible in range from  $1 \cdot 10^{-8}$  to  $5 \cdot 10^{-8}$  g/cm<sup>3</sup> with error of  $\pm 4.7\%$ .

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KINETIČKO ODREĐIVANJE TRAGOVA Mn(II) U FeCl<sub>2</sub> I MgCl<sub>2</sub>

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Izvod. Kinetička metoda za određivanje tragova mangana u rastvoru, zasnovana na katalitičkom dejstvu koje Mn(II) joni pokazuju na reakciju oksidacije karminske kiseline (KA) u amonijačnom puferu, primenjena je za analizu tragova Mn(II) u FeCl<sub>2</sub>·4H<sub>2</sub>O (čistoće p.a.) i MgCl<sub>2</sub>·6H<sub>2</sub>O (čistoće p.a.).

Budući da 2,2'-dipiridil pokazuje aktivatorsko dejstvo na primenjenu indikatorsku reakciju, a kalijum-natrijum tartarat znatno poboljšava njenu selektivnost, određivanje tragova Mn(II) u FeCl<sub>2</sub>·4H<sub>2</sub>O vršeno je u prisustvu 2,2'-dipiridila, a u MgCl<sub>2</sub>·6H<sub>2</sub>O u prisustvu kalijum-natrijum tartarata. Nađeno je da srednja vrednost koncentracije Mn(II) u FeCl<sub>2</sub>·4H<sub>2</sub>O iznosi 5·10<sup>-3</sup>%, sa relativnom greškom od ± 10%, odnosno u MgCl<sub>2</sub>·6H<sub>2</sub>O - 5·10<sup>-4</sup>% sa relativnom greškom od ± 4.7%.