

## 새로운 지시약 반응에 의해 극미량 수준의 망간 측정을 위한 촉매 반응의 분광 광도 측정법

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### Catalytic Spectrophotometry for the Determination of Manganese at Trace Levels by a Novel Indicator Reaction

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**요약.** 새로운 동적 분광 광도 측정법은 천연의 물 샘플에서 망간(II)의 측정을 위해 개발되었다. 그 방법은 620 nm에서 활성 화제로서 nitrilotriacetic acid (NTA)를 사용하면서  $\text{KIO}_4$ 에 의한 갈로시아닌(Galloycyanin)의 산화와 함께 망간(II)의 촉매 효과에 기초했다. 최적조건은 갈로시아닌(Galloycyanin)  $4.00 \times 10^{-5}$  M,  $\text{KIO}_4$   $1.00 \times 10^{-4}$  M, NTA  $1.00 \times 10^{-4}$  M, pH = 3.50인 0.1 M HAc/NaAc 완충용액, 5분의 반응시간 그리고 30 °C의 온도에서 얻어졌다. 최적조건 하에서 제안된 방법은 0.1 - 4.0 ng mL<sup>-1</sup>의 범위에서 망간(II)의 측정을 허용했고 0.025 ng mL<sup>-1</sup>이하의 검출한계를 가지고 있다. 표준 망간(II) 용액을 측정하는 것에서 회수율은 98.5 - 102% 범위에 있다. 그리고 상대표준편차(RSD)는 0.76 - 1.25%의 범위에 있다. 새롭게 개발된 동적 방법은 약간의 주위의 물과 만족할 만한 결과를 갖는 JAC-0031의 공인된 표준 기준 강물 샘플 둘 다에서 망간(II)의 측정에 성공적으로 응용되었다. 또한, 얼마 안 되는 양이온과 음이온은 망간(II)의 측정을 방해한다. 다른 촉매-동적 방법과 기기적 방법과 비교했을 때, 제안된 동적 방법은 상당히 좋은 선택성과 감도, 낮은 가격, 저렴함, 낮은 검출한계와 신속함을 보인다. 상대적으로 낮은 염분을 갖는 진짜 물 샘플과 병으로 된 마시는 물, 차갑고 뜨거운 용천수, 호수, 강물 샘플 같은 복잡한 모체들에 적용하는 것은 쉽고 성공적으로 적용될 수 있다.

**주제어:** 망간(II), 동적-분광 광도 측정법, 촉매 효과, 갈로시아닌 (Galloycyanin), 천연 물 샘플,  $\text{KIO}_4$

**ABSTRACT.** A new kinetic spectrophotometric method is developed for the measurement of Mn(II) in natural water samples. The method is based on the catalytic effect of Mn(II) with the oxidation of Galloycyanin by  $\text{KIO}_4$  using nitrilotriacetic acid (NTA) as an activation reagent at 620 nm. The optimum conditions obtained are  $4.00 \times 10^{-5}$  M Galloycyanin,  $1.00 \times 10^{-4}$  M  $\text{KIO}_4$ ,  $1.00 \times 10^{-4}$  M NTA, 0.1 M HAc/NaAc buffer of pH = 3.50, the reaction time of 5 min and the temperature of 30 °C. Under the optimum conditions, the proposed method allows the measurement of Mn(II) in a range of 0.1 - 4.0 ng mL<sup>-1</sup> and with a detection limit of down to 0.025 ng mL<sup>-1</sup>. The recovery efficiency in measuring the standard Mn(II) solution is in a range of 98.5 - 102%, and the RSD is in a range of 0.76 - 1.25%. The newly developed kinetic method has been successfully applied to the measurement of Mn(II) in both some environmental water samples and certified standard reference river water sample, JAC-0031 with satisfying results. Moreover, few cations and anions interfere with the measurement of Mn(II). Compared with the other catalytic-kinetic methods and instrumental methods, the proposed kinetic method shows fairly good selectivity and sensitivity, low cost, cheapness, low detection limit and rapidity. It can easily and successfully be applied to the real water samples with relatively low salt content and complex matrices such as bottled drinking water, cold and hot spring waters, lake water, river water samples.

**Keywords:** Mn(II), Kinetic-spectrophotometry, Catalytic effect, Galloycyanin, Natural water samples,  $\text{KIO}_4$

## INTRODUCTION

Manganese is one of the most abundant natural metals after iron in the continental Earth's crust and is recognized as one of ten elements essential to life. It takes part largely

in enzymatic activity, in particular relating to the metabolism of lipids and glucose, and it plays a major part in photosynthesis and antioxidant actions.<sup>1</sup> However, manganese can also be very toxic in high concentrations and contribute for example to the development of Parkinson's symptoms.<sup>2</sup>

Manganese, along with iron, also creates serious problems in many public water supplies.<sup>3</sup>

Aquatic sediments are the ultimate sink of trace elements in the marine environment. However, sediment-incorporated trace elements do not stay fixed in the solid phase but can be partly remobilized in pore-water by physical, chemical and biological processes. Degradation of organic matter is the driving force for early diagenesis in sediment compartment. The bacterially mediated oxidation of organic matter is reflected in a well-established depth sequence of redox reactions in which oxygen is reduced near the sediment-water interface, followed by the reduction of nitrate, manganese- and reactive iron oxides, sulfate, and finally carbon dioxide. A strong vertical gradient of dissolved manganese in pore waters is thus observed. The transformation of oxidized manganese to reduced forms (and vice versa) is directly or indirectly controlled by the supply of oxygen, which is strongly coupled to the oxidation of organic matter in sediments.<sup>4,5</sup>

In the natural environment manganese occurs in several oxidation states (+II, +III, and +IV) and in soluble and insoluble forms as a function of pH and oxidoreduction potential.<sup>6</sup> Despite the high abundance of manganese in the Earth's crust (0.0716% (w/w)), dissolved manganese in rivers and oceans is present at very low levels of nanomoles per liter or less, due to its low solubility in oxygenated water. Mn(II) concentration levels are normally about 0.01 mg L<sup>-1</sup> in ocean water, and about 4 mg L<sup>-1</sup> in rivers.<sup>7,8</sup> The manganese concentrations in surface waters can also increase temporarily but drastically when sediment pore waters are mixed with overlying water during intensive fluvial traffic.

Various techniques are used for manganese analysis, of which atomic emission and absorption spectrometry are the most common methods.<sup>9</sup> These techniques necessitate sampling, pre-treatment and analyses in the laboratory.<sup>10</sup> For these reasons, catalytic kinetic methods are interesting alternatives due to the sensitivity and the selectivity for trace metal detection without requiring any significant sample pretreatment.

Catalytic methods provide an attractive and cost effective way for the determination of trace amounts of manganese in comparison with more expensive techniques such as atomic absorption spectrometry, atomic emission spectrometry, neutron activation analysis, mass spectrometry. Recently, several catalytic and spectrophotometric methods have been described for the determination of manganese.<sup>11-21</sup> However, only some of these methods have sufficient sensitivity for determination of Mn(II) at or below ng mL<sup>-1</sup> levels.

Among the most sensitive methods described so far the

following methods were developed. The use of the method of Bartkus and Naekaitis<sup>22</sup> (detection limit of 0.014 ng mL<sup>-1</sup>) is limited because of Fe<sup>3+</sup>, Pb<sup>2+</sup>, and I<sup>-</sup> ions interference at the same concentration level. In the case of the method of Rubio et al.<sup>23</sup> (detection limit of 0.050 ng mL<sup>-1</sup>) some ions, such as Co<sup>2+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup> interfere with the manganese(II) content determination, and therefore various masking agents are necessary. The flow injection method of Kolotyrykina et al.<sup>24</sup> (detection limit of 0.010 ng mL<sup>-1</sup>) is relatively sensitive and interference free, but it requires a separation-preconcentration step in order to remove the seawater matrix effect, and to increase the precision of the determination of manganese content.

Some of the methods cited, however, show a sufficient sensitivity and selectivity and they were successfully applied to determine Mn<sup>2+</sup> content in real samples without the use of masking agents and special sample pretreatment steps.<sup>11-15,19,20</sup> The principal disadvantages of these methods are the need to synthesize the new selective chromogenic dye and dye derivatives<sup>14,19,20</sup> and the longer analysis time required.<sup>11-13</sup>

An alternative approach to improve sensitivity is the use of activator ligands. An activator is a chemical species that is not the catalyst, but its presence increases the reaction rate considerably and, "from an analytical point of view, yields a better sensitivity and lower limit of detection in a catalytic determination".<sup>25</sup> NTA has been used as an activator in a batch method<sup>26</sup> for the oxidation of malachite green by periodate, a reaction catalyzed by manganese. The enhanced catalytic effect exerted by the presence of NTA appears to be related to the formation of NTA-Mn complexes,<sup>27,28</sup> although the exact mechanism is not well understood. One hypothesis is that NTA participates in the regeneration of Mn(II)<sup>25</sup> by keeping Mn(III) in solution. A second hypothesis is that the NTA-Mn complex introduces favorable steric factors<sup>25</sup> that facilitate the catalytic role of Mn.

In this work, Galloxyanin was employed for the first time in a kinetic system for the determination of manganese (II). The catalytic effect of Mn(II) on the oxidation of Galloxyanin with KIO<sub>4</sub> in the presence of NTA was investigated. A catalytic kinetic spectrophotometric method for the determination of Mn(II) was developed applicable for Mn(II) concentrations of 0.1 - 4 ng mL<sup>-1</sup> using the fixed-time method with a detection limit of 0.025 ng mL<sup>-1</sup>. The proposed method is also highly sensitive and selective, and, moreover, more simple compared to all methods mentioned above. The principal advantages of this method are the small reaction volume (only 10 mL), the smaller number of reagents, and the shorter time needed for analysis. The method

was successfully applied to determine manganese content in environmental water samples. This is the first attempt to apply a catalytic method based on the usage of Galloctyanin to determine manganese levels in real samples.

## EXPERIMENTAL

### Instrumentation

A Shimadzu Model UV-1800 spectrophotometer equipped with a 1 cm quartz cell was used for absorbance measurements. This spectrophotometer has a wavelength accuracy of  $\pm 0.2$  nm and a bandwidth of 2 nm in the wavelength range of 190 - 1100 nm. A Grant LTG-6G model thermostatic water bath with good temperature control was used. A stopwatch was used for recording the reaction time. A pH meter consisting of a glass-calomel electrode double was used to determine pH values of solutions. Two standard buffer solutions of pH  $7 \pm 0.01$  and pH  $4 \pm 0.01$  were used for the calibration of pH meter. The temperature was maintained constant in the reaction cell by circulating water at appropriate temperature around the cell compartment of the spectrophotometer throughout the experiment. All solutions were preheated to a working temperature of  $25^\circ\text{C}$  with an accuracy of  $\pm 0.1^\circ\text{C}$  before the initiation of the indicator reaction. The absorbance measurements were made at a working wavelength of 620 nm for indicator system. In establishment of optimum conditions, the standard micropipettes of 5 - 50, 50 - 500 and 10 - 1000  $\mu\text{L}$  were used in distribution of volumes of reagent and working solutions of anionic and cationic interfering ions in interference studies.

### Reagents and standards

All the chemicals used were of analytical reagent grade, and doubly distilled water was used throughout experiments.  $\text{KIO}_4$  solution ( $2.0 \times 10^{-3}$  M) was prepared by dissolving 0.1161 g solid reagent and diluting to 250 mL with deionized water. A stock solution of Galloctyanin ( $2.25 \times 10^{-3}$  M) was prepared by dissolving 0.0190 g of indicator dye in 25 mL of  $1.00 \times 10^{-3}$  M NaOH solution and diluting to 500 mL with deionized water. A stock solution of NTA ( $5.0 \times 10^{-4}$  M) was prepared by dissolving 0.0048 g of pure NTA and diluting to 250 mL with deionized water. The acetate buffer solution, 0.1 M pH 3.50 was prepared by dissolving solid  $\text{CH}_3\text{COONa}$  at the known amounts with HCl solution and diluting to 100 mL with deionized water. The pH of solution media was controlled by using a pH meter when necessary. Stock solution of Mn(II) ( $200 \text{ mg L}^{-1}$ ) was prepared by dissolving 0.1540 g of manganese sulfate monohydrate in water and diluted to 250 mL. The working standard solutions of

Mn(II) were obtained by stepwise dilution of the stock solution immediately before use. All stock solutions were stored in polyethylene containers. All labware used for handling solutions were cleaned with detergent solution, soaked in the diluted  $\text{HNO}_3$  solution of 2.0% (v/v), followed by vigorous shaking, rinsed thoroughly with deionized water.

### General procedure

All the reagent solutions, deionized water and empty volumetric flasks were thermostated, usually at  $30^\circ\text{C}$ , in a water bath. A suitable aliquot of a solution containing 0.2  $\mu\text{g}$  of Mn(II) was transferred into a 10-mL volumetric flask. Exactly 2.0 mL of buffer solution (0.1 M pH = 3.50 HAc/NaAc) and 2.0 mL of  $2.25 \times 10^{-3}$  M Galloctyanin solution and finally 2.0 mL of  $2.0 \times 10^{-3}$  M  $\text{KIO}_4$  and 2.0 mL of  $5.0 \times 10^{-4}$  M NTA were added to the flask, and the final solution was diluted to the mark with water and shaken. The time recording was started with the last reagent addition. A portion of the solution was transferred into a 1.0-cm cell within 30 sec from initiation of the reaction, and the reaction was followed by recording the absorbance changes at 620 nm for a fixed time of 0.5 to 5.0 min ( $\Delta A_c$ ). The same measurements were performed in the absence of manganese and regarded as analyte blank ( $\Delta A_0$ ). The net changes in the absorbance, as a measure of the catalyzed-reaction rate, were calculated from the difference in the absorbance change of the catalyzed and uncatalyzed reactions ( $\Delta(\Delta A) = \Delta A_c - \Delta A_0$ ).

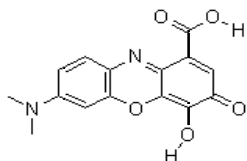
### Sample preparation

Prior to analysis, river and lake water samples were treated as follows: 50 mL of sample was evaporated to about 5 mL in a 100 mL beaker on a hot plate at about  $90^\circ\text{C}$ . The 1 mL of concentrated  $\text{HNO}_3$  and 0.5 mL of  $\text{H}_2\text{O}_2$  (30%) was added and the contents were heated to dryness at  $90^\circ\text{C}$ . After cooling, the digest was diluted to 25 mL with water and adjusted to pH 3.50 with diluted HCl and NaOH. It was boiled for 5 min to expel the dissolved  $\text{CO}_2$ . After cooling, the solution was transferred to a 50 mL volumetric flask and diluted to the mark with deionized water, which was ready for analysis. Lake water sample was collected from Hafik Lake (Sivas, Turkey), and river water sample was freshly collected from Kızılırmak river (Sivas, Turkey). All the water samples including hot and cold spring water were filtered through a 0.45  $\mu\text{m}$  pore size membrane filter to remove suspended particulate matter and were stored at  $4^\circ\text{C}$  in the dark. Bottled mineral water samples were obtained from a local convenient store and analyzed directly without pretreatment.

## RESULTS AND DISCUSSION

### Absorption spectra

Gallocyanin is an oxazin group cationic dye containing vicinal hydroxy groups next to carboxyl group that selectively undergoes oxidation reaction with periodate at pH = 3.50 to form a colorless product.

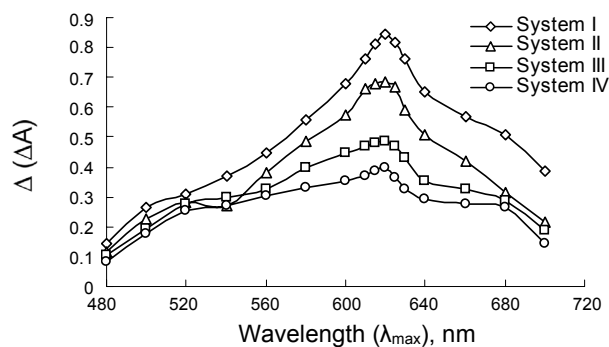


**Schema 1.** The molecular structure of Gallocyanin

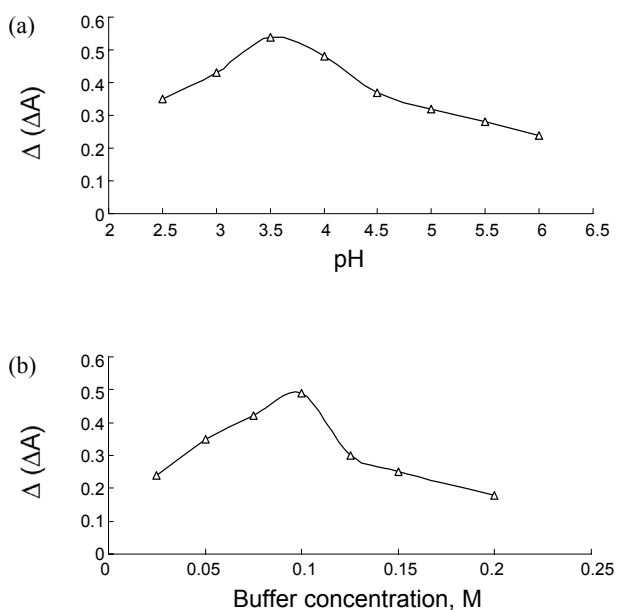
Absorption spectra of the catalytic and non-catalytic systems against water in the range of 480 - 700 nm were determined and shown in Fig.1. The analytical results suggested that the absorbance values of different systems reach their maximum at 620 nm, and oxidation of Gallocyanin by potassium periodate in weak acidic medium is very slow. In the presence of trace amounts of Mn(II), the oxidation rate of Gallocyanin increases. Mn(II) catalyses the decolorizing oxidation of indicator dye. The absorbance changes are proportional to the Mn(II) concentrations in certain concentration range, and when NTA as an activator is added, the absorbance of the catalytic system is getting smaller. This showed that the addition of NTA can increase the sensitivity of the indicator reaction. Therefore, the determination should be carried out at 620 nm for further experimental studies.

### Optimization of reaction conditions

In order to take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimized; providing that the optimum concentration of each component will give the smallest relative standard deviation and its reaction order will be zero according to its relevant species for the kinetic measurements, except for the analyte (where catalyst). The conditions of which the small fluctuations in concentration have not any effect on the initial rate are desired. These conditions should be selected providing that the initial rate will be first order according to the analyte ( $\Delta(\Delta A) = k_c[Mn(II)]$ ). In this context, the optimization data for each analytical variable was repeated at least three times during the kinetic absorbance measurements. The effect of analytical variables such as the pH, Gallocyanin and periodate concentration, concentration of NTA as activator, and



**Fig. 1.** Absorption spectra of indicator systems at optimum conditions ( $[GC] = 4.00 \times 10^{-5} M$ ,  $[NTA] = 1.00 \times 10^{-4} M$ ,  $[KIO_4] = 4.00 \times 10^{-4} M$ , 0.1 M HAc-NaAc buffer pH 3.50 for the fixed time of 5 min at 620 nm and 30 °C). System I: Gallocyanin-pH 3.5 HAc/NaAc buffer System II: Gallocyanin-pH 3.5 HAc/NaAc buffer-KIO<sub>4</sub> System III Gallocyanin-pH 3.5 HAc/NaAc buffer-KIO<sub>4</sub>-Mn(II) System IV: Gallocyanin-pH 3.5 HAc/NaAc buffer-KIO<sub>4</sub>-Mn(II)-NTA



**Fig. 2.** (a) Effect of pH on analytical sensitivity for the net catalyzed-reaction rate. Conditions:  $[NTA] = 1.00 \times 10^{-4} M$ ,  $[KIO_4] = 4.00 \times 10^{-4} M$ ,  $[GC] = 4.00 \times 10^{-5} M$  for the fixed time of 5 min at 620 nm and 30 °C. (b) Effect of pH on analytical sensitivity for the net catalyzed-reaction rate. Conditions:  $[NTA] = 1.00 \times 10^{-4} M$ ,  $[KIO_4] = 4.00 \times 10^{-4} M$ ,  $[GC] = 4.00 \times 10^{-5} M$  for the fixed time of 5 min at 620 nm and 30 °C

temperature and ionic strength of environment on the rate of catalyzed and uncatalyzed reaction was studied in detail. In reaction rate-concentration curves according to their tradition in literature the concentration of reactants or inert

salt were taken into consideration. In order to reconcile sensitivity ( $\Delta(\Delta A)$ ) and short analysis time the fixed-time method for the first 5 minutes was adopted as kinetic detection method in the catalytic determination of Mn(II).

#### Effect of pH on sensitivity

The effect of pH on sensitivity in presence of  $2 \text{ ng mL}^{-1}$  Mn(II) was studied by adjusting the sample pH to a value ranging from 2.5 to 6.0. For this purpose, acetic acid-boric acid-orthophosphoric acid and NaOH solutions were used. Based on the data shown in Fig. 2(a), the optimum pH value of 3.5 was selected. The influence of several buffer solutions at pH 3.5 was tested. The best buffer solution was selected using the slope of the calibration graph as the optimization criterion. In the case of sodium citrate-HCl and potassium hydrogen phthalate-HCl buffer solutions, the slope of calibration graph was unsatisfactory. On the other hand, if  $\text{H}_3\text{PO}_4$ -NaOH or NaAc-HCl buffers were used, the slope of calibration graph was higher. However, better results were obtained for the latter one. Moreover, preparation of NaAc-HCl buffer is less time-consuming compared to the preparation of  $\text{H}_3\text{PO}_4$ -NaOH buffer solution. Later on, the NaAc-HCl concentration was varied within 0.025 - 0.2 M in order to discriminate the optimum HAc-NaAc content in samples. It was found that the highest slope of the calibration graph was achieved for the buffer concentration of 0.1 M (Fig. 2(b)).

#### Effect of $\text{KIO}_4$ concentration on sensitivity

The effect of the periodate concentration on the rate of reaction in presence of  $2 \text{ ng mL}^{-1}$  Mn(II) was studied in the range of  $1.0 \times 10^{-4}$  -  $12 \times 10^{-4}$  M (Fig. 3). The results show that the net reaction rate increases with increasing periodate concentration up to  $4.0 \times 10^{-4}$  M and decreases at higher concentrations. This means that the rate of uncatalyzed reaction increases with periodate concentration ( $> 4.0 \times 10^{-4}$  M) to a greater extent than the catalyzed reaction, and the difference between the rates of catalyzed and uncatalyzed reactions ( $\Delta A_c - \Delta A_0$ ) diminishes at higher periodate concentrations. Therefore, a periodate concentration of  $4.0 \times 10^{-4}$  M was selected for further study.

#### Effect of Gallocyanin concentration on sensitivity

Fig. 4 shows the effect of Gallocyanin concentration on the sensitivity for the range of  $1.0 \times 10^{-5}$  -  $7.0 \times 10^{-5}$  M in presence of  $2 \text{ ng mL}^{-1}$  Mn(II). This sensitivity (net reaction rate) increases with increasing Gallocyanin concentration up to  $4.5 \times 10^{-5}$  M and decreases at higher concentrations. This may be due to the aggregation of the dye at higher concentrations. Therefore, a final concentration of  $4.5 \times 10^{-5}$  M

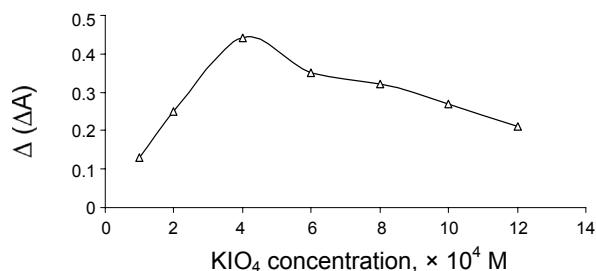


Fig. 3. Effect of  $\text{KIO}_4$  concentration on analytical sensitivity for the net catalyzed-reaction rate. Conditions:  $[\text{NTA}] = 1.00 \times 10^{-4}$  M,  $[\text{GC}] = 4.00 \times 10^{-5}$  M, 0.1 M HAc-NaAc buffer pH 3.50 for the fixed time of 5 min at 620 nm and  $30^\circ\text{C}$

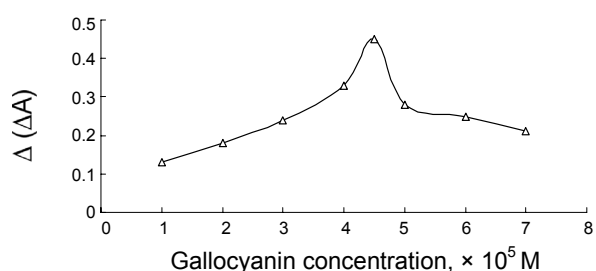


Fig. 4. Effect of Gallocyanin concentration on analytical sensitivity for the net catalyzed-reaction rate. Conditions:  $[\text{NTA}] = 1.00 \times 10^{-4}$  M,  $[\text{KIO}_4] = 4.00 \times 10^{-4}$  M, 0.1 M HAc-NaAc buffer pH 3.50 for the fixed time of 5 min at 620 nm and  $30^\circ\text{C}$

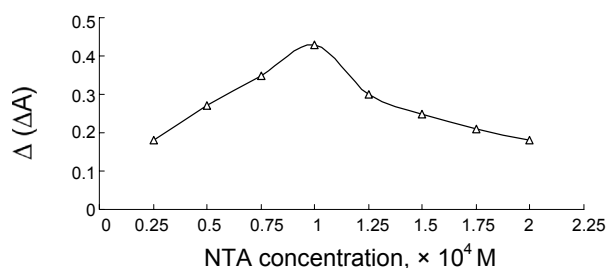
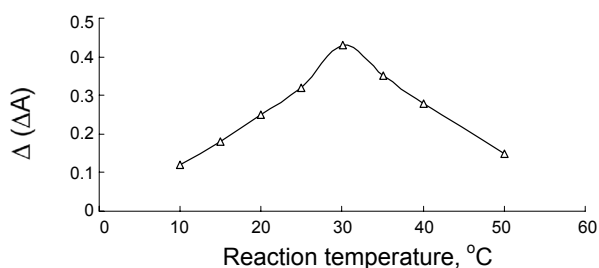


Fig. 5. Effect of activator concentration on analytical sensitivity for the net catalyzed-reaction rate. Conditions:  $[\text{KIO}_4] = 4.00 \times 10^{-4}$  M,  $[\text{GC}] = 4.00 \times 10^{-5}$  M, 0.1 M HAc-NaAc buffer pH 3.50 for the fixed time of 5 min at 620 nm and  $30^\circ\text{C}$

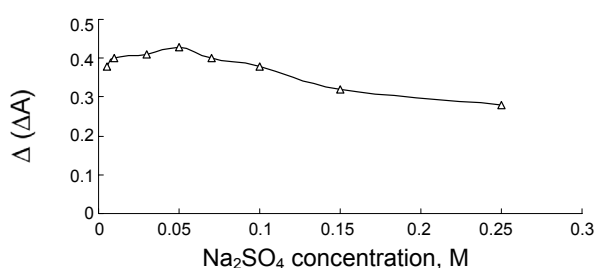
of Gallocyanin was selected as the optimum concentration.

#### Effect of activator concentration on sensitivity

The effect of NTA concentration on the rate of net reaction was studied in the range of  $2.5 \times 10^{-5}$  -  $2.0 \times 10^{-4}$  M in presence of  $2 \text{ ng mL}^{-1}$  Mn(II) (Fig. 5). This sensitivity increases with increasing NTA concentration up to  $1.0 \times 10^{-4}$  M and decreases at higher concentrations. This is due to the ion-pair complex formation with indicator dye in blank solution and change in the activation effect of the activator in the solution.



**Fig. 6.** Effect of reaction temperature on analytical sensitivity for the net catalyzed-reaction rate. Conditions:  $[GC] = 4.00 \times 10^{-5} \text{ M}$ ,  $[NTA] = 1.00 \times 10^{-4} \text{ M}$ ,  $[KIO_4] = 4.00 \times 10^{-4} \text{ M}$ , 0.1 M HAc-NaAc buffer pH 3.50 for the fixed time of 5 min at 620 nm



**Fig. 7.** Effect of ionic strength on analytical sensitivity for the net catalyzed-reaction rate. Conditions:  $[GC] = 4.00 \times 10^{-5} \text{ M}$ ,  $[NTA] = 1.00 \times 10^{-4} \text{ M}$ ,  $[KIO_4] = 4.00 \times 10^{-4} \text{ M}$ , 0.1 M HAc-NaAc buffer pH 3.50 for the fixed time of 5 min at 620 nm and 30°C

Therefore, a final concentration of  $1.0 \times 10^{-4} \text{ M}$  was selected as the optimum concentration of NTA.

#### Effect of reaction temperature on sensitivity

The effect of the temperature on the sensitivity was studied in the range 10 - 50 °C with the optimum pH and other reagent concentrations in presence of  $2 \text{ ng mL}^{-1} \text{ Mn(II)}$  (Fig. 6). The results showed that, as the temperature increases up to 30 °C, the net reaction rate increases, whereas higher temperature values decrease the sensitivity ( $\Delta(\Delta) = \Delta A_c - \Delta A_0$ ). This means that the rate of uncatalyzed reaction increases with temperature to a greater extent, and the uncatalyzed reaction occurred at a suitable rate. Therefore, 30 °C was selected for further study.

To calculate the activation energy,  $-\ln(\Delta(\Delta A)/\Delta t)$  was measured over the range of 10 - 30 °C, the results suggest that  $\ln(\Delta(\Delta A)/\Delta t)$  is linearly related to  $(1/T)$ , and the calibration curve obeys the following linear regression equations :  $-\ln(\Delta(\Delta A)/\Delta t) = 5.3776 \times 1/T - 16.914$  (for catalyzed reaction) with a regression coefficient ( $r$ ) of 0.9945. According to the Arrhenius equation, the activation energy of the Mn(II)-catalyzed reaction calculated from the equation mentioned above is  $22.48 \text{ kJ}\cdot\text{mol}^{-1}$ . In this study, the catalyzed-reaction

is heated during the fixed-time of 5 min.

#### Effect of ionic strength of media on sensitivity

Under optimal conditions selected, the effect of ionic intensity of environment onto the analytical sensitivity,  $\Delta(\Delta A)$  was examined in the concentration range of 0.005 - 0.25 M  $\text{Na}_2\text{SO}_4$ . Results showed that the reaction rate has changed very little with increasing concentration approximately up to 0.05 M, after this concentration exhibited a negative change with increasing inclination. This case predicted that the catalyzed- indicator reaction would give right responds for catalyst in real life samples with low matrix such as fresh waters. It can be expressed that inert salt effect should be checked at matrix systems with the high salt content such as sea water and wastewaters. Standard addition method can be suggested for analyzing Mn(II) in real samples having high salt content (Fig. 7).

#### The calibration graph, detection limit and precision

Calibration graphs were obtained using the fixed-time method. This method was applied to the change in absorbance over an interval of 0.5 - 5 min from initiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration graph was obtained for Mn(II) in the concentration range  $0.1 - 4 \text{ ng mL}^{-1} \text{ Mn(II)}$ . The equation of the calibration graph is  $\Delta(\Delta A) = 0.0043 + 0.183C_{\text{Mn(II)}}$  ( $r = 0.998$ ,  $n = 10$ ), where  $c$  is the concentration of Mn(II) in  $\text{ng mL}^{-1}$ .

The limit of detection, defined as  $C_{LOD} = \Delta A_{blank} + 3S_{blank}$  (where  $\Delta A_{blank}$  is the average of the absorbance change for the blank solution for ten replicate determinations and  $S_{blank}$  is its standard deviation) was equal to  $0.025 \text{ ng mL}^{-1} \text{ Mn(II)}$ .

The relative standard deviations of 0.80, 2.00 and 3.00  $\text{ng mL}^{-1}$  of Mn(II) were 2.38, 1.21 and 0.66%, respectively. Table 1 shows the accuracy and precision of the kinetic method developed under optimum reagents conditions at 620 nm and 30 °C.

#### Interference studies

In order to assess the application of the proposed method to synthetic samples, the effect of various ions on the determination of  $2 \text{ ng mL}^{-1} \text{ Mn(II)}$  was studied. The tolerance limit was defined as the concentration of added ions causing a relative error less than 5%. The results are summarized in Table 2. Many ions did not interfere, even when they were present in 50-3000 fold excess over Mn(II). A 10-25-fold excess of Cr(III) and Ni(II) showed almost a significant effect on the catalytic signal of Mn(II). However, some reductive

**Table 1.** The accuracy and precision of the present kinetic method Conditions: ([NTA] =  $1.0 \times 10^{-4}$  M, [KIO<sub>4</sub>] =  $4.0 \times 10^{-4}$  M, 2 mL 0.1 M pH = 3.5 HAc/NaAc buffer solution, [GC] =  $4.0 \times 10^{-5}$  for the fixed time of 5 min at 620 nm and 30 °C)

Added Mn(II) (ng mL <sup>-1</sup> )	Found Mn(II) (ng mL <sup>-1</sup> )	RSD%	RE%
0.8	0.84	2.38	5.00
2	2.05	1.21	2.50
3	3.04	0.66	1.30

**Table 2.** Interference study for determination of 2 ng mL<sup>-1</sup> Mn(II) in the presence of optimum reagent concentrations

Interfering species (K <sup>n+</sup> or A <sup>m-</sup> )	Tolerance limit (W <sub>interfering ion</sub> /W <sub>Mn(II)</sub> )
K <sup>+</sup> , Na <sup>+</sup> , Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , NH <sub>4</sub> <sup>+</sup>	3000 - 4500
Ca(II), Mg(II), F <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup>	2000 - 3000
Cd(II), Al(III), C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	1000 - 1750
Cr(VI), Cu(II), Zn(II)	350 - 500
Ag <sup>+</sup> , Fe(III)	200
V(V), Co(II), Bi(III)	100 - 150
SO <sub>3</sub> <sup>2-</sup> , V(IV)	25 - 50
Cr(III), Ni(II)	10 - 25
Fe(II)	7.5
S <sup>2-</sup>	5
NO <sub>2</sub> <sup>-</sup>	2.5

**Table 3.** Determination of Mn(II) present in three different commercially bottled drinking water samples by using the present kinetic method

Samples	Added (ng mL <sup>-1</sup> )	Found (ng mL <sup>-1</sup> )	Recovery%	RSD%
Drinking water-I	-	1.34 ± 0.03	-	2.24
	1.00	2.35 ± 0.02	101	0.85
Drinking water-II	2.00	3.34 ± 0.02	100	0.60
	-	1.51 ± 0.03	-	1.98
Drinking water-III	1.00	2.52 ± 0.02	101	0.79
	2.00	3.54 ± 0.02	103	0.56
Drinking water-III	-	1.61 ± 0.03	-	1.86
	1.00	2.65 ± 0.02	104	0.75
	2.00	3.63 ± 0.02	103	0.55

**Drinking water-I** Specific properties (Damla, Tokat): 21 mg L<sup>-1</sup> Cl<sup>-</sup>, pH:7.8, 21 µg mL<sup>-1</sup>, 1.3 mg L<sup>-1</sup> Mn(II), 6 mg L<sup>-1</sup> SO<sub>4</sub><sup>2-</sup>, 2.5 mg L<sup>-1</sup> Na<sup>+</sup>. After the water sample was diluted to 1 L with deionized water at 1:1000 ratios, 1 mL of diluted water sample was analyzed.

**Drinking water-II** Specific properties (Üç Çamlar, Tokat): Nitrite, ammonium and fluoride are not present. pH:7.4, 5 mg L<sup>-1</sup> Cl<sup>-</sup>, 0.22 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>, 13.2 mg L<sup>-1</sup> SO<sub>4</sub><sup>2-</sup>, 12.3 mg L<sup>-1</sup> Na<sup>+</sup>, 1.5 mg L<sup>-1</sup> Mn<sup>2+</sup>. After the water sample was diluted to 1 L with deionized water at 1:1000 ratios, 1 mL of diluted water sample was analyzed.

**Drinking water-III** Specific properties (Akdağ, Yozgat): Sulfate is not present. 0.014 mg L<sup>-1</sup> Na<sup>+</sup>, 0.033 mg L<sup>-1</sup> NH<sub>4</sub><sup>+</sup>, 132 mg L<sup>-1</sup> Al<sup>3+</sup>, 92.16 mg L<sup>-1</sup> Cl<sup>-</sup>, pH:7.77, 36.1 mg L<sup>-1</sup> Fe<sup>3+</sup>, 1.61 mg L<sup>-1</sup> Mn<sup>2+</sup>. After the water sample was diluted to 1 L with deionized water at 1:1000 ratios, 1 mL of diluted water sample was analyzed.

ions such as NO<sub>2</sub><sup>-</sup> (> 5 ng mL<sup>-1</sup>), S<sup>2-</sup> (> 10 ng mL<sup>-1</sup>) and Fe<sup>2+</sup> (> 15 ng mL<sup>-1</sup>) could yield serious adverse effects on sensitivity. It is perceptible that these reductive ions may interfere in the indicator redox reaction, on which the measurement is based, although they were rarely mentioned and discussed in the previous catalytic kinetic systems. In natural waters in the local area, their concentrations generally range from 20 to 200, 10 to 100, and 5 to 50 µg mL<sup>-1</sup> for NO<sub>2</sub><sup>-</sup>, S<sup>2-</sup>, and Fe<sup>2+</sup>, respectively.<sup>29</sup> In order to eliminate their potential interference, water samples were treated with strong oxidizing agents such as HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, prior to analysis as described in Section 2. Therefore, no attempt was made to individually avoid the adverse effects from each of the above-mentioned ions. The results show that the method is relatively selective for manganese determination. All results are averages of three replicate measurements with 1.20 - 3.50% RSD.

#### Analytical applications of the developed kinetic method

In order to determine the analytical accuracy and validity of the developed kinetic method in different water samples with complex matrix, the manganese concentrations were determined by spiking the standard manganese solutions at different concentrations into different drinking water samples for analysis separately. The results, which are found by adding standard manganese solutions into different water samples for determining manganese, are also given in Table 3 in detail. All of the results found with four replicate analyses were statistically in 95% confidence interval. The relative standard deviations less than 2.5% were evaluated in the analysis of bottled drinking waters for 1.34 - 1.64 ng mL<sup>-1</sup> manganese. Also, the recovery results prove clearly the accuracy and validity of kinetic spectrophotometric method described in the present study.

The proposed method was applied to the determination in some environmental water samples such as river, lake, hot- and cold-spring water. After being collected, the samples were filtered with membrane filter having the pore size of 0.45 µm and the filtrates were acidified at approximately pH 3.50 by adding 5.0 M HCl. After pretreatment at suitable dilution ratios, in order to control a possible systematic error, both the calibration curve method and standard addition method were carried out. Applications of standard addition yielded linear calibration curves with the same slopes as that of standard calibration curves and showed reasonably good agreement in manganese concentrations determined by both methods. These results show that the proposed method gives reasonably precise and accurate determinations, especially from the standpoint of trace metal analysis with

**Table 4.** Determination of manganese in certified standard river water (JAC-0031) and some environmental water samples such as river, lake, hot- and cold-spring water

Samples	Mn added (ng mL <sup>-1</sup> )	Mn found <sup>a</sup> (ng mL <sup>-1</sup> )	Mn in sample (ng mL <sup>-1</sup> )	Recovery (%)	RSD (%)
River water after dilution at 1:1000 ratio (Kızılırmak, Sivas)	0	2.48 ± 0.02 (2.47 ± 0.02) <sup>c</sup>	-	-	0.81
	0.5	3.01 ± 0.02	-	106	0.66
	1.0	3.51 ± 0.02	-	103	0.57
Lake water after dilution at 1:250 ratio (Hafik, Sivas)	0	1.35 ± 0.02 (1.36 ± 0.02)	-	-	1.48
	1	2.37 ± 0.02	-	102	0.84
	2	3.37 ± 0.02	-	101	0.59
Hot-spring water after dilution at 1:250 ratio (Sivas)	0	0.76 ± 0.02 (0.78 ± 0.02)	-	-	2.63
	1	1.78 ± 0.02	-	102	1.12
	2	2.80 ± 0.02	-	102	0.71
Cold-spring water after dilution at 1:250 ratio (Sivas)	0	1.03 ± 0.02 (1.05 ± 0.02)	-	-	1.94
	1	2.05 ± 0.02	-	100	0.98
	2	3.07 ± 0.02	-	97.0	0.65
JAC-0031 <sup>b</sup>	0	0.23 ± 0.02 (0.23 ± 0.02)	0.46 ± 0.02	-	4.35
	1	1.24 ± 0.02	-	101	1.62
	2	2.24 ± 0.02	-	100.5	0.89
	3	3.24 ± 0.02	-	100.3	0.62

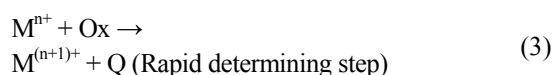
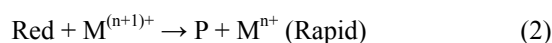
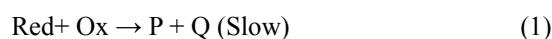
<sup>a</sup>Average values plus their standard deviations for four replicate measurements. <sup>b</sup>Dilution, 1/2; certified value (ng mL<sup>-1</sup>), 0.46 ± 0.02. <sup>c</sup>Values in paranthesis are the results of applying the standard addition method.

very simple procedure. In order to validate the present method, the recovery tests were also made by adding two standard Mn(II) solutions at known concentrations Analytical results are summarized in *Table 4*. The recovery values obtained were highly good. In order to test the analytical validation of the newly developed kinetic method, the method was also applied to the determination of Mn(II) in certified standard river water sample. The standard reference material was employed without any pretreatment procedure. For comparison of the results found by using the present method, the standard reference water sample was also analyzed by recoveries of the Mn(II) spiked water samples. It was found that the results obtained by the present method were in agreement with the certified value. To confirm both the accuracy and precision of the kinetic method with the recovery experiments, the known amounts of Mn(II) were added to the certified sample solution. The results are shown in *Table 4*. The recovery of spiked Mn(II) was found to be quantitative and the reproducibility was satisfactory. It was observed that the results obtained with the certified reference material, JAC-0031 were in good agreement with the certified value. Application of t-test to the results of the proposed method and the certified values for manganese demonstrated that there were no significant differences at the 5% probability level for the results. It can be concluded that the proposed kinetic method for determining the trace amounts of Mn(II)

available in real samples is a useful and applicable method.

#### The catalytic reaction mechanism

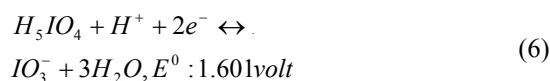
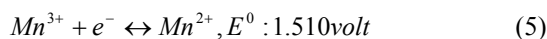
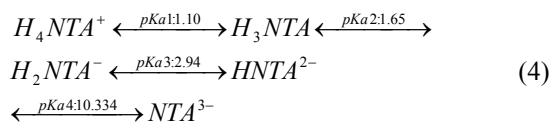
A detailed study of the kinetics of a catalytic indicator reaction is necessary for obtaining a complete understanding of the system and helpful for designing new methods and recovery technologies. Moreover, knowledge of kinetic parameters like apparent rate constant (k) and apparent activation energy (E<sub>a</sub>) is desirable for strict control of the experimental conditions (e.g. temperature, pH, reaction time). Kinetic laws and reaction mechanisms of different studies have been reported. In indicator reactions, the catalyst usually changes its oxidation state during the reaction in a cyclic manner as exemplified below:<sup>30</sup>



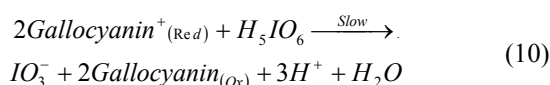
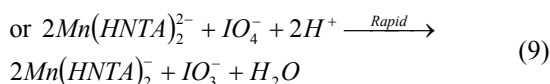
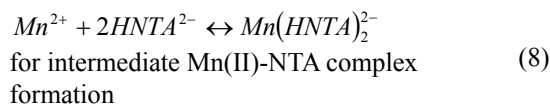
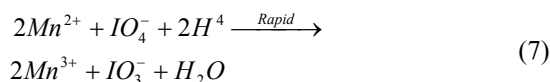
where Red and Ox are the reactants of a redox system and P and Q are the reaction products. When an ion M<sup>(n+1)+</sup> acts as a catalyst, it accelerates the formation of the product P and is then reduced to a lower oxidation state, M<sup>n+</sup>. If M<sup>n+</sup>



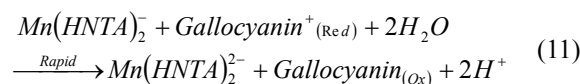
is oxidized again to  $M^{(n+1)+}$  by reaction (3), the oxidation of Red to P is catalyzed by a minute amount of  $M^{(n+1)+}$ . Even small amounts of catalyst at subnanogram levels can effect high conversions of Red to P. As the concentration of the catalyst is directly proportional to the rate of reaction, the reaction rate can be employed for the determination of catalyts. The kinetics of the uncatalyzed and the Mn(II)-catalyzed oxidation of Galloctyanin by  $KIO_4$  has been studied in presence of NTA as an activator. The absorbance of Galloctyanin at 620 nm was found to be dramatically decreased by the presence of Mn(III) or  $Mn(HNTA)_2^-$ , and the absorption spectrum of oxidation product was the same as that obtained from Galloctyanin oxidation by  $KIO_4$  at pH 3.50. The possible catalytic reaction mechanism for the indicator system at pH 3.50 may be indicated by a series of reactions as follows:



Because the pH of catalytic reaction system is 3.50, the predominant species of NTA present in media is  $HNTA^{2-}$ . In presence of Mn(II) at trace levels, this activating species reacts with  $Mn^{2+}$  ions forming stable  $Mn(HNTA)_2^{2-}$  complex. In presence of activator, this intermediate Mn(II)-NTA complex participates into the catalytic cycle in the kinetic determination of manganese(II) at pH 3.50.



In presence of  $Mn(HNTA)_2^-$ ;



The concentration of Mn(III) or  $Mn(HNTA)_2^-$  complex in (9) was greatly increased with increasing temperature in the range of 10 - 30 °C, which improved the decoloration rate of Galloctyanin (11), thus the reaction rate was effectively enhanced on Galloctyanin oxidation by  $KIO_4$ . The calculated apparent activation energy ( $E_A = 22.48 \text{ kJ mol}^{-1}$ ) was in line with the need for a low reaction temperature of 30 °C.

## CONCLUSIONS

In conclusion, catalytic spectrophotometric detection based on the oxidation of Galloctyanin by  $KIO_4$  at pH 3.50 acetate buffers and 30 °C is proved to be a new attractive approach for the determination of trace amounts of Mn(II) in natural waters. The use of NTA as an activator in acetate media makes efficiently it easy to monitor the present catalytic processes successfully. The present approach was found to provide a very simple method with high sensitivity and selectivity. Any sample treatment other than initial filtration and simple acidification which does not require close control of acidity are not needed and removal of reducing species such as Fe(II),  $NO_2^-$  and  $S^{2-}$  from the initial solution media with  $HNO_3$  and  $H_2O_2$  is the only major operation involved in the catalytic determination. The precision and accuracy of the proposed kinetic method are satisfactory in the application to natural waters such as river and lake waters.

The proposed kinetic method is based on the catalytic effect of Mn(II) on the oxidation of Galloctyanin by  $KIO_4$  in presence of NTA as an activator at pH 3.50 acetate buffer. In order to determine the manganese at trace levels, the sensitivity and selectivity of newly developed kinetic method is highly good even in presence of reducing species such as Fe(II),  $NO_2^-$  and  $S^{2-}$ . Therefore, the newly kinetic method, which is developed for determining the manganese present in real life samples such as hot and cold spring water, lake water, river water and various natural drinking water samples, except for complex seawater with high salt contents has a great analytical potential. It was verified with the results of the analysis of three different drinking water samples, some environmental water samples and certified reference river water sample, JAC-0031 (Table 3 and 4). The data presented in Table 3 and 4 to determine Mn(II) in real samples have

**Table 5.** Comparison of the proposed kinetic method with other Mn(II)-catalyzed kinetic methods previously mentioned in literature

Indicator reaction	Dynamic range (ng m <sup>-1</sup> )	Detection limit (ng mL <sup>-1</sup> )	Conditions (Temperature, λ <sub>max</sub> , method)	Type of samples	Kinetic parameters and remarks	References
Nile blue A+H <sub>2</sub> O <sub>2</sub>	6.6-65.9	0.08	640 nm, 25 °C, initial rate method	Mineral water	Ribavirin as activator and thiaofurin as inhibitor	[31]
Methylthymol blue+H <sub>2</sub> O <sub>2</sub>	0.2-40	0.64	610 nm, 70 °C, fixed time method, 15 min	Mongolian medicine	k: 5.62 × 10 <sup>-4</sup> s <sup>-1</sup> , E <sub>a</sub> : 73.2 kJ mol <sup>-1</sup>	[32]
Naphtol blue black+H <sub>2</sub> O <sub>2</sub>	0.08-4	0.025	618 nm, 60 °C, fixed time method, 5 min	Cucumbers, garlic cloves and parsley leaves		[33]
1,3-Dimethyl-2 [4-N(N,N-dimethylamino)phenazo]im idazolium perchlorate + KIO <sub>4</sub>	0.1-4.5	0.03	540 nm, 70 °C fixed time method, 5 min	Medicinal plants	1,10-phenantroline as activator	[34]
Tropaeolin+KIO <sub>4</sub>	0.05-2.5	0.02	445 nm, fixed time method	Dococtions of some medicinal plants	1,10-phenantroline as activator	[35]
2',4'-Dihydroxy-azobenzen-4-sulphonic acid sodium salt	0.1-5	0.03	490 nm, 70 °C fixed time method, 8 min	Dococtions of some medicinal plants	1,10-phenantroline as activator	[36]
Alizarin green+KIO <sub>4</sub>	0.4-2.4	0.097	620 nm, 80 °C fixed time method, 6 min	Cereal and wine samples	NTA as activator and β-cyclodextrin as sensitizer	[37]
Dahlia violet+KIO <sub>4</sub>	0.4-5.6	0.0375	580 nm, 70 °C, fixed time method, 14 min	Foodstuff samples	NTA as activator and nonionic microemulsion system k: 1.31 × 10 <sup>-3</sup> s <sup>-1</sup> , E <sub>a</sub> : 10.2 kJ mol <sup>-1</sup>	[38]
Nile blue+KIO <sub>4</sub>	0.4-5.6	0.054	634 nm, 50 °C fixed time method, 11 min	Water samples and vegetables	NTA as activator and cetylpyridinium bromide as sensitizer	[39]
Azure II+KIO <sub>4</sub>	0.4-2.0; 2.0-6.0	0.053	655 nm, 75 °C, fixed time method, 12 min	Tea sample	NTA as activator and dodecyl dimethylamino acetic acid as sensitizer	[40]
Gallocyanin-KIO <sub>4</sub>	0.1-4.0	0.025	620 nm, 30 °C, fixed time method, 5 min	Environmental water samples	NTA as activator, E <sub>a</sub> : 22.48 kJ mol <sup>-1</sup>	The present method

shown that the performance of the proposed kinetic method is a very good. Due to the relatively high selectivity of the method, for removal of reducing species Fe(II), NO<sub>2</sub><sup>-</sup> and S<sup>2-</sup> ions depending on pH of environment, there is no need for any separation and preconcentration except for prefiltration and acid treatment. The current method is simple and fast, but also without the need to make any separation and preconcentration can be used to determine Mn(II) at low levels. The kinetic method is a comparable method with many of spectrophotometric and kinetic spectrophotometric methods reported in the literature in view of selectivity and sensitivity, so it can be successfully implemented for trace analysis of the manganese in real samples. The main advan-

tage of the proposed method is related to its selectivity and sensitivity, simple procedure, and short analysis time in comparable levels when comparing with the other kinetic methods previously reported in literature.

A comparison between the proposed method with the previously reported methods for kinetic spectrophotometric determination of Mn(II) (Table 5) indicates that this method provides a lower detection limit and/or wider linear range for the determination of trace quantities of Mn(II) present in real samples.<sup>14,15,21-23</sup>

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