

## Kinetic-spectrophotometric determination of manganese

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**Abstract.** A simple and fairly selective kinetic method has been developed for the determination of manganese(II) based on its catalytic activity on the autoxidation of *o*-hydroxyphenylthiourea (OHPTU). It is found that the rate of the reaction is proportional to the concentration of manganese(II) ions. The reaction is carried out in a borate buffer of pH 7.5 and determined effectively in the range of 0.05–0.50  $\mu\text{g}$  of manganese per ml. The methods of tangents and of fixed time are employed. The former method is more accurate than the latter. The present method has been applied to foodstuff like cabbage, tomato and potato wherein manganese plays a vital role in various physiological functions. Many associated metal ions do not interfere in the determination.

**Keywords.** Manganese(II); *o*-hydroxyphenylthiourea; catalytic action; autoxidation.

### 1. Introduction

The concept of kinetic methods of analysis, especially those based on catalysed reactions, for determination of trace elements has gained considerable importance in analytical chemistry as is evident from the literature (Mottola and Mark 1982; Yatsimirskii 1966; Harris and Kratochvil 1981; Laitinen and Harris 1975) because of their simplicity, sensitivity and fairly wide selectivity over the activation analysis and atomic absorption spectrophotometric methods. In the present investigation, the catalysed autoxidation reaction is monitored with an ordinary spectrophotometer which is simple, less expensive and easily available to researchers in developing countries like India. The present method can be well adopted to determine manganese, an essential micronutrient, in foodstuff.

### 2. Experimental

#### 2.1. Reagents

All the chemicals used are of AnalaR grade.

*Manganese(II) solution:* About 3.0768 g of manganese sulphate monohydrate is weighed exactly, dissolved and made up to 250 ml with distilled water. The solution is standardised with EDTA (Vogel 1962).

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*o*-Hydroxyphenylthiourea (OHPTU): It is prepared as per the standard procedure given in Beilstein (1943). The reagent solution (1 mg/ml) is prepared in 95% ethanol just before use.

Michaeli's borate buffer of pH 7.5 is prepared.

## 2.2 Apparatus

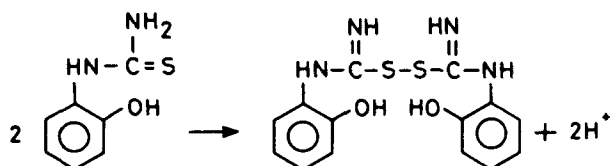
Toshniwal Spectrophotometer model RL02 and Elico pH meter model L1-10 were used in the present investigation. The plant samples were dried in a muffle furnace (Tempo).

## 2.3 Procedure

An aliquot of manganese solution (1.0–12.5  $\mu\text{g}$ ) was transferred to a 25 ml standard flask. 2.5 ml of the reagent solution (1 mg/ml) and 10 ml of borate buffer (pH 7.5) were added to the same flask. The solution was made up to the mark with distilled water and absorbance of the solution was measured with time using a reagent blank at 416 nm.

## 3. Results and discussions

OHPTU undergoes autoxidation with the formation of yellow coloured disulfide, 1,1'-dithiobis N-(*o*-hydroxyphenyl)-formamidine, which is confirmed by analysis (Santhanam 1964; Feigl 1966). The reaction may be represented as



The above reaction is very slow and the rate of the reaction increases abruptly in the presence of microquantities of manganese. The increase in the concentration of manganese increases the rate of the catalysed oxidation and it is found from the results that the rate of the reaction is proportional to the concentration of manganese. The  $\lambda_{\text{max}}$  values for OHPTU and its disulphide are 280 and 416 nm respectively. Despite the wide difference in  $\lambda_{\text{max}}$  values, the reagent has some absorbance at 416 nm. However, this can be compensated by measuring absorbance against a reagent blank. In the present studies the 'method of tangents' is followed. The plot of slope against concentration of manganese is linear (figure 1) in the range of 0.05–0.50  $\mu\text{g}/\text{ml}$ .

The reaction rate is sufficiently fast in borate buffer of pH 7.5–8.0. The catalysed autoxidation is slow below pH 5.0 and the uncatalysed reaction itself is fast above pH 10.5. The rate of the reaction is enhanced on raising the temperature of the system. Hence, the reaction system is maintained at laboratory temperature by keeping it in a thermostat bath. The sensitivity of the reaction is improved by the addition of 1 ml of 0.05 M ethylenediamine as evidenced by increase in the value of the slope from 1.0 to 1.3

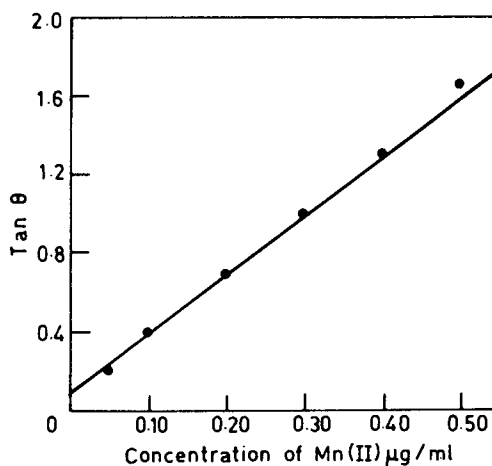


Figure 1. Calibration curve for determination of manganese(II) by the tangents method.

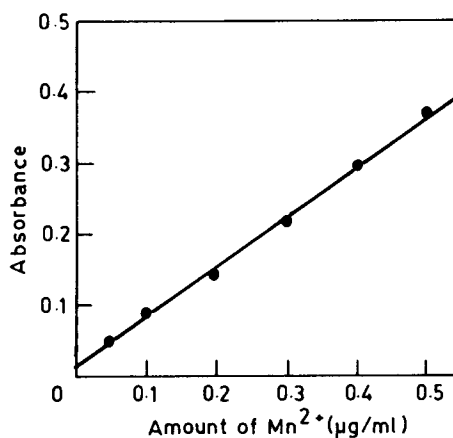


Figure 2. Calibration curve for determination of manganese(II) by the fixed time method.

for 0.3  $\mu\text{g}$  of manganese per ml. It is observed that 2.0 mg of the reagent is sufficient for the investigation.\*

Metal ions like aluminium(III), molybdenum(VI), tungsten(VI), gold(III), platinum(VI), vanadium(V) and zinc(II) do not interfere upto 35-fold excess by weight whereas cobalt(II), palladium(II) and silver(I) interfere by slightly enhancing the reaction rate when they are present below 20-fold excess. The interference of iron is eliminated by the addition of fluoride. Among the anions chloride, sulphate, nitrate and fluoride have no effect on the determination.

\*The precision of the method is determined by taking 10 measurements each containing 0.3 mg of metal. The relative standard deviation is found to be 1.53%.

**Table 1.** Determination of manganese in some kinds of food stuff

Sample	Mn(II) found by	
	the present method ( $\mu\text{g/g}$ )*	the periodate method ( $\mu\text{g/g}$ )
1. Cabbage ( <i>Brassica oleracea capitata</i> )	11.9	12.1
2. Potato ( <i>Solanum tuberosum</i> )	5.8	5.8
3. Tomato ( <i>Lycopersicon esculentum</i> )	9.8	9.7

\*An average value for five determinations.

#### 4. Application

The present method has been applied for the determination of micro quantities of manganese present in plant materials like cabbages, tomatoes and potatoes. The samples are thoroughly washed, dry ashed and made into solution as per the procedure of Chapman and Pratt (1961). The amounts of manganese in the above samples are computed from the calibration plot and are comparable with the values obtained by the standard periodate method (Vogel 1962) for the same samples (table 1).

#### 5. Conclusions

The method developed here is simple and does not require any sophisticated or complicated equipment. The accuracy of the method is improved by following the 'method of tangents'. This method is applied to plant materials for determination of the manganese present.

#### Acknowledgements

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