Chem. Pharm. Bull. 23(10)2376—2380(1975) UDC 545.81 : 547.783.9.04 : 546.712.04

Studies on 3-Substituted-2-thiohydantoins as Analytical Reagent. III.[1) Determination of Trace Amounts of Manganese by Catalytic Oxidation of 3-Ethyl-2-thiohydantoin

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(Received March 27, 1975)

A highly sensitive method for the determination of trace amounts of Mn(II) is based on the catalytic effect of Mn(II) on the autoxidation of 3-ethyl-2-thiohydantoin (ETH). Under given conditions of concentrations of reactants, temperature and reaction time, the coloration due to the oxidation of ETH in alkaline solution is proportional to the concentration of Mn(II) present. Mn(II) is determined by measuring the absorbance of the colored sample solution at 500 nm. Concentrations in the range of 2 to 16 ng of Mn(II) may be determined. The present method was applied to the analysis of natural water.

Based on the consideration of sensitivity and specificity, catalytic methods have offered an excellent alternative choice for the determination of trace concentration of many elements. Catalytic oxidation of some organic compounds such as alizarin S,[3) eriochrom black T,[4) leucomalachite green,[5) and *o*-dianisidine[6) have been employed in a trace analysis of Mn(II). Catalytic reaction between potassium permanganate and oxalic acid has also been reported for trace determination of Mn(II).[7)

In the previous paper,[1) we have described the color reaction of 3-methyl-2-thiohydantoin (MTH), which is based on the formation of highly colored bis(3-methyl-2-thiohydantoinylidene-5) in alkaline media, is catalyzed by the presence of Mn(II). In the present study, 3-ethyl-2-thiohydantoin (ETH) was selected for the most sensitive reagent from some 3-substituted-2-thiohydantoins investigated, and the catalytic oxidation was applied to the determination of trace amounts of Mn(II).

Experimental

All glasswares used were treated with 10% HCl for 12 hr and then washed with water. Redistilled water was used in all experiments unless otherwise noted. All chemicals used in this study were of analytical reagent grade.

Reagents——ETH was prepared from ethyl isothiocyanate and glycine, a method for the phenyl derivative[8) being applied, and recrystallized twice from water, mp 143—144°. The compound was slightly soluble in cold water and easily soluble in acetonitrile, dioxane and EtOH. *Anal.* Calcd. for $C_5H_8ON_2S$: C, 41.63; H, 5.60; N, 19.43. Found: C, 41.93; H, 5.82; N, 19.22. Acetonitrile solution (10^{-2}M) was prepared and used in aliquots as needed. This solution was stable for about one month.

Mn(II) Stock Solution——The solution (10^{-2}M) was prepared by dissolving 0.1979 g of $MnCl_2\cdot 4H_2O$ in 100 ml of water containing a few drops of concentrated HCl. This solution was standardized by titration with ethylenediaminetetraacetic acid.

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1) Part II: A. Sugii, M. Matsuo, and Y. Ohara, *Chem. Pharm. Bull.* (Tokyo), **22**, 1366 (1974).
2) Location: *Oe-honmachi, Kumamoto.*
3) T.J. Janjic, G.A. Milovanovic, and M.B. Celap, *Anal. Chem.*, **42**, 27 (1970).
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Buffer Solution——A sodium borate–boric acid buffer solution was prepared by dissolving 13.4 g of sodium borate and 3.7 g of boric acid in water and diluting up to 1000 ml.

Apparatus——Spectrophotometric measurements were carried out in the same manner as described in a previous paper.[9]

Standard Procedure——Take 1.0 ml of sample solution containing less than 16 ng of Mn(II), 1 ml of the reagent solution (10^{-2}M), 1 ml of 10^{-2}M potassium cyanide and 5 ml of the buffer solution in a 10 ml volumetric flask. After the solution is diluted to the mark with water, the solution is kept at 50±0.5° in a thermostat for 2 hr. Then it is cooled quickly with tap-water to stop the reaction, and the absorbance is read at 500 nm using a similarly treated reagent blank as a reference.

Separation and Identification of Colored Substance——Reddish brown precipitate was obtained by acidification of red colored solution which was prepared from 1 ml of 0.1M ETH acetonitrile solution, 50 ml of the borate buffer solution and 1 ml of 10^{-5}M Mn(II). The resultant precipitate was washed with EtOH twice. The elemental analyses and spectral data of this compound were identical with those of bis(3-ethyl-2-thiohydantoinylidene-5) which was prepared by a known synthetic method for phenyl derivative.[10] mp>350°, *Anal.* Calcd. for $C_{10}H_{12}O_2N_4S_2$: C, 42.22; H, 4.20; N, 19.71. Found: C, 42.31; H, 4.33; N, 19.55. Mass Spectrum *m/e*: 284 (M^+), 213 (M^+–$CONC_2H_5$), 197 (M^+–$CSNC_2H_5$), 169 (M^+–$CSNC_2H_5CO$).

Result and Discussion

Spectral Characteristics

3-Substituted-2-thiohydantoins show an analogous red coloration in alkaline solutions containing small amounts of Mn(II). In this experiment, ETH was chosen for the reagent because this showed the highest sensitivity among the tested thiohydantoins, namely MTH, ETH and 3-phenyl-2-thiohydantoin. Fig. 1 shows the absorption spectra, in the useful portion of the visible region, of a colored solution of ETH in the presence of trace amounts of Mn(II) and potassium cyanide and of a solution of authentic Bis-ETH. The shapes of the absorption spectra for the colored solutions of ETH are identical with that of Bis-ETH. In addition, mass spectrum and data of elemental analysis of the colored substance support the structure of Bis-ETH. Accordingly, it is clear that the coloration of ETH in alkaline solutions is due to the formation of oxidation product (Bis-ETH) as well as the MTH previously reported.[9]

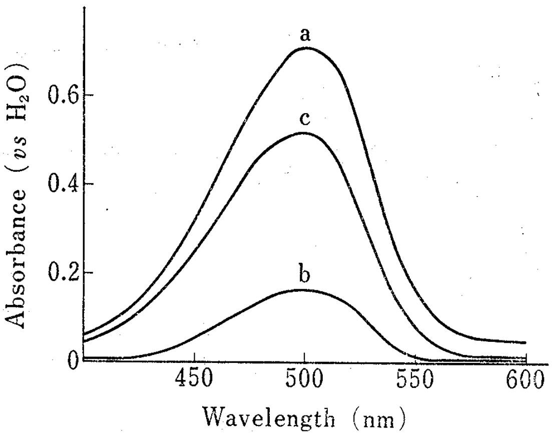

Fig. 1. Absorption Spectra of Colored Solution of ETH and Bis-ETH

reaction conditions: potassium cyanide (1×10^{-3}M) buffer (50%), acetonitrile (10%), pH (9.2), reaction time (2 hr, at 50°)
a : 1×10^{-3}M ETH, 2×10^{-8}M Mn(II)
b : 1×10^{-3}M ETH, without Mn(II)
c : 1.6×10^{-5}M Bis-ETH, 2×10^{-8}M Mn(II)

Determination of Reaction Conditions

Although the color development of ETH is affected by its concentration, the concentration was held constant at 1×10^{-3}M in this experiment because the color reaction attained equilibrium more rapidly in this concentration.

The autoxidation of ETH in the presence of Mn(II) is very sensitive to pH and reaction temperature. Fig. 2 and Fig. 3 show the effect of pH and temperature on the color development of ETH, respectively. The highest sensitivity can be realized at 50° for the reaction time of 2 hr in the solution of pH 9.2—9.3. Accordingly, this condition was selected for the standard procedure.

Since it is known that the autoxidation of organic compounds is affected by the presence of some organic solvents, the effect of solvents on the color development of ETH in the presence

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[9] A. Sugii, Y. Ohara, and K. Kitahara, *Chem. Pharm. Bull.* (Tokyo), 22, 109 (1974).
[10] R. Mayer and H. Tiem, *J. Prakt. Chem.*, 27, 213 (1965).

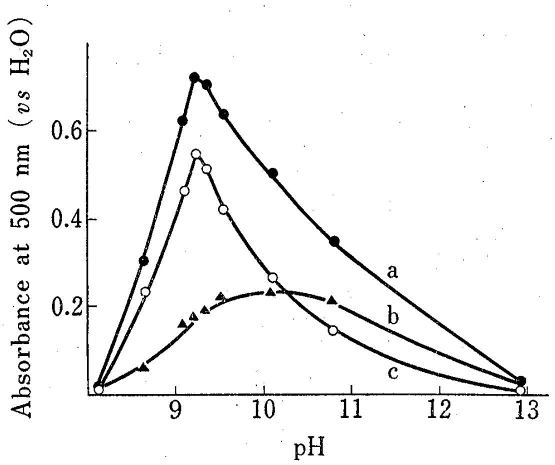

Fig. 2. Effect of pH

Reaction conditions are the same as Fig. 1-a,c except for pH.

a : 2×10^{-8}M Mn(II)
b : without Mn(II)
c : differences between a and b

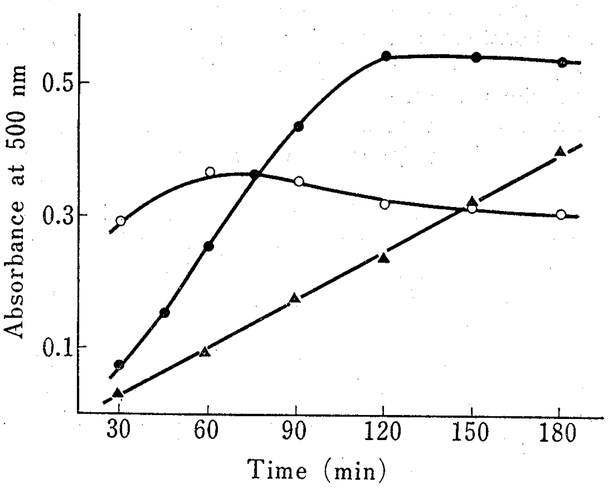

Fig. 3. Effect of Reaction Temperature

Reaction conditions are the same as Fig. 1-c except for temperature and absorbances are measured against reagent blank.

—▲—: 40°, —●—: 50°, —○—: 60°

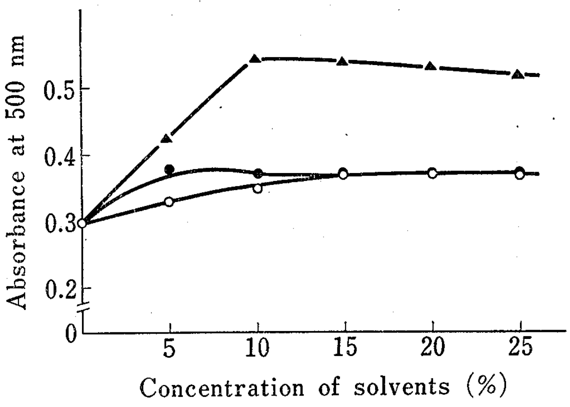

Fig. 4. Effect of Solvents

Reaction conditions are the same as Fig. 1-c except for solvent and absorbances are measured against reagent blank.

—▲—: acetonitrile, —●—: dioxane —○—: ethanol

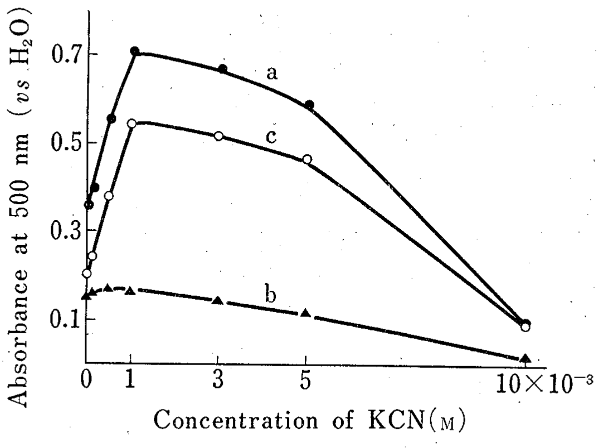

Fig. 5. Effect of Concentration of Potassium Cyanide

Reaction conditions are the same as Fig. 1-a, c except for potassium cyanide.

a : 2×10^{-8}M Mn(II)
b : without Mn(II)
c : differences between a and b

of Mn(II) was investigated. As is shown in Fig. 4, the highest sensitivity is obtained in the presence of acetonitrile, and all other experiments were carried out in the solution containing 10% (v/v) acetonitrile.

During the investigation of the effect of masking agent, it was found that the addition of potassium cyanide showed not only masking effect for some interfering metal ions, such as Cu(II) and Co(II), but also enhancement of color development. Fig. 5 shows the effect of concentration of potassium cyanide. When the concentration of potassium cyanide is 1×10^{-3}M the highest sensitivity is obtained. Thus the standard procedure was carried out in 1×10^{-3}M potassium cyanide solution. The reason of enhancement of color intensity with potassium cyanide is not yet clear. The details are now under investigation.

Calibration Curve and Sensitivity

Calibration curve obtained by the standared procedure passes through the zero point and is linear for 0—16 ng/10 ml of Mn(II). The sensitivity of the method, expressed as the weight of Mn(II) corresponding to an absorbance of 0.001 at 500 nm is 2.0×10^{-6} μg/cm². The minimum determinable amount is nearly equal to that of the kinetic method by using alizarin S.[3] In the measurement of 10 identical colored solutions containing 13 ng of Mn(II), the mean absorbance at 500 nm was 0.636 with a standard deviation of 0.025.

Influence of Diverse Ions

The influence of diverse ions on the determination of Mn(II) was investigated by adding the known amounts of test ions to a standard Mn(II) solution and by comparing the final absorbance with the standard. Table I shows that the presence of most of the ions investigated (Al(III), Ba(II), Ca(II), Hg(II), Mg(II), Ni(II), Zn(II), Ag(I), Cd(II), Co(II) and Cr(VI)) do not interfere the reaction at concentration 1×10^4 or 1×10^3 times with respect to Mn(II). However, the interference of some ions is not negligible when present more than 10 times; Cu(II) accelerates the reaction, while Pb(II), Fe(II) and Fe(III) decelerate the reaction. The interference of latter group may be concerned in the adsorption of Mn(II) with their hydroxides. On the other hand, chloride, carbonate, bromide, fluoride, nitrate, nitrite, phosphate, silicate, sulfate and ammonium ions do not interfere the color reaction, even when present in a 10^4 to 1 ratio.

Table I. Influence of Diverse Ions on the Determination of Mn(II)

Diverse ions	[Ion]/[Mn(II)][a]	Absorbance at 500 nm
—	—	0.544
Al(III)	1×10^4	0.526
Ba(II)	1×10^4	0.534
Ca(II)	1×10^4	0.564
Hg(II)	1×10^4	0.511
Mg(II)	1×10^4	0.572
Ni(II)	1×10^4	0.559
Zn(II)	1×10^4	0.530
Ag(I)	1×10^3	0.549
Cd(II)	1×10^3	0.557
Co(II)	1×10^3	0.550
Cr(VI)	1×10^3	0.510
Fe(II)	5×10	0.525
Cu(II)	1×10	0.543
Fe(III)	1×10	0.532
Pb(II)	1×10	0.536

a) concentration of Mn(II): 11 ng/10 ml

Determination of Mn(II) in Natural Water

The present method was applied to the natural water samples and the analytical results were compared with those obtained by the formaldoxime method.[11] As is shown in Table II,

Table II. Determination of Mn(II) in Natural Water

Sample number	Mn(II) by proposed method[a] μg/l	Mn(II) by formaldoxime method[b] μg/l
1	45 ± 3	43 ± 2
2	120 ± 12	110 ± 10

a) One ml of the sample solutions previously diluted to 5—10 times with water was employed for the color reaction.
b) Sample solutions concentrated to one-tenth volume were used for color development.

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[11] K. Goto, T. Komatsu, and T. Furukawa, *Anal. Chim. Acta*, **27**, 331 (1962).

both analytical results are in good agreement. Since the present method is more sensitive than the formaldoxime method, this method can be applied to the sample solutions containing smaller amounts of Mn(II) without troublesome concentration which may be responsible for error.

Conclusion

The proposed method is almost completely free from interference from several anions and cations and should find wide application where traces of Mn(II) are to be determined. Its outstanding features are that it is highly sensitive, rapid and no special calculation is necessary as kinetic method. Therefore, this method should be very convenient for routine analyses.

Acknowledgement The authors are indebted to Mrs. M. Ito, Mrs. K. Soe, Miss Y. Hamada, and Miss E. Fukunaga for their technical assistances.