

## A kinetic method for the determination of phenol

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**Abstract:** A kinetic method for the determination of phenol is proposed. The method is based on the inhibiting effect of phenol on the Mn(II) catalysis of the oxidation of malachite green with potassium periodate. The reaction rate was followed spectrophotometrically at 615 nm. Kinetic expression for the reaction in the presence and absence of phenol are postulated. The optimal experimental conditions for the determination of phenol were established and phenol was determined in concentrations from 30.0 to 188.0 ng/cm<sup>3</sup> with a relative standard deviation of 5.5 %. The lower detection limit is 7.8 ng/cm<sup>3</sup>. The effects of certain foreign ions upon the reaction rate were determined for the assessment of the selectivity of the method. The method was applied for the determination of phenol in tap and river water.

**Keywords:** phenol kinetic determination, malachite green oxidation, potassium periodate.

### INTRODUCTION

Phenols, defined as hydroxy derivatives of benzene and its condensed nuclei, may occur in domestic and industrial waste waters, natural waters and potable water supplies. Chlorination of such waters may produce odorous and objectionable-tasting chlorophenols. For that reason it is necessary to determine the phenols.

Advances have been made in phenols analyses using gas-liquid chromatographic procedure with flame ionization detector.<sup>1</sup> The method can be applied to samples containing more than 1 mg phenolic compounds in 1 dm<sup>3</sup>. Sensitive spectrophotometric methods have been used to determine lower concentrations of phenols based on the formation of colored antipyrine dye with 4-aminoantipyrine at high pH in the presence of potassium ferricyanide.<sup>1,2</sup>

Only a few kinetic methods for the determination of phenol have been reported. Price *et al.*<sup>3</sup> proposed a kinetic method for the determination of alkyl-, nitro- and chlorophenols at subppb levels based on peroxyoxalate chemiluminescence after liquid chromatographic separation.

In this paper a sensitive and simple kinetic method for the determination of phenol is proposed. The oxidation of malachite green (MG) with potassium periodate in an acetate

buffer solution gives a colorless product. The reaction is catalysed by traces of Mn(II) and is used for its kinetic-catalytic determination.<sup>4</sup> We observed that small amounts of pyridoxine hydrochloride and ascorbic acid strongly inhibit the catalysis of this reaction, a fact which was used for their kinetic determination.<sup>5,6</sup> In a continuation of our studies of the inhibiting effect, we have also observed that small amounts of phenol strongly inhibit the catalysis of this reaction. The rate of the reaction decreases proportionally with increasing concentration of phenol. This fact was used as the basis of the kinetic method for determining ultramicro amounts of phenol.

## EXPERIMENTAL

### *Apparatus*

A Perkin-Elmer Lambda 15 UV/VIS spectrophotometer connected to a thermocirculating bath, was used for the absorbance measurements. The absorbance of a solution was measured at 615 nm every 30 s over a period of 7 min from the onset of the reaction. The pH was measured by means of a Radiometer PHM 29b pH meter with a combined glass-calomel electrode. The solutions were thermostated at  $25 \pm 0.1$  °C before the beginning of the reaction.

### *Reagents*

A stock MG solution ( $1 \times 10^{-3}$  mol/dm<sup>3</sup>) was prepared by dissolving MG in deionised water. The working MG solution ( $4 \times 10^{-5}$  mol/dm<sup>3</sup>) was obtained by diluting the stock MG solution with water, and was used within 3 weeks of preparation.

The periodate solution ( $1 \times 10^{-3}$  mol/dm<sup>3</sup>) was prepared by dissolving potassium periodate in deionised water.

The acetic acid solution (10 mol/dm<sup>3</sup>) was prepared from 99.0 % reagent.

The phenol solution ( $1 \times 10^{-3}$  mol/dm<sup>3</sup>) was prepared by dissolving phenol in deionised water.

The Mn(II) solution ( $1 \times 10^{-5}$  mol/dm<sup>3</sup>) was prepared by dissolving manganese chloride in deionised water.

All chemicals were of analytical reagent grade and were provided by Merck unless indicated otherwise. All the stock solutions were stored in polyethylene containers. The working solutions of Mn(II), periodate and phenol were prepared immediately before the use. All the polyethylene containers and glassware used were cleaned in aqueous HCl (1:1) and then thoroughly rinsed with deionised water.

### *Procedure*

The selected volumes of reagents were transferred into a 10 cm<sup>3</sup> volumetric flask in the order: MG, acetic acid, catalyst and inhibitor. Water was added to give a predetermined volume. The flask was thermostated for 10 min and the solution was then made up to the mark with periodate and vigorously shaken. The spectrophotometer cell was rinsed well and filled with the solution. The absorbance at 615 nm was measured every 30 s over a period of 5 – 8 min after the addition of periodate. Instead of the reaction rate ( $dc/dt$ ), the quantity  $d \log A/dt$  was used. The measurements were made at  $25 \pm 0.1$  °C.

### *Determination of phenol in tap and river water by kinetic method*

One liter of freshly collected tap (river) water was filtered through a 0.45 µm Millipore filter and 0.05 g (0.094 g) of phenol was added to the filtrate. Phenol is distilled from nonvolatile impurities.

10.0 cm<sup>3</sup> of distilled phenol solution was diluted to 1000 cm<sup>3</sup> with freshly boiled and cooled deionised water; 1 cm<sup>3</sup> = 0.5 µg phenol in tap water (1 cm<sup>3</sup> = 0.94 µg phenol in river water). After these treatments, 1 cm<sup>3</sup> of the sample was used for the recommended procedure.

### *Determination of phenol in tap and river water by standard method*

One liter of freshly collected tap (river) water was filtered through a 0.45 µm Millipore filter and 0.050 g (0.094 g) of phenol was added to the filtrate. Cupric sulphate solution is added and the filtrate is transferred to an

all-glass still, acidified with phosphoric acid and distilled. Ammonium chloride solution is added to the distillate and the pH of the solution is adjusted to 10.0 by the addition of ammonium hydroxide solution. Following the addition of 4-aminoantipyrine and potassium ferricyanide solutions, the mixture is extracted with chloroform in a separatory funnel. The absorbance (at 460 nm) of the chloroform extract is measured in a spectrophotometer and the phenol concentration is determined from a calibration curve prepared with phenol.

## RESULTS AND DISCUSSION

### Kinetic studies

The kinetics of the catalytic reaction of potassium periodate and malachite green, both in the presence and absence of phenol was investigated by following the changes of  $\text{tg } \alpha$  when varying the concentration of one component while keeping the concentration of all the other reaction components constant. Figs. 1 – 5 show the effect of the individual components taking part in the reaction.

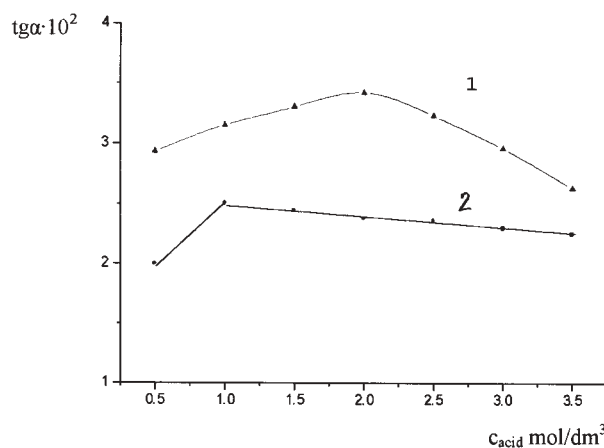


Fig. 1. Dependence of the rate of the catalyzed (1) and inhibited (2) reaction on the acetic acid concentration. Initial concentrations  $\text{mol/dm}^3$ : MG –  $1.6 \times 10^{-6}$ ,  $\text{KIO}_4$  –  $1 \times 10^{-4}$ ,  $\text{Mn(II)}$  –  $1.5 \times 10^{-6}$ , phenol –  $5 \times 10^{-7}$ ,  $t = 25 \pm 0.1$  °C.

Figure 1 shows the influence of pH on the rate of both reactions. It can be seen that the greatest difference between the reaction rates occurs at concentration of acetic acid 1.5

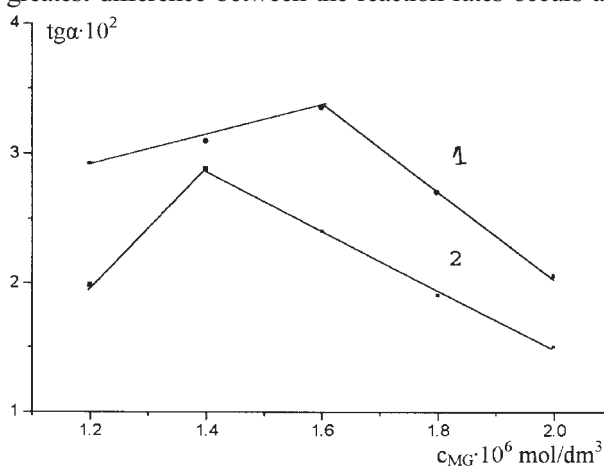


Fig. 2. Dependence of the rate of the catalyzed (1) and inhibited (2) reaction on the MG concentration. Initial concentrations  $\text{mol/dm}^3$ :  $\text{CH}_3\text{COOH}$  – 1.5,  $\text{KIO}_4$  –  $1 \times 10^{-4}$ ,  $\text{Mn(II)}$  –  $1.5 \times 10^{-6}$ , phenol –  $5 \times 10^{-7}$ ,  $t = 25 \pm 0.1$  °C.

mol/dm<sup>3</sup>, when phenol maximally decreases the catalytic reaction rate. From Fig. 1 it appears that there is a complicated relationship between the  $c_{\text{CH}_3\text{COOH}}$  and the catalytic and inhibited reaction rates, *i.e.*, the order of the reaction is variable with respect to the hydrogen-ion concentration for the range of concentrations studied.

The dependence of the reaction rate on the concentration of MG is shown in Fig. 2, which shows that the inhibited reaction is first order with respect to the MG concentration up to  $1.4 \times 10^{-6}$  mol/dm<sup>3</sup> and negative first order for higher concentrations, whereas the catalytic reaction is first order with respect to the MG concentration up to  $1.6 \times 10^{-6}$  mol/dm<sup>3</sup> and negative first order for higher concentrations. The maximal difference between the reaction rates in the presence and absence of phenol occurs at an MG concentration of  $1.6 \times 10^{-6}$  mol/dm<sup>3</sup>. This concentration is optimal and was used in further work.

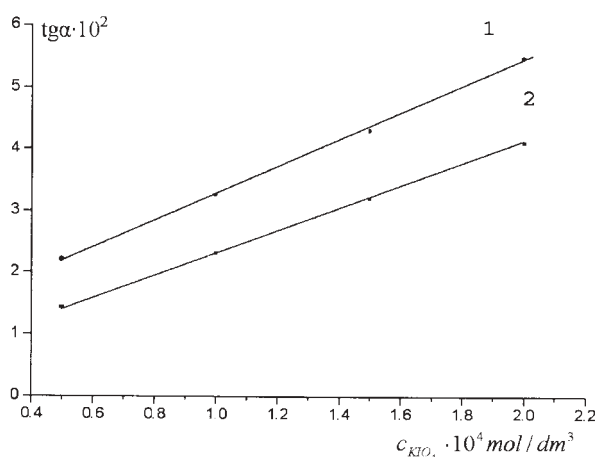


Fig. 3. Dependence of the rate of the catalyzed (1) and inhibited (2) reaction on the  $\text{KIO}_4$  concentration. Initial concentrations mol/dm<sup>3</sup>:  $\text{CH}_3\text{COOH} - 1.5$ ,  $\text{MG} - 1.6 \times 10^{-6}$ ,  $\text{Mn(II)} - 1.5 \times 10^{-6}$ , phenol  $- 5 \times 10^{-7}$ ,  $t = 25 \pm 0.1$  °C

It may be also seen, from Fig. 3 and Fig. 4 that the reaction rates increase with increasing concentration of the catalyst and potassium periodate. Both reactions are first order with respect to the catalyst and potassium periodate concentration. For further work the catalyst and

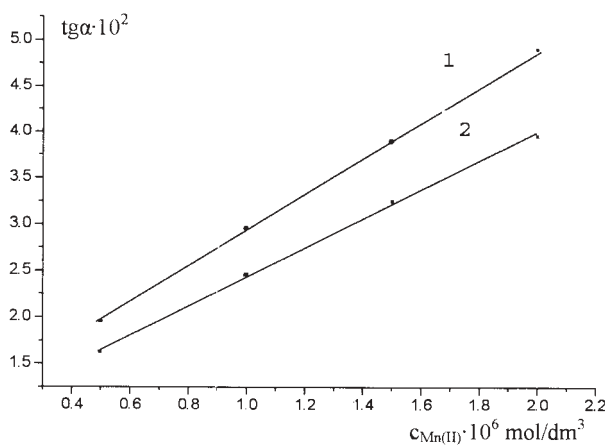


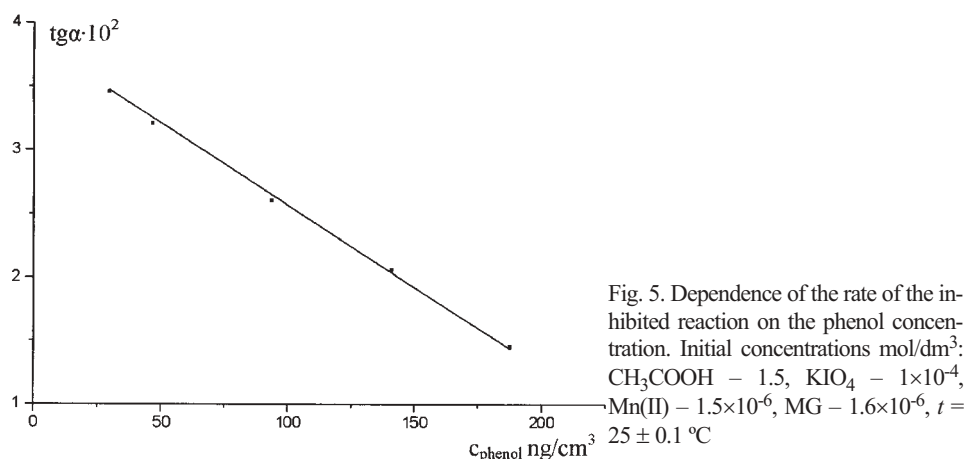
Fig. 4. Dependence of the rate of the catalyzed (1) and inhibited (2) reaction on the  $\text{Mn(II)}$  concentration. Initial concentrations mol/dm<sup>3</sup>:  $\text{CH}_3\text{COOH} - 1.5$ ,  $\text{KIO}_4 - 1.5 \times 10^{-4}$ ,  $\text{MG} - 1.6 \times 10^{-6}$ , phenol  $- 5 \times 10^{-7}$ ,  $t = 25 \pm 0.1$  °C

periodate concentrations of  $1.5 \times 10^{-6}$  mol/dm<sup>3</sup> and  $1.5 \times 10^{-4}$  mol/dm<sup>3</sup> were used, respectively, because at higher concentrations the linear part of the kinetic curve ( $\log A-t$ ) is rather short.

Under the optimal reaction conditions (MG –  $1.6 \times 10^{-6}$  mol/dm<sup>3</sup>, potassium periodate –  $1.5 \times 10^{-4}$  mol/dm<sup>3</sup>; Mn(II) –  $1.5 \times 10^{-6}$  mol/dm<sup>3</sup>; CH<sub>3</sub>COOH – 1.5 mol/dm<sup>3</sup>), the phenol concentration was varied from 30.0 – 188.0 ng/cm<sup>3</sup>. The calibration line which can be used for the determination of the phenol concentration in the interval mentioned is shown in Fig. 5. A linear dependence was established between  $\text{tg } \alpha$  and the concentration of phenol:

$$\text{tg } \alpha = -0.134 \cdot c_{\text{phenol}} + 0.0389 \quad (r = 0.994) \quad (1)$$

for phenol concentrations in the range 30.0 – 188.0 ng/cm<sup>3</sup>.



On the basis of all the obtained results, the following kinetic expressions were derived for the proposed indicator reaction in the absence and presence of phenol (at constant pH 3.36):

$$-\frac{d[\text{MG}]}{dt} = k_1 \cdot [\text{KIO}_4] \cdot [\text{MG}]^{-1} \cdot [\text{Mn}(\text{II})] \quad (2)$$

where  $k_1$  is a constant proportional to the rate constant of the catalyzed reaction and

$$-\frac{d[\text{MG}]}{dt} = k_2 \cdot [\text{KIO}_4] \cdot [\text{MG}]^{-1} \cdot [\text{Mn}(\text{II})] \cdot [\text{phenol}]^{-1} \quad (3)$$

where  $k_2$  is a constant proportional to the rate constant of the inhibited reaction.

The above equations are valid for the following concentration ranges: MG  $1.6 \times 10^{-6}$  –  $2.0 \times 10^{-6}$  mol/dm<sup>3</sup> (Eq. 2) and  $1.4 \times 10^{-6}$  –  $2.0 \times 10^{-6}$  mol/dm<sup>3</sup> (Eq. 3); KIO<sub>4</sub>  $0.5 \times 10^{-4}$  –  $2.0 \times 10^{-4}$  mol/dm<sup>3</sup> (Eqs. 2 and 3); Mn(II)  $0.5 \times 10^{-6}$  –  $2.0 \times 10^{-6}$  mol/dm<sup>3</sup> (Eqs. 2 and 3).

#### Analytical characteristics

On the basis of our kinetic investigations the chemical conditions for the kinetic method set out in the experimental part are proposed (Table I).<sup>7</sup> The spectrophotometric

method was also used. In both cases, the calibration graph is linear in the concentration range indicated in Table I. The accuracy and precision of the two methods applied for 47.0 ng phenol/cm<sup>3</sup> are included in Table I, from which it is concluded that the kinetic and spectrophotometric method has a negative systematic error and that both are accurate and precise. The kinetic method is simpler and more precise than the spectrophotometric method.

TABLE I. Linear concentration range, accuracy and precision of the methods for determination of phenol

| Method             | Concentration range<br>ng phenol/cm <sup>3</sup> | Relative standard<br>deviation (%) | $t_{\text{exp}}$    |
|--------------------|--|------------------------------------|---------------------|
| Kinetic            | 30–188   | 5.4                                | 0.96 ( $t = 2.77$ ) |
| Spectrophotometric | 10–100   | 6.8                                | 1.08 ( $t = 2.77$ ) |

The influence of foreign ions on the determination was investigated by the  $2S$  ( $S$ -standard deviation) criteria<sup>8</sup> for a phenol concentration of 94 ng/cm<sup>3</sup>. The presence (individually in the ratio to phenol given in the brackets) of B<sub>4</sub>O<sub>7</sub><sup>2-</sup>, Cu<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, F<sup>-</sup> (100:1), Sr<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Al<sup>3+</sup> (10:1), Co<sup>2+</sup>, Hg<sup>2+</sup> (1:1) have no practical effect upon the inhibited reaction. The presence of AsO<sub>2</sub><sup>-</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> (1:1) interfere.

TABLE II. Determinations of phenol in waters

| Sample      | Phenol (ng/cm <sup>3</sup> ) |                    |                              |
|-------------|------------------------------|--------------------|------------------------------|
|             | Taken                        | Found <sup>a</sup> |                              |
|             |                              | Kinetic method     | Spectrophotometric<br>method |
| River water | 94.00                        | 91.26 ± 1.28       | 90.90 ± 1.38                 |
| Tap water   | 50.00                        | 47.90 ± 1.34       | 47.18 ± 1.39                 |

<sup>a</sup>Mean of 5 determinations

The influence of some aromatic hydroxy compounds was also investigated. The presence of (individually in the ratio 1:1) resorcinol, pyrogallol and catechol interfere.

#### *Determination of phenol in waters*

Results obtained by application of a tangent variant of the kinetic method<sup>9</sup> as well as the spectrophotometric method for the determination of phenol in water samples are shown in Table II. The results were reproducible as indicated by the standard deviation values. The accuracy of the method was evaluated by statistical comparison of the results with those obtained by the spectrophotometric method, based on the reaction between phenol and 4-aminoantipyrine.

## ИЗВОД

## КИНЕТИЧКА МЕТОДА ЗА ОДРЕЂИВАЊЕ ФЕНОЛА

СНЕЖАНА С. МИТИЋ и ВАЛЕНТИНА В. ЖИВАНОВИЋ

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Предложена је нова кинетичка метода за одређивање фенола. Метода се заснива на инхибиторном дејству фенола у реакцији оксидације малахитног зеленог калијум-перјодатом, у киселој средини, коју катализује манган. Брзина реакције праћена је спектрофотометријски на 615 nm. Постављени су кинетички изрази за реакцију у присуству и одсуству фенола и нађени оптимални услови за његово одређивање. Фенол је одређиван у концентрацијама од 30,0 до 188,0 ng/cm<sup>3</sup>, са релативном стандардном девијацијом до 5,5 %. Граница детекције је 7,8 ng/cm<sup>3</sup>. Метода је примењена за одређивање фенола у чесменској и речној води.

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