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# Determination of chlorine in atmosphere by kinetic spectrophotometry

Jian-Xin Meng\*, Xiao-Bo Wang, Ge-Lan Ruan, Guo-Qiang Li, Zhao-Xia Deng

Department of Chemistry, Jinan University, Guangzhou 510632, China

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# Abstract

A kinetic method for determination of chlorine in air was described in the present work. The method based on fading of methyl orange (MO) containing solution in air absorption process. A determination limit of 2.64  $\mu$ g L<sup>-1</sup> was found. With the present method, chlorine concentration could be determined in several minutes with convenient manipulation. As concentration variation of methyl orange in the absorption solution did not affect the experimental results, fabrication and preservation of the stock absorption is also convenient. The present method is promising in monitoring chlorine concentration in atmosphere.

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# 1. Introduction

A lot of methods have been applied to determine chlorine in atmosphere, most of them employ photometry technique [1,2], while the others based on chlorine sensitive sensors [3–8] or by barrier discharge radio frequency helium plasma [9]. Although the later technique is simpler, photometry methods often give more reliable results. Photometry using methyl orange (MO) has been recommended by the environmental protect council of People's Republic of China and is among the most widely used methods. Besides giving good accuracy and precision, the method has a wide linear range and is excellent in eliminate interfere of coexist HCl. However, the method is very onerous in manipulation owing to unstable of the stock solution, and results are prone to be interfered by temperature and concentration of the reagent. In the present paper, a kinetic method for chlorine determination also using MO as a color reagent was proposed. The method is convenient in manipulation. The principle of the method is based on the fading velocity of MO solution in air absorption process against concentration of chlorine, which was test with a self-made apparatus and satisfaction results was got.

# 2. Principle of the kinetic spectrophotometry

As a recommended method, the photometry method using MO as color reagent has been widely used in chlorine determination. In which the absorption solution contain MO, H<sub>2</sub>SO<sub>4</sub>, and KBrO<sub>3</sub>. In the recommended method, a definite volume of absorption solution containing with known absorbency  $(A_0)$  was put in a bubble absorption tube and effervesces with chlorine containing air samples. Several minutes later, the absorption solution faded and its absorbency  $(A_1)$ was measured. The difference  $\Delta A = A_0 - A_1$  was calculated. A working curve about  $\Delta A$  versus quantity of chlorine was made in advance, from which the quantity of chlorine in the air sample could be determined. Since  $A_0$  was taken as constant in the experiment, varying of  $A_0$  will influence value of  $\Delta A$  and thus the resulted chlorine concentration. As the absorption solution is unstable,  $A_0$  always change with time and thus the working curve must be regenerated frequently, which made the experimental manipulation very complicated.

Obviously, chlorine concentration of samples will directly influence the fading velocity of the solution. If we could measure color fading character of the solution, or varying of the solution absorbency in the air absorption process, the concentration of chlorine could be determined. An apparatus as shown in Fig. 1 was made to test varying of the solution absorbency in the air absorption process. Similar to the

<sup>\*</sup> Corresponding author. Tel.: +86 203 3011499.

E-mail address: tmjx@jnu.edu.cn (J.-X. Meng).

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Fig. 1. Diagram of the experimental setup.

recommended MO photometry, a definite volume of absorption solution was put into the absorption tube first, air sample was driven with an air compressor pump (Pump 1) to effervesce and chlorine in the sample was absorbed. To measure the varying of the absorbency, a flowing cell was connecting to bottom of the absorption tube. Absorption solution was drive to circulate between the tube and the cell by another wriggling pump (Pump 2). As absorption spectrum of the solution peaks at 510 nm, a ultra-bright LED with peak at 510 nm was used as light source. Transparent light was detected with a PIN photodiode. The signal was amplified and processed with a microcomputer equipped with an A/D converter card. Running of the wriggling pump could also be controlled with the computer.

With the above setup, varying curve of the transparent light intensity ( $I_t$ ) was recorded. A typical  $I_t-t$  curve was shown in Fig. 2. The curve could be divided into four stages: oa, ab, bc and cd. In the beginning stage oa, as solutions in the flowing cell and wriggling pump tube did not react with air sample, varying of  $I_t$  is very small. In stage ab, the  $I_t$  curve



Fig. 2. Typical  $I_t$ -*t* curves in Cl<sub>2</sub> absorption.

is linear, the slope of the curve is related with concentration of chlorine in samples. In the next stage bc, most MO in absorption solution was consumed, the fading velocity was determined by the concentration of MO and varying of  $I_t$ became slower. After all the MO was consumed, absorbency of the solution did not change any more and  $I_t$  keep constant as shown in stage cd.

According to Lambert-Beer's Law, the absorbency of the solution in the absorption process could be expressed as

$$A = \varepsilon bc = \frac{\varepsilon bn}{V} = \frac{\varepsilon b(n_1 - n_2)}{V} = \frac{\varepsilon bn_1}{V} - \frac{\varepsilon bn_2}{V}$$
(1)

where *V* is the volume of the absorption solution, *n* the quantity of MO in solution that varies in the absorption process,  $n_1$  the quantity of MO in the absorption liquid before the air sample is absorbed and  $n_2$  is that consumed in the reaction. A first-order derivative could be made to formula (1)

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -\frac{\varepsilon b}{V} \times \frac{\mathrm{d}n_2}{\mathrm{d}t} \tag{2}$$

Since  $A = -\log T = -\log(I_t/I_0) = -\log I_t + \log I_0$  and

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -\frac{\mathrm{d}(\log I_{\mathrm{t}})}{\mathrm{d}t} \tag{3}$$

We get

$$\frac{\mathrm{d}(\log I_{\mathrm{t}})}{\mathrm{d}t} = \frac{\varepsilon b}{V} \times \frac{\mathrm{d}n_2}{\mathrm{d}t} \tag{4}$$

in which  $(dn_2/dt)$  is the velocity of MO consumed during absorption.

Fading of MO in the absorption solution could be explained with the following mechanism:

$$Cl_2 + 2KBr \rightarrow 2KCl + Br_2$$

$$2Br_2 + (CH_3)_2NC_6H_4N = NC_6H_4SO_3Na$$
  

$$\rightarrow (CH_3)_2NC_6H_4NBr_2 + Br_2NC_6H_4SO_3Na$$

Experiment has been done on a air sample with 10% of Cl<sub>2</sub>, and fading of MO taken place instantly. It could be concluded that the velocity of both reaction are very large. Consuming of MO will take place as soon as Cl<sub>2</sub> is absorbed, and thus the fading velocity of MO,  $(dn_2/dt)$ , is determined by the absorbing rate of chlorine, which is proportional to the concentration of chlorine when the velocity of air is unchanged. Now we get  $d(\log I_t)/dt \propto c_{Cl_2}$  which means slope of logarithm of stage ab is proportional to the chlorine concentration in the air sample, and this relationship was applied to chlorine determination in the present work.

As calculation of logarithm was complicated, the following strategy was adopted in the experiment. Because stage ab is almost linear, the value of  $d(\log I_t)/dt$  could be determined with the equation  $d(\log I_t)/dt = (\log I_{t_2} - \log I_{t_1})/(t_2 - t_1)$ , where  $t_1$  and  $t_2$  are the time at which  $I_t = I_{t_1}$  and  $I_{t_2}$ , respectively. If the value of  $I_{t_1}$  and  $I_{t_2}$  were fixed up, the value of J.-X. Meng et al. / Spectrochimica Acta Part A 61 (2005) 823–827

log  $I_{t_2}$  – log  $I_{t_1}$  will be constant. We can get another expression  $1/(t_2 - t_1) \propto c_{\text{Cl}_2}$  or  $1/(t_2 - t_1) = Kc_{\text{Cl}_2}$ , where *K* is a proportional constant, which means, if we could measure  $t_1$  and  $t_2$ , chlorine concentration could be determined from a working curve.

# 3. Experimental

#### 3.1. Reagents

All the chemicals were of analytical reagent grade except MO, which was of indicator grade. All solutions were prepared with double distilled water.

#### 3.2. Absorption solution

A 0.1000 g of MO was dissolved in 60 mL water at  $\sim$ 50 °C and the solution was cooled to room temperature. After adding 60 mL ethanol, the solution was further diluted to 1 L with water to get a stock solution. One gram of potassium bromide was dissolved in 50 ml of the stock solution and dilute to 500 mL to get solution A. The absorption solution was fabricated by mixing 8 mL solution A and 2 mL 3 M sulfuric acid solution.

## 3.3. Standard air sample

Pure chlorine is made from reaction of potassium permanganate and concentrated hydrochloric acid. Which was desiccated with concentrated sulfuric acid and preserved in a glass bottle. To make a standard air sample, definite volume of pure chlorine was injected into a 10L glass bottle. The air was left to mix for more than 5 h before use. The above produce may be repeated if necessary to get a more dilute sample. Concentration of the standard air sample was confirmed before experiments with the recommended method [1].

## 3.4. General procedure for kinetic photometry

Ten milliliters of absorption solution was put into the modified bubble absorption tube. Pump 2 was controlled to run firstly for 2 s to ensure the flow cell give a stable signal. Then Pump 1 began to run and drive air sample effervescem in the absorption tube. In the mean time, the transparent light intensity was measured and recorded with the computer. With the present experimental apparatus,  $I_t$  is ~0.03 before air absorption (which may vary with the concentration of MO in the absorption solution) and 0.61 when all MO were consumed. After measuring large number of samples with different chlorine concentration, good linear was found between  $1/(t_2 - t_1)$ and  $c_{Cl_2}$  when  $I_{t_1} = 0.3$  and  $I_{t_2} = 0.5$ , which was adopted as  $I_{t_1}$  and  $I_{t_2}$  in the following experiments. The computer program was written to record  $I_t$ -*t* curve and output value of  $t_1$ and  $t_2$  after the experiment.

Fig. 3. Effect of the flow velocity of air samples.

# 4. Results and discussion

## 4.1. Effect of air flowing velocity

Air velocity could be adjusted with Pump 1 in the experimental setup.  $I_t-t$  curve at different air velocity were shown in Fig. 3. If the flow velocity of air sample is too large, effervesce in the absorption tube would be very furious and lead to unstable of the transparent intensity. Large air velocity also leads to small values of  $(t_2 - t_1)$  and thus big relative errors. Although a small velocity could give stable results, it cost too long time to be adopted. A favorable velocity should give medium values of  $(t_2 - t_1)$  and short analytical time. A velocity no more than  $0.5 \text{ L} \text{ min}^{-1}$  is appropriate for low concentration samples (no more than  $15.30 \text{ µg L}^{-1}$ ) and rise with chlorine concentration.

## 4.2. Effect of the absorption solution

Similar to the effect in MO photometry method, acidity of the absorption solution also affects fading velocity of the solution and thus shapes of  $I_t$ -*t* curve as shown in Fig. 4. High acidity caused fast fading and was favor to determination of low chlorine concentration sample, while low acidity was favor to that of chlorine rich sample. For most samples, an acidity of 0.25 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> was reasonable.

A big drawback for MO photometry method is complicated manipulation caused by unstable of the stock absorption solution. Since shift of  $A_0$  of the absorption will lead to great error in  $\Delta A$  and determination of chlorine concentration. However, value of  $(t_2 - t_1)$  and thus the experimental result are insensitive to shift of stock solution, as  $A_0$  is not used in the present technique. Experiment has been done with a stock solution preserved for 1 month at room temperature and similar result with a fresh prepared solution was found.





Fig. 4. Effect of acidity of the absorption solution.

#### 4.3. Effect of speed of Pump 2

The circulation speed of the absorption solution could be adjusted with Pump 2. It was found that varying of the circulation speed in a wide range made no obvious effect on the  $I_t$ -*t* curve. However, if the speed is too slow or too fast, wrong results may be got. A speed of 1.47 mL s<sup>-1</sup> was adopted in the following experiment.

## 4.4. Calibration curve

Determination of low concentration of chlorine in air sample was done with an absorption solution containing  $0.25 \text{ mol } \text{L}^{-1} \text{ H}_2 \text{SO}_4$ , speed of Pumps 1 and 2 was adjusted to  $0.4 \text{ L} \text{min}^{-1}$  and  $1.47 \text{ mL s}^{-1}$ , respectively. Good linearity was found between  $1/(t_2 - t_1)$  and concentration of chlorine in the range of  $2.64-15.30 \text{ } \mu \text{g} \text{L}^{-1}$  as shown in Fig. 5. The detection limits have been determined according to the formula  $c = 3\sigma/k$ , where  $\sigma$  is the standard deviation of the measurements of  $1/(t_2 - t_1)$ , k is the sensitivity calculated from the slope of the plot  $1/(t_2 - t_1)$  versus concentration. However, an air sample with big chlorine concentration could not be determined with the presented speed of wriggling Pump 1. Because the value of  $t_2 - t_1$  is too small for samples with large chlorine concentration, which would induce big error to value of  $1/(t_2 - t_1)$ . Determination of more



Fig. 5. Plot of  $1/(t_2 - t_1)$  versus concentration of chlorine.

Table 1Determination of chlorine in real samples

${(\mu g  L^{-1})}$	Found $(\mu g L^{-1})$		Average $(\mu g L^{-1})$	Recovery $R(\%)$		R.S.D. (%)
3.73	3.70 4.11	4.06 3.94	3.95	99.2 110.2	108.8 105.6	4.63
8.49	7.838 7.837	8.10 7.83	7.90	92.2 92.2	95.4 95.4	0.85

<sup>a</sup> Determined with the recommended MO photometry method.

concentrated air sample has also been done with a reduced Pump 1 speed.

## 4.5. Samples analysis

Two air samples from a chemical plant was determination with the present method as shown in Table 1. These samples were also tested with the recommended MO photometry method for comparison, which were also shown in Table 1. The results from the two method correlate each other in satisfactory.

## 5. Conclusion

The kinetic method described in the present work employ similar absorption solution and chemical reaction with that of MO photometry method, which has been proposed by environmental protect council of People's Republic of China. By choosing favorable sample speed, samples with different chlorine concentration could be determined with good accuracy. The manipulation is very convenient and the process could be finished in several minutes compared with complicated manipulation in the recommended MO photometry method. Preservation of the stock absorption is also conveniently since the value of  $1/(t_2 - t_1)$  in the present method is insensitive to the small variation of the stock solution. Obviously, the present method is easy to be automatized sand is promising in monitor of chlorine concentration in atmosphere.

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