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Determination of trace amount of formaldehyde base on a bromate-Malachite Green system

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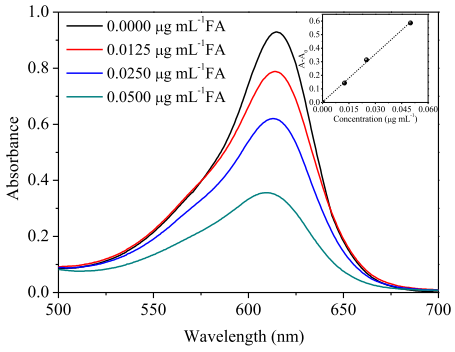
HIGHLIGHTS

- A method to determinate FA has been developed based on MG-bromate system.
- The developed method was sensitive, selective and accurate.
- The developed method was optimized to determinate trace amount of FA in samples.
- A good repeatability and accuracy were obtained from the determination of FA in samples.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel catalytic kinetic spectrophotometric method for determination of trace amount of formaldehyde (FA) has been established, based on catalytic effect of trace amount of FA on the oxidation of Malachite Green (MG) by potassium bromate in presence of sulfuric acid medium, and was reported for the first time. The method was monitored by measuring the decrease in absorbance of MG at 617 nm and allowed a precise determination of FA in the range of 0.003–0.08 μg mL^{-1}, with a limit of detection down to 1 ng mL^{-1}. The relative standard deviation of 10 replicate measurements was 1.63%. The method developed was approved to be sensitive, selective and accurate, and adopted to determinate free FA in samples directly with good accuracy and reproducibility.

Introduction

FA, a simplest aldehyde, is a highly productive industrial chemical and a ubiquitous environmental pollutant [1]. It is widely used in consumer goods, such as foods, wood, furniture and others, to protect the products from spoilage by microbial contamination. But this chemical is highly reactive and poses a threat to human health. For example, it gives rise to eye irritation, respiratory irritation, dermatitis, asthma and pulmonary edema. The International Agency for Research on Cancer (IARC) has classified FA as a human carcinogen that causes nasopharyn-geal cancer in 2006 [2] and human leukemia, particularly myeloid leukemia, in 2012 [3]. Recently, the U.S. National Toxicology Program also classified FA as human leukemogen [4].

The FA has received a great deal of attention due to its toxic activity to human body in the past ten years. Therefore, a number of methods for determination of FA have been reported, such as Fourier Transform Infrared Absorption (FTIA), Differential Optical Absorption Spectroscopy (DOAS), Tunable Diode Laser Absorption

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Spectroscopy (TDLAS), Laser-Induced Fluorescence Spectroscopy (LIFS) [5]. However, the requirement of large, complex, and expensive instrumentation makes these methods unsuitable for routine applications. The chemical derivatization bonding with high-performance liquid chromatography (HPLC) [6–8] and gas chromatography (GC) [9,10] is commonly used for determination of FA too, and these methods have high sensitivity. But the problem associated with these methods is the interference of many carbonyls substances, including acetaldehyde, acetone. The enzymatic method [11,12] is very sensitive and selective. However, the enzyme is expensive and unstable. Other methods such as 3-methyl-2-benzothiazolone hydrazone (MBTH) [13], 4-aminohydrazine-5-mercapto-1,2,4-triazole(AHMT) [14], chromotropic acid [15] and pararosaniline [16] are commonly used for determination of FA. But these methods are in generally time-consuming, of low sensitivity, poor limits of detection or prone to interference by phenols, alcohols and cyclohexanone and hence unsuitable for determination of FA too. Consequently, developing a simple, rapid, highly sensitive, better selective and accurate determination method for the FA is especially important.

In recent years, more sensitive methods have been developed based on spectrophotometric method. Catalytic kinetic Spectrophotometric methods are based on the catalytic effect of trace amount of compound on the reactions in colored or colorless solutions. The methods can offer specific advantages, such as low cost, simplicity, high sensitivity and more selectivity alternatives for determination of trace amount of compound and become important means in trace analysis. The methods have been reported for determination of trace amount of numerous elements [17–19], and trace amount of FA in foods, such as bromate-rhodamine B system [20], bromate-Janus green system [21] and bromate-cresyl violet system [22]. Our team has established sensitive and stable bromate-esion Y system to determinate trace amount of FA in food [23].

MG is a kind of basic triphenylmethane dye, it is excited in the visible part of the spectrum (at about 617 nm) and apt to be oxidized. The structure schematic of MG was shown in Fig. 1. Pourreza [24] used the Malachite Green–Ti(III) redox reaction and a thiocyanate activator to determinate tungsten. Afkhami [25] determinated formaldehyde by using ultratrace quantities of formaldehyde to inhibit the Malachite Green–Sulfite Reaction. But few reports refer to MG-bromate system based on the catalytic effect of FA on the oxidation of MG by bromate in the presence of sulfuric acid for determination of FA.

The current paper developed a simple, sensitive, selective and accurate spectrophotometric kinetic method for the determination of trace amount of FA based on the catalytic effect of FA on the oxidation of MG by bromate in the presence of sulfuric acid. To our knowledge, this system was reported for the first time and the limit of detection was down to 1 ng mL^{-1}, which was more lower than those reported [20,21,26]. The method could be successfully applied to determinate unknown levels of FA in samples.

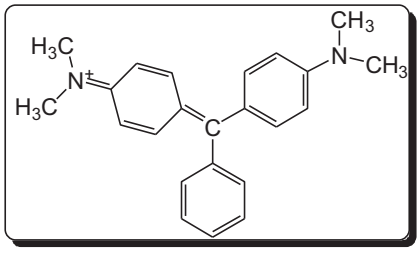

Fig. 1. The structure schematic of MG.

Experimental

Reagents

All chemicals used in this study were of analytical reagent grade and the water used in the experiment was doubly distilled water (DDW). Working solution of FA was prepared freshly appropriately by diluting the stock solution (37%) with DDW and the accurate concentration was determinated by the iodometric method. Potassium bromate solution (0.2 mol L^{-1}) was prepared by dissolving 8.35 g of $KBrO_3$ in DDW in a 250 mL volumetric flask [23]. The concentrated stock MG solution (8.8×10^{-4} mol L^{-1}) was prepared by dissolving 0.0803 g of MG in DDW in a 250 mL volumetric flask. Sulfuric acid solution was prepared by diluting the appropriate volume concentrated sulfuric acid with DDW.

The samples of food were purchased from retail stores in Xiangtan, Hunan, China. The medicinal samples used were purchased from local drug stores.

Apparatus

A spectrophotometer (UV-2450) equipped with 1.0 cm path length quartz cell was used to record the absorbance spectra and absorbance curves at 617 nm [23].

Recommended experiment procedure

To a series of 10 mL volumetric flasks, 1 mL of 8.8×10^{-4} mol L^{-1} MG solution, 1 mL of 0.011 mol L^{-1} sulfuric acid and 1 mL of different concentration of FA were added in sequence, then 2 mL of 0.2 mol L^{-1} potassium bromate solution was added and the mixed solution was diluted to the mark with DDW. After shaking, all volumetric flasks were kept in a 95 °C thermostat water batch for 10 min. The tested volumetric flasks were then cooled in ice water to stop the reactions. After that, a portion of the solution was transferred into a 1.0 cm quartz cell and the absorbance was measured. The zero time was taken as the moment at which the last drop of potassium bromate solution was added and mixed well. The blank reaction was performed according to the same procedure without addition of FA and the absorbance was labeled as A_0. The standard curve which the difference of absorbance ($A_0 - A$) of MG at different concentration of FA versus the concentration of FA was constructed. The $A_0 - A$ was defined as the sensitivity of reaction system [23].

For each sample and blank, five replicated determinations were made and the means were used. The determination of catalytic and non-catalytic reaction (blank reaction) was simultaneously measured.

Results and discussion

The absorption spectra of reaction system

The changes in the absorption spectra by scanning the spectrum of the several reaction systems from the 500 to 700 nm were examined. As shown in Fig. 2, the absorbance of MG in system 2–4 at 617 nm decreased in large range comparing with the system 1, and the difference of absorbance (A_0–A) increased linearly with increasing of the concentration of FA (as shown in insert of Fig. 2) and initial green color of MG disappeared. The results suggested that the MG was oxidized by bromate in acidic media and the trace amount of FA could accelerate the oxidation reaction.

The possible mechanism of the reaction between MG and potassium bromate may be contributed to the equations below [21,23]:

$$BrO_3^- + H^+ + MG_{Red}(\text{green}) \rightarrow Br^- + MG_{Ox}(\text{colorless}) \quad (1)$$