



## Short communication

## A practical headspace gas chromatographic method for the determination of oxalate in bleaching effluents

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## ABSTRACT

This paper reports an improved headspace gas chromatographic (HS-GC) technique for the determination of oxalate content in bleaching effluents. The method is based on the redox reaction between potassium iodate and oxalate, from which the carbon dioxide is generated and measured by HS-GC. The results showed that the reaction in a sulfuric acid solution (0.05 mol/L) was complete in 35 min at 95 °C. The RSD of the method in the repeatability testing was less than 4.5%, the LOQ was 0.35 µg, and the recovery ranged from 95 to 103%. The present method is simpler, more reliable, and more practical compared to the methods reported previously.

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## 1. Introduction

Oxalate, resulted from the oxidations of lignin and hemicelluloses, is a minor product generated during pulp bleaching processes [1–3]. The hard scales of oxalates (such as calcium oxalate), due to their solubility limits, could be precipitated on the surfaces of the reactor walls, pumps, pipelines, and evaporation units and cause severe operational and quality related problems [4]. Therefore, the analysis of oxalate in bleaching effluents is very important for the process study [5] to clarify how the process parameters (e.g., temperature, nature of pulps, and dosage of bleaching chemicals) affect the formation of oxalate ions in the effluents, aiming at minimizing the scaling problems associated with oxalates in the operations.

There are several methods reported in the literatures for the oxalate quantification in mill effluents, i.e., ion chromatography [6,7] and capillary electrophoresis [8,9]. However, besides the complicated and time-consuming procedures in the sample pretreatment and testing, the measurement errors in these methods are quite significant. In 2006, we proposed a headspace gas chromatographic method (HS-GC) for the determination of oxalate in pulping spent liquors (also called black liquor) based on

the carbon dioxide (CO<sub>2</sub>) generated from the reaction between permanganate and oxalate [10]. Because permanganate is a strong oxidant and could react with many coexisting organic compounds (e.g., methanol and formic acid) to form CO<sub>2</sub>, a multiple headspace extraction (MHE) measurement technique was applied. In this way, the kinetics of formation of the carbon dioxide from the other organic species in the sample can be determined and thus a correction can be made for minimizing the interferences. More recently, we reported a very simple HS-GC for the determination of oxalate in oxygen delignification (bleaching) effluents [11]. The method uses manganese dioxide (MnO<sub>2</sub>) as an oxidant to convert oxalate to CO<sub>2</sub>. Although the oxidation ability of MnO<sub>2</sub> is not so strong as that of permanganate, it is still not selective. By carefully selecting the reaction conditions (i.e., the temperature and time, the dosage of the oxidant and acidity of the medium), the CO<sub>2</sub> formation from the slow reactions caused by the coexisting species can be minimized. Since the poor reaction selectivity is problem in both permanganate and MnO<sub>2</sub> cases, the HS-GC testing in these methods must be immediately performed after adding the oxidant, since the conversion reactions with the coexisting species also took place in room temperature. Thus, the method only allows us to perform the HS-GC measurement once a sample, which makes the testing less efficient. Therefore, it is necessary to develop a practical HS-GC method that is capable of performing an automatic HS-GC measurement in the batch (multiple) sample.

In this work, we developed an improved HS-GC method for the quantification of oxalate in bleaching effluents based on potassium iodate (KIO<sub>3</sub>), a more selective oxidant. The focuses were to explore

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the suitable reaction conditions (such as the temperature, dosage of  $\text{KIO}_3$ , and acidity of the medium) that could speed up the conversion for oxalate while minimizing the interferences caused by the other species in the testing samples.

## 2. Experimental

### 2.1. Chemicals and samples

All chemicals used in the experiment were purchased from commercial sources. A set of sulfuric acid solutions in which the concentration of hydrogen ion was from 0.001 to 1.0 mol/L was prepared by adding right amount of  $\text{H}_2\text{SO}_4$  to distilled water. A standard oxalate sodium solution (0.100 mol/L) was prepared by dissolving 1.06 g of pure anhydrous sodium oxalate in 100 mL sulfuric acid solution ( $[\text{H}^+] = 0.1 \text{ mol/L}$ ). A potassium iodate solution (10 g/L) was prepared by adding 1.0 g of  $\text{KIO}_3$  in 100 mL of solution containing  $5 \times 10^{-4}$ –0.5 mol/L of sulfuric acid. A barium chloride solution (1.0 mol/L) was prepared by dissolving 20.8 g of  $\text{BaCl}_2$  in 100 mL of distilled water.

A bleaching effluent was obtained from our lab-scale oxygen delignification process for the eucalyptus pulps from a kraft pulping process.

### 2.2. Apparatus and operations

All measurements were carried out using an automatic headspace sampler (DANI HS 86.50, Italy) and a GC system (Agilent GC 7890A, US) equipped with a TCD and a GS-Q capillary column (30 m  $\times$  0.53 mm, J&W Scientific, US) operating at a temperature of 120 °C with nitrogen carrier gas (flow rate = 10.3 mL/min). Headspace operating conditions were as follows: the equilibration temp. = 60 °C; needle and sampling coil temp. = 105 °C; transfer line temp. = 115 °C; vial pressurization time = 0.2 min; and sample loop fill time = 0.2. The volume of the headspace sample loop is 3.0 mL.

### 2.3. Procedures of sample preparation, reaction and measurement

#### 2.3.1. Sample preparation

5 mL of sample solution was directly mixed with 5 mL of sulfuric acid solution (1.0 mol/L). After one min of ultrasonic agitation, ~3 mL of the supernatant was filtered by a membrane filter (0.45  $\mu\text{m}$ ).

#### 2.3.2. Reaction and HS-GC measurement

A 300  $\mu\text{L}$  of the filtered solution was added to a headspace vial containing 3 mL of  $\text{KIO}_3$  solution and 1.7 mL of sulfuric acid solution ( $[\text{H}^+] = 0.1 \text{ mol/L}$ ). The vial was immediately sealed with a PTFE/butyl rubber pad. The sealed sample vials were placed in a lab oven for 45 min at 95 °C, and then they were cooled to a room temperature. After injecting a 1.0 mL of barium chloride solution (1.0 mol/L) to each vial, the vials were placed in the headspace sampler to perform an automatic HS-GC measurement for  $\text{CO}_2$  converted from oxalate during the reaction. The headspace of the vials was equilibrated for 1 min at 60 °C with a GC measurement cycle time of 4 min.

## 3. Results and discussion

### 3.1. Effects of reaction conditions on oxalate conversion

The present method is based on measuring the  $\text{CO}_2$  that is quantitatively generated by the reaction between potassium iodate and oxalate in an acidic medium. The effects of the reaction conditions, i.e., the dosages of potassium iodate, concentration of

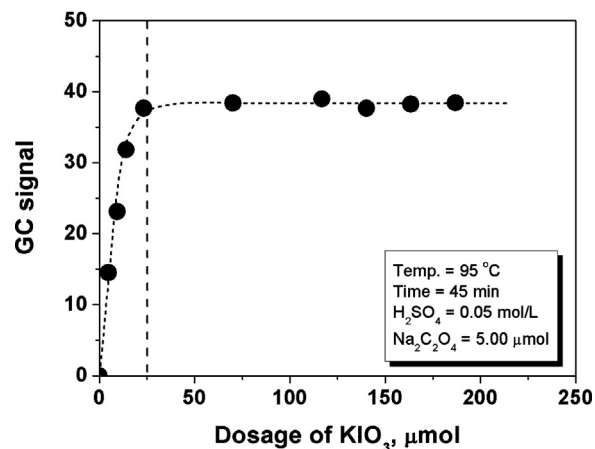


Fig. 1. Effect of  $\text{KIO}_3$  dosage on the oxidation of oxalate.

sulfuric acid, and the reaction temperature and time, on the completion of the conversion should be investigated.

#### 3.1.1. Dosage of potassium iodate

To ensure complete conversion of oxalate to  $\text{CO}_2$  and accelerate the redox reaction, an excess amount of  $\text{KIO}_3$  is required. As shown in Fig. 1, a conversion equilibrium is obtained by adding 25  $\mu\text{mol}$  (at least) of  $\text{KIO}_3$  for a sample containing 5.00  $\mu\text{mol}$  of oxalate at the given reaction conditions. In the following study, a sufficient amount (140  $\mu\text{mol}$ ) of  $\text{KIO}_3$ , i.e. 3 mL of  $\text{KIO}_3$  solution (10 g/L), was used in the reaction

#### 3.1.2. Effect of acidity

Fig. 2 shows that an appropriate acidity in the reaction medium is necessary for achieving the conversion equilibrium of oxalate, in which the concentration of sulfuric acid should be greater than 0.015 mol/L. Therefore, we spiked sulfuric acid into the  $\text{KIO}_3$  solution and ensured its concentration greater than 0.1 mol/L in the following work.

#### 3.1.3. Reaction temperature and time

Fig. 3 shows the time-dependent  $\text{CO}_2$  formations from the oxalate conversion reaction with  $\text{KIO}_3$  at temperature of 70, 80, 90 and 95 °C, respectively. It can be seen that the temperature effect on the conversion reaction with  $\text{KIO}_3$  is very significant and it takes 35 min to achieve the conversion equilibrium at 95 °C, which is much slower than those observed when using  $\text{MnO}_2$  [11]. Obviously, the slow reaction for oxalate also avoids the  $\text{CO}_2$

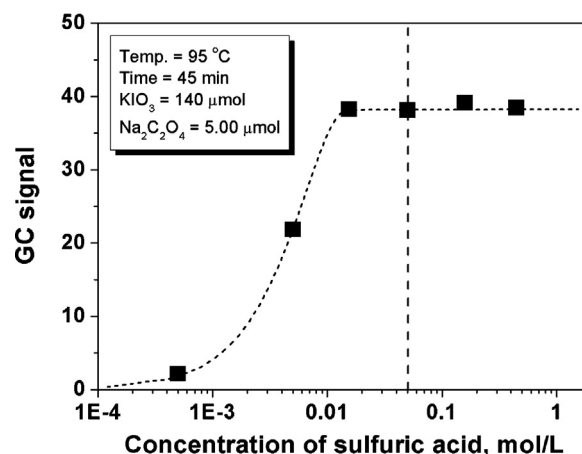


Fig. 2. Effect of acidity on the oxalate conversion.

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