DETERMINATION OF SULPHUR DIOXIDE (residual SO_2) BY RANKINE METHOD B : COLORIMETRIC METHOD

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INTRODUCTION

The sulphur dioxide in foods is distilled under acidic condition (phosphoric acid, H_3PO_4) in the presence of nitrogen (N_2) gas.

The receiver contains alkali (sodium hydroxide). By heating, the sulphur dioxide from foods are immediately stabilized in the form of a salt-alkali complex in the receiver.

An aliquot of the solution from the receiver is used and acidified using phosphate buffer solution. Then the addition of ρ-rosaniline-formaldehyde solution results in the development of a reddish colour. The intensity of the colour developed is measured by the colorimetric method.

This method is applicable to all foods.

APPARATUS

1. Round bottomed flasks, 100 ml
2. Oval shaped flasks, 50 ml
3. Graduated test tubes with stoppers, 10 ml
4. Distillation apparatus (Fig. 1)

REAGENTS

1. 1% sodium azide (NaN_3)

   Weigh 1 g of NaN_3 and dissolve in distilled water. Make up to 100 ml.

2. 95% (v/v) ethanol

3. Hydrochloric acid - sodium acetate solution

   Measure 600 ml hydrochloric acid (HCl, 1N). Add 500 ml of sodium acetate ($CH_3COONa.3H_2O$, 1 M) and mix well.

4. ρ-rosaniline-HCl solution ($[NH_2C_6H_4]_3COH$-HCl)

   Weigh 0.2 g ρ-rosaniline-HCl (analytical grade) and add 100 ml distilled water. Mix well. Stand overnight, then filter using filter paper (No. 1). Take 20 ml of the filtrate and add 6 ml HCl (12N or 36%). Make up to 100 ml with distilled water.

5. ρ-rosaniline-formaldehyde solution

   Add 1 volume of 0.2% ρ-rosaniline-HCl solution with 1 volume of 0.2% formaldehyde solution (1:1). Mix well.

6. 0.2% formaldehyde solution

   Take 1 ml of 37% formalin and add 184 ml of distilled water or 1 ml of 35% formalin and add 174 ml distilled water. To be prepared fresh for each use.

7. 5% dimedone ($C_8H_{12}O_2$)-ethanol

   Weigh 5 g dimedone and dissolve in ethanol. Make up to 100 ml.

8. Silicon oil as antifoaming agent (food additive)

9. 25% phosphoric acid (H_3PO_3) solution

   Take 100 ml of 85% H_3PO_3 and add 240 ml of distilled water. Mix well.

10. 0.1N sodium hydroxide (NaOH) solution.

11. Sulfurous standard solution

    Weigh 0.5 g sodium bisulphite ($NaHSO_3$) and dissolve in distilled water. Make up to 100 ml in a volumetric flask.

    Take 10 ml of this solution and add 15 ml of 0.1N iodine (I_2) solution. Also add 2 ml of HCl (12N or 36%). Titrate against 0.1 N sodium thiosulphate solution. From the titration, calculate A ml using formula below :

$$A\ (ml) = \frac{93.75}{(b - a)} \times \frac{1}{f}$$

Where a = titration volume of sulfurous standard solution (ml)

b = titration volume (ml) of blank (using 10 ml of distilled water instead of $NaHSO_3$)

f = factor of 0.1N sodium thiosulphate

Take A ml of $NaHSO_3$ solution and make up to 300 ml with 0.1N NaOH solution to give the **original sodium bisulphite** solution. Finally take 2 ml of the original bisulphite solution and make up to 100 ml with 0.1N NaOH solution, in a volumetric flask. This gives the **sulphurous standard solution** ($NaHSO_3$ solution). 1 ml of this solution contains 0.002 mg (2 ug) SO_2. This solution must not be used after more than 2 - 3 days in the refrigerator.

PROCEDURE

(Refer to Figs. 1 and 2)

1. Pipette 8 ml of 0.1N NaOH solution into Flask A, then fix Flask A to C.
2. Pipette 1 ml 5% dimedone-ethanol into Flask B, followed by 1 ml 1% NaN_3, 2 drops of silicone oil and 10 ml of 25% H_3PO_4.
3. Flow in nitrogen gas at a speed of 0.5 - 0.6 l/min for 5 min.
4. Remove Flask B from E and quickly put the sample into Flask B.
5. Connect Flask B to glass capillary E.
6. Flow nitrogen gas at 0.5 - 0.6 l/min.
7. Heat Flask B with micro-burner for 10 min using a flame height of 4 - 5 cm.
8. Remove Flask A and wash the tip of the delivery tube with small amounts of 0.1N NaOH solution into Flask A.
9. Make up the solution in Flask A to 10 ml in a graduated test tube (stoppered) with washings from Flask A.
10. Take 5 ml of the above sample solution and add 5 ml of ρ-rosaniline-formaldehyde solution. Stand for 35 min at room temperature (20° - 25°C).
11. Determine by colorimetry at wavelength of 560 nm.
12. For testing standard solution, 5 ml of standard solution is used instead of sample solution.

CALCULATION

$$SO_2\ (g/kg) = 10 \times \frac{\text{absorption value of sample solution (A)}}{\text{absorption value of standard solution (B)}} \times \frac{10}{5} \times W \times \frac{1}{1000}$$

$$= \frac{W}{50} \times \frac{A}{B}$$

Where, A = absorption value of sample solution

B = absorption value of standard solution

W = sample weight(g)

Detection limit = 0.2 ppm (0.0002 g/kg)

REMARKS

1. This colorimetric method is suitable for samples with titration values of less than 0.1 ml of 0.01N NaOH solution (alkali titration method).

2. Nitrogen gas is used to prevent the oxidation of SO_2 to H_2SO_4.

3. If a high level of SO_2 is obtained, dilute 5 ml of the sample solution (in a graduated test tube with stopper) with 0.1N NaOH solution and make up to 10 ml i.e. two times dilution.

4. This method is suitable for low levels of SO_2 (0.2 ppm) as well as high levels of SO_2.

5. To prevent carbonization in the case of low moisture foods an adequate amount of distilled water must be used in the Flask B.

REFERENCE

Shokuhin Eisei Kensa Shishin, Guidelines for Food Hygiene Inspection. (Analytical Methods for Food Additives), Japan Food Hygiene Association (1989).

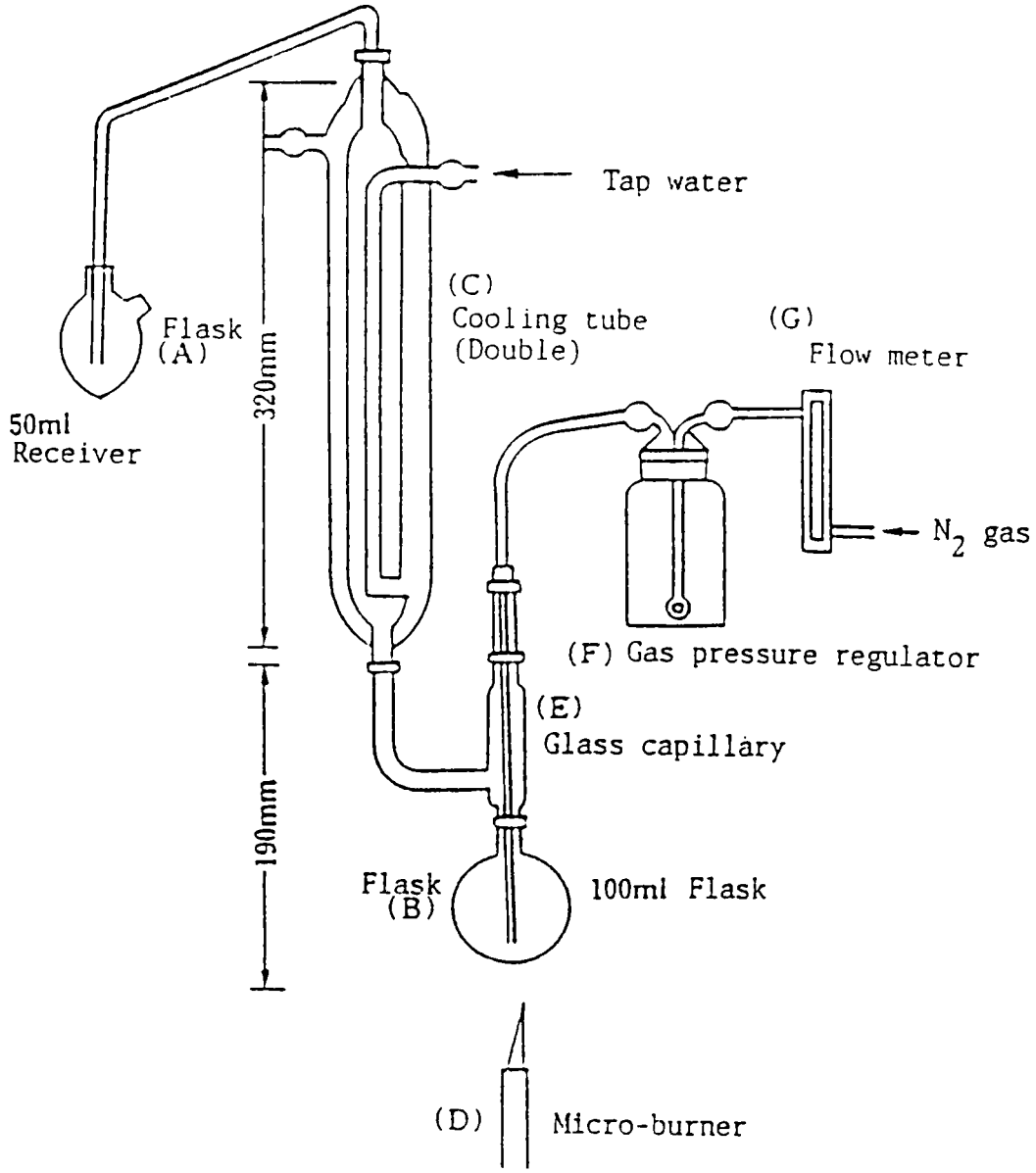

Fig. 1. APPARATUS FOR DISTILLATION
(RANKINE METHOD)

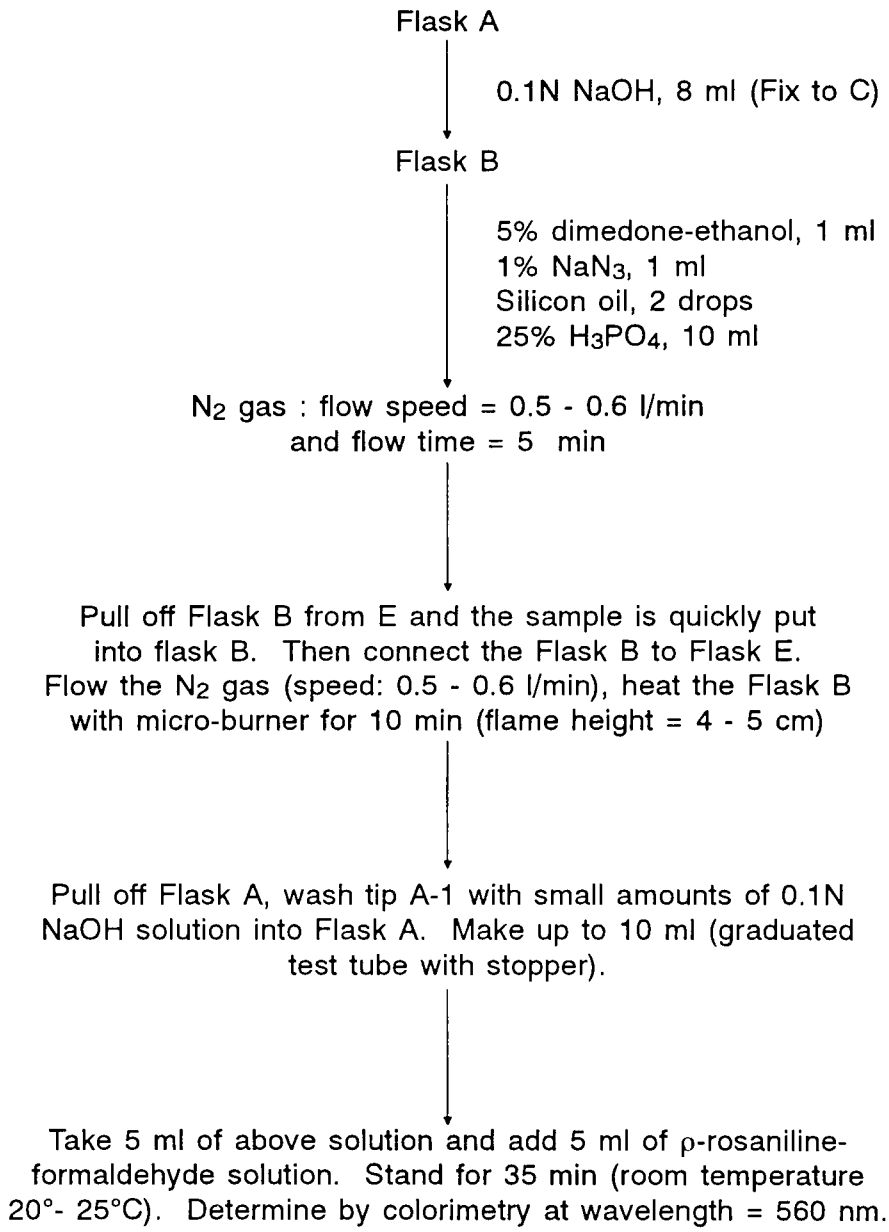

Fig. 2. Analytical procedure for the analysis of SO_2 by Rankine Method