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Frederick, Maryland, 21701

GAS ANALYSIS BY MEANS OF DETECTOR TUBES (PART 7)

RAPID METHOD FOR THE DETERMINATION OF ETHYLENE

Journal of the Chemical Society of Japan, Industrial Chemistry Section; Vol. 56, No. 6, pages 446-449 (1953)

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1. Introduction

Ethylene presently is becoming increasingly important as a starting material for synthetic resins and other organic substances, however, the mixing of ethylene and air presents an explosive hazard in plants which handle ethylene. The lower explosive limit of ethylene in air is 2.8 percent and 2.9 percent in oxygen[1]. It is also known that explosive incidents of unknown origin frequently occur at air separation plants which separate nitrogen and oxygen for industrial use[2]. There has been recent suspicion that the sudden oxidation of hydrocarbons accumulated in the liquid nitrogen, particularly unsaturated compounds like acetylene and ethylene, could be responsible for these explosions[3]. There is need, therefore, for a simple method to determine ethylene. It is not overstating the case when we say that there is no method available as yet which will fulfill the objectives mentioned above. The authors reported on the use of detector tubes in explosion prevention with respect to the detection of acetylene[4], and the following is a concise description of the application of detector tubes to the determination of ethylene.

2. Analytical Equipment and Operating Procedure

(a) Analytical equipment: The analytical equipment included the gas collector and detector tubes. The gas collector was a 30 cc or 100 cc syringe made of glass or metal.

The ethylene detector tube was prepared by letting ammonium molybdate and palladium sulfate permeate 40-60 mesh silica gel, vacuum drying this gel material at room temperature, and packing 0.30 g of

this dried material into a thin glass tube of 2 mm I.D. (total length of packed column 6-8 cm). A small amount of glass beads were placed at either end of the packed column to prevent contact between this detector material and the cotton plugs. The two ends of this glass tube were then sealed to protect the contents. This detector tube has a light yellow color which on exposure to ethylene generates a lower molybdenum oxide (Mo_5O_8) which imparts a brilliant deep blue color. Measuring the length of this colored column then gives a measure of the ethylene concentration.

(b) Operating procedure

First of all, both ends of the detector tube were cut off with the aid of a file. The gas to be analyzed was drawn into the gas collector after which the detector tube and gas collector were connected together with a short length of thick wall rubber tubing. The gas to be analyzed was passed through the detector tube at the flow rate of 10 cc per 40 seconds or 400 cc per 400 seconds. The ethylene concentration in the gas being analyzed was determined with the use of Figs. 1 and 2 and applying the temperature corrections of Tables 1 and 2. The description of the use of these figures and tables are deleted here (see Part 1[5]).

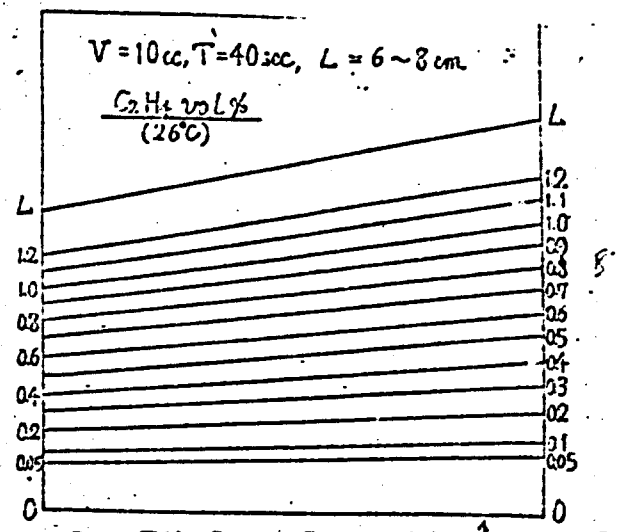

Figure 1. Ethylene Concentration Table

3. Ethylene Concentration Tables and Temperature Correction Tables

The ethylene concentration tables shown in Figs. 1 and 2 and the temperature correction tables of Tables 1 and 2 were derived in the manner described below.

(a) Preparation of ethylene samples: Pure ethyl alcohol was dripped on to activated alumina maintained at about 400°C to generate ethylene gas which was purified by passage through a layer of silica gel to remove impurities. This gas was stored in a dry and clean glass bottle of about 20 liter capacity. The ethylene concentration in this gas was determined

by drawing a 50-100 cc volume into a gas collector, and this gas was absorbed into a potassium bromide-potassium bromate solution acidified with hydrochloric acid. This solution was then titrated with standard sodium thiosulfate solution to establish the ethylene concentration[6].

(3) Velocity of gas passage through detector tube: A variation in the speed at which the sample gas passes through the detector tube will cause variations in the length of the colored zone for any given concentration of ethylene. The velocity of flow-through was varied, and the relation between the velocity and length of color layer was determined. The results were evaluated for sharpness of the color boundary, precision, and ease of operation from which it was decided that a flow-through velocity of F - 0.25 cc/sec (V = 10 cc, T = 40 sec; V = 100 cc, T = 400 sec) be selected.

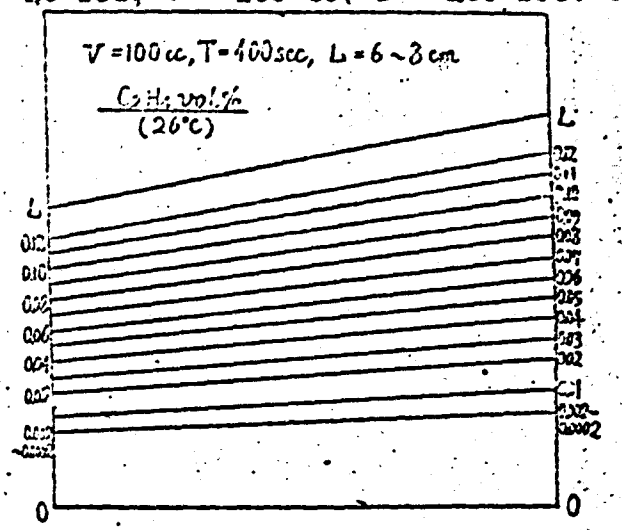

Figure 2. Ethylene Concentration Table

Table 1. Table for Temperature Correction

V=10cc, T=40sec

1 読取表の読み (%)	C_2H_4 (%) 10°C	15°C	20°C	25°C	30°C
0.6	0.6_8	0.6	0.6	0.6	0.6
0.7	0.7_8	0.7_8	0.7	0.7	0.7
0.8	0.9	0.8_8	0.8	0.8	0.8
0.9	1.0	0.9_8	0.9_8	0.9	0.9
1.0	1.1	1.1	1.0	1.0	1.0
1.1	1.2	1.2	1.1	1.1	1.1
1.2	1.3	1.3	1.2_8	1.2	1.2

Key: 1. reading on concentration table (%)

Table 2. Table for Temperature Correction

V = 100 cc, T = 400 sec

1 Reading on concentration table (%)	C_2H_4 (%)				
	10°C	15°C	20°C	25°C	30°C
0.02	0.01	0.01_5	0.02	0.02	0.02
0.03	0.02	0.02_5	0.02_5	0.03	0.03
0.04	0.02_5	0.03	0.03	0.04	0.04
0.05	0.03	0.04	0.04	0.05	0.05
0.06	0.04	0.05	0.05	0.06	0.06
0.07	0.04_5	0.06	0.06	0.07	0.07_5
0.08	0.05	0.06_5	0.07	0.08	0.08_5
0.09	0.06	0.07_5	0.08	0.09	0.09_5
0.10	0.07	0.08	0.09	0.10	0.10_5
0.11	0.08	0.09	0.10	0.11	0.11_5
0.12	0.09	0.10	0.11	0.12	0.12_5

Key: 1. reading on concentration table (%)

(c) Volume of gas passed through: Gas of constant composition was passed through at constant flow-through rate, and the relation between the volume of gas passed through and the length of the colored portion of the detector tube was determined. The length of this colored portion gradually increased with increasing volume of gas passed through, however, the length was not proportional to the volume. Taking into account the range of concentrations to be determined and the operating conditions, V = 10 cc and V = 100 cc were selected.

(d) Correction for the inner diameter of the detector tube: The inner diameter of the glass tubing used to prepare these detector tubes is not necessarily constant so that fixing the weight of detector material to be packed into each tube will cause variations in length L of the packed material due to the constancy in density of the material and the uneven cross section of the tubing. In this case, the length of the colored layer l of a gas of fixed ethylene concentration is proportional to the length of the packed column. By determining the ratio ($\ell_0 = \ell/L \times 80$) in which ℓ_0 is the length of the colored zone in tube of standard packing lengthL, it is possible to determine the ethylene concentration independent of the inner diameter of the tubing.

(e) Relation between the length of the colored layer in the detector tube and ethylene concentration: Sample gas was collected with the 30 cc gas sampler, and a volume of 10 cc was sent through the detector tube in the course of 40 seconds. The relation between the length of the color layer that was developed and the corresponding ethylene concentration was then determined. The plot of this relation taking the ordinate to be the length ℓ_0 (mm) of the colored layer and the abscissa to be the ethylene concentration is shown in Fig. 3. (The curve for V = 100 cc and T = 400 sec is not shown here). Using the inner diameter correction for the detector tube and the relation between the length of the colored layer and the ethylene concentration, ethylene concentration tables shown in Figs. 1 and 2 covering the range 0.05-1.2 percent and 0.002-0.12 percent were constructed. The detection limit here was about 0.00005 percent (V = 100 cc, T = 400 sec).

(3) Temperature of the determination: The length ℓ_0 of the colored layer in the detector tube also varies with the temperature of the determination. The length ℓ_0 corresponding to a given ethylene concentration was determined at various temperatures between 10-30°C using a constant temperature bath. When the ethylene concentration was relatively high (the range represented by the curves in Fig. 1), increasing temperature brought about a slight but linear increase in the length of this colored layer. On the other hand, this length conversely decreased with increasing temperature when the concentration was low (the range covered by the curves of Fig. 2). This behavior probably results from the effects of physical adsorption coming into play in the first mentioned case, and in contrast, the volume expansion and reaction velocity effects becoming more important than the physical adsorption effects in the latter case. The results of these studies were used to construct the temperature correction tables of Tables 1 and 2. These tables are used to make corrections for temperature between 10-30°C.

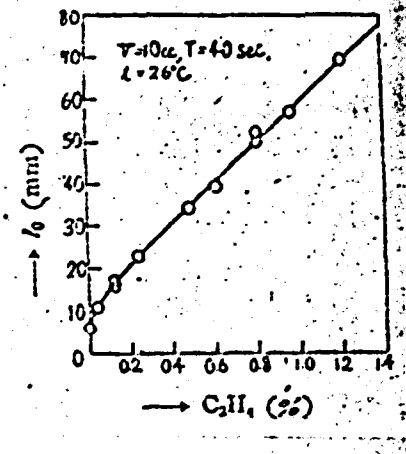

Figure 3. Relation Between the Length of the Colored Layer and Ethylene Concentration

4. Precision, Time Required, and Effect of Gases

Parallel studies were conducted to determine the precision of this determination. The results showed the mean error in each case to be within ± 5 percent indicating sufficient degree of reproducibility for practical applications. A measurement required two minutes for the first method and eight minutes for the second.

The effect of other gases on this detector tube was discussed in the paper on the determination of acetylene[4] and is not discussed here.

5. Summary

(1) A mixed solution of ammonium molybdate and palladium sulfate was sorbed onto silica gel particles which were ~~then~~ dried in vacuum to

prepare gas detection material which was loaded into a thin glass tube to make the detector tube.

(2) Using a gas sampler and running a 10 cc gas sample through the tube in 40 seconds or 100 cc in 400 seconds, ethylene concentrations in the range 0.05-1.2 percent and 0.002-0.12 percent can be determined within a few seconds.

(3) The effects of various parameters on the length of the colored layer of the detector tube were studied, and direct reading concentration and temperature correction tables were constructed. Precision studies showed the reproducibility to be adequate for practical application. ( )

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References

[1] Jones, Vant, Miller, Kennedy, U.S. Bur. Mines, Rept. Inv. No. 3278 (1935).

[2] Japan Ammonium Sulfate Industrial Cooperative, Data of the Committee to Devise Countermeasures against Explosions of Air Separation Units (1950).

[3] Eizo Kanda, Ryuan Gijutsu 4, No. 3, 2 (1951).

[4] Tetsuzo Kitagawa, Yoshitaka Kobayashi, Kcatsu Gasu 15, 169 (1951); Tetsuzo Kitagawa, Tadahiko Ogawa, Yoshitaka Kobayashi, Denka 20, 423 (1952).

[5] Tetsuzo Kitagawa, Yoshitaka Kobayashi, Koka 55, 191 (1952).

[6] De Wilde, Ber. 7, 353 (1874).