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GAS ANALYSIS BY MEANS OF DETECTOR TUBES (PART 3)

RAPID DETERMINATION OF LOW CONCENTRATIONS OF ETHYLENE AND ACETYLENE

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1. Introduction

One of the authors (Kitagawa) reported[1] that it was possible to detect at an early stage the buildup of traces of carbon monoxide and ethylene resulting from the spontaneous combustions that sometimes takes place within coal mines. In another direction, traces of acetylene are mixed in with ethylene and other low hydrocarbons to become responsible for explosions sometimes taking place in air fractionating plants [2]. As a result, a rapid method of determining trace quantities of these gases both at the intake and outlet of these air fractionating units is desirable. While there are a few methods of determination for these gases, there are none which are adaptable to the situations described above. The authors utilized the sensitive response of silicomolybdate detector material to the presence of reducing gases to fashion detector tubes to be used in determining trace quantities of ethylene and acetylene in air. The results are reported here.

2. Experimental Equipment

The equipment included the two rubber bulbs in tandem shown in Fig. 1 and the detector tube shown in Fig. 2. This detector tube is a 4 mm I.D. glass tube packed with alternate layers of yellow silicomolybdate detector material and white silica gel particles used as absorber material [3]. The two ends of the packed layers are stoppered with cotton plugs, and the ends of the glass tube are sealed shut for storage. This detector material was prepared by soaking silica gel particles in a solution mixture of ammonium molybdate and palladium sulfate followed by drying in vacuum at room temperature. When this material makes contact with a number of reducing gases, a low molybdenum oxide is produced which is colored. For example, ethylene brings out a deep blue color while acetylene causes a brownish green color. Thus, it is possible to detect and estimate trace quantities of these gases from the degree of coloring. The absorbant is placed in the tube to remove moisture from the air that is passed through.

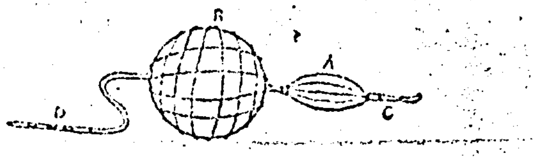


Figure 1. Detector Tube Hooked to Two Bulbs in Series

A: rubber squeeze bulb B: mesh coated sphere
C: gas sampling port D: detector tube

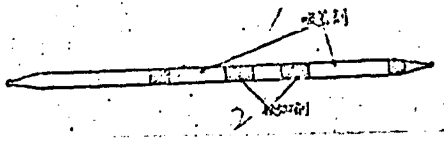


Figure 2. Detector Tube

Key: 1. absorbant 2. detecting reagent

3. Method of Determining Trace Quantities of Ethylene

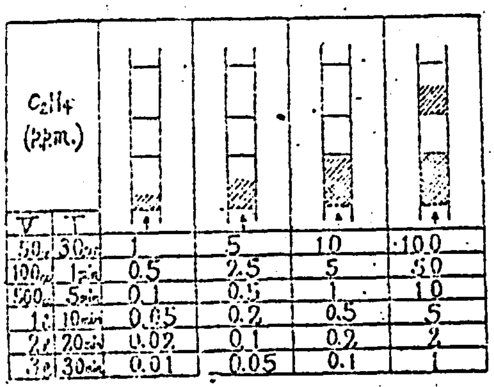
(1) Blank run: The air within a laboratory is more frequently somewhat contaminated, and passing laboratory air through these detector tubes often produces a light green coloration. This color is due to traces of carbon monoxide [3], and passing the gas first through a layer of hopcalite effectively removes this interference. When a silica gel tube and a hopcalite tube were placed before the detector tube, no coloration of the detector tube by room air was observed.

(2) Preparation of sample gas: Ethylene was generated by dripping ethyl alcohol on alumina maintained at 400°C in an electric furnace and passed through a layer of silica gel to remove impurities. This purified gas was stored in a 20 liter glass container. The ethylene concentration was determined by absorbing a known volume of this gas into a potassium bromide-potassium bromate solution and titrating the resulting solution with N/100 sodium thiosulfate. A known volume of the gas which was standardized in this manner was then diluted with a volume of air purified

in the manner described before and taken up in two 20 liter glass flasks, connected in series. The necessary amount of sample gas was drawn from these two spheres in series and sent to the detector tubes.

(3) Method of passing through sample gas: The ends of the sealed tube were cut away with the aid of a file, and the detector tube D was hooked to the rubber tube lead to the two bulbs in series as shown in Fig. 1. The rubber tube was squeezed shut with the fingers while bulb A of about 100 cc capacity was squeezed four times to blow up air reservoir B to suitable size. The hold on the rubber tube was released while a stop-watch was started at the same time, and gas passage through the detector tube was initiated. After one minute, the bulb A was again squeezed once. This operation was repeated the prescribed number of times. This technique passed gas through the detector tube at the uniform rate of 100 cc/min, and measurement of the total time of passage enabled the calculation of the total volume of gas V that passed through. While this method seemingly appears to have low precision on first glance, it is only necessary to get results within the order of magnitude. As a result, this technique gave results of adequate precision.

(4) Detector tube coloring test using trace quantity of ethylene: Sample gas containing ethylene in concentration ranging between 100 ppm to the minimum 0.01 ppm (1 ppm = 0.0001 vol%) was passed through the detector tube at the flow rate of 100 cc/min utilizing the two flasks in series, and the relation between the degree of coloring of the detector tube versus the ethylene concentration, total volume passed through is shown in Fig. 3. When the requisite volume of gas had been passed through, the detector tube was placed against Fig. 3 to determine the ethylene concentration. This figure shows it is possible to determine ethylene concentration as low as 0.01 ppm by passing through a 3 liter volume of gas sample in a period of 30 minutes.



V	T				
50 ml	30 sec	1	5	10	100
100 ml	1 min	0.5	2.5	5	50
500 ml	5 min	0.1	0.5	1	10
1 l	10 min	0.05	0.2	0.5	5
2 l	20 min	0.02	0.1	0.2	2
3 l	30 min	0.01	0.05	0.1	1

Figure 3. Coloring of Detector Tube by Trace Quantities of Ethylene

(5) Effect of volume of gas passed through: The relation between the time following gas passage when coloration is observable and the volume of gas passed through for gas containing 0.01 ppm ethylene is shown in Table 1. The relation between the log of the ethylene concentration required to bring about the same coloration in Fig. 3 versus the log of the gas volume is shown in Fig. 4, and the result is nearly a straight line.

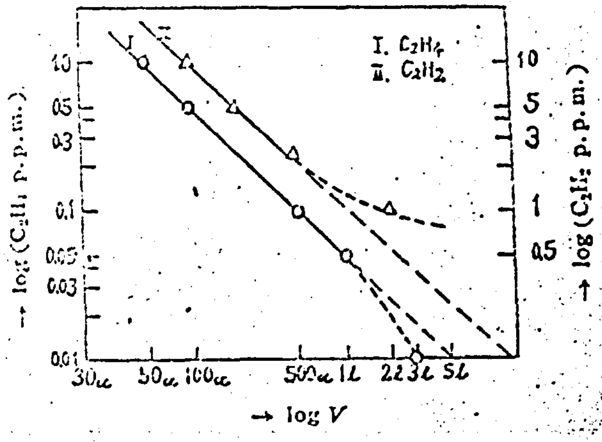


Figure 4. Relation between Ethylene and Acetylene Concentrations and the Gas Volume Required for the Determinations

Table 1. Relation between Time Required for Detector Color to be Developed and Gas Volume Passed Through

(Room temperature t = 18°C)

C_2H_4	Sample Gas Volume (l)	Flow-Through Rate (cc/min)	Time of Passage (min)	Elapsed Time After Passage of Gas Until Color Developed	
				When Viewed Directly from the Side	When Viewed from an Oblique Angle
0.01	3.0	100	30	Just after	Just after
"	2.0	"	20	" "	" "
"	1.5	"	15	70 min later	" "
"	1.0	"	10	Not evident in 70 min	" "
"	0.6	"	6	" " " " "	After 15 min
"	0.3	"	3	" " " " "	After 60 min

(6) Effect of rate of gas flow-through: The coloring of the detector tubes when the rate of flow-through was varied between 50 cc/min and 200 cc/min was compared. A slow flow-through rate tended to give obscure boundaries, but any distinction resulting from difference in flow-through rates can be considered negligible.

(7) Effect of temperature: The appearance of color tends to be delayed the lower the temperature but the length of the colored layer and the

depth of color are independent of temperature between 10-30°C. Consequently, no temperature corrections are necessary at room temperature.

4. Method of Determining Trace Quantities of Acetylene

(1) Preparation of sample gas: Acetylene was generated by passing water into carbide and purified by passage through catalyzol /phonetic/ [illegible] compound and silica gel before it was run into an evacuated flask of about 20 liter capacity. The air was adjusted to give acetylene concentration between 0.2-0.4 percent. The concentration of the acetylene in this bottle was determined by the detector tube method that was described in a preceding paper [4].

Next a fixed volume of gas with known composition of acetylene was placed in the system consisting of two 20 liter flasks in series, and this system was used to prepare gas samples of desired concentrations.

(2) Detector tube coloring test using trace quantity of acetylene: The two rubber bulbs in series were used just as with ethylene to pass sample gas through the detector tube at the rate of 100 cc/min, and the results of this study are shown in Fig. 5. It was found that acetylene could be detected from 1000 ppm down to a minimum of 1 ppm.

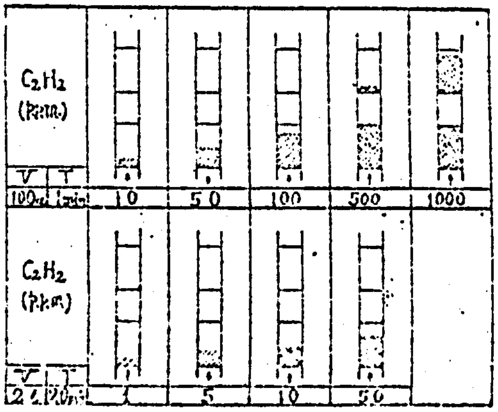


Figure 5. Coloring of Detector Tube by Trace Quantities of Acetylene

Geissman et al. [5] condensed ethylene gas from air containing about 1 ppm by passing the air through a copper tube cooled in liquid air and analyzed the acetylene by a spectrophotometric method using the Ilosvay reagent. The Ilosvay reagent contains a copper (I) salt, and passing a large volume of air directly through the reagent oxidizes the copper (I) such that the reagent becomes useless. On the other hand, the reagent used here is completely unaffected by oxygen in air, and this detector tube presents the advantage that several liters of air can be sampled through each tube without causing any error.

(3) Effect of volume of gas passed through: The relation between the concentration of acetylene giving the same degree of coloration and the flow-through volume is shown in Fig. 4, and the relation is nearly linear.

(4) Effect of rate of gas flow-through: The rate of flow-through was varied between 50 cc/min to 200 cc/min in the concentration range 1-10 ppm, and no variations in the degree of coloring were observed with changes in rate of flow of this range. The length of the colored layer became longer with increasing flow rate when the acetylene concentration was increased to about 500 ppm.

(5) Effect of inner diameter size of detector tube: Detector tubes whose internal diameters varied in small increments between 3.9-4.5 mm were tested with 1 ppm and 50 ppm acetylene containing gases, but no effect of inner diameter size was seen. This study showed that no corrections were necessary for inner diameter at least at these concentration levels.

(6) Effect of temperature: Air containing 1 ppm of acetylene was passed through the detector tubes at 13°, 25°. and 35°C, and no difference in the degree of coloring was found. As the acetylene concentration was raised to about 500 ppm, the degree of coloring became somewhat stronger with increasing temperature while the length of the colored layer became a little shorter at the same time.

5. Effect of Other Gases

This detector reagent is completely unaffected by oxygen (O_2), nitrogen (N_2), hydrogen (H_2), methane (CH_4), carbon dioxide gas (CO_2), or sulfur dioxide gas (SO_2). It is colored black by hydrogen sulfide (H_2S). Water vapor interferes with color formation, however, it is removed by the layer of absorbant at the detector tube inlet. Besides giving a sharp coloration with carbon monoxide (CO) [3], this reagent reacts rather sensitively to propane (C_3H_8) as well as to butane (C_4H_{10}), pentane (C_5H_{12}), and hexane (C_6H_{14}). It is particularly sensitive to unsaturated hydrocarbons of the olefin series like ethylene (C_2H_4) and propylene (C_3H_6) which impart brilliant blue color. On the other hand, it is completely insensitive to the aromatic hydrocarbons.

6. Summary

(1) Mixed ammonium molybdate and palladium sulfate reagent was sorbed on to silica gel particles, the granules were dried in vacuum, and the granules were packed into thin glass tubes to prepare ~~these~~ gas detector tubes.

(2) By passing a sample gas through this detector tube at the rate of 100 cc/min, ethylene concentration between 0.01-100 ppm and acetylene concentration between 1-1000 ppm could be determined in a simple manner

within a few tens of minutes or less from the color-volume relations.

(3) This method of detecting trace quantities of ethylene and acetylene can be put to practical use to detect the initial stages of the spontaneous combustion of coal in mines as well as to analyze the air that is taken into air fractionating units. ( )

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