Gas Chromatography Method for Traces of Carbon Dioxide in Air

SIR: A new approach has been developed for determination of trace components in a "light" major component using a modified hot-wire-detector gas chromatograph. The method has been applied to the determination of CO_2 in air. A similar method has been reported previously (1).

EXPERIMENTAL

Apparatus. The basic instrument used in these experiments was an F&M Scientific Corp. Model 720 dual column gas chromatograph equipped with type W filaments and a -0.2 to $+1.0$ mv. Minneapolis-Honeywell Electronic Model 15 recorder. The revised gas flow streams are shown in Figure 1. Helium was used as the carrier gas for the analysis of air samples. Air samples were dried by passing over Drierite and then introduced through either a 26.0 ± 0.5-cc. or 94 ± 1-cc. sample loop in conjunction with a F&M, GV-11 gas sampling valve. The four-way valve (Figure 1) is a gas chromatograph selector valve (No. A3-30-2) manufactured by Republic Valves. The precut column was 3.5 feet of $1/4$ inch o.d. copper tubing containing 30- to 60-mesh silica gel. The tubing was wrapped with asbestos insulation and an electrothermal heating tape. Temperature of this precut column was maintained at $60°$ C.
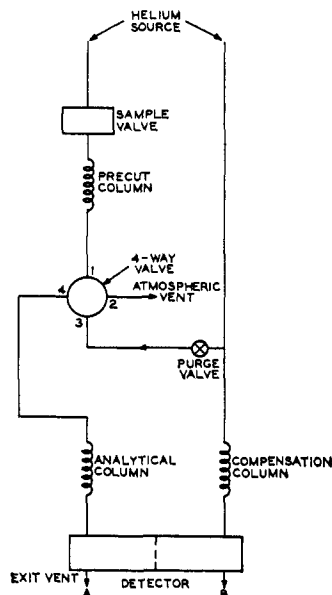

Figure 1. Revised gas flow streams

Analytical and compensation columns were 2.5 feet of $1/4$ inch o.d. copper tubing containing 30- to 60-mesh silica gel. These columns were maintained at $40°$ C.

Procedure. An air sample containing approximately 300 p.p.m. of CO_2

by volume was injected at the gas sample inlet port and swept by the helium carrier gas into the silica gel precut column. The four-way valve was set so that the N_2 and O_2 were vented to the atmosphere while the analytical column was purged with helium carrier gas. At an experimentally determined time, usually $1\frac{1}{2}$ minutes, the four-way valve was turned so that the CO_2 portion of the sample was passed into the analytical column. Here, the residual air and CO_2 were separated and then detected by the T/C detector. The CO_2 concentration was measured at the maximum sensitivity of the detector. A typical chart record obtained during one of these analyses is shown in Figure 2A compared with an "unvented" sample in Figure 2B.

The four-way valve "vent time" setting of $1\frac{1}{2}$ minutes is dependent upon carrier gas flow rates. Adjustment of flow rates was determined by the following method: (a) retention times of air and CO_2 in the analytical system were determined using the analytical column by itself at an optimum flow rate: then, (b) retention times were determined through the entire precut analytical column system without "venting" air. From steps (a) and (b), the differences in retention times equal to precut column retention times. Utilizing this information, the
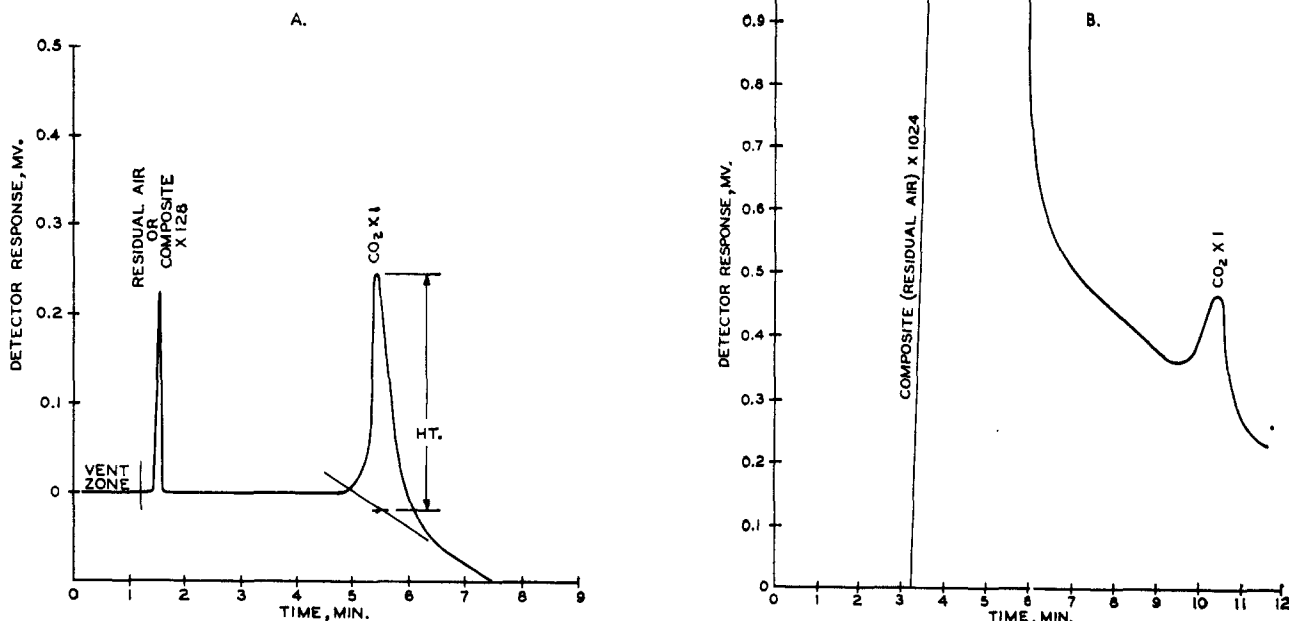

Figure 2. Comparison of typical chart record (A) left with unvented sample (B) right

A. Sample volume, 26.0 ± 0.5 cc.; precut column, 3.5 feet silica gel; analytical column, 2.5 feet silica gel; compensation column, 2.5 feet silca gel; precut column temp. $60°C$. Analytical and compensation column temp. $40°C$.; helium flowrate, analytical column, 50 cc./min., compensation column, 70 cc./min.; tungsten (hot-wire) bridge setting, 200 ma. B. Sample volume, 26.0 ± 0.5 cc.; analytical column, 2.5 feet silica gel; compensation column, 2.5 feet silica gel; analytical and compensation column temp., $40°$ C.; helium flowrate, analytical column, 50 cc./min.; compensation column, 70 cc./min.; tungsten (hot-wire) bridge setting, 200 ma.

Sample vol., cc.	No. of samples	Av. peak height, cm.	Std. dev., %	Average peak area, cm.^{2}	Std. dev, %
26.0	8	5.82	±2	3.63	±2
95	9	8.77	±2	13.55	±5

[a] Conditions of analysis are given in Figure 2A.

"vent time" for air was ascertained. Since the analytical column must be continually purged, the flow rate through the compensation column was adjusted so that helium stream divides equally between these two columns at the original flow rate through the analytical column.

CALIBRATION AND DISCUSSION

Where the CO_2 content was reasonably large, a detectable signal was obtained as is shown in Figure 2A for a 500-p.p.m. CO_2 utilizing the 26-cc. inlet loop.

The T/C detector was calibrated with a standard gas blend containing 500 p.p.m. of CO_2 in N_2 obtained from the Matheson Co., Inc. The typical results presented in Table I illustrate the relative merits of peak height vs. peak area for this analysis. A comparison of the area data for 26.0-cc. and 95-cc. samples indicated a 3.7 increase in signal area for the 3.7-fold increase of sample. However, the peak height data showed only a 1.5 increase in signal for the 3.7-fold sample increase. Although the peak height calibration may be more convenient, the peak area data, having shown excellent agreement with the sample size, was used for calibration purposes. The peak height was an aid in the determination of the method detection limits. Therefore, with the apparatus conditions as previously described, the calibration values were 138 p.p.m. of CO_2 per sq. cm. and 37 p.p.m. of CO_2 per sq.cm. for the 26- and 95-cc. loops, respectively. The deviations observed during the calibration are shown in Table I.

In the analysis with the 26-cc. loop sample, the average CO_2 peak height was 5.82 cm. for approximately 500 p.p.m. Because the lowest measurable peak height is about 0.24 cm., the minimum detectability would be 20 p.p.m. of CO_2. With the 95-cc. gas blend sample, the average CO_2 peak height was 8.77 cm. for approximately 500 p.p.m. As the lower limit of readable peak heights is again about 0.24 cm., 13 p.p.m. of CO_2 would be the minimum concentration detectable.

LITERATURE CITED

(1) Brenner, Nathaniel, Ettre, Leslie S., ANAL. CHEM. 31, 1815 (1959).

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Nitrite Interference in Spectrophotometric Determination of Atmospheric Sulfur Dioxide

SIR: The West-Gaeke (7) modification of the Schiff reaction is used extensively to measure concentrations of sulfur dioxide in the atmosphere. Monitoring instruments utilizing other principles for the determination of sulfur dioxide are quite commonly standardized, by assay (7) of known concentrations prepared for calibration. To eliminate NO_2 interference in the method, West and Ordoveza (8) proposed a modified sodium tetrachloromercurate (II) collecting solution containing 0.06% sulfamic acid. Zurlo and Griffini (9) have described the use of o-toluidine to eliminate this interference. We have found that the use of sulfamic acid in the collecting solution produces small but significant errors upon aeration. The increased use of this method for monitoring over long periods of time and the attachment of significance to small trends over the same periods of time require that the aeration effect be eliminated.

A project involving atmospheric sampling in Denver (2) enabled us to evaluate the West-Ordoveza modification for measuring sulfur dioxide. Parallel samples were collected during the study, using the unmodified West-Gaeke method and the West-Ordoveza modification. The results from these samples are shown in Figures 1 and 2. These figures have a dual ordinate. The lower gives the concentration found for nitrogen dioxide, which was determined by concurrent sampling. The upper ordinate shows the results obtained by the unmodified West-Gaeke method and the West-Ordoveza modification. In the first day's sampling (9 January), the two methods used for SO_2 gave parallel results but showed a difference in magnitude. The West-Ordoveza modification gave lower values than did the unmodified method. This was contrary to expectations since nitrogen dioxide interferes with the development of the color and thus leads to lower results in any method which does not compensate for this interference. The figure also shows that as the concentration of nitrogen dioxide decreased, the values for the sulfur dioxide concentration obtained by the two methods approached more closely to each other. The West-Ordoveza method still gave a lower value and, in the case of three samples, actually yielded negative values for the concentrations.

Figure 2 gives the results obtained from samples collected on 18 and 19 March. In this case, the West-Ordoveza method was modified by increasing the concentration of sulfamic acid in the collecting solution. With the exception of the one aberrant value obtained at five o'clock in the afternoon, the values for the concentration of sulfur dioxide given by the two methods were relatively divergent. The modified West-Ordoveza technique gave large negative values for the sulfur dioxide concentration, which could not be explained on the basis of errors in the experimental procedures.

The methods proposed by West-Gaeke (7), West-Ordoveza (8), and Zurlo and Griffini (9) were evaluated in a laboratory study. The reagents used