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GAS CHROMATOGRAPHIC METHODS FOR MIXTURES OF INORGANIC GASES AND C_1–C_2 HYDROCARBONS

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SUMMARY

Five gas chromatographic methods have been developed whereby gas mixtures containing H_2, A (or O_2), N_2, CO, CO_2, CH_4, and C_2H_6 can be analyzed on various lengths and combinations of three kinds of gas–solid adsorption columns. The adsorbents employed are molecular sieve 5A, silica gel and activated charcoal. Volume of gas mixture injected into the column is fixed at 0.5 ml, and therefore, volume percent of each component can be directly determined from its calibration curves. The calibration curves are constructed by plotting peak area versus percentage of the component in 0.5 ml sample of a series of standard mixtures with attenuation of the instrument as the parameter. When greater accuracy is desired, a normalization method is used.

Preparation of gas samples for chromatography, including sampling and conditioning, are also presented and discussed in detail.

All five methods are simple, rapid, and accurate. They have been satisfactorily applied to gas samples from coal gasification. Two of them are also applicable for on-stream analyses.

INTRODUCTION

The gas generator research project at Bituminous Coal Research, Inc., called for development of rapid and accurate methods for analyzing gaseous products containing inorganic gases and C_1–C_2 hydrocarbons. Due to its versatility and rapidity, gas chromatography was extensively employed.

Gas chromatography using thermal conductivity detection has been applied to gas mixtures of fixed gases and light hydrocarbons by many authors. For a review of the literature, see also ref. 5. Generally, two or more columns—a molecular sieve column with either a gas–solid adsorption or a gas–liquid partition column—are used for a complete analysis. CVEJANOVICH[1] separated mixtures of C_1–C_5 hydrocarbons and inorganic gases on three columns, namely a squalane on chromosorb, an adiponitrile on chromosorb and a molecular sieve 5A. The technique is rather involved and the arrangement of the columns is complicated. SWINNERTON and co-workers[2] employed, in series, a hexamethyl-phosphoramide on Columpak and a molecular sieve 13X, to

determine dissolved CO_2, O_2, N_2, CH_4, and CO in aqueous solutions. Later MANKA[3] also used, in series, a silica gel and a molecular sieve 13X, to analyze the same components in gas samples. In the latter case, only one detector was employed; therefore, switching polarity of the detector was necessary. These methods all have their merits and are good for their specific applications.

In our laboratory, a large number of gas samples either from coal gasification studies or from coal pyrolysis studies were to be analyzed. The components were: major, H_2, A, N_2, CO, CO_2, and CH_4, minor, C_2H_6, and traces, C_2H_4 plus some sulfides, which were undesirable impurities. Argon was present only in the gasification samples and was purposely added to the gasifier as a reference for making material balance in coal gasification studies[4]. To meet our need, the analytical procedures had to be highly accurate, rapid, and simple. After examining and testing the existing procedures, none of them met all the criteria. To suit our various purposes, five methods, using silica gel, activated charcoal, and molecular sieve 5A columns, were developed. Of the five, two (methods A and B) have become routine procedures to handle daily samples in the laboratory, another two (methods D and E) have been satisfactorily applied to our own on-stream analysis, and only method C appears to have limited usage.

This paper describes the five methods, their operating conditions, method of determining component concentrations, precision, and sample preparation.

EXPERIMENTAL

Gas chromatographs and columns

Two F & M gas chromatographs, Model 720 and Model 700-231, were used. Both were equipped with thermal conductivity detectors, dual columns, and Honeywell 1-mV recorder with automatic disc integrators for peak areas. The Model 720 was provided with a single gas sampling valve and the 700-231 with two valves, one for each column.

Helium was chosen as the carrier gas. As pointed out in the literature[5], a suitable mobile phase for the thermoconductivity detector is helium or hydrogen with a slight preference of the latter. However, in our case, hydrogen was a major component of the sample, and helium was, therefore, the natural choice.

Columns were all 0.25 in. O.D. aluminum tubing packed in this laboratory with one of the three packing materials, namely silica gel (30–60 mesh), molecular sieve 5A (30–60 mesh), or activated charcoal (30–60 mesh). The materials were purchased from F & M Scientific Company. Packing material per foot of column was 5 g for silica gel, 4 g for molecular sieve, and 2.5 g for charcoal. The columns were packed by a combination of vacuum and vibration techniques. The newly packed columns and exhausted columns were activated with helium. The activation was accomplished for molecular sieve and charcoal columns at 350° for 3 hours and for silica gel at 160° for 4 hours.

Column design and operating conditions

Design of column and establishment of operating conditions were partially guided by the principles discussed in the literature[5–7] and partially based on experience for finer adjustments. After extensive experimentation, satisfactory combinations were achieved for various gas mixtures. The final results are shown in Table I.

TABLE I

DESCRIPTION OF FIVE GC METHODS FOR MIXTURES OF INORGANIC GASES AND SOME LIGHT HYDROCARBONS

	A	*B*	*C*	*D*	*E*
Column	6 ft. (or 3 ft.) Molecular Sieve 5A + 3 ft. Silica gel (Independent)	12 ft. Silica gel	3 ft. Silica gel in series with 12 ft. Molecular Sieve 5A	3 ft. Molecular Sieve 5A	2 ft. Carbon column
Model of gas chromatograph	F & M 700-231	F & M 720	F & M 720	F & M 720	F & M 720
Elution order of components	H_2, A(O_2), N_2, CH_4, CO (M.S.); composite, C_2H_6, CO_2, C_2H_4 (S.g.)	H_2, A(O_2) + N_2, CO, CH_4, C_2H_6, CO_2, C_2H_4, C_3H_8	H_2, A(O_2), N_2, (all from M.S.) CO_2 (S.g.), CH_4 (M.S.) CO (M.S.)	H_2, A(O_2), N_2, CH_4 CO	H_2, composite (A, O_2, N_2, CO) CH_4, CO_2
Operating conditions					
Column temperature (°C)	50	50	50	50	80
Detector temperature (°C)	140	120	120	120	120
Bridge current (mA)	200	190	190	190	190
Injection port temperature (°C)	90	90	90	110	110
Helium pressure (p.s.i.)	30	30	30	30	30

Column temperature (°C)	50	50	60	50	50	50
Pressure at exit of the column (ml/min)						
Sampling loop (ml)	½	½	½	½	½	½
Remarks	(a) CO_2 removed from sample prior to admission to molecular sieve column. (b) A and O_2 can be determined by CHANG's differential method[8]. (c) Sample may be stripped of CO_2 prior to admission to silica gel column when determination of minute quantity of C_2H_4 is desired.	(a) O_2 and (A + N_2) as a group can be determined by the differential method[8].	(a) Two columns connected with a 10 in. × 1/8 in. teflon tubing; switching detector polarity is necessary. (b) A small CO_2 trap is inserted between the connecting tubing and the molecular sieve column. (c) A and O_2 can be individually determined[8].	(a) CO_2 removed from sample prior to admission to column. (b) Good for on-stream application.	(a) Good for on-stream application.	

Preparation of gas samples

Sampling

Depending on whether the analysis was to be made in the laboratory or on-stream in the pilot plant, two different means of sampling were used. For laboratory use, batch samples were collected in either a glass sampler or a metal sampler. For on-stream analysis, the gas was introduced directly into the instrument.

The glass sampling system for low gas pressure as devised in this laboratory is shown schematically in Fig. 1. (T) is a 500 ml glass sampling tube connected to a manifold (M). Each tube was filled with a confining liquid containing a saturated solution of Na_2SO_4 acidified with H_2SO_4 to 20% concentration. Methyl orange was added to the liquid to indicate the acidity of the solution. Basic constituents, such as NH_3, reacted with the acid and stayed in the liquid while all acidic components, such as CO_2 and H_2S, as well as neutrals, remained in the gas phase. (C) is a leveling bulb serving as a reservoir for the confining liquid. This system was satisfactorily used with gas line pressures from 10 in. to 40 in. water. Time for each collection was manually adjusted from a few seconds to a few minutes at a constant flow rate as desired. When samples were collected by this system, CO_2 could be determined by other wet methods for higher accuracy, such as the standard Orsat absorption method[9] used in this laboratory. This point will be discussed later in the paper.

For higher gas line pressure and larger volume of the gas sample, an all stainless steel batch sampling system was devised. It consisted of several 1500 ml-cylinders, each equipped with a packless valve and $^1/_8$ in. tubing fittings. The cylinders were connected to short parallel pieces ($^3/_4$ in. long) of $^1/_8$ in.-O.D. tubing welded on a $^1/_4$ in.-O.D. tubing used as manifold. The inlet end of the manifold was equipped with a single-stage pressure regulator in series with an MSA filter cartridge; the outlet end with a control valve. The system was connected to the gas line at the filter cartridge and

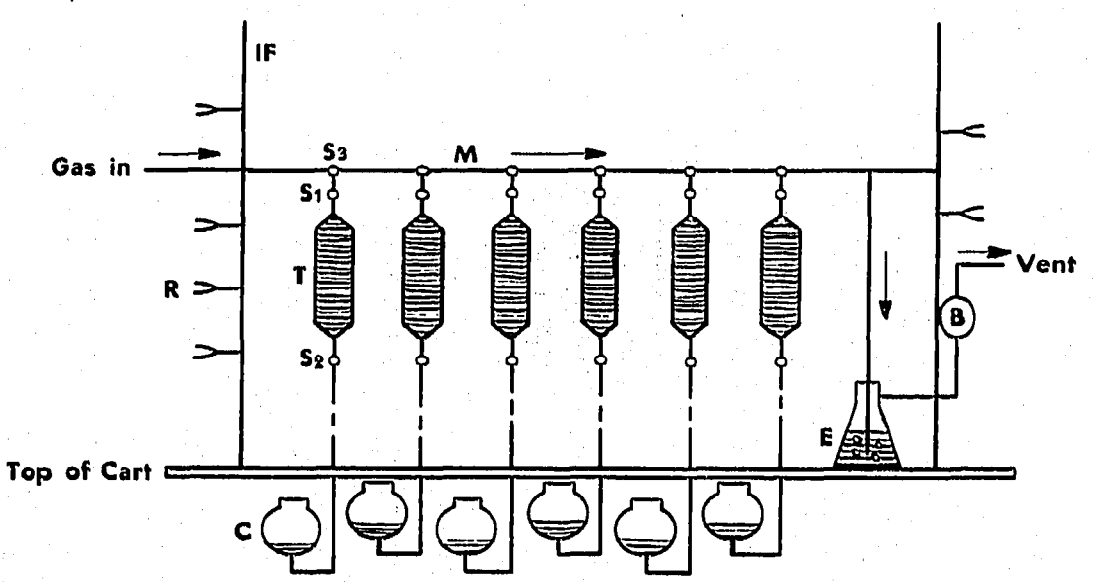

Fig. 1. Batch sampling system on cart. T = Sampling tube; S_1, S_2 = two-way stopcock on sampling tube; S_3 = three-way stopcock on manifold; M = manifold; IF = iron frame; C = confining liquid reservoir connected to sampling tube by long tygon tubing; E = Erlenmeyer flask containing water to indicate gas flow; B = double action bulb; R = iron ring for reservoir.

evacuated prior to sampling. After evacuation, all cylinders were kept under vacuum by closing their valves. The gas to be sampled was let in at the cartridge through the manifold and vented to atmosphere at a regulated pressure of 1 to 2 p.s.i. for purging. The control valve at the outlet was then closed. One of the cylinder valves was opened to sample the gas. The pressure of the gas was gradually increased at approximately constant rate to 20 p.s.i. within a few seconds to a few minutes as desired. At the end of the sampling period, the cylinder valve was closed and the outlet control valve opened again. The pressure was returned to 1 to 2 p.s.i. for purging. This procedure was repeated for the next sampling. The sample so collected represented an average product within the sampling period.

Conditioning of samples

Regardless of the sampling devices, the sample must be conditioned prior to admission to the gas chromatograph. A glass purification train, shown in Fig. 2, was inserted between the sample and the inlet of the chromatograph. Absorber (A) of 20 ml-capacity contained 10 to 15 ml $CdCl_2$ solution to trap sulfides[10]. Refrigerator (B) was made of a 2 mm I.D. coiled glass tubing attached to a 6 mm tubing and was placed in a Dewar flask packed with cracked ice. Drying tube (C) was a 3 in. $\times$ $^1/_4$ in. I.D. tygon tubing filled with indicating drierite (10 to 20 mesh). The total hold-up volume of the train was 30 ml. For the analysis of batch samples, the train and the sampling loop must be purged thoroughly with the sample prior to injection. For this reason, a minimum of 150 ml gas was needed for each analysis.

For on-stream gas chromatography, a much larger sulfide trap (50 ml), or two traps in series, and a longer drying tube (C) were needed. Exhausted traps could be

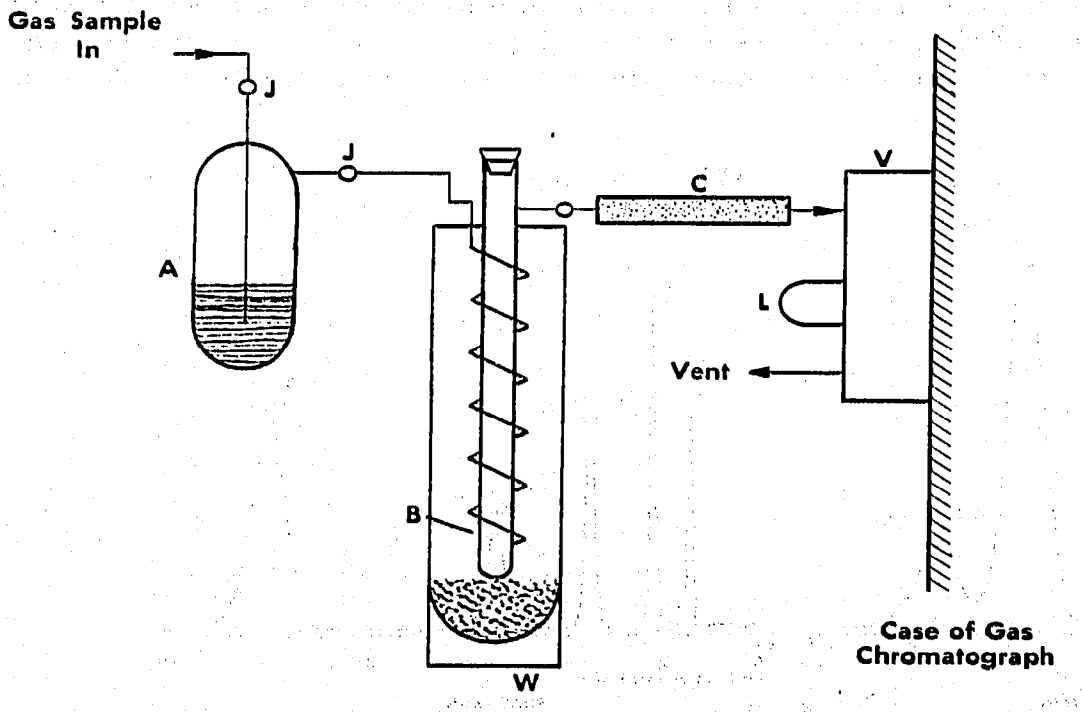

Fig. 2. Purification train for gas samples. A = Sulfide absorber; B = refrigeration tube; C = drying tube; V = sampling valve; L = sampling loop; J = ball joints; W = Dewar flask. Connecting tubing: 2 mm I.D. heavy wall capillary.

replaced with fresh ones between injections. The proper flow rate for gas flowing through the train was found to be about 100 ml/min.

Removal of CO_2 in samples

Presence of CO_2 in samples presented a problem on the molecular sieve column in methods (A), (C), and (D). CO_2 was rather strongly adsorbed on this column and eluted very slowly at 50°. This caused delay in readying the column for other injections. Removal of CO_2 from the sample eliminated the problem. A cartridge made of a 4 in. $\times$ $^3/_{16}$ in. I.D. glass tubing filled with Indicarb (10 to 20-mesh) was used for this purpose. The ends of the cartridge were loosely plugged with glass wool and tightly fitted with $^1/_8$ in.-holed rubber plugs. Stainless steel tubing of $^1/_8$ in. O.D. connects the cartridge between the sampling valve and the inlet of the column. Such a cartridge may be similarly employed in method (E) should on-stream measurement be limited to H_2 and CH_4 only.

Determination of concentration of each component

For each of the five methods, a family of calibration curves was established for each component by chromatographing standard mixtures of increasing concentration at various instrument attenuations. The curves were constructed by plotting integrated peak area directly *versus* the percentage of component in 0.5 ml of standard at ambient conditions with attenuation as the parameter. When an unknown was chromatographed under the standard operating conditions, the percentage of a component was determined from its peak area on the calibration curve.

However, if the total percentages of components in the unknown differed from 100, a normalization method was used to improve the accuracy of the result.

When the 500 ml-glass sampler with confining liquid was used, it was found that appreciable amounts of CO_2 would dissolve in the liquid if prolonged contact of the two was allowed. This condition was encountered when the gas in the sampler was

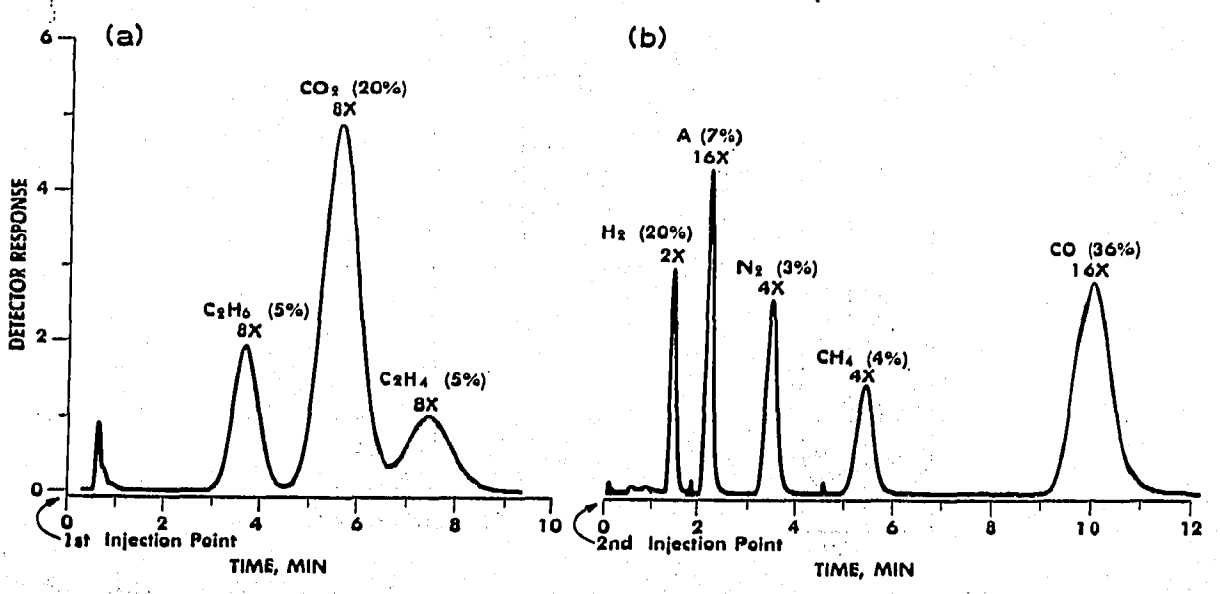

Fig. 3. Chromatograms produced by method A. (a) 3 ft. silica gel at 50°. (b) 6 ft. molecular sieve 5A at 50°.

repeatedly expelled by the incoming liquid. As discussed later, loss of CO_2 could amount to a few percent depending on its partial pressure. To eliminate this trouble, CO_2 was determined by the standard Orsat method immediately after sampling. The remaining components were determined by a suitable GC method. For this case, the calculation is as follows:

$$f_n = \frac{100 - CO_2\% \text{ (from Orsat)}}{(H_2{}^R\% + N_2{}^R\% + CH_4{}^R\% + ...)}$$

$$H_2\% = f_n\,(H_2{}^R\%)$$
$$N_2\% = f_n\,(N_2{}^R\%)$$
$$CH_4\% = f_n\,(CH_4{}^R\%)$$

where:

f_n = normalization factor,

$H_2{}^R\%$, $N_2{}^R\%$, $CH_4{}^R\%$..... = read out % of H_2, N_2, CH_4 ....., from their calibration curves.

$H_2\%$, $N_2\%$, $CH_4\%$ ..... = normalized % of H_2, N_2, CH_4 .....

For on-stream analysis, using methods (D) and (E), only a few important components were generally determined. Their percentages were found directly from the peak areas on the calibration curves.

RESULTS AND PRECISION OF THE METHODS

Chromatograms produced by each of the five methods are shown in Figs. 3, 4, 5, and 6. Relative retention times referring to N_2 for the components are presented in Table II.

The time requirements for the five methods are as follows: method (A), 30 min

TABLE II

RELATIVE RETENTION TIME (R_t) OF GAS COMPONENTS ON DIFFERENT COLUMNS

Method	*Column*	R_t*							
		H_2	$A(O_2)$	N_2	CH_4	C_2H_6	CO	CO_2	C_2H_4
(A)	6 ft. molecular sieve 5A	0.31	0.55	1 (2.9 min)	1.66	16.80	3.31	—	—
	3 ft. silica gel	0.50	1.0	1 (0.6 min)	1.0	6.30	1.0	10.0	13.00
(B)	12 ft. silica gel	0.65	1.0	1 (2.1 min)	1.55	7.45	1.20	10.70	14.1
(C)	3 ft. silica gel	0.09	0.14	0.14	0.20	—	0.14	1.52	—
	in series with 12 ft. molecular sieve	0.35	0.67	1 (6.4 min)	1.95	—	2.50	—	—
(D)	3 ft. molecular sieve 5A	0.36	0.64	1 (1.4 min)	1.71	21.5	2.57	—	—
(E)	2 ft. carbon	0.57	1.00	1 (0.7 min)	2.14	—	1.00	4.86	—

* Reference: N_2.

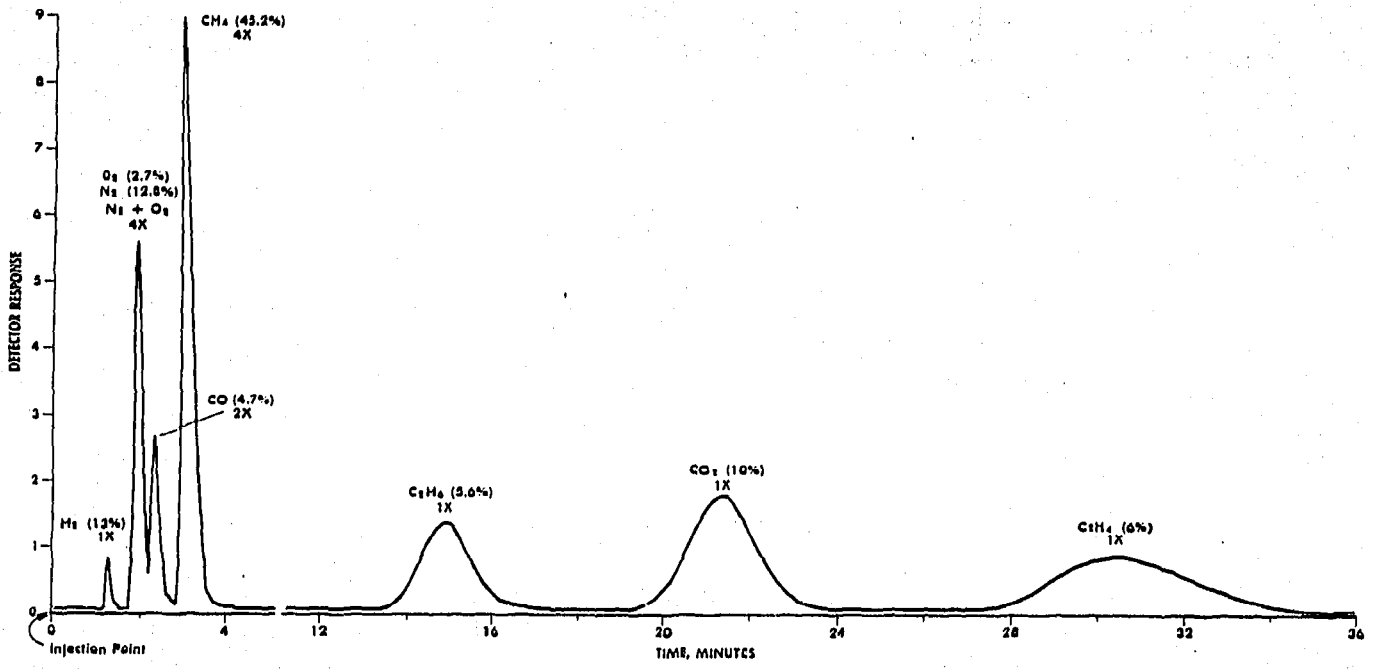

Fig. 4. Chromatogram produced by method B.

to C_2H_6; method (B), 35 min to C_2H_4; method (C), 18 min to CH_4; method (D), 4 min for analyzing H_2, $A(O_2)$, N_2, CH_4, and CO; method (E), 4 min for determining H_2, CH_4 and CO_2, or only 2 min for H_2 and CH_4.

Generally speaking, precision of any GC method depends on several factors,

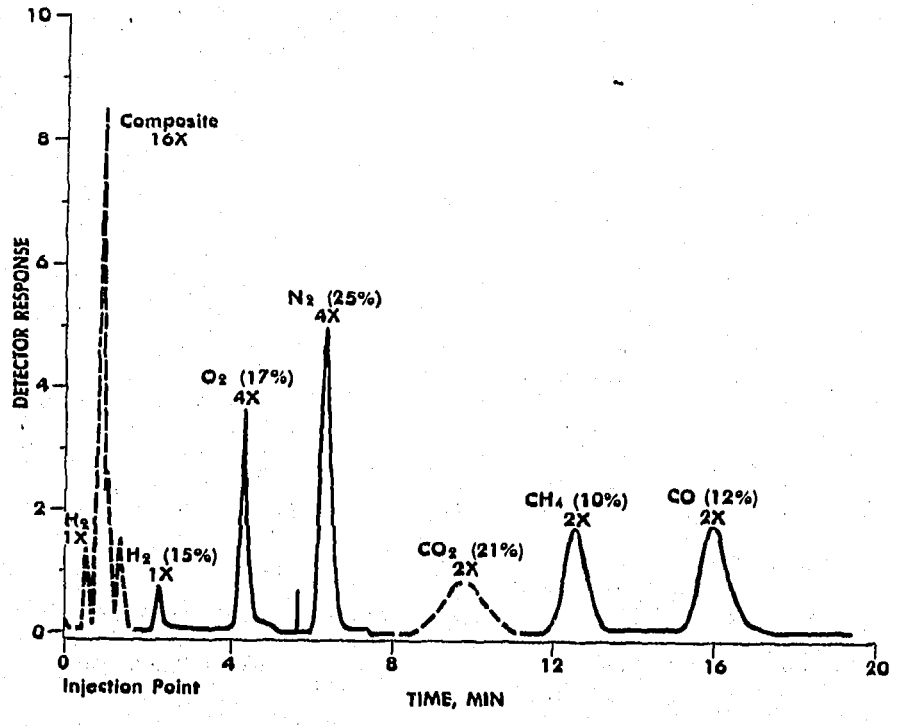

Fig. 5. Chromatogram produced by method C. 3 ft. silica gel (- - - -) in series with 12 ft. molecular sieve 5A (————) at 50°.

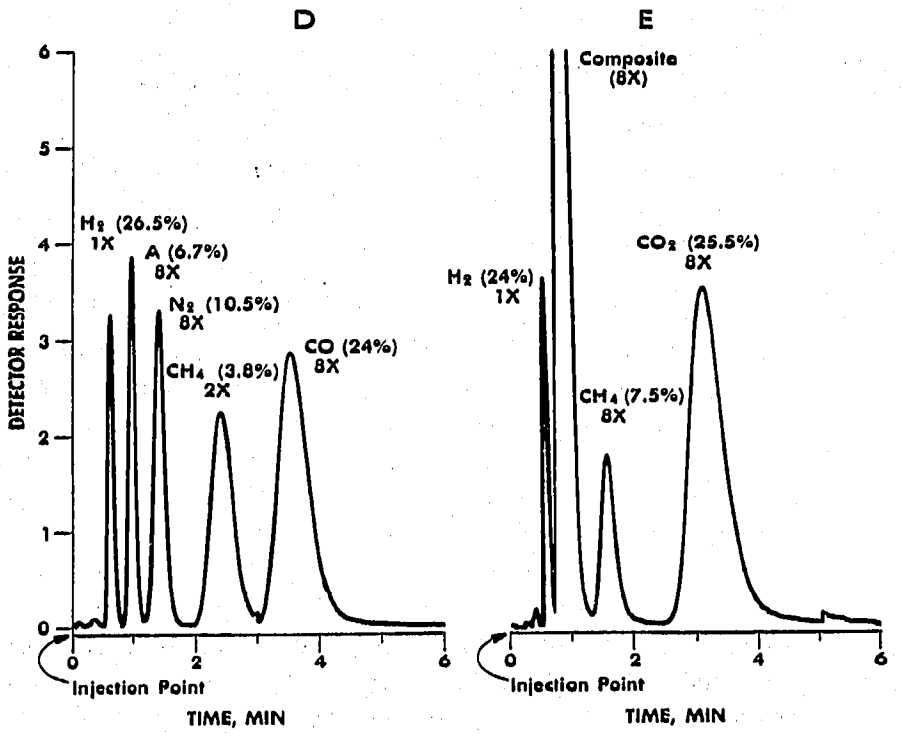

Fig. 6. Chromatograms produced by method D and method E. (Result of on-stream application.) Method D: 3 ft. molecular sieve 5A at 50°. Method E: 2 ft. charcoal at 80°.

namely, sampling and injection techniques, chromatograph and recorder performances, and ambient conditions. For method (A), the F & M 700-231 gas chromatograph was used. The precision of this method using this instrument for analyzing H_2, A, N_2, CH_4, CO and C_2H_6 plus CO_2 by the Orsat determination is expressed as standard deviations[11] as shown in Table III. These deviations were calculated from the results of replicate analyses of a sample from coal gasification. For applying methods (B), (C), (D), and (E), the F & M 720 gas chromatograph was employed. It is felt sufficient to present the precision data from one method for this instrument. As shown in Table IV, the precision

TABLE III

REPLICATE ANALYSES OF A GAS SAMPLE BY METHOD (A)

Run No.	*Volume (%)*						
	CO_2*	C_2H_6	H_2	*A*	N_2	CH_4	*CO*
1	18.6	1.8	24.8	11.9	1.9	10.5	30.5
2	18.5	1.9	24.6	11.9	2.0	10.7	30.4
3	18.5	1.8	24.8	11.9	1.9	10.7	30.4
4	18.3	1.3	25.9	11.8	1.8	10.7	30.2
5	18.6	1.5	25.9	11.8	1.9	10.2	30.1
6	18.5	1.5	25.1	11.7	1.9	10.8	30.5
Mean	18.50	1.63	25.18	11.84	1.90	10.60	30.35
Std. dev. (σ)	0.110	0.233	0.577	0.082	0.100	0.219	0.164

* CO_2 by Orsat method.

TABLE IV

REPLICATE ANALYSES OF A KNOWN MIXTURE BY METHOD (B)

Run No.	*Volume (%)*				
	H_2	CO	CO_2	CH_4	C_2H_6
1	6.2	0.80	1.0	2.50	0.75
2	5.9	0.85	1.05	2.50	0.95
3	5.8	0.85	1.20	2.60	0.80
4	6.0	0.80	1.00	2.50	0.95
5	5.7	0.85	1.00	2.80	0.90
Mean	5.9	0.83	1.05	2.60	0.87
% Present*	6.06	0.80	1.10	2.44	0.85
Std. dev. (σ)	0.193	0.042	0.141	0.042	0.091

* Balance of the mixture was helium.

of method (B) and the instrument is expressed as standard deviations determined by replicate analyses of a simulated gas sample from the coal pyrolysis. These deviations are considered to be small for components at such low concentrations.

DISCUSSION

As described in the experimental section, two sampling systems were used in this work to obtain batch samples. One was an all glass unit for low pressure gas, and the other an all stainless steel unit for high pressure gas. The former system used a confining liquid which absorbs appreciable amounts of CO_2 when its partial pressure was high.

When CO_2 was determined by gas chromatography, the purification train and the sampling loop were slowly and thoroughly purged with a large volume of the sample, which was gradually forced out by admitting the confining liquid into the sampling tube. Before an injection of the sample could be made to the column, CO_2 in the gas sample was gradually absorbed by the liquid tending to establish an equilibrium between the two phases. As a result, CO_2 concentration in the gas phase became less as time passed and the peaks produced by consecutive injections of the sample became smaller and smaller. It was found that for samples having 25% CO_2, the area difference of the highest and the lowest peaks reached 2 to 3%, and for those with 35% CO_2, 3 to 4%. To correct this error, CO_2 was determined by the Orsat method prior to gas chromatography of the sample. Immediately after sampling, the tube was full of gas under a pressure slightly higher than 1 atm. Less than 10 ml of the confining liquid was left inside, and this small amount of liquid was already saturated with CO_2. When the first portions of the sample were taken out for Orsat CO_2 determination, the result would closely represent the true concentration of this component. It was also found that for samples with less than 10% CO_2, the loss to confining liquid was not large enough to cause significant error. Therefore, Orsat CO_2 determination was not applied to samples having CO_2 less than 5%. This absorption of gas by the confining liquid was observed with CO_2 but not with other components.

By using the metal sampling system, loss of CO_2 was avoided. Besides, the basic constituents, *i.e.*, NH_3 and pyridine homologs, if present, would still remain in the sample. The large quantity of an intact sample so collected could supply the need for many other purposes. On the other hand, the cost of the metal system was high and it could not be assembled in the laboratory as easily as the glass unit.

As described in the section *Determination of concentration*, calibration curves for all five methods were established from areas produced by 0.5 ml standard mixtures measured at ambient conditions. Theoretically, gas sampled at ambient conditions must be corrected to standard temperature and pressure; however, we found that the correction was unnecessary. In our locality, barometric pressure recorded for a period of four months was 730 $\pm$ 5 mm and room temperature in the air-conditioned laboratory was 26° $\pm$ 2°. The error introduced to the volume by these variations was found insignificant. To simplify the procedure, no correction of temperature and pressure was made for the 0.5 ml volume of the standard mixtures during calibration. For unknown samples, it is noted that the procedure of normalization also tends to cancel out the effect of pressure and temperature.

In method (A), as shown in Table I, either a 6 ft. or a 3 ft. molecular sieve column completely separates H_2, A, N_2, CH_4, and CO. However, the longer column was preferred because the resolution values between adjacent peaks were greater than on the shorter column; thus providing a safety factor against wide variations in the molar ratios of adjacent components.

Also in method (A), the 3 ft. silica gel column did not completely resolve CO_2 and C_2H_4 at a molar ratio (C_2H_4 to CO_2) of 0.25 as shown in Fig. 3, and a 10 ft. column was needed for complete separation. But on this longer column, retention times of these two components were too long. It was impractical to couple the 10 ft. column with the 6 ft. molecular sieve for routine use. Fortunately the majority of the gas samples encountered contained no C_2H_4. Whenever samples containing minute amounts of C_2H_4 were determined on the 3 ft. silica gel, the analysis was made by removing CO_2 from the sample with an "Indicarb" cartridge installed between the column inlet and the sampling valve. In this manner, C_2H_4 appeared as a small individual peak. Therefore, for speed, the 3 ft. silica gel column was employed in method (A).

The precision of methods (A) and (B) shown in Tables III and IV is high; these two methods, therefore, have become routine procedures for use in our laboratory.

Methods (D) and (E) were generally used for on-stream analysis of a few important components. Since normalization could not be accomplished, the precision was sometimes slightly lower than that of methods (A) and (B). For operation control purposes, methods (D) and (E) were found satisfactory.

Method (C), which uses a 3 ft. silica gel column in series with a 12 ft. molecular sieve, is similar to the method developed by MANKA[3]. In method (C), as shown in Fig. 5, CO_2 from the silica gel column is eluted between N_2 and CH_4, both from the molecular sieve. But in MANKA's method, elution of CO_2 from the silica gel can be adjusted either ahead of or behind the other components emerged from the molecular sieve column. It may be true that by varying the length of the connecting tubing between the two columns and the operating conditions of the gas chromatograph, elution of CO_2 could be spaced anywhere as desired; however, spacing CO_2 at the beginning or in the middle of the chromatogram was found undesirable. When the

concentration of CO_2 and its adjacent components differed greatly, the elution curve for these two would be distorted somewhat and quantitative estimation could not be made accurately. For two closely eluted peaks, as CO_2 and CH_4 in this case, resolution is affected by their molar ratio[5]. In gas–solid chromatography, retention time and peak broadening usually increase with concentration and thus influence the difference of retention time between the two peaks. The resolution will deteriorate with decreasing molar ratio of CH_4 to CO_2 and vice versa. For example, from our experience, when a high percent CO_2 was eluted between N_2 and low percent CH_4, the small CH_4 peak was only partially shown or entirely lost. This is due to the fact that the last part of the major CO_2 peak at a lower instrument attenuation overlapped with the small CH_4 peak which was partially or entirely cancelled while reversing the detector polarity. To avoid this situation, CO_2 elution must be spaced at the end, far away from the last eluate from the molecular sieve. When the molar ratio of CH_4 to CO_2 was in the range of 0.75 to 0.25 with $CO_2 < 25\%$ in a 0.5 ml sample, the elution pattern produced by method (C) was not distorted.

In conclusion, all five methods as described above have been satisfactorily applied to coal gasification samples in our laboratory. It is believed that methods (A), (B), (D), and (E) can be equally well applied to similar gas samples from other sources. In addition, methods (D) and (E) are extremely useful for on-stream application in gas-making processes.

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