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Note

Analysis of coke oven gas by gas chromatography

PERTTI KOKKONEN*
Department of Chemistry, University of Oulu, 90570 Oulu (Finland)
ERKKI OJANIEMI
Research Centre, Rautaruukki Oy, 92170 Raahensalo (Finland)
and
RISTO PÖYKIÖ
Department of Chemistry, University of Oulu, 90570 Oulu (Finland)
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The use of gas chromatography (GC) in the analysis of coke oven gas has been reported by several workers[1–5]. The method has been used to control the purification and chemical recovery process of coke oven gas in iron and steel works. Compared with classical procedures of gas analysis, *e.g.*, IR and UV–fluorescence spectroscopy, chemiluminescence, gamma absorption and titrimetry, GC increases the speed and precision of determinations[6,7]. Doran and Cross[8] studied a sample containing O_2, N_2, CH_4, CO, CO_2, C_2H_6, C_3H_8 and n-C_4H_{10} using a molecular sieve and Chromosorb P columns. Terry and Futrell[9] analysed gases containing C_2–C_6 hydrocarbons in the presence of O_2 and N_2 using a three-column system. For the analysis of mixtures of permanent gases and C_1–C_2 hydrocarbons, Marchio[10] used Porapak and molecular sieve columns.

Although much work has been carried out in this field, no papers on the dependence of the different operational parameters on the separation of these molecules have been published. We have therefore carried out experiments with various packing materials, column lengths, temperatures and flow-rates of the carrier gas in order to establish the optimal conditions for coke oven gas analysis.

EXPERIMENTAL

Column packings

As the stationary phase we used molecular sieves 5A (60–80 and 80–100 mesh) (Ohio Valley Specialty Chemical), Porapak QS (80–100 mesh) (Waters) and Chromosorb 102 (60–80 mesh) (Manville Products). The columns were filled in the usual manner with pure stationary phase material. Each column was pre-conditioned at a temperature at least 30 K higher than its working temperature. All the connections between the columns (1/8 in. O.D.) and the valves and also the column tubes were made of stainless steel. Columns of Porapak QS (500 × 0.2 cm I.D., 80–100 mesh), Chromosorb 102 (360 × 0.2 cm I.D., 60–80 mesh) and Carbosieve S-II (300 × 0.2 cm I.D., 100–120 mesh) were supplied by Perkin-Elmer.

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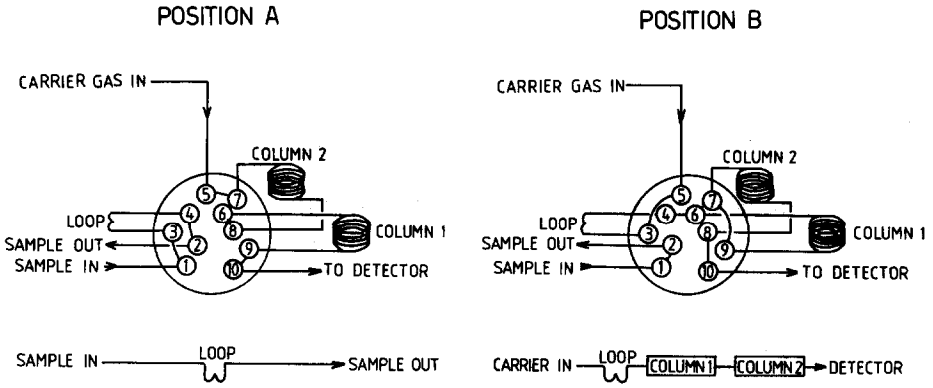

Fig. 1. Schematic diagram of gas sampling and column switching during the analytical run.

Apparatus

The analyses are accomplished by using a Perkin-Elmer Model Sigma 300 dual-column temperature-programmed gas chromatograph equipped with an integrator (Perkin-Elmer LCI-100), instruments for thermal conductivity (TCD) and flame ionization detection (FID), a ten-port valve and a 2.5-ml sample loop. The flow circuit of the instrument is shown in Fig. 1.

Column 1 refers to a Porapak QS or Chromosorb 102 column and column 2 contains molecular sieves. The sample is introduced by means of a gas-sampling valve from a sample loop to the Porapak QS (or Chromosorb 102) column. With the valve in position B, injection of the sample into column 1 permits a portion of the sample to flow into column 2. The separation of CO, CO_2, C_2H_6 and H_2S molecules takes place in this first column, but H_2, O_2, N_2 and CH_4 pass quickly into the molecular sieve column, where they are separated. The valve is thrown from position B to position A just before the CO_2 would elute from the porous polymer, and the components that were in the porous polymer column enter the detector directly. Instead of pure helium, a gas mixture containing hydrogen (8.6 ± 0.3%) mixed with helium manufactured by AGA (Oulu, Finland) was used as the carrier gas. This gas mixture, together with the programmed polarity changing of the recorder at the beginning of each run and back again after the H_2 peak, make it possible to transform an M-shaped negative peak of hydrogen into a normal positive peak for the quantitative determination. The composition of the calibration gas supplied by AGA was as follows: O_2, 0.989 ± 0.020; CO_2, 1.99 ± 0.04; C_2H_6, 2.10 ± 0.04; N_2, 3.05 ± 0.06; CO, 6.89 ± 0.14; CH_4, 26.17 ± 0.26%; and H_2S, 4920 ± 246 ppm; remainder H_2 (*ca.* 58.319%).

The temperature programmes were as follows: time (1), 3–10 min at the initial temperature (15–35°C), after which the column oven was heated to 60°C at a rate (1) of 20–25°C/min, held for time (2) = 0 min in all instances; this was followed by an immediate rise from 60°C to 225°C at a rate (2) of 4–32°C/min, then held for time (3) = 25–35 min. The injector and detector temperatures were 150°C. The flow-rate of the carrier gas varied between 30 and 50 ml/min.

TABLE I

INFLUENCE OF THE OVEN TEMPERATURE, THE FLOW-RATE OF THE CARRIER GAS AND THE PARTICLE SIZE OF THE PACKING MATERIAL ON THE RETENTION TIMES, t_R, OF H_2, O_2, N_2 AND CO GASES USING A MOLECULAR SIEVE 5A COLUMN (200 × 0.2 cm I.D.)

Injector and detector (TCD) temperatures, 150°C.

Component	*Flow-rate (ml/min)*	*Particle size (mesh)*	*t_R (min)*			*Flow-rate (ml/min)*	*t_R (min)*		
			40°C	*50°C*	*60°C*		*40°C*	*50°C*	*60°C*
H_2	30	60–80	0.518	0.504	0.498	50	0.406	0.398	0.401
O_2	30		1.314	1.148	1.074	50	1.021	0.954	0.818
N_2	30		3.05	2.433	2.01	50	2.38	1.829	1.578
CO	30		16.40	11.24	8.62	50	12.66	8.76	6.62
H_2	30	80–100	0.668	0.657	0.650	50	0.520	0.502	0.500
O_2	30		1.489	1.404	1.281	50	1.169	1.090	0.997
N_2	30		3.609	3.116	2.60	50	2.82	2.44	2.03
CO	30		17.17	13.46	9.97	50	13.59	10.10	7.67

RESULTS AND DISCUSSION

The first approach was to test various packing materials and their ability to separate the gas components. Several runs were carried out to find the optimal working conditions. Figs. 2–4 show the chromatograms for different types of packing material. Apart from H_2, O_2 and N_2, the order of separation of the other gas components in the mixture is different for all the columns studied. The peak were verified for all the columns studied. The peaks were verified for all the column types by the standard addition method.

The separation of the O_2 and N_2 using a single Carbosieve S-II column involves long retention times, and the whole run therefore takes a long time although

TABLE II

INFLUENCE OF THE OVEN TEMPERATURE, THE FLOW-RATE OF THE CARRIER GAS AND THE PARTICLE SIZE OF THE PACKING MATERIAL ON THE RETENTION TIMES, t_R, OF H_2, O_2, N_2 AND CO GASES USING A MOLECULAR SIEVE 5A COLUMN (100 × 0.2 cm I.D.)

Injector and detector (TCD) temperatures, 150°C.

Component	*Flow-rate (ml/min)*	*Particle size (mesh)*	*t_R (min)*		*Flow-rate (ml/min)*	*t_R (min)*	
			20°C	*40°C*		*20°C*	*40°C*
H_2	30	60–80	0.262	0.253	50	0.210	0.184
O_2	30		0.666	0.541	50	0.449	0.417
N_2	30		1.98	1.261	50	1.481	0.998
CO	30		12.51	6.15	50	9.20	4.64
H_2	30	80–100	0.276	0.262	50	0.213	0.210
O_2	30		0.696	0.545	50	0.552	0.434
N_2	30		1.85	1.193	50	1.474	0.950
CO	30		15.35	6.94	50	11.59	5.51

a heating rate of 32°C/min is used to raise the oven temperature from 60 to 225°C. In addition this column does not separate H_2S. We therefore considered the influence of the different operational parameters on the separation of the gas components using only Porapak QS and Chromosorb 102 columns together with the molecular sieve 5A column.

Next we tested the influence of the flow-rate of the carrier gas, the oven temperature, the particle size of the packing material and the length of the column on the separation of H_2, O_2, N_2 and CO using the single colecular sieve column. The gas mixture was prepared by mixing nearly equal volumes of the pure components. The results are given in Tables I and II. The retention times and the chromatograms (not presented) show that the separation of H_2 and O_2 sets the limit for the operational parameters. When a flow-rate of 50 ml/min and a column 1 m long filled with 60–80 mesh molecular sieves are used, the highest temperature for a quantitative analysis is 40°C. Tables I and II also show the normal behaviour of the operational parameters: the retention times of the gas components increase with increasing length of the column and decreasing particle size of the packing material, and decrease with increasing oven temperature and flow-rate of the carrier gas. The most influential of these parameters seems to be the length of the column; the particle size of the packing material has only a minor effect on the retention times under otherwise constant conditions.

The third approach was to compare the polymer columns, Porapak QS and Chromosorb 102, with each other using the double column system. Because the 1-m molecular sieve column is full enough to separate the first three components (H_2, O_2 and N_2), we used it together with the two above-mentioned polymer columns.

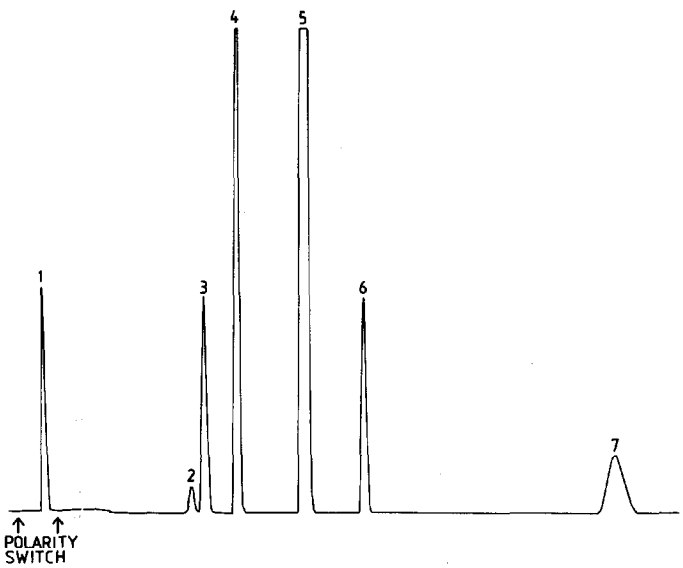

Fig. 2. Chromatogram of the separation of a gas mixture. Column 1 = stainless steel, 300 cm × 2 mm I.D., Carbosieve S-II, 100–120 mesh. Carrier gas, helium–hydrogen mixture, flow-rate 30 ml/min. Oven temperature programme: 20°C for 3 min, then 10°C/min to 60°C, held for 0 min, 32°C/min to 225°C, held for 25 min. Peaks: 1 = H_2; 2 = O_2; 3 = N_2; 4 = CO; 5 = CH_4; 6 = CO_2; 7 = C_2H_6.

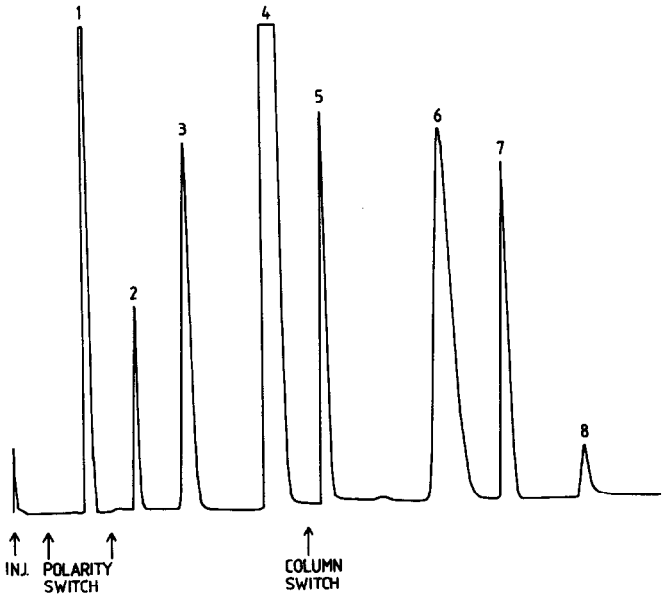

Fig. 3. Typical chromatogram of the separation of permanent and hydrocarbon gases. Column 1 = stainless steel, 500 cm × 2 mm I.D., Porapak QS, 80–100 mesh. Column 2 = stainless steel, 100 cm × 2 mm, I.D., molecular sieve 5A, 60–80 mesh. Carrier gas, helium–hydrogen mixture, flow-rate 10 ml/min. Oven temperature programme: 25°C for 8.5 min, then 25°C/min to 60°C, held for 0 min, 4°C/min to 225°C, held for 25 min. Peaks: 1 = H_2; 2 = O_2; 3 = N_2; 4 = CH_4; 5 = CO_2; 6 = CO, 7 = C_2H_6; 8 = H_2S.

It was found that with the Porapak QS column the critical step in the gas mixture analyses is the separation of CO and C_2H_6. We tested the dependence of Δt_R, the difference between the retention times of C_2H_6 and CO gases, on the flow-rate of the carrier gas and the oven heating rate (2) using the following operational parameters: time (1) = 8.5 min, time (2) = 0 min, time (3) = 25 min, initial oven temperature = 25°C and rate (1) = 25°C/min. The results are given in Fig. 5. Sufficient separation of CO and C_2H_6 for quantitative determination using the molecular sieve column 5A (1 m × 1/8 in. O.D., 60–80 mesh) and the Porapak QS column (5 m × 1/8 in O.D., 80–100 mesh) is achieved when the flow-rate of the carrier gas is 20 ml/min and the oven heating rate (2) is 4°C/min. The total time for the separation of all the components from which H_2S (19.61 min) is the last one. A significantly better separation is achieved with a lower flow-rate (10 ml/min), as shown in Fig. 2. The retention time of H_2S is then 22.65 min.

When the Chromosorb 102 and molecular sieve column system is used, the critical step in the analyses is the separation of H_2S and CO. The operational parameters are given in Fig. 4. It seems that the separation of the components is sufficient at a flow-rate of 50 ml/min when the heating rate (2) is 15°C/min or higher (Fig. 5). When a flow-rate of 50 ml/min and a heating rate (2) of 15°C/min are used, the retention time of the last component is 10.31 min. Fig 5 shows that Δt_R for the separation of CO and H_2S at a constant heating rate (2) increases with decreasing flow-rate of the carrier gas.

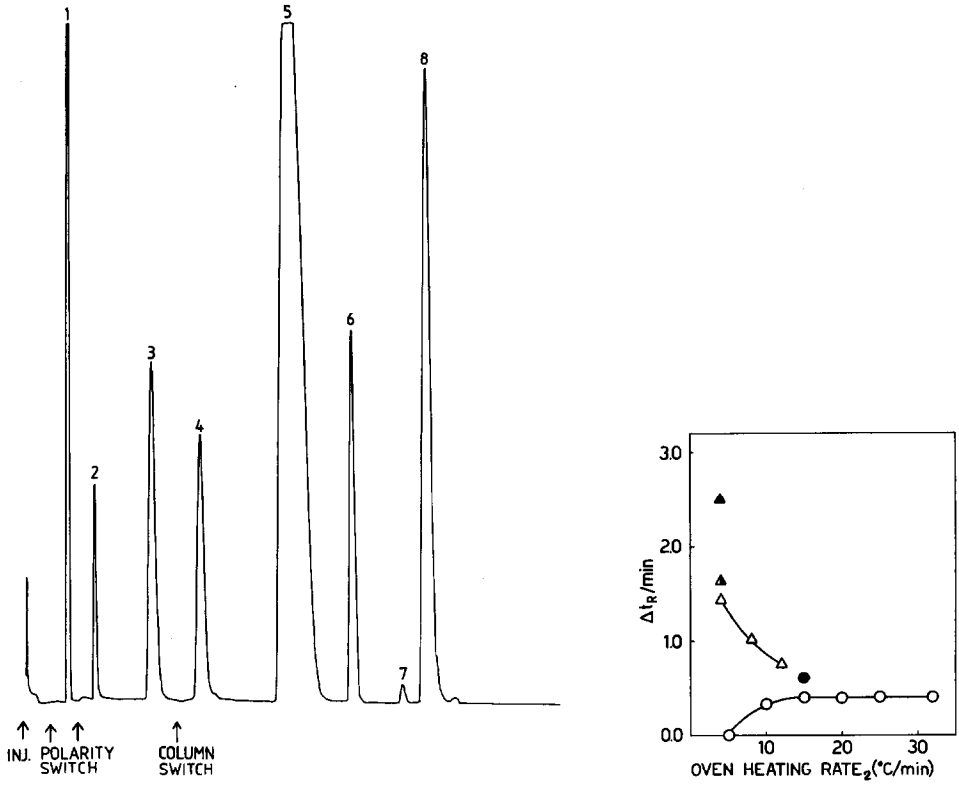

Fig. 4. Chromatogram of the separation of a gas mixture. Column 1 = stainless steel, 360 cm × 2 mm, I.D., Chromosorb 102, 60–80 mesh. Column 2 = stainless steel, 100 cm × 2 mm, I.D., molecular sieve 5A, 60–80 mesh. Carrier gas, helium–hydrogen mixture, flow-rate 30 ml/min. Oven temperature programme: 15°C for 5.5 min, then 20°C/min to 60°C, held for 0 min, 15°C/min to 250°C, held for 35 min. Peaks: 1 = H_2; 2 = O_2; 3 = N_2; 4 = CO_2; 5 = CH_4; 6 = C_2H_6; 7 = H_2S; 8 = CO.

Fig. 5. Δt_R versus heating rate (2) for the separation of successive peaks. The triangles refer to the Porapak QS column and the separation of the CO and C_2H_6 peaks. The symbols △, ▲ and ▲ refer to flow-rates of 30, 20 and 10 ml/min, respectively. The circles relate to the separation of H_2S and CO with the Chromosorb 102 column. The symbols ○ and ● refer to flow-rates of 50 and 30 ml/min, respectively. Oven temperature programmes as in Figs. 3 and 4, except that rate (2) varies.

It can be concluded that a single column system is not sufficient for coke oven gas analysis, although the Carbosieve S-II column alone is able to separate all components except H_2S from the gas mixture studied. When a double column system (molecular sieve column + polymer column) is used, the results show that the shorter Chromosorb 102 column yields a good separation of all the components in nearly half of the time required by the Porapak QS column. The Chromosorb 102 packing material is hence recommended for the GC analysis of coke oven gas.

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