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A New Method of Continuous Gas Chromatography

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A method is proposed for the continuous analysis of multi-components mixture of volatile compounds by means of gas chromatograph. In the method, a sinusoidal concentration wave of sample gas mixture is introduced continuously into a column of gas chromatograph and the mole fraction of each component can be determined from the amplitude attenuation and the phase-shift measured at the points of several length along the column. The principle of the method is described and the conditions which have to be considered in selecting the column and the angular frequency are discussed. Experiments with two components, nitrogen and oxygen, gas mixture employing a Molecular Sieve 5A column and the hydrogen carrier gas indicate that the principle is valid and that the continuous analysis of multi-components mixture is successful.

It is almost needless to say that the gas chromatography has provided the most efficient and versatile method for the analysis of volatile compounds since its first appearance.[1] In these days, with the aid of automatic gas sampling, peak reading and programming devices, the gas chromatograph has become to repeat the analysis periodically.[2] However, while rapid compared with the ordinary chemical analysis, the gas chromatography is essentially a batch operation analysis and requries several minutes to complete one cycle of analysis. This may sometimes be too slow to follow rather rapid change in the concentration such as required in the analysis of a batch reaction. It is quite desirable, therefore, to develop the method for the continuous analysis of multi-components mixture by means of gas chromatograph. Recently Izawa and Furuta[3] proposed a way of obtaining the results of analysis continuously using a correlation function between the input and the output of a gas chromatograph. Though continuous, this method can only give the average value of concentration for the time interval which corresponds to a period of one cycle of analysis in the ordinary gas chromatograph. The continuous gas chromatograph presented in this paper will give the instantaneous results of analysis and will provide a way of the continuous analysis of multi-components gas mixture.

Theoretical

Principle. Figure 1 shows a schematic diagram of the proposed continuous gas chromatograph. A number of concentration detectors are installed to measure the sum of concentration of each component at the points of several different length along the column. Sample gas and carrier gas are introduced into the column in such a way that the concentration of the sample gas mixture varies with time sinusoidally at the inlet of the column. Since individual components have their characteristic moving velocities in the column, the wavelength of components within the column are different each other and thus the phase-shift of each component wave at a specified length of the column has its own characteristic value. It may be possible, therefore, to determine the concentration of each component by measuring the magnitude of the phase-shift of the sinusoidal wave at the points of several length along the column.

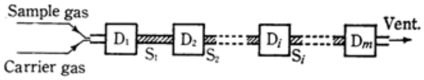

Fig. 1. Schematic diagram of continuous gas chromatograph.
S: Column segment, D: Concentration detector

Let consider a gas mixture consists of n components. The concentration of component j at the detector 1 can be written as:

$$C_{1j}(t) = C_{sj} + A_1 x_j \sin \omega t \qquad j = 1, 2, \cdots, n \quad (1)$$

where C_{sj} is the stationary concentration of component j ; A_1: the amplitude of sinusoidal wave of sample gas mixture; x_j: the mole fraction of component j in the sample gas and ω is the angular frequency of the sinusoidal wave. The output signal of the detector 1 will be then:

$$y_1(t) = \sum_{j=1}^{n} C_{sj} + \sum_{j=1}^{n} A_1 x_j \sin \omega t \qquad (2)$$

where, without loss of generality, the sensitivity of the detector is assumed to be the same unity for

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[1] A. T. James and A. J. P. Martin, *Analyst,* **77,** 915 (1952).

[2] H. R. Karp, *Control Engineering,* **8,** 87 (1961).

[3] K. Izawa and K. Furuta, 36th International Congress on Industrial Chemistry, Brussel (1966).

each component.*1

If all the phenomena which occur within the column are of linear characteristics, that is, if Henry's law of adsorption holds within the column and its constant is not influenced by the presence of other components, the concentration of each component at the detector i will be completely characterized by the amplitude attenuation and the phase-shift of the sinusoidal wave. Thus:

$$C_{ij}(t) = C_{sj} + \alpha_{ij}A_1x_j\sin(\omega t + \theta_{ij}) \qquad (3)$$
$$i = 2,3,\cdots,m; \quad j=1,2,\cdots,n$$

where C_{ij}, α_{ij} and θ_{ij} are the concentration, the attenuation factor and the phase-shift, respectively, of j component at the detector i. Therefore, the output signal of detector i will be:

$$y_i(t) = \sum_{j=1}^{n} C_{sj} + \sum_{j=1}^{n} \alpha_{ij}A_1x_j\sin(\omega t + \theta_{ij}) \qquad (4)$$
$$i = 2,3,\cdots,m$$
$$= \sum_{j=1}^{n} C_{sj} + A_i\sin(\omega t + \theta_i) \qquad (5)$$

where

$$A_i = A_1\{(\sum_{j=1}^{n}\alpha_{ij}x_j\cos\theta_{ij})^2 + (\sum_{j=1}^{n}\alpha_{ij}x_j\sin\theta_{ij})^2\}^{1/2} \qquad (6)$$

and

$$\theta_i = \tan^{-1}(\sum_{j=1}^{n}\alpha_{ij}x_j\sin\theta_{ij}/\sum_{j=1}^{n}\alpha_{ij}x_j\cos\theta_{ij}) \qquad (7)$$

are the amplitude and the phase-shift of the sinusoidal wave observed at the detector i.

Since the amplitude attentuation factor α_{ij} and the phase-shift θ_{ij} of j component at the detector i are of characteristic value under the specified column condition and may be determined preliminarily using pure component as sample gas, the $m=n-1$ number of the amplitude and/or the phase-shift measurements made at the points of different length along the column will suffice to calculate the mole fraction of all the components according to Eqs. (6) and/or (7). From computation point of view, the use of Eq. (7) instead of Eq. (6) is preferable because of the simplicity in data reduction process. Rearranging Eq. (7). together with the definition of the mole fraction the following linear algebraic simultaneous equations are obtained.

$$\begin{aligned} &\sum_{j=1}^{n} x_j = 1 \\ &\sum_{j=1}^{n}\alpha_{ij}x_j\sin(\theta_i - \theta_{ij}) = 0 \quad i = 2,3,\cdots,n \end{aligned} \qquad (8)$$

Solving Eq. (8), the mole fraction of each component is expressed as:

$$x_j = \Delta_j/\Delta \qquad j = 1,2,\cdots,n \qquad (9)$$

where

$$\Delta = |a_{ij}|$$
$$a_{ij} = \begin{cases} 1 & \text{for } i = 1 \\ \alpha_{ij}\sin(\theta_i - \theta_{ij}) & \text{for } i = 2,3,\cdots,n \end{cases}$$

is the determinant associated with the coefficient matrix of Eq. (8) and Δ_j is the minor determinant obtained by deleting the 1st row and the jth column.

Column Conditions and Angular Frequency. It should be noted on the principle that in contrast with the ordinary gas chromatograph the column length needs not to be long enough to separate the peaks of the components in this method. Even if the very short column is used the large magnitude of the phase-shift can be attained by employing sufficiently large angular frequency. This suggests the possibility of obtaining the very high speed response continuous gas chromatograph.

As clearly seen from Eq. (9), the column conditions and the anglular frequency should be selected so that the determinant Δ may not be zero. Inspecting the elements of the determinant Δ, the following three conditions which have to be satisfied in the selection of the column and the angular frequency are obtained. i) The characteristic phase-shift of all the components observed at one detector should not be identical with those observed at any other detectors. ii) The characteristic phase-shift of one component should not be identical with those of any other components for every detector. If any such components exist, they should be treated together just like one component. iii) At any detector i the relation

$$\theta_{ij} - \theta_{ik} = p\pi \qquad \begin{matrix} p = 0,\pm1,\pm2,\cdots \\ j,k = 1,2,3,\cdots,n \\ j\neq k \end{matrix} \qquad (10)$$

should not be satisfied for every possible combination of two components. If all of Eq. (10) are satisfied, it possibly happen that all the elements of ith row of the determinant Δ become zero.

Sensitivity. To increase the sensitivity and thus minimize the measurement error in this method, it is desirable to have the large magnitude of the phase-shift variation whena certain change in the sample gas concentration arises. From this point of view, the sensitivity indices of this method may be defined as $S_{ij}=\partial\theta_i/\partial x_j$ for a particular component j.

Differentiating Eq. (7), we have:

$$S_{ij} = \alpha_{ij}\sum_{k=1}^{n}\alpha_{ik}x_k\sin(\theta_{ij} - \theta_{ik}) \qquad (11)$$

Thus, the sensitivity index S_{ij} may be maximized by selecting the column conditions and the angular frequency so that the following equation

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*1 For extention, if the relative sensitivity γ_{ij}, the inverse of the correction factor, of the detector i to the component j is introduced, C_{ij} should be replaced by $\gamma_{ij}C_{ij}$ in the succeeding equations. This results in the use of $\gamma_{ij}\alpha_{ij}$ instead of α_{ij} in Eq. (3) and thereinafter.

$$\theta_{ij} - \theta_{ik} = \frac{\pi}{2} + 2p\pi \quad \begin{array}{l} p = 0, \pm 1, \pm 2, \cdots \\ j, k = 1,2,3,\cdots,n \\ j \neq k \end{array} \tag{12}$$

may be satisfied for every component. When it is impossible to do that for every component because of the limited variety of the column property, the components having larger values of $\alpha_{ik}x_k$ should be selected to satisfy some of Eq. (12).

Parallel Type. Besides the series connection of the column segments shown in Fig. 1, the parallel connection of the column segments can be used as well. The principle discussed so far will be applied to the parallel type without any modification.

Estimation of Amplitude Attenuation and Phase-shift. When the assumption of the ideal gas chromatograph[4] can be applied, the amplitude attenuation factor and the phase-shift of each component wave can be estimated simply by:

$$\begin{array}{ll} \alpha^k{}_j = 1 & k = 1,2,\cdots,m-1 \\ \theta^k{}_j = \omega t^k{}_j = \omega(1+\mu^k)t^k{}_c & j = 1,2,\cdots,n \end{array} \tag{13}$$

where t_j is the retention time of j component; μ: the distribution coefficient and t_c is the residence time of the carrier gas; and supperscript k indicates the kth column. The amplitude attenuation factors and the phase-shift at the detector j will be obtained by:

$$\alpha_{ij} = \prod_{k=1}^{i-1} \alpha^k{}_j, \quad \theta_{ij} = \sum_{k=1}^{n-1} \theta^k{}_j \quad \begin{array}{l} i = 2,3,\cdots,m \\ j = 1,2,\cdots,n \end{array} \tag{14}$$

for a series type. Equation (14) seems to be appropriate for predicting the proper column and angular frequency in the preparation procedure of the continuous gas chromatograph.

For further accurate estimation, the dissipation of the concentration waves has to be considered. Employing the rate theory[4] of the gas chromatograph, the following basic equations are obtained:

$$\begin{aligned} E^k \frac{\partial^2 C^k{}_j(l,t)}{\partial l^2} - u\frac{\partial C^k{}_j(l,t)}{\partial l} &= f_g \frac{\partial C^k{}_j(l,t)}{\partial t} + f_b \frac{\partial b^k{}_j(l,t)}{\partial t} \\ f_b \frac{\partial b^k{}_j(l,t)}{\partial t} &= K_g a C^k{}_j(l,t) - H^k{}_j b_j(l,t) \end{aligned} \tag{15}$$

$$k = 1,2,\cdots,m-1, \quad j = 1,2,\cdots,n$$

Initial and boundary conditions are:

$$C(0,t) = C_{1j}(t)$$
$$C(l,0) = 0, \qquad C(\infty,t) = 0$$

where E is the longitudinal dispersion coefficient; C: the concentration in gas phase; u: the linear gas velocity; f_g: the volume fraction of gas phase; f_b: the volume fraction of liquid phase; b: the concentration in liquid phase; K_g: the mass transfer coefficient; a: the surface area of liquid phase per unit volume of the column; H: Henry's constant of adsorption and superfix k indicates the kth column segment. Solving Eq. (15) with sinusoidal concentration input $C_{ij}(t) = C_{sj} + A_1 x_j \sin \omega t$, the amplitude attenuations and the phase-shift at stationary state are obtained as follows:

$$\begin{aligned} \alpha^k{}_j &= \exp\left[\frac{uL^k}{2E^k}\{1 - (a_1{}^2 + a_2{}^2)^{1/4}\cos a_3\}\right] \\ \theta^k{}_j &= -\frac{uL^k}{2E^k}(a_1{}^2 + a_2{}^2)^{1/4}\sin a_3 \end{aligned} \tag{16}$$

where

$$a_1 = 1 + \frac{2E^k}{u^2}\left[\frac{\omega^2 f_b{}^2 K_g a}{(K_g a H)^2 + (\omega f_b)^2}\right]$$

$$a_2 = \frac{4E^k}{u^2}\left[\omega f_g + \frac{f_b H (K_g a)^2}{(K_g a H)^2 + (\omega f_b)^2}\right]$$

$$a_3 = \frac{1}{2}\tan^{-1}\frac{a_2}{a_1}$$

The constants included in Eq. (16) may be estimated[4] from the expected operation conditions and the gas chromatograms obtained by the ordinary method.

Linearity of Adsorption Isotherm. The linear adsorption isotherm is assumed in the derivation of the principle. This is, however, only for a matter of mathematical convenience. Since the linearity can be assured approximately using small amplitude of sinusoidal wave, the calibration made over the range of practical interest using the known composition gas mixture will allow to use this method regardless of the linearity of the adsorption isotherm.

Experimental

Experiments were carried out with two components, nitrogen and oxygen, gas mixture employing hydrogen carrier gas and a Molecular Sieve 5A column.

Apparatus. The apparatus used in the experiments is shown schematically in Fig. 2. A column assembly consisted of column and two thermal conductivity cells which were connected to the both ends of the column. The column assembly was placed in an air bath regulated at 20±0.5°C by a thermostat. Flow rate of the carrier gas and the sample gas were regulated by means of pressure regulators and were measured by a soap film flowmeter connected to the outlet of the column assembly. A dummy column of Molecular Sieve 5A was inserted between the column assembly and the flowmeter to seal the column assembly from moisture.

To generate sinusoidal wave of concentration, the sample gas and the carrier gas were alternated by a three-way solenoid valve and then partially mixed during flow through an inert column which is placed at the inlet of the column assembly. The inert column served

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[4] J. J. van Deemter, F. J. Zuiderweg and A. Klinkenberg, *Chem. Eng. Sci.*, **5**, 271 (1956).

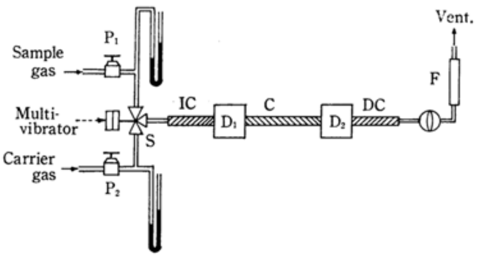
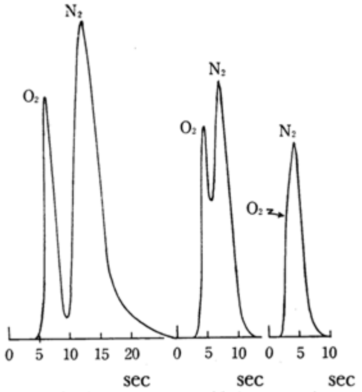


Fig. 2. Apparatus.

C: Molecular Sieve 5A column;
D: Thermal conductivity cell; IC: Inert column;
DC: Dummy column; P: Pressure regulator;
S: Three-way solenoid valve;
F: Soap film flowmeter.



(a) (b) c)

Fig. 3. Gas chromatograms.
Column length; (a) 15.0 cm, (b) 7.0 cm
(c) 4.0 cm.

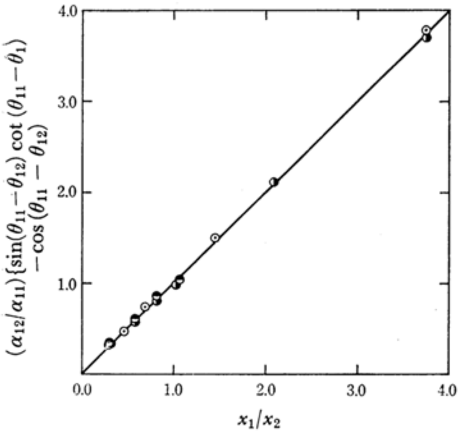


Fig. 4. Comparison with the theory.
Column length, ⊙: 15.0 cm, ◓: 7.5 cm
◑: 4.0 cm

TABLE 1. TYPICAL EXPERIMENTAL RESULTS

a) Column length is 15.0 cm; carrier gas flow rate: 100 cc/min; angular frequency: 0.251 rad/sec; phase-shift of nitrogen: 184.0 deg; phase-shift of oxygen: 93.9 deg and α_{11}/α_{12}: 0.910.

Phase-shift deg.	Mole fraction of N_2	Mole fraction of N_2 obtained	Relative error %
167.8	0.790	0.791	0.12
147.0	0.593	0.593	0.0
126.0	0.408	0.408	0.0
115.4	0.312	0.322	3.2
109.3	0.241	0.231	4.2

b) Column length is 7.5 cm; carrier gas flow rate: 100 cc/min; angular frequency: 0.522 rad/sec; phase-shift of nitrogen: 196.2 deg; phase-shift of oxygen 111.9 deg and α_{11}/α_{12}: 0.995.

Phase-shift deg.	Mole fraction of N_2	Mole fraction of N_2 obtained	Relative error %
152.6	0.489	0.514	5.1
147.9	0.438	0.441	0.69
138.8	0.359	0.350	2.5
128.1	0.242	0.237	2.1

c) Column length is 4.0 cm; carrier gas flow rate: 100 cc/min; angular frequency: 1.25 rad/sec; phase-shift of nitrogen: 266.5 deg; phase-shift of oxygen: 172.9 and α_{11}/α_{12}: 1.00.

Phase-shift deg.	Mole fraction of N_2	Mole fraction of N_2 obtained	Relative error %
215.3	0.788	0.790	0.25
240.3	0.674	0.677	0.45
220.9	0.512	0.499	2.6
210.5	0.439	0.425	3.2
202.7	0.360	0.358	0.55
190.9	0.242	0.252	4.2

to remove most of harmonics from the approximate square waves introduced by the three-way solenoid valve. A variety of the column length were used while keeping the carrier gas flow rate constant at 100 cc/min. For each column length the angular frequency of the sinusoidal wave was adjusted first by Eq. (13) approximately and then finely by trial and error search so that the maximum sensitivity condition, Eq. (12), was nearly satisfied. The inert column having the suitable length to produce a satisfactory sinusoidal wave was selected and installed for each angular frequency.

The output of the two thermal conductivity cells were fed to a two pen recorder and the magnitude of the amplitude attenuation and the phase-shift were read from the recorded traces.

Results. Typical experimental results are summarized in Table 1. And the ordinary gas chromatograms obtained at the same column conditions as the continuous gas chromatograph are also shown in Fig. 3.

Discussion. From Eq. (9) the ratio of the mole fraction can be written as:

$$\frac{x_1}{x_2} = (\alpha_{12}/\alpha_{11}) \sin(\theta_{11} - \theta_{12}) \cot(\theta_{11} - \theta_1) - \cos(\theta_{11} - \theta_{12}) \quad (17)$$

Figure 4 shows that the experimental data are in very good agreement with Eq. (17) regardless of the column length and the angular frequency. The following two points should be emphasized about the results. First, the experimental data agree well with the theory in spite of the nonlinear adsorption isotherms of nitrogen and oxygen on Molecular Sieve 5A. Second, even when the column length was chosen to be too short to separate the peaks of nitrogen and oxygen Eq. (17) was still valid. Therefore, it can be concluded that the principle of the continuous gas chromatograph is verified experimentally and the continuous analysis of multi-components gas mixture is successful.

The good regulation in the conditions which influence on the magnitude of the phase-shift are essential to assure the good accuracy of the analysis. Of particular importance among these conditions are the flow rate of carrier gas, the angular frequency and the column activity. During the course of this experiment, the decay in the activity of Molecular Sieve 5A caused by moisture adsorption made very severe hazard on the measurements. The dummy column of Molecular Sieve 5A was for preventing this hazard.

The output of the continuous gas chromatograph may easily be converted to the form of the direct indication of the component concentration by means of automatic phase-shift detectors and computing devices for Eq. (9) which will be mechanized with an analog and/or digital device.

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