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Pyrolytic Sulfurization Gas Chromatography. XI. An Improved Apparatus and Procedure for Practical Use

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With the objectives of reducing the time necessary for an analysis and of improving the precision and accuracy of the analysis value, the isothermal gas-chromatographic optimum conditions were investigated and established. By the present method, the time necessary for an analysis is reduced to 25 min, from 35 min under the previous conditions, and both precision and accuracy are further improved together with an improvement of the calculation method of the calculation factors used in the calculation of the atomic ratio between C, H, O, and N. Thus many standard samples, including some liquid ones which are newly examined in this study, can be analyzed within an absolute error of about ±0.2%.

In order to establish a new elemental analysis method by which several elements can be simultaneously determined, pyrolytic sulfurization gas chromatography (PSGC) was originated[1] and has been investigated[2-9] fundamentally by the present authors to provide a simultaneous determination of the atomic ratio between C, H, O, and N in an organic compound. It has been successfully applied to an ordinaly organic compound,[1] a metal organic chelate compound,[3] a polymer,[5] and an organic halogen compound.[7,8]

The present study also intended to reduce the time necessary for an analysis and to improve both precision and accuracy of the analytical values. According to the PSGC, the reaction products from the pyrolytic sulfurization of a sample were restricted to nitrogen (N_2), carbon dioxide(CO_2), hydrogen sulfide(H_2S), calbonyl sulfide(COS), and carbon disulfide(CS_2). The additional products, water(H_2O) and sulfur dioxide (SO_2), were obtained only in the case of the atomic ratio C/O<1 in a sample. These products were separated and determined under the programmed gas-chromatographic conditions in the previous study.[2] According to this procedure, the next sample could not be applied until the column temperature went down at 85 °C and this led to an increase of the total analysis time. In the present study which aimed at the minimization of the total analysis time, the isothermal gas-chromatographic conditions were examined and optimum column conditions were obtained by combining a 150 cm Porapak QS column with a 50 cm Chromosorb 104 column in series and by interposing a six-way cock at a proper position of the column so as to reduce the retention time of CS_2. The present study reduced the net analysis time by gas chromatography to about 8 min, from about 18 min under the previous conditions. Thus the total time(including reaction time, standing time, and so on) necessary for an analysis is also reduced to about 25 min from about 35 min. Moreover, both precision and accuracy are also improved, together with the improvement of the calculation method of the calculation factors used in the calculation of the atomic ratio between C, H, O, and N. Thus many standard samples, including liquid ones which are newly examined in this study, can be analyzed within an absolute error of about ±0.2%.

Experimental

Reagents. All of the reagents used as the analytical samples were of reagent grade for elemental analysis except for cyanoguanidine, which was of reagent grade for melting point standard.

Apparatus. An analyzer used in the present study is shown in Fig. 1. It consists of a Shimadzu GC 4B gas chromatograph mounted with two six-way cocks in the column oven and a sampler similar to that in the previous work.[1] The gas chromatograph was operated under the following conditions: Columns a 45 cm stainless steel column C_1 packed with Porapak QS(80—100 mesh), a 105 cm stainless steel column C_2 with Porapak QS(80—100 mesh), and a 50 cm stainless steel column C_3 with Chromosorb 104 (80—100 mesh); the insides of the stainless steel columns were treated preliminarily by coating with water glass; column temperature 85 °C; flow rate of He as a carrier gas 50 cm³/min.

A high-frequency induction furnace was used for the pyrolytic sulfurization reaction under the same conditions as in the previous work.[9]

Procedure. The quartz ampule containing 0.3—0.5 mg of sample and 5 mg of S was prepared and treated for 1 min by the high-frequency induction furnace as in the previous study.[9] After standing for 3 min in the furnace, the ampule was inserted into the sampler. Replacing the inside of the sampler with He for 5 min, the sampler was connected with the gas chromatograph by operating the

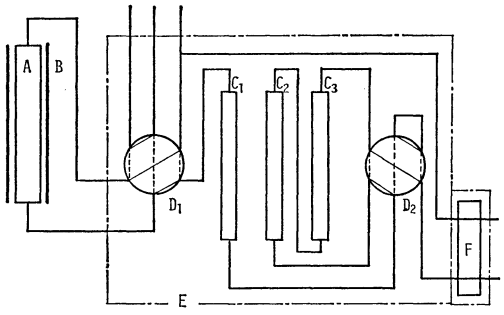

Fig. 1. Schematic flow diagram of the analyzer.
A: Gas sampler, B: vice, C_1: Porapak QS column (45 cm), C_2: Porapak QS column (105 cm), C_3: Chromosorb 104 column (50 cm), D_1, D_2: six-way cocks, E: column oven held at 85 °C, F: thermal conductivity detector.

six-way cock D_1. After 5 min, the time necessary for the stabilization of the base line in a gas chromatogram, the ampule was broken with a vice B and the evolved gases were subjected to gas-chromatographic analysis. After 4.5 min, the separation column was shortened to only a 45 cm Porapak QS column by operating the six-way cock D_2. On the basis of the data obtained by a digital integrator, the atomic ratio between C, H, O, and N in a sample was calculated by the use of calculation factors of the products.

Results and Discussion

Gas-chromatographic Separation of the Reaction Products under the Isothermal Conditions. According to the PSGC, the gaseous products of the pyrolytic sulfurization reaction were limited as follows: N_2, CO_2, H_2S, COS, H_2O, SO_2, and CS_2. Then, an investigation was undertaken to separate them under the isothermal gas-chromatographic conditions, instead of the programmed ones in the previous studies. Porapak Q, Porapak QS, Chromosorb 104, silica gel, Carbon molecular sieve B, and Molecular sieve 13X were chosen as representative gas-chromatographic packings to separate the above gaseous products. Each packing was investigated to determine the elution behavior of the products under the following standard conditions: Column length 100 cm, flow rate of He as a carrier gas 30 cm³/min, and column temperature 100 °C. All of the above-mentioned products were found to elute within 1 h when Porapak Q, Porapak QS, and Chromosorb 104, respectively, were used as a column packing. As can be seen from the retention time of each product in Table 1, H_2S cannot be separated from H_2O by Porapak Q or Porapak QS nor from COS by Chromosorb 104. It was suggested that the optimum column conditions to separate the seven kinds of products would be obtained by the combination of Porapak Q with Chromosorb 104(Q-104 type) or by that of Porapak QS with Chromosorb 104(QS-104 type) in series. Therefore, an examination was undertaken to separate the products by the above combination columns, and optimum conditions to separate them were obtained. Since two kinds of optimum conditions, however, indicated fairly large retention times for CS_2, the column was shortened by interposing the six-way cock at a proper position of the column so as to reduce the retention time of CS_2. Thus, the following optimum column conditions were obtained: (Q-104 type) first column a 50 cm Porapak Q(80—100 mesh) column, second column a 100 cm Porapak Q(80—100 mesh) column, third column a 45 cm Chromosorb 104(80—100 mesh) column, column temperature 90 °C, and flow rate of He 50 cm³/min. (QS-104 type) first column a 45 cm Porapak QS(80—100 mesh) column, second column a 105 cm Porapak QS (80—100 mesh) column, third column a 50 cm Chromosorb 104 (80—100 mesh) column, column temperature 85 °C, and flow rate of He 50 cm³/min. The six-way cock was interposed between the first column and the second column in each type. Typical chromatograms under the above-mentioned conditions are shown in Fig. 2. As can be seen from Fig. 2, the separation of the products is achieved

Table 1. The retention time of the products under the standard column conditions

Column packing	Retention time/min						
	N_2	CO_2	H_2S	COS	H_2O	SO_2	CS_2
Porapak Q	0.3	0.5	1.1	1.6	1.1	2.0	13.8
Porapak QS	0.3	0.5	1.0	1.3	1.0	1.8	12.5
Chromosorb 104	0.3	0.5	1.2	1.2	4.1	2.8	7.3

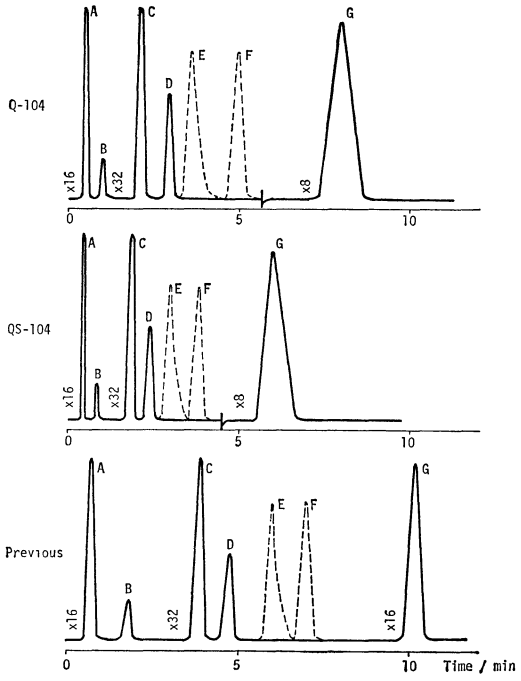

Fig. 2. Typical chromatograms of alanine as a standard sample.
A: N_2, B: CO_2, C: H_2S, D: COS, E: H_2O, F: SO_2, G: CS_2.

Table 2. Fluctuation of the ratio[a] of peak areas obtained by the previous and the present anayltical conditions

	C. V. (%)[b] of peak area ratio				
	N_2	CO_2	H_2S	COS	CS_2
Q-104 type	1.81	2.44	1.34	1.48	1.89
QS-104 type	0.897	2.73	0.614	0.736	0.924
Previous	1.31	2.67	1.31	1.69	1.48

a) The ratio of each peak area of N_2, CO_2, H_2S, COS, and CS_2 to their sum was represented as a percentage. b) Calculated from 10 runs for alanine.

Table 3. Fluctuation of K(COS) and $K(CO_2)$

	C. V. (%)	
	K(COS)	$K(CO_2)$
Present	0.443[a]	0.778[b]
Previous	1.25[b]	1.18[b]

a) Calculated from 5 runs for 8-quinolinol. b) Calculated from 5 runs for sucrose.

Table 4. Analytical results of various organic compounds

Sample[a]	C (wt%)			H (wt%)			O (wt%)			N (wt%)		
	Calcd	Found	Error	Calcd	Found	Error	Calcd	Found	Error	Calcd	Found	Error
Acetanilide	71.09	71.03	−0.06	6.71	6.77	+0.06	11.84	11.95	+0.11	10.36	10.25	−0.11
Acetone 2,4-dinitrophenylhydrazone	45.38	45.41	+0.03	4.23	4.20	−0.03	26.87	27.04	+0.17	23.52	23.35	−0.17
DL-α-Alanine	40.44	40.27	−0.17	7.92	7.90	−0.02	35.92	36.09	+0.17	15.72	15.74	+0.02
Anthracene	94.34	94.43	+0.09	5.66	5.57	−0.09						
Antipyrine	70.19	70.06	−0.13	6.43	6.47	+0.04	8.50	8.66	+0.16	14.88	14.81	−0.07
Benzoic acid	68.85	68.68	−0.17	4.95	4.98	+0.03	26.20	26.34	+0.14			
Benzoin	79.22	79.20	−0.02	5.70	5.71	+0.01	15.08	15.09	+0.01			
Butyl *p*-hydroxybenzoate	68.02	68.01	−0.01	7.27	7.16	−0.11	24.71	24.83	+0.12			
Caffeine	49.48	49.51	+0.03	5.19	5.15	−0.04	16.48	16.56	+0.08	28.85	28.78	−0.07
Cholesterol	83.87	84.07	+0.20	11.99	11.93	−0.06	4.14	4.00	−0.14			
Cyclohexanone 2,4-dinitrophenylhydrazone	51.80	51.64	−0.16	5.07	5.05	−0.02	23.00	23.21	+0.21	20.13	20.10	−0.03
Cyclohexanone oxime	63.68	63.56	−0.12	9.80	9.85	+0.05	14.14	14.28	+0.14	12.38	12.31	−0.07
Cyclohexanone semicarbazone	54.17	54.05	−0.12	8.44	8.43	−0.01	10.31	10.26	−0.05	27.08	27.26	+0.18
m-Dinitrobenzene	42.87	42.80	−0.07	2.40	2.42	+0.02	38.07	38·08	+0.01	16.66	16.70	+0.04
N,N'-Diphenylthiourea	79.57	79.63	+0.06	6.16	6.12	−0.04				14.27	14.25	−0.02
Ethyl *p*-aminobenzoate	65.44	65.37	−0.07	6.71	6.80	+0.09	19.37	19.29	−0.08	8.48	8.54	+0.06
Guaiacol carbonate	65.68	65.69	+0.01	5.15	5.16	+0.01	29.17	29.15	−0.02			
Hippuric acid	60.33	60.24	−0.09	5.06	5.13	+0.07	26.79	26.66	−0.13	7.82	7.97	+0.15
Methyl α-D-glucoside	43.3^	43.13	−0.17	7.27	7.28	+0.01	49.43	49.59	+0.16			
Naphthalene	93.71	93.58	−0.13	6.29	6.42	+0.13						
Nicotinic acid	58.54	58.42	−0.12	4.09	4.10	+0.01	25.99	25.96	−0.03	11.38	11.52	+0.14
p-Nitroaniline	52.17	52.20	+0.03	4.38	4.42	+0.04	23.17	23.28	+0.11	20.28	20.10	−0.18
Phenacetin	67.02	66.82	−0.20	7.31	4.41	+0.10	17.85	17.94	+0.09	7.82	7.83	+0.01
Stearic acid	75.99	75.90	−0.09	12.76	12.70	−0.06	11.25	11.40	+0.15			
Succinic acid	40.68	40.63	−0.05	5.12	5.10	−0.02	54.20	54.27	+0.07			
Sulfanilamide	51.43	51.29	−0.14	5.75	5.84	+0.09	22.83	22.78	−0.05	19.99	20.09	+0.10
Sulfathiazole	56.53	56.51	−0.02	4.75	4.86	+0.11	16.74	16.67	−0.07	21.98	21.96	−0.02
Thiourea	27.26	27.27	+0.01	9.15	9.15	0				63.59	63.58	−0.01
p-Toluenesulfonamide	60. ?	60.33	−0.09	6.52	6.53	+0.01	22.99	23.03	+0.04	10.07	10.11	+0.04
Triphenylphosphine	93.46	93.28	−0.18	6.54	6.72	+0.18						
Vanillin	63.15	63.29	+0.14	5.30	5.36	+0.06	31.55	31.35	−0.20			
Anthraquinone	80.76	80.71	−0.05	3.87	3.83	−0.04	15.37	15.46	+0.09			
2,2'-Bis(ethylsulfonyl)propane	51.21	51.25	+0.04	9.82	9.65	−0.17	38.97	39.10	+0.13			
Bis(2,4-pentanedionato)magnesium(II)	51.27	51.21	−0.06	7.75	7.85	+0.10	40.98	40.98	−0.04			
Tris(2,4-pentanedionato)iron(III)	60.59	60.58	−0.01	7.12	6.95	−0.17	32.29	32.47	+0.18			
Phenylmercury(II) acetate	70.58	70.55	−0.03	5.92	5.97	+0.05	23.50	23.48	−0.02			

a) Sulfur and metal atoms were neglected in the calculation of the compositions of samples, since they could not be determined.

Table 5. Analytical results of liquid samples

Sample	C (wt%)			H (wt%)			O (wt%)			N (wt%)		
	Calcd	Found	Error	Calcd	Found	Error	Calcd	Found	Error	Calcd	Found	Error
Anisole	77.75	77.92	+0.17	7.46	7.32	−0.14	14.79	14.76	−0.03			
Nitrobenzene	58.54	58.53	−0.01	4.09	4.11	+0.02	25.99	25.80	−0.19	11.38	11.56	+0.18

under the isothermal gas-chromatographic conditions, and moreover the elution time of the products is reduced from 13 min under the previous conditions to 8 min under the present conditions.

Reproducibility of the Analytical Values. The reproducibility of the PSGC was examined using N_2, CO_2, H_2S, COS, and CS_2 obtained from alanine, since the atomic ratio of C/O in alanine was more than 1 and neither H_2O nor SO_2 was produced. The two sets of column conditions were compared with the previous column conditions by analyzing 10 samples of alanine and by estimating the coefficient of variation(C.V.) in the ratio of the individual peak area (Table 2). Table 2 shows that QS-104 type has the best reproducibility of the analytical values. Therefore, QS-104 type was employed in the present study.

Calculation Factor. In the PSGC, the atomic ratio between C, H, O, and N was calculated by using both the factors obtained by analyzing the standard compounds preliminarily and the peak areas of the individual product obtained from the sample. Judging from the meaning of the above factors, the term "calculation factor" is hereafter adopted instead of "correction factor" used in the previous papers.

The calculation factors of $N_2(K(N_2))$ and $CS_2(K(CS_2))$ were obtained by solving the following equations on the basis of the analytical data of cyanoguanidine:

$$\left(\frac{N}{H}\right) = \frac{2K(N_2)A(N_2)}{2K(H_2S)A(H_2S)}, \quad (1)$$

$$\left(\frac{C}{H}\right) = \frac{K(CS_2)A(CS_2)}{2K(H_2S)A(H_2S)}. \quad (2)$$

Here $A(X)$ is the peak area of X and $K(H_2S)$ is 1, as in the previous papers. The calculation actors of $CO_2(K(CO_2))$ and COS ($K(COS)$) were o tained by solving the following simultaneous equations on the basis of the analytical data of sucrose:

$$\left(\frac{O}{H}\right) = \frac{2K(CO_2)A(CO_2)+K(COS)A(COS)}{2K(H_2S)A(H_2S)}, \quad (3)$$

$$\left(\frac{C}{H}\right) = \frac{K(CO_2)A(CO_2)+K(COS)A(COS)+K(CS_2)A(CS_2)}{2K(H_2S)A(H_2S)}. \quad (4)$$

However, the values of $K(CO_2)$ and $K(COS)$ obtained by Eqs. 3 and 4 were accompanied with the fluctuation of the value of $K(CS_2)$ in Eq. 4. Therefore an equation which is free from $K(CS_2)$ was necessary for an improvement of the values of $K(CO_2)$ and $K(COS)$. In the present study, $K(COS)$ was obtained from Eq. 5, which was obtained by neglecting $2K(CO_2)A(CO_2)$ in Eq. 3, by the use of the analytical data of 8-quinolinol in which the amount of CO_2 was negligibly small.

$$\left(\frac{O}{H}\right) = \frac{K(COS)A(COS)}{2K(H_2S)A(H_2S)} \quad (5)$$

Then $K(CO_2)$ was calculated by Eq. 3 by the use of the analytical data of sucrose. Table 3 shows the fluctuation of $K(CO_2)$ and $K(COS)$ in the present and in the previous procedures. The values of C.V. in Table 3 indicate that the present procedure is superior to the previous one.

Analysis of Various Organic Compounds. Various organic compounds were analyzed by the present procedure (Table 4). Judging from the results in Table 4, both precision and accuracy were superior to those in the previous procedure.

Analysis of Liquid Samples. Liquid samples were newly analyzed in the following manner. A liquid sample was taken in a quartz capillary tube (0.5 mm i.d., 2 mm long) by the capillary action; 5 mg of S were inserted in the quartz tube which was closed at one end, and the inside of the quartz tube was replaced with He as in the previous study.[1] Ten minutes later, the stream of He was stopped, and the other end of the quartz tube was sealed. Each ampule thus obtained was analyzed by the present procedure. Analytical results of liquid samples are shown in Table 5. It shows that high boiling point liquid organic compounds can be analyzed with satisfactory results by the PSGC.

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