Pyrolytic Sulfurization Gas Chromatography. XIV. Simultaneous Determination of the Absolute Contents of C, H, O, and N in an Organic Compound by Means of a Calibration Method

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The absolute content of C, H, O, and N in an organic compund including a metal organic chelate was satisfactorily determined on the basis of pyrolytic sulfurization gas chromatography. A 1.0—1.3 mg sample was weighed on a microbalance, and was subjected to pyrolytic sulfurization. The gases evolved by the reaction were estimated by gas-chromatography. By using both the analytical result of each product and its calibration factor previously obtained by analyzing cyanoguanidine, 8-quinolinol, and sucrose as standard samples, the absolute content of C, H, O, and N was calculated satisfactorily for each substance.

Pyrolytic sulfurization gas chromatography (PSGC) was originated[1] and has been reported[2-13] by the authors for the purpose of establishing a new method of elemental analysis by which several elements in an organic compound can be simultaneously determined. By using PSGC, the atomic ratio between C, H, O, and N in a usual organic compound,[1] a metal organic chelate compound,[3,13] a polymer,[5] and an organic halogen compound[7,9] have been successfully and simultaneously determined.

In PSGC, a 0.3—0.5 mg sample is subjected to pyrolytic sulfurization with 5 mg of high purity sulfur[4] in a sealed quartz tube. The gaseous products from this reaction, carbon dioxide (CO_2), carbonyl sulfide (COS), carbon disulfide (CS_2), hydrogen sulfide (H_2S), and nitrogen molecule(N_2), are estimated by gas-chromatography, followed by the calculation of the atomic ratio between C, H, O, and N. Organic elemental analysis by PSGC is mainly characterized by the followings: 1) The atomic ratio between C, H, O, and N can be simultaneously determined within an absolute error of about $\pm 0.2\%$;[12] 2) no weighing is necessary for sampling and thus a microbalance is not necessary; 3) no additional combustion is required for a less combustible compound; 4) this method is applicable to various compounds such as metal organic chelates, thermosetting polymers, and organic halogen compounds; 5) the atomic ratio between C, H, O, N, Cl, Br, and I in an organic halogen compound can be determined[9] in a single analysis; and 6) the measurement is inexpensive because with a slight modification commercial apparatus is available. However, PSGC is not yet as satisfactory as conventional organic elemental analysis based on an oxygen combustion technique in the following respects; 1) the absolute amount of each element in a sample cannot be determined; as in PSGC only the atomic ratio between C, H, O, and N in a sample is calculated from the analytical data of the gaseous products. 2) Compounds which contain elements additional to C, H, O, and N cannot be analyzed. These problems must be solved by further improvement of PSGC, to establish a method by which each absolute content of C, H, O, and N in a sample can be determined. Therefore, the present study has been carried out with this objective in mind. Since the reaction products obtained by pyrolytic sulfurization of a common organic compound sample is restricted to CO_2, COS, CS_2, H_2S, and N_2, calibration curves of these products were easily obtained by analyzing three standard samples which were previously weighed. By using such calibration curves, various samples could be analyzed and the absolute content of C, H, O, and N in a sample was successfully and simultaneously determined.

Experimental

Apparatus and Reagents. The apparatus used in this study was the same as that previously reported.[11] A definite amount of sample was measured on a Shimadzu microbalance MDP-5.

The organic compounds used as analytical samples were of reagent grade for elemental analysis except for cyanoguanidine, which was of reagent grade for melting-point standard.

Procedure. A sample in the range of 1.0 to 1.3 mg was weighed exactly in a quartz tube, which was closed at one end, and about 10 mg of S was also added. The air inside the quartz tube containing the sample and S was next displaced with He for 10 min, after which the other end of the tube was sealed. The ampule was next heated for 1 min in a high-frequency induction furnace as described in the previous study.[10] The gaseous products evolved in the reaction between a sample and S were analyzed by gas-chromatography under the same conditions as those previously reported.[11] From the analytical data, the absolute contents of C, H, O, and N in a sample were separately calculated by use of calibration curves of the products which had been previously obtained by analyzing three standard samples, such as cyanoguanidine, 8-quinolinol, and sucrose.

Results and Discussion

Sample Amount. According to the conventional PSGC, 0.3—0.5 mg of sample has been subjected to pyrolytic sulfurization. Since a sample had to be weighed, in the present study, to four significant figures with the microbalance which could weigh to a precision of 1 μg, a sample more than 1 mg was used for an analysis. Therefore, the following examinations were undertaken to confirm whether PSGC could be applied or not to the analysis using about 1 mg of sample. 1) Approximately 0.5—1.3 mg of alanine as a standard sample and 10 mg of S (5 mg of S was

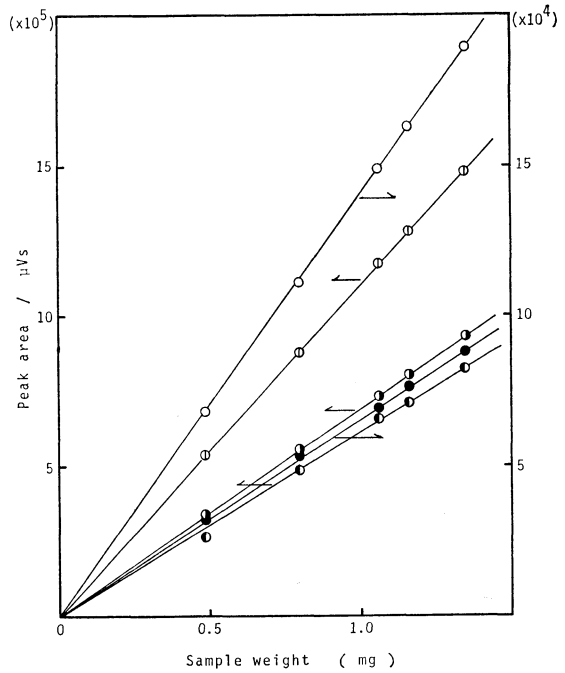

Fig. 1. Relationship between sample weight and peak area of each product. ○: N_2, ●: CO_2, ◑: H_2S, ◑: COS, and ◐: CS_2.

used in the conventional PSGC) were subjected to PSGC analysis, and the relationship between the sample weight and the peak area of each product was determined. Figure 1 shows that a plot of peak area of each product *vs.* sample weight gives a straight line. 2) In order to examine the reproducibility of the analytical value under the present conditions, the present PSGC analysis was repeated 10 times using 1 mg of alanine and 10 mg of S. The same procedure was repeated 10 times with 0.5 mg of alanine and 5 mg of S. By using these analytical data, the analytical values under the present conditions were compared with those under the previous ones by estimating the coefficient of variation (CV) of the peak area ratio of each product to their sum (Table 1). These examinations indicate that PSGC analysis is also feasible for use with 1 mg samples though the reproducibility of the analytical values under the present conditions is slightly inferior to those under the conventional ones, as is inferred from Table 1.

Calculation Method of C, H, O, and N Content. The individual absolute content of C, H, O, and N in a sample can be calculated theoretically by the following equations.

$$\mathrm{C(wt\%)} = \frac{W_A(\mathrm{C})[f_C(\mathrm{CO_2})N(\mathrm{CO_2}) + f_C(\mathrm{COS})N(\mathrm{COS}) + f_C(\mathrm{CS_2})N(\mathrm{CS_2})]}{w} \times 100 \quad (1)$$

$$\mathrm{H(wt\%)} = \frac{W_A(\mathrm{H})f_H(\mathrm{H_2S})N(\mathrm{H_2S})}{w} \times 100 \quad (2)$$

$$\mathrm{O(wt\%)} = \frac{W_A(\mathrm{O})[f_O(\mathrm{CO_2})N(\mathrm{CO_2}) + f_O(\mathrm{COS})N(\mathrm{COS})]}{w} \times 100, \quad (3)$$

Table 1. Reproducibility of the peak area ratio of each procuct to their sum

Sample weight (mg)	CV/%[a]				
	N_2	CO_2	H_2S	COS	CS_2
1	0.850	1.84	0.385	0.508	1.29
0.5	0.451	0.942	0.230	0.484	1.06

a) Calculated from 10 runs for alanine.

Table 2. Products from each standard sample

Standard sample	Products
Cyanoguanidine	N_2, H_2S, CS_2
8-Quinolinol	N_2, H_2S, COS, CS_2
Sucrose	CO_2, H_2S, COS, CS_2

$$\mathrm{N(wt\%)} = \frac{W_A(\mathrm{N})f_N(\mathrm{N_2})N(\mathrm{N_2})}{w} \times 100, \quad (4)$$

where $W_A(\alpha)$ is the atomic weight of α(α=C, H, O, and N), $N(\beta)$ is the mole number(mol) of β(β=CO_2, COS, CS_2, H_2S, and N_2), w is the sample weight(mg), and $f_\alpha(\beta)$ is the number of element α in a reaction product β. Then the following equation is defined in the case of gas-chromatographic analysis.

$$A(\beta) = F(\beta)N(\beta), \quad (5)$$

where $A(\beta)$: peak area(μV s) of β and $F(\beta)$: proportional constant (μV s/mol), which is called calibration factor. Moreover, $f_\alpha(\beta)$ are offered by the following values.

$$f_C(\mathrm{CO_2}) = f_C(\mathrm{COS}) = f_C(\mathrm{CS_2}) = f_O(\mathrm{COS}) = 1 \quad (6)$$

$$f_H(\mathrm{H_2S}) = f_O(\mathrm{CO_2}) = f_N(\mathrm{N_2}) = 2 \quad (7)$$

Therefore, by introducing Eqs. 5—7 into Eqs. 1—4, Eqs. 1—4 are rewritten as follows.

$$\mathrm{C(wt\%)} = W_A(\mathrm{C})\left[\frac{A(\mathrm{CO_2})}{F(\mathrm{CO_2})} + \frac{A(\mathrm{COS})}{F(\mathrm{COS})} + \frac{A(\mathrm{CS_2})}{F(\mathrm{CS_2})}\right] \times \frac{1}{w} \times 100 \quad (8)$$

$$\mathrm{H(wt\%)} = W_A(\mathrm{H}) \times \frac{2A(\mathrm{H_2S})}{F(\mathrm{H_2S})} \times \frac{1}{w} \times 100 \quad (9)$$

$$\mathrm{O(wt\%)} = W_A(\mathrm{O}) \times \left[\frac{2A(\mathrm{CO_2})}{F(\mathrm{CO_2})} + \frac{A(\mathrm{COS})}{F(\mathrm{COS})}\right] \times \frac{1}{w} \times 100 \quad (10)$$

$$\mathrm{N(wt\%)} = W_A(\mathrm{N}) \times \frac{2A(\mathrm{N_2})}{F(\mathrm{N_2})} \times \frac{1}{w} \times 100 \quad (11)$$

Each absolute content of C, H, O, and N in a sample can be calculated by use of Eqs. 8—11 from the analytical data of a sample if the values of $F(\beta)$ have been determined by Eqs. 8—11 from the analytical data of standard samples.

Determination of Calibration Factors. According to the PSGC method, the carbon in a sample is converted to CO_2(its amount is negligibly small when the value of C/O exceeds about 8), COS, and CS_2, hydrogen is converted to H_2S, oxygen to CO_2 and COS, and nitrogen to N_2 by the pyrolytic sulfurization. Therefore, in order to determine $F(\beta)$ of the products, the

TABLE 3. CALIBRATION FACTOR

Standard sample	Calibration factor/μV s mol^{-1}[a)]				
	$F(N_2)$	$F(CO_2)$	$F(H_2S)$	$F(COS)$	$F(CS_2)$
Cyanoguanidine	269.5		297.4		473.4
8-Quinolinol	268.2		302.6	401.3	
Sucrose		300.1	296.4		
Average	268.9	300.1	298.8	401.3	473.4

a) Average of 3 runs for each standard sample.

TABLE 4. ANALYTICAL RESULTS OF VARIOUS ORGANIC COMPOUNDS

Sample	C (wt%)			H (wt%)			O (wt%)			N (wt%)		
	Calcd	Found	Error	Calcd	Found	Error	Calcd	Found	Error	Calcd	Found	Error
Acetoanilide	71.09	71.28	+0.19	6.71	6.78	+0.07	11.84	12.02	+0.18	10.36	10.26	−0.10
Acetone 2,4-dinitrophenylhydrazone	45.38	45.67	+0.29	4.23	4.20	−0.03	26.87	27.01	+0.14	23.52	23.22	−0.30
Anthracene	94.34	94.06	−0.28	5.66	5.66	0.00						
Anthraquinone	80.76	80.49	−0.27	3.87	3.86	−0.01	15.37	15.48	+0.11			
Benzoic acid	68.85	68.97	+0.12	4.95	4.98	+0.03	26.20	26.26	+0.06			
Benzoin	79.22	79.34	+0.12	5.70	5.65	−0.05	15.08	15.37	+0.29			
2,2-Bis(ethylsulfonyl)-propane	36.82	37.00	+0.18	7.06	7.08	+0.02	28.03	28.20	+0.17			
Bis(2,4-pentanedionato)-magnesium(II)	46.45	46.14	−0.31	7.02	7.08	+0.06	37.13	37.09	−0.04			
Caffeine	49.48	49.23	−0.25	5.19	5.21	+0.03	16.48	16.18	−0.30	28.85	28.79	−0.06
Cholesterol	83.87	83.39	−0.48	11.99	11.87	−0.12	4.14	4.30	−0.16			
Cyclohexanone 2,4-dinitrophenylhydrazone	51.80	51.88	+0.08	5.07	5.18	+0.11	23.00	23.19	+0.19	20.13	20.25	+0.12
Cyclohexanone oxime	63.68	63.53	−0.15	9.80	9.75	−0.05	14.14	14.15	+0.01	12.38	12.28	−0.10
Cyclohexanone semicarbazone	54.14	54.57	+0.43	8.44	8.49	+0.05	10.31	10.57	+0.26	27.07	27.00	−0.07
N,*N*′-Diphenylthiourea	68.39	68.35	−0.04	5.30	5.33	+0.03				12.27	12.33	+0.06
Ethyl *p*-aminobenzoate	65.44	65.26	−0.18	6.71	6.79	+0.08	19.37	19.65	+0.28	8.48	8.48	0.00
Guaiacol carbonate	65.69	65.71	+0.02	5.15	5.07	−0.08	29.17	29.14	−0.03			
Hippuric acid	60.33	60.07	−0.26	5.06	5.08	+0.02	26.79	26.78	−0.01	7.82	7.83	+0.01
α-Methyl D-glucoside	43.30	43.54	+0.24	7.27	7.29	+0.02	49.44	49.46	+0.02			
Nicotinic acid	58.54	58.52	−0.02	4.09	4.13	+0.04	25.99	26.15	+0.16	11.38	11.25	−0.13
p-Nitroaniline	52.17	52.27	+0.10	4.38	4.42	+0.04	23.17	23.24	+0.07	20.28	20.32	+0.04
Phenacetin	67.02	67.19	+0.17	7.31	7.18	−0.13	17.85	17.83	−0.02	7.82	7.77	−0.05
Phenylmercury(II) acetate	28.53	28.55	+0.02	2.39	2.40	+0.01	9.50	9.59	+0.09			
Succinic acid	40.68	40.43	−0.25	5.12	5.12	0.00	54.19	54.03	−0.16			
Sulfathiazole	42.34	42.48	+0.14	3.55	3.57	+0.02	12.53	12.52	−0.01	16.46	16.38	−0.08
Thiourea	15.78	15.61	−0.17	5.30	5.34	+0.04				36.80	36.59	−0.21
p-Toluenesulfonamide	49.11	48.92	−0.19	5.30	5.30	0.00	8.18	8.00	−0.18			
Triphenylphosphine	82.43	82.33	−0.10	5.76	5.80	+0.04						
Tris(2,4-pentanedionato)iron(III)	51.01	50.79	−0.22	5.99	5.98	−0.01	27.18	27.18	0.00			
Vanillin	63.15	63.49	+0.34	5.30	5.31	+0.01	31.55	31.34	−0.21			

compounds which satisfy the following requirements must be selected as the standard samples; 1) N-containing compound, 2) H-containing compound, 3) C-containing and O-free compound, 4) C-containing and O-rich compound from which CO_2 is produced, and 5) C-containing and O-poor compound from which CO_2 is produced in small amounts. In the present study, cyanoguanidine will satisfy the requirements of 1), 2), and 3), sucrose will satisfy that of 4), and 8-quinolinol will satisfy that of 5). Accordingly there substances were selected as the standard samples for the determination of $F(\beta)$. The reaction products from each standard sample on pyrolytic sulfurization are shown in Table 2. As can be seen from Table 2, $F(N_2)$ can be calculated by Eq. 11 from the analytical results for cyanoguanidine and 8-quinolinol; $F(H_2S)$ by Eq. 9 from that of cyanoguanidine, 8-quinolinol, and sucrose; $F(COS)$ by Eq. 10 from that of 8-quinolinol; and $F(CS_2)$ by Eq. 8 from that of cyanoguanidine. $F(CO_2)$ can also be calculated by Eq. 10 from both $F(COS)$ and the analytical result of sucrose. The calibration factor of each product was shown in Table 3. All of the calibration factors (Table 3) were used for the calibration of each absolute content of C, H, O, and N in a sample.

Analysis of Various Organic Compounds. Various organic compounds including metal organic chelates were analyzed by the present procedure; the results are shown in Table 4. Table 4 indicates that each absolute content of C, H, O, and N in an organic compound can be successfully and simultaneously determined by the present method.

Comparison of the Present Method with the Conventional PSGC. The present method was compared with the conventional PSGC in the following manner. An analysis using about 1 mg of sample is repeated 10 times by use of alanine as a standard sample, and both the absolute content of C, H, O, and N in alanine and the atomic ratio between C, H, O, and N were calculated by the present method and by the conventional PSGC, respectively. Moreover, fluctuation of analytical data by the present method and the conventional PSGC, respectively, was also calculated and the value of CV for each value of C, H, O, and N was compared (Table 5). Table 5 indicates that the present method is superior to the conventional PSGC with regard to the value of H but inferior for C and O.

Table 5. Comparison of the present method with the conventional PSGC

Method	CV/%[a]			
	C	H	O	N
Present	0.820	0.217	0.562	0.646
Conventional PSGC	0.351	0.685	0.357	0.654

a) Calculated from 10 runs for alanine.

From the results obtained by the present study, it can be concluded that the absolute content of C, H, O, and N in an organic compound can also be determined, if necessary, by PSGC. This makes possible the simultaneous determination of the atomic ratio between C, H, O, and N in an organic compound without weighing a sample. This will make PSGC a more valuable method in organic elemental analysis.

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