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Pyrolytic Sulfurization Gas Chromatography. VI. The Continuous and Simultaneous Determination of the Atomic Ratio between C, H, O, and N in Various Compounds

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The simultaneous determination of the atomic ratio between C, H, O, and N in various compounds including a metal organic chelate one has been presented in our previous papers.[1-3] With the objective of reducing the analysis time, an apparatus by which a continuous and simultaneous determination of the atomic ratio between C, H, O, and N can be carried out has been newly designed and constructed. Using this apparatus, many samples can be treated continuously at the rate of about 20 min for one sample, with satisfactory results.

It has been reported in the previous papers[1-3] that the simultaneous determination of the atomic ratio between C, H, O, and N in various compounds, including a metal organic chelate one, can be achieved with satisfactory results by pyrolytic sulfurization gas chromatography (PSGC). Since the analysis by the PSGC is, however, batch-by-batch, time-consuming, and laborious, an apparatus which made it possible to determine the atomic ratio between C, H, O, and N in a sample continuously and simultaneously was newly designed and constructed. An analysis can be carried out more rapidly and simply by this apparatus than by the previous one. In place of a Teflon-made gas sampler,[1] a new gas sampler consisting of three stainless steel crushing devices was constructed. The quartz ampule containing a sample was easily dashed to pieces in the present apparatus by driving the plunger of the crushing device in place of the jack used in the previous paper.[1] In the present gas sampler, the crushing device can be used for many analyses, unlike the more fragile Teflon tube in the previous paper. The analytical procedure using the crushing device consists of the following steps; 1) the introduction of an ampule, 2) the replacement of the air in the crushing device with helium(He) as a carrier gas, 3) analysis by gas chromatography, and 4) the recycling of these steps. Three crushing devices are set up in parallel with a gas chromatograph and operated separately in different steps. By this procedure the time necessary for an analysis was minimized; a sample could be analyzed within about 20 min, while it took about 30 min in the previous procedure. Using the present procedure, operating at the rate of 3 samples per hour, about three times as many samples as in the previous procedure could be treated; precision could also be improved by optimizing the reaction conditions.

Experimental

Apparatus. The new gas sampler is shown in Fig. 1. The gas sampler consists of three stainless steel crushing devices A(Fig. 2) and electric valves for the regulation of the gaseous flow. The inside of the crushing device was treated preliminarily by coating it with an aqueous solution of water glass, by drying it at room temperature under the reduced pressure, and by then elevating the temperature. The three crushing devices(A_1, A_2, and A_3) were laid out so as to connect them in parallel with a gas chromatograph by operating electric valves. The temperature of the gaseous flow between A and a gas chromatograph was held at 150 °C. The gas sampler was heated by connecting the crushing devices and electric valves with a hot brass plate into which cartridge heaters had been inserted. A Shimadzu GC-4B gas chromatograph was used for the analysis, while the other parts of the apparatus were the same as in the previous paper.

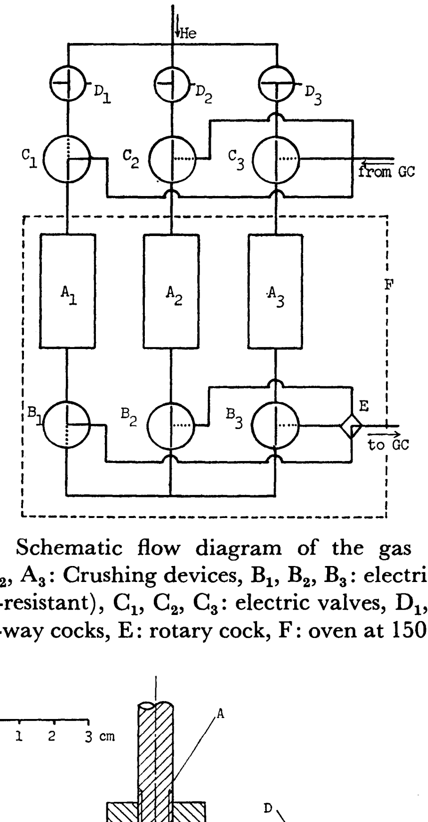

Fig. 1. Schematic flow diagram of the gas sampler. A_1, A_2, A_3: Crushing devices, B_1, B_2, B_3: electric valves-(heat-resistant), C_1, C_2, C_3: electric valves, D_1, D_2, D_3: three-way cocks, E: rotary cock, F: oven at 150 °C.

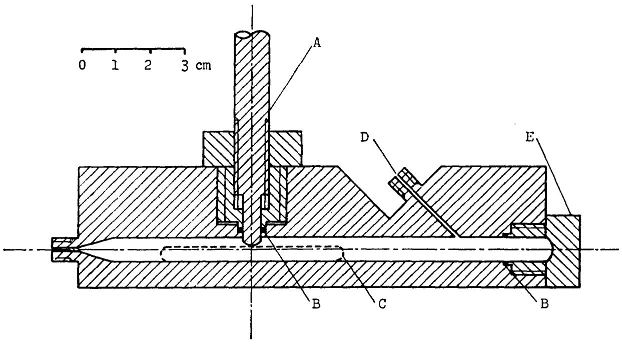

Fig. 2. Crushing device. A: Plunger for crushing an ampule, B: seals, C: an ampule containing a sample, D: carrier gas inlet, E: screwed cap for an ampule insertion.

Reagents. The sulfur used as an oxidizing agent was obtained by purifying[4] commercially available sulfur (chemically pure). The organic compounds used as standard samples were of an analytical grade, while the metal organic chelate compounds were prepared carefully by the method found in the literature for their gravimetric analysis. The polymer samples were the same as in the previous paper.[5]

Procedure. The ampule containing a sample was prepared and the sample was made to react with sulfur as follows: Definite amounts of sulfur and a sample were placed in a quartz tube in which one end had been sealed, and the inside of the quartz tube was replaced with He, after which the other end of the quartz tube was sealed. The ampule thus obtained was held at 600 °C for 10 min and at 950 °C for 30 min. Thereafter, the ampule at 950 °C was slowly cooled in an electric furnace to room temperature by lefting it stand. Three ampules were at first inserted into the crushing devices, A_1, A_2, and A_3, and then the three flows including A_1, A_2, and A_3 were replaced with He, after which one of the three flows was connected with a gas chromatograph. Figure 1 shows that the flow-1 is in a state of an analyzing system, while the flows-2 and -3 are in a state of a replacing system. Here, A_2 is connected in series with A_3. Thus, the system replaced with He is shown by Scheme 1:

$$\mathrm{He} \rightarrow \mathrm{D_2—C_2—A_2—B_2—B_3—A_3—C_3—D_3} \rightarrow \mathrm{Exhaust}$$

Scheme 1.

After the sample in the flow-1 has been completely analyzed, the flow-2 is connected with a gas chromatograph by turning the rotary cock, E, to the flow-2, while the flows-1 and -3 are in a state of a replacing system. Thus, the system replaced with He is shown by Scheme 2:

$$\mathrm{He} \rightarrow \mathrm{D_3—C_3—A_3—B_3—B_1—A_1—C_1—D_1} \rightarrow \mathrm{Exhaust}$$

Scheme 2.

Here, the residual quartz pieces in A_1 are taken off and the next ampule is newly charged. After the 5 min necessary for the stabilization of the base line in a gas chromatogram, the column of the gas chromatograph is cooled for 5 min; then the ampule is broken with the plunger of A_2, followed by the gas-chromatographic analysis. In the present gas sampler, B and C in the same flow are designed so as to operate simultaneously. The analysis was carried out continuously by repeating the above-mentioned operation. The gas chromatogram was obtained under conditions similar to those used in a previous paper.[2]

Results and Discussion

Reaction Conditions. In the previous procedure the ampule at 950 °C was cooled to 90 °C immediately after the reaction, while it is cooled slowly to room temperature by being left standing in the electric furnace in the present procedure. The results obtained by the present procedure are superior to those obtained by the previous one in the following points; 1) the fluctuation of the individual peak area ratio on the chromatogram, 2) the evolution of carbon monoxide (CO) as an impurity, and 3) the fluctuation of the correction factors. The fluctuation of the ratio of the peak areas in the previous and the present procedures, which was obtained by analyzing 5 samples of glycine and by estimating the coefficient of variation in the ratio of the individual peak area, is shown in Table 1.

TABLE 1. FLUCTUATION OF THE RATIO OF PEAK AREAS IN THE PREVIOUS AND THE PRESENT PROCEDURES

Procedure	Coefficient of variation (%)[a]				
	N_2	CO_2	H_2S	COS	CS_2
Present	0.2365	1.026	0.3895	0.1678	1.141
Previous	1.331	2.437	0.8553	1.406	1.940

a) Calculated from five runs for glycine.

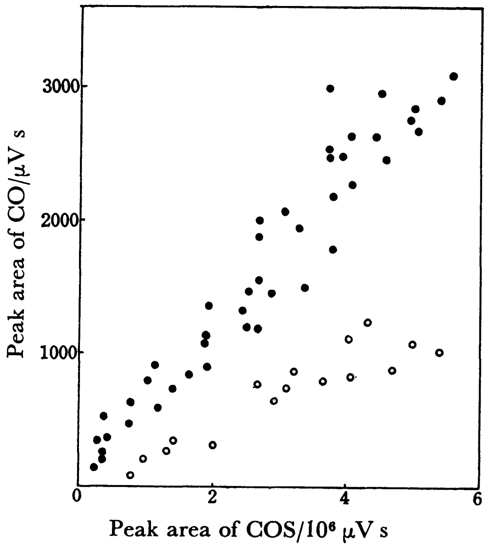

Fig. 3. Relationship between peak areas of COS and of CO in the compound consisting of C, H, and O.
○: Present procedure, ●: previous procedure.

The amount of CO evolved in the present procedure was smaller than that in the previous procedure and was neglected much as before. As may be seen from the fact that the peak of CO overlaps with that of nitrogen(N_2) on the chromatogram, the present procedure may be expected to be more precise than the previous one. This is shown in Fig. 3 with regard to the compound consisting of C, H, and O, the relationship between the peak areas of carbonyl sulfide (COS) and of CO is plotted. It can easily be seen from Fig. 3 that the peak area of CO is approximately proportional to that of COS. No linear relationship was, however, obtained experimentally between CO and carbon dioxide or carbon disulfide. On the basis of these results, CO was considered to evolve by means of the equilibrium shown in Eq. 1:

$$\mathrm{CO(g)} + \frac{1}{x}\mathrm{S}_x\mathrm{(g)} \rightleftharpoons \mathrm{COS(g)}. \qquad (1)$$

By taking the complete decomposition of COS at high temperatures into consideration, and by supposing that the above equilibrium could not be established completely when the temperature was suddenly lowered to 90 °C from 950 °C, the evolution of a larger amount of CO in the previous procedure as compared with that in the present one was easily understood. The amount of CO evolved by dropping the ampule into water at 950 °C was found to be several times as great as the amount of CO evolved by the present procedure. This makes the above considerations reasonable.

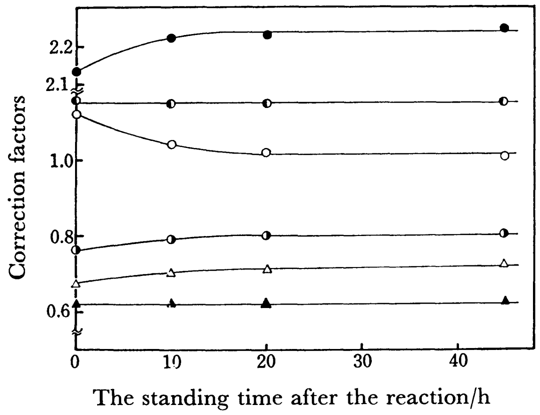

Fig. 4. Effect of the standing time on correction factors. ◐: K(N_2), ○: K(CO_2), △: K(COS), ●: K(H_2O), ◑: K(SO_2), ▲: K(CS_2).

According to the experimental results, the correction factors changed with the standing time within several hours after the completion of the reaction (Fig. 4). It may also be seen from Fig. 4 that a definite period of standing for an ampule is indispensable for obtaining a good result. The correction factor of $N_2(K(N_2))$, which was defined by $K(N_2)=A(H_2S)/A(N_2)$, was obtained by the use of dicyandiamide.[2] Hydrogen sulfide was concluded to be stable, irrespective of the standing time of the ampule throughout the experiment, since N_2 was stable under the conditions of PSGC and since $K(N_2)$ was also constant experimentally. Though hydrogen (H_2) could not be detected under the conditions of PSGC, it was unnecessary, in the light of the above results, to pay much attention to H_2. Based on these results, the previous procedure was improved as in the present one, in which the ampule was analyzed for a definite period of standing after the reaction.

Pretreatment of a Crushing Device. The results obtained by the use of a crushing device without pretreating the internal surface fluctuated from sample to sample, and the peak of water (H_2O) was observed in spite of the fact that the H_2O should not evolve under the present experimental conditions. To avoid these phenomena, the internal surface of the crushing device was treated with an aqueous solution of disodium phosphate or water glass. The pretreatment with an aqueous solution of water glass was found to improve the analytical results markedly and to reduce the amount of evolved water to traces from $H_2O/N_2=0.0381$, which was obtained as the mean value of the peak-area ratio in 5 analyses of glycine. Therefore, the internal surfaces of all the crushing devices were coated with water glass for use.

Gas Sampler. The gas sampler used in the previous papers was made of Teflon and was occasionally broken with a piece of quartz. The previous procedure was also time-consuming, since such operations as 1) the removal of quartz pieces and the insertion of a sample, 2) the replacement of the air in the inside of a gas sampler with He, and 3) the analysis of the reaction products with a gas chromatograph were carried out with only one gas sampler. By setting up three crushing devices in parallel with a gas chromatograph, the gas sampler could be used for a long time and the time necessary for an analysis was minimized to about 20 min from the period of about 30 min needed in the previous procedure. According to the present procedure, the analysis could be carried out continuously at the rate of 3 samples per hour.

Analysis of Various Compounds. Various organic compounds, metal organic chelate compounds, and polymers were analyzed by the present procedure; the results are shown in Tables 2, 3, and 4, respectively. As may be seen from Tables 2—4, both precision and accuracy were superior to those by the previous procedure. After the sample in an ampule treated at 950 °C

Table 2. Analytical results of organic compounds

Sample	C wt%			H wt%			O wt%			N wt%		
	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error
Glycine	32.00	31.93	−0.07	6.71	6.86	+0.15	42.63	42.30	−0.33	18.66	18.91	+0.25
L-Glutamine	41.09	41.04	−0.05	6.90	7.04	+0.14	32.84	32.78	−0.04	19.17	19.13	−0.04
Cholesterol	83.87	83.62	−0.25	11.99	12.03	+0.04	4.14	4.35	+0.21			
8-Quinolinol	74.47	74.40	−0.07	4.86	4.88	+0.02	11.02	10.94	−0.08	9.65	9.78	+0.13
Benzophenone	85.69	85.66	−0.03	5.53	5.51	−0.02	8.78	8.83	+0.05			
p-Dimethylamino-benzaldehyde	72.46	72.47	+0.01	7.43	7.53	+0.10	10.72	10.93	+0.21	9.39	9.08	−0.31
2,2′,3,3′,4,4′,5,5′,6-Nonamethyl-diphenylmethane	89.73	89.84	+0.11	10.27	10.16	−0.11						
Lauric acid	71.95	72.17	+0.22	12.08	12.07	−0.01	15.97	15.76	−0.21			
Myristic acid	73.63	73.76	+0.13	12.36	12.15	−0.21	14.01	14.09	+0.08			
Stearic acid	75.99	75.63	−0.36	12.76	12.75	−0.01	11.25	11.62	+0.37			
Palmitic acid	74.94	74.72	−0.22	12.58	12.51	−0.07	12.48	12.77	+0.29			
Suberic acid	55.16	55.01	−0.15	8.10	8.23	+0.13	36.74	36.77	+0.03			

TABLE 3. ANALYTICAL RESULTS OF METAL ORGANIC CHELATE COMPOUNDS

Sample[a]	C wt%			H wt%			O wt%			N wt%		
	Theor.[b]	Found	Error	Theor.[b]	Found	Error	Theor.[b]	Found	Error	Theor.[b]	Found	Error
Bis(8-quinolinolato)-magnesium(II) $Mg(C_9H_7ON)_2$	74.99	75.04	−0.05	4.20	4.19	−0.01	11.10	10.82	−0.28	9.72	9.93	+0.21
Tris(8-quinolinolato)-chromium(III) $Cr(C_9H_6ON)_3$	74.99	74.95	−0.04	4.20	4.18	−0.02	11.10	11.26	+0.16	9.72	9.61	−0.11
Bis(anthranilato)-manganese(II) $Mn(C_7H_6O_2N)_2$	61.76	62.15	+0.39	4.44	4.47	+0.03	23.51	23.44	−0.07	10.29	9.94	−0.35
Tris(8-quinolinolato)-iron(III) $Fe(C_9H_6ON)_3$	74.99	75.30	+0.31	4.20	4.04	−0.16	11.10	11.29	+0.19	9.72	9.36	−0.36
Bis(anthranilato)-cobalt(II) $Co(C_7H_6O_2N)_2$	61.76	62.01	+0.25	4.44	4.51	+0.07	23.51	23.23	−0.28	10.29	10.25	−0.04
Bis(8-quinolinolato)-nickel(II) $Ni(C_9H_6ON)_2$	74.99	75.23	+0.24	4.20	4.16	−0.04	11.10	11.12	+0.02	9.72	9. 6	−0.26
(Benzoin oximato)-copper(II) $Cu(C_{14}H_{11}O_2N)$	74.65	74.60	−0.05	4.92	4.65	−0.27	14.21	14.55	+0.34	6.23	6.20	−0.03
Bis(salicylaldehyde oximato)copper(II) $Cu(C_7H_6O_2N)_2$	61.76	61.61	−0.15	4.44	4.44	0	23.51	23.44	−0.07	10.29	10.50	+0.21
Bis(anthranilato)-copper(II) $Cu(C_7H_6O_2N)_2$	61.76	62.04	+0.28	4.44	4.55	+0.11	23.51	23.28	−0.23	10.29	10.11	−0.18
Bis(anthranilato)-zinc(II) $Zn(C_7H_6O_2N)_2$	61.76	61.96	+0.20	4.44	4.28	−0.16	23.51	23.66	+0.15	10.29	10.10	−0.19
Bis(8-quinolinolato)-cadmium(II) $Cd(C_9H_6ON)_2 \cdot 2H_2O$	66.66	67.01	+0.35	4.94	4.88	−0.06	19.75	19.49	−0.26	8.65	8.62	−0.03
Tris(8-quinolinolato)-gallium(III) $Ga(C_9H_6ON)_3$	74.99	74.96	−0.03	4.20	4.15	−0.05	11.10	11.30	+0.20	9.72	9.59	−0.13
Tris(8-quinolinolato)-indium(III) $In(C_9H_6ON)_3$	74.99	75.39	+0.40	4.20	4.06	−0.14	11.10	11.14	+0.04	9.72	9.41	−0.31
Dioxobis(8-quinolinolato)molybdenum(VI) $MoO_2(C_9H_6ON)_2$	67.50	67.37	−0.13	3.78	3.70	−0.08	19.98	20.25	+0.27	8.75	8.68	−0.07
Dioxobis(8-quinolinolato)tungsten(VI) $WO_2(C_9H_6ON)_2$	67.50	67.35	−0.15	3.78	3.58	−0.20	19.98	20.19	+0.21	8.75	8.89	+0.14

a) Metal atoms were neglected in considering the composition of metal organic chelate compounds, since they couldn ot be determined. b) These values were also found to be correct by the C and H analysis carried out in the Elemental analysis Center of the Pharmaceutical Department of Kyoto University.

TABLE 4. ANALYTICAL RESULTS OF VARIOUS POLYMERS

Sample	C wt%		H wt%		O wt%	
	CH analysis[a]	PSGC	CH analysis[a]	PSGC	CH analysis[b]	PSGC
Phenol resin	82.49	82.75	10.76	10.38	6.78	6.87
Xylene resin	82.10	82.31	8.83	8.70	9.07	8.97
Terpene resin	85.37	85.31	11.42	11.31	3.21	3.37
Acrylonitrile/butadiene/stylene terpolymer A	85.63	85.67	7.92	7.65	6.45	6.69
B	85.52	85.86	7.81	7.76	6.67	6.39
Ethylene/vinyl acetate copolymer A	81.36	81.19	13.71	13.41	4.93	5.39
B	76.27	76.34	12.15	12.04	11.58	11.62
C	72.99	73.36	11.27	11.18	15.74	15.48

a) The composition of the samples were confirmed by the C and H analysis carried out in the Elemental Analysis Center of the Pharmaceutical Department of Kyoto University. b) Determined by subtracting the sum of the C and H values from the total amount of a sample.

Table 5. Analytical results of organic compounds which were left standing for 3 weeks after the reaction

Sample	C			H			O			N		
	wt%			wt%			wt%			wt%		
	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error
Glycine	32.00	31.79	−0.14	6.71	6.62	−0.09	42.63	42.45	−0.18	18.66	19.14	+0.48
8-Quinolinol	74.47	74.41	−0.06	4.86	4.87	+0.01	11.02	10.93	−0.09	9.65	9.79	+0.14
Benzophenone	85.69	85.80	+0.11	5.53	5.48	−0.05	8.78	8.73	−0.05			
Suberic acid	55.16	55.47	+0.31	8.10	8.21	+0.11	36.74	36.31	—0.43			

was left standing for 3 weeks at room temperature, it was analyzed (Table 5). It may be seen from Table 5 that a good analytical value was obtained irrespective of the standing time after the temperature of a sample had been brought to room temperature in accordance with the present procedure.

The present gas sampler could also be used for the previous procedure so long as the correction factors obtained previously were used.

References

1) K. Tsuji, K. Fujinaga, and T. Hara, *Bull. Chem. Soc. Jpn.*, **50**, 2292 (1977).

2) T. Hara, K. Fujinaga, and K. Tsuji, *Bull. Chem. Soc. Jpn.*, **51**, 1110 (1978).

3) T. Hara, K. Fujinaga, and K. Tsuji, *Bull. Chem. Soc. Jpn.*, **51**, 2951 (1978).

4) T. Hara, K. Fujinaga, K. Tsuji, and F. Okui, *Bull. Chem. Soc. Jpn.*, **51**, 3079 (1978).

5) T. Hara, K. Fujinaga, and F. Okui, *Bull. Chem. Soc. Jpn.*, in press.