Simultaneous Determination of the Atomic Ratio between C, H, O, and N by the Pyrolytic Sulfurization Method

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From a sample subjected to pyrolytic sulfurization in a sealed quartz tube, the evolved gases, carbon disulfide, carbon monoxide, carbon dioxide, carbonyl sulfide, hydrogen sulfide, and a nitrogen molecule were simultaneously estimated. Determination of the atomic ratio between C, H, O, and N was carried out by means of three calibration curves obtained by use of glycine, L-glutamic acid, L-citrulline, and fumaric acid. They are applicable to carboxylic acids and the other compounds, but not to compounds including nitro and/or sulfo groups.

Various carboxylic acids were subjected to pyrolysis in sulfur(S) vapor and the reaction products such as hydrogen sulfide(H_2S), carbon dioxide(CO_2), and carbon disulfide(CS_2) were analyzed gas chromatographically, followed by determination of the chemical composition and functional group.[1] However, complete sulfurization of carboxylic acids apparently was not accomplished, since the amount of evolved CS_2 was much smaller than the expected one and a black carbonaceous residue remained. The method could not be applied to compounds other than carboxylic acids since the reaction products except for CO_2 were given in terms of the amount of CO_2 and the reaction in addition did not go to completion.

The present study was undertaken to establish an improved method in which a sample is subjected to pyrolytic sulfurization in a sealed quartz tube containing S, and the evolved gases such as H_2S, carbonyl sulfide (COS), CS_2, and a nitrogen molecule(N_2) are simultaneously estimated, followed by determination of the atomic ratio between C, H, O, and N. The calibration curves obtained from four compounds were applicable to carboxylic acids and other compounds, but not to the compounds including nitro and/or sulfo groups. Sulfurization seemed to be complete since no black carbonaceous residue remained. The present method gives more accurate results, no weighing being necessary during the procedure.

Experimental

Apparatus. A sampler, a displacement apparatus and an electric furnace were used. Gas chromatograms were taken on a Yanagimoto GCG-5DH and a Shimadzu GC-4B.

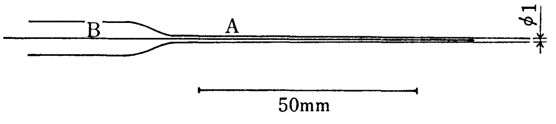

Fig. 1. Sampler.
(A) Quartz capillary, (B) plunger(nickel-chromium alloy).

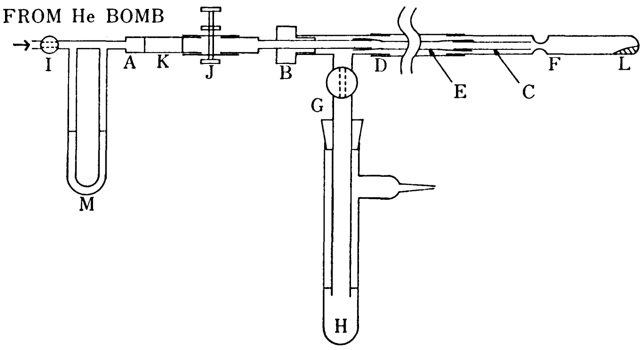

Fig. 2. Displacement apparatus.
A: Joint, B: silicone rubber packing, C: stainless steel tube, D: poly(vinyl chloride) tube, E: silicone rubber tube, F: reaction tube, G: two-way cock, H: water, I: needle valve, J: pinch cock, K: silica gel packing, L: sulfur and sample, M: flow meter.

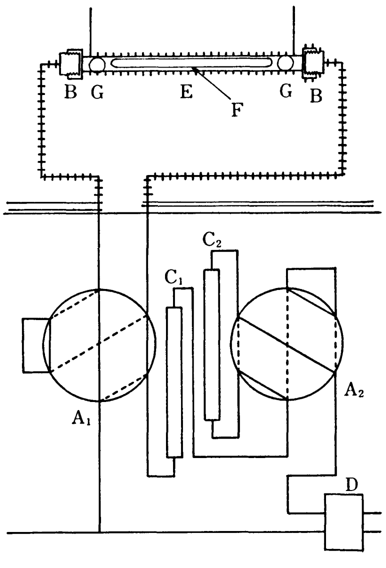

Fig. 3. Schematic diagram of the flow system.
A_1, A_2: Six-way cocks, B: joint, C_1: silica gel column, C_2: molecular sieve 5A column, D: thermal conductivity detector, E: Teflon tube, F: reaction tube, G: quartz wool.

Reagents. Various purification methods including (1) vacuum sublimation, (2) contact with sulfuric acid, (3) nitric acid oxidation of sodium sulfide, (4) decomposition of sodium thiosulfate with hydrochloric acid, and (5) refluxing with magnesium oxide(MgO)[2] were examined, the last one being found the best. The procedure is as follows: 500 g S was gradually heated in a 500 ml four-holed flask with a reflux condenser, with an electric furnace, MgO being added after cessation of gas evolution. The temperature was held at *ca.* 450 °C, S being refluxed for 24 h. The melts were filtered at 120—150 °C through a sintered glass filter protected by a ribbon heater. About 450 g S was obtained as a filtrate to which was added 4.5 g (1%) MgO, the contents being refluxed for 24 h. The operation was repeated six times, *ca.* 150 g S being finally obtained. The S obtained was dried at 150 °C for 3 h. A blank test was carried out using the sealed tube containing 20 mg S. Though slight peaks of air, COS and CS_2 were confirmed at the highest sensitivity of the Shimadzu GC-4B gas chromatograph, they were negligible in the present study.

The other reagents were of analytical grade. Helium was of commercial grade.

Materials. A transparent quartz tube was found suitable as the reaction tube, since an opaque tube gives a large peak owing to the N_2 present in foams. The maximal strength of the quartz tube was estimated to be *ca.* 390 atm at 950 °C from the relationship between the amount of S and the explosion temperature during the course of heating, and on the assumption that S is present as a diatomic molecule[3] at 950 °C. The internal pressure being *ca.* 20 atm, the operation was safely carried out.

The gas sampler E shown in Fig. 2 should be heat-resistant, strong and elastic. A silicone rubber tube is heat-resistant but mechanically weak, a poly(vinyl chloride) tube less heat-resistant, giving a number of impurity peaks. A Teflon tube meets all requirements and can be used more than 100 times at 55 °C, not giving any impurity peaks even at 120 °C.

Procedure. A transparent quartz tube, 3.8 mm i.d., 5.6 mm o.d. and 110 mm long, was treated for 5 h in a Bransonic-52 ultrasonic cleaner, washed, dried, and closed at one end by use of a town gas-oxygen flame, followed by being made narrow at *ca.* 50 mm from the closed end and being heated at 850 °C for 10 min.

Five mg of S was placed in the quartz tube and a definite volume of powdered sample was added to it with the sampler (Fig. 1), a definite length of capillary sample thus being prepared. The reaction tube was connected with the displacement apparatus (Fig. 2). A stream of helium regulated at a flow rate of 100 ml/min by a manometer M and valve I was passed through it to displace the air. Cock G and pinch cock J were closed. The internal pressure of the reaction tube (*ca.* 890 Torr) was balanced with the atmospheric pressure by operating cock G just before glass blowing, followed by sealing. The time required for sealing was *ca.* 15 s. The sealed tube was placed in a quartz case 11 mm i.d. × 90 mm and heated in an electric furnace for 10 min at 600 °C and for 30 min at 950 °C. The sealed tube was held at 90 °C for 5 min in an oven and inserted into a Teflon sampler E (Fig. 3) maintained at 55 °C. E was connected with the gas chromatograph by operating the cock A_1. The sealed tube was broken into pieces by driving a jack across the Teflon sampler and evolved gas was introduced into the gas chromatograph, the column temperature being raised immediately to the programmed one at a rate of 8 °C/min. The molecular sieve 5A column C_2 was separated from the flowing system in *ca.* 5 min after the introduction of evolved gas, and the constituents of relative higher boiling point, which come out of the silica gel column C_1, were analyzed with a thermal conductivity detector after passing through cock A_2.

The gas chromatograph was operated under the following conditions: A 1.5 m stainless steel column C_1 was charged with silica gel (80—100 mesh) and a 0.6 m stainless steel column C_2 with molecular sieve 5A (80—100 mesh), column temperature being programmed between 40 and 185 °C at a rate of 8 °C/min. The flow rate of helium was 30 ml/min at 185 °C. Davison grade 08 silica gel[4] was used instead of Deactigel.[5] The latter is known to be effective for the separation of S-containing compounds. In order to separate the individual constituents in the evolved gas, a combination of the silica gel column and the molecular sieve 5A column was utilized, by which N_2 was completely separated from carbon monoxide(CO). Glycine was chosen as an example and analyzed. Its chromatogram is shown in Fig. 4. All the peaks were identified by use of an authentic sample and their peak areas were estimated by the half-width method.

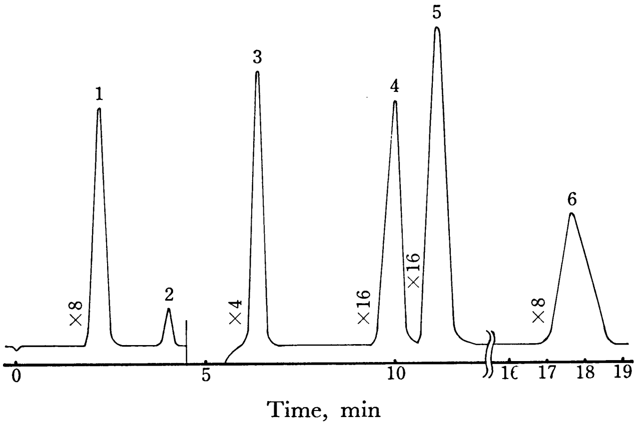

Fig. 4. Typical chromatogram of reaction products.
1: N_2, 2: CO, 3: CO_2, 4: COS, 5: H_2S, 6: CS_2.

Results

Reaction Temperature and Reaction Time. The relationship between reaction products and reaction temperature (Fig. 5) or reaction time (Fig. 6) was examined using glycine. The composition of the reaction products was almost definite at a temperature in the range 750—1050 °C and in more than 20 min after the start of the reaction.

Pyrolytic Sulfurization. The sealed tube containing S and glycine was processed by five separate procedures (Table 1). The coefficients of variation in the values of (N/H), (C/H), and (O/H) were smaller in procedures C and E than in any other, and were thus re-examined using 5 mg S and 0.1—2.0 mg glycine. The results are given in Fig. 7 and Table 2. Procedure C was chosen since it gave a better result.

Amounts of Sample and S. Since the values of (N/H), (C/H) and (O/H) were approximately definite

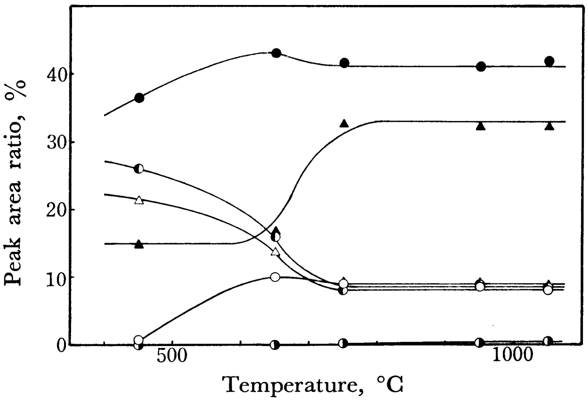

Fig. 5. Effect of reaction temperature on products.
20 mg S and 0.1—1.0 mg glycine made to react for 30 min. ○: N_2, ◑: CO, ◐: CO_2, ▲: COS, ●: H_2S, △: CS_2.

Table 1. Comparison of individual pyrolytic sulfurization procedures[a)]

Procedure	Coefficient of variation (%)[b)]								
	Individual peak area ratio[c)]						Observed atomic ratio[d)]		
	N_2	CO	CO_2	COS	H_2S	CS_2	$(N/H)_f$	$(C/H)_f$	$(O/H)_f$
A	4.0	24.5	3.6	2.9	1.9	8.2	4.7	2.8	4.5
B	4.5	9.1	4.9	2.5	4.9	4.3	9.5	7.8	7.4
C	2.1	20.0	2.4	3.3	1.8	11.1	2.7	3.5	4.2
D	6.1	0	6.6	2.0	4.0	10.9	9.5	6.9	6.9
E	6.8	5.6	6.9	2.0	1.8	10.9	8.5	2.3	2.8

a) 20 mg S and 0.3—1.0 mg glycine used. b) Calculated from five runs for each procedure. c) Ratio to the sum of all peaks. d) Estimated by Eqs. 6, 7, and 8, respectively. A: Heated at 950 °C for 40 min in a quartz case and held in an oven at 90 °C for 5 min, B: Heated at 950 °C for 40 min in a quartz case and held in water for 1 min, C: Heated at 600 °C for 10 min, at 950 °C for 30 min in a quartz case and held in an oven at 90 °C for 5 min, D: Heated at 950 °C for 40 min and held in an oven at 90 °C for 5 min, and E: Heated at 950 °C for 40 min and held in water for 1 min.

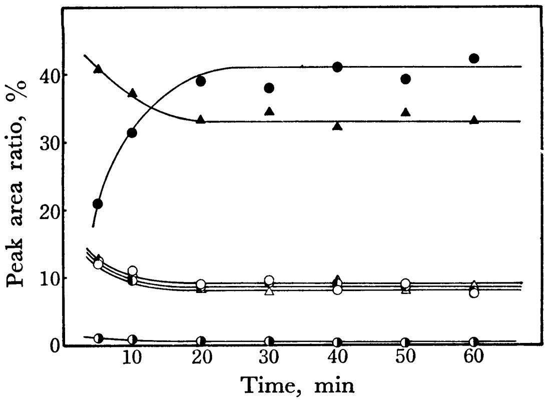

Fig. 6. Effect of reaction time on products.
20 mg S and 0.1—1.0 mg glycine made to react at 950 °C. ○: N_2, ◑: CO, ◐: CO_2, ▲: COS, ●: H_2S, △: CS_2.

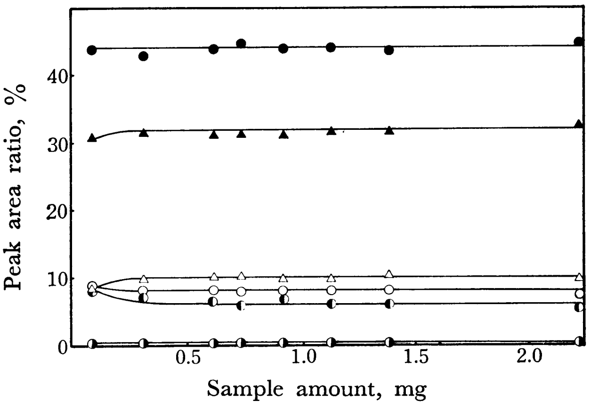

Fig. 7. Effect of the amount of sample on peak area ratios. 5 mg S and glycine made to react by procedure C. ○: N_2, ◑: CO, ◐: CO_2, ▲: COS, ●: H_2S, △: CS_2.

Table 2. Re-examination of the pyroltic sulfurization procedures[a)]

Procedure	Coefficient of variation(%)[b)]		
	$(N/H)_f$	$(C/H)_f$	$(O/H)_f$
C	3.9	1.4	2.4
E	5.0	1.9	2.1

a) Five mg S and 0.3—2.0 mg glycine used. b) Calculated from five runs for each procedure.

in the reaction between a definite amount of S and 0.3—2.0 mg glycine, the compounds other than glycine were also sampled by the sampler (Fig. 1) so that their amounts would be in the range 0.3—2.0 mg. From the relation between the weight of sample and the peak area in the gas chromatogram, the amount of samples taken was 0.3—1.0 mg. The relation between the amount of sample and the amounts of S was examined. The contents of N_2, CO, and CO_2 in the evolved gas were constant for the weight ratio of S to sample greater than 20. The contents of H_2S and COS decreased with an increase in the amount of S. Five mg of S was used.

Temperature of Gas Sampler. The effect of the internal temperature of the gas sampler E on the peak area of the reaction products was examined (Fig. 8). The peak area ratios of reaction products to N_2 were approximately constant at temperatures 50—120 °C. Thus the internal temperature of the gas sampler E

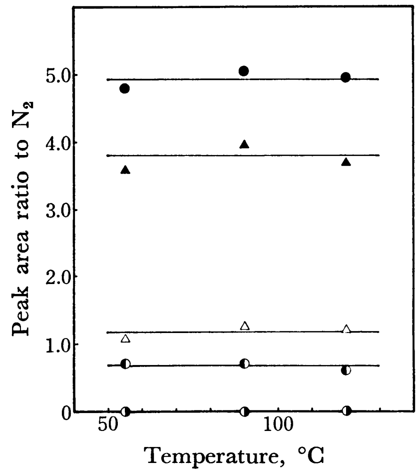

Fig. 8. Effect of the internal temperature of a Teflon tube on peak area ratios.
5 mg S and glycine made to react. ◑: CO/N_2, ◐: CO_2/N_2, ▲: COS/N_2, ●: H_2S/N_2, △: CS_2/N_2.

Table 3. Correction factors

Run number	Peak area ratio[a]				Correction factor[b]		
	CO	CO_2	COS	CS_2	$K(CO_2)$	K(COS)	$K(CS_2)$
1	0.8	13.6	65.0	20.6	1.00	1.26	1.51
2	0.6	13.4	65.3	20.4	1.00	1.26	1.52
Average	0.7	13.5	65.2	20.5	1.00	1.26	1.52

a) Individual peak area divided by the sum of all peaks. b) Estimated by Eqs. 4 and 5, respectively.

was held at 55 °C.

Correction Factors for the Relative Peak Area of CO_2, COS, and CS_2. The compound containing C, H, O, and N was subjected to pyrolytic sulfurization to form the following products: CO, CO_2, COS, and CS_2 from carbon atom, H_2S from hydrogen atom, CO, CO_2, and COS from oxygen atom and N_2 from nitrogen atom. In order to determine the composition of the compound, each peak area of N_2, C- and O-containing compounds was divided by the peak area of H_2S, and the atomic ratios between H and C or O or N were estimated from the calibration curves. The relationship between the peak areas of CO, CO_2, COS, and CS_2 and their mole numbers was used to estimate the sum of individual peak areas. Since the peak area of CO was negligibly small in comparison with that of CO_2, COS, and CS_2, no care was taken of the correction factor of CO. CO was sealed into a quartz tube containing S by use of the displacement apparatus (Fig. 2), and the gases evolved by the reaction were analyzed (Table 3). The major products were CO_2, COS, and CS_2, only a minute amount of CO remaining as an unreacted component. The reaction between CO and a diatomic S molecule[3] at 950 °C was assumed to proceed according to the following equations.

$$2CO + S_2 = 2COS, \tag{1}$$

$$2COS = CO_2 + CS_2. \tag{2}$$

CO_2 and CS_2 were formed in equimolecular amounts. On the basis of $K(CO_2)=1.00$, the correction factors were estimated by Eqs. 4 and 5, where $A'(CO)$, $A'(CO_2)$, $A'(COS)$ and $A'(CS_2)$ refer to percent peak area ratios of CO, CO_2, COS, and CS_2 to the sum of all peaks.

$$K(CO_2) = 1.00, \tag{3}$$

$$\frac{K(COS)}{K(CO_2)} = K(COS) = \frac{\{100-[A'(CO)+A'(COS)]\}}{2A'(CO_2)}, \tag{4}$$

$$\frac{K(CS_2)}{K(CO_2)} = K(CS_2) = \frac{A'(CS_2)}{A'(CO_2)}. \tag{5}$$

The value of $100-[A'(CO)+A'(COS)]$ corresponds to the amount of COS consumed. Thus the value of $A'(CO_2)$, $A'(COS)$, and $A'(CS_2)$ divided by $K(CO_2)$, $K(COS)$, and $K(CS_2)$ in that order imply their mole ratios. The correction factors thus obtained were used.

Calibration Curves. Glycine, L-glutamic acid, L-citrulline, and fumaric acid in high purity were analyzed and the numerical ratios of each atom were calculated as follows.

$$\left(\frac{C}{H}\right)_f = \frac{[A(CO)+A(CO_2)+A(COS)/1.26+A(CS_2)/1.52]}{2A(H_2S)}, \tag{6}$$

$$\left(\frac{O}{H}\right)_f = \frac{[A(CO)+2A(CO_2)+A(COS)/1.26]}{2A(H_2S)}, \tag{7}$$

$$\left(\frac{N}{H}\right)_f = \frac{A(N_2)}{A(H_2S)}. \tag{8}$$

Here, $A(CO)$, $A(CO_2)$, $A(COS)$, $A(CS_2)$, $A(H_2S)$, and $A(N_2)$ are referred to the individual peak areas in mm^2 at the chart speed of 5 mm/min. Simultaneous determination of the atomic ratio among C, H, O, and N was made by use of the calibration curves. Experimental values (f) are plotted against theoretical values (t) in Fig. 9.

Analysis of Various Compounds. Amino acids (Table 4) and other carboxylic acids (Table 5) were

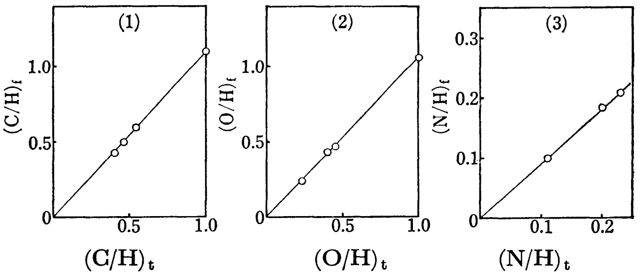

Fig. 9. (1) Calibration curve for (C/H). (2) Calibration curve for (O/H). (3) Calibration curve for (N/H).

Table 4. Analytical results of amino acids

Compound	Formula	
	Theoretical	Found[a]
γ-Aminobutyric acid	$N_1C_4O_2H_9$	$N_{1.0}C_{3.9}O_{2.0}H_9$
L-Phenylalanine	$N_1C_9O_2H_{11}$	$N_{1.0}C_{8.6}O_{2.2}H_{11}$
Tryptophan	$N_2C_{11}O_2H_{12}$	$N_{2.1}C_{10.6}O_{2.2}H_{12}$
L-Methionine	$N_1C_5O_2S_1H_{11}$	$N_{1.0}C_{5.0}O_{2.1}H_{11}$
L-Aspartic acid	$N_1C_4O_4H_7$	$N_{1.0}C_{4.1}O_{4.1}H_7$
L-Threonine	$N_1C_4O_3H_9$	$N_{1.0}C_{3.9}O_{3.0}H_9$
L-Homoserine	$N_1C_4O_3H_9$	$N_{1.0}C_{3.9}O_{2.9}H_9$

a) Calculated from two runs for each sample.

Table 5. Analytical results of carboxylic acids

Compound	Formula	
	Theoretical	Found[a]
Malonic acid	$C_3O_4H_4$	$C_{3.1}O_{4.1}H_4$
Succinic acid	$C_4O_4H_6$	$C_{3.9}O_{3.9}H_6$
Lauric acid	$C_{12}O_2H_{24}$	$C_{12.3}O_{2.2}H_{24}$
Myristic acid	$C_{14}O_2H_{28}$	$C_{13.6}O_{2.3}H_{28}$
Terephthalic acid	$C_8O_4H_6$	$C_{7.9}O_{4.1}H_6$

a) Calculated from two runs for each sample.

Table 6. Analytical results of other compounds

Compound	Formula	
	Theoretical	Found[a]
2,2′,3,3′,4,4′,5,5′,6-Nonamethyldiphenylmethane	$C_{22}H_{30}$	$C_{22.1}H_{30}$
2,2′-Bipyridine	$N_2C_{10}H_8$	$N_{1.9}C_{10.1}H_8$
Cyanoguanidine	$N_4C_2H_4$	$N_{4.0}C_{1.9}H_4$
Benzil	$C_{14}O_2H_{10}$	$C_{14.1}O_{2.2}H_{10}$
Benzophenone	$C_{13}O_1H_{10}$	$C_{13.0}O_{1.2}H_{10}$
meso-Erythritol	$C_4O_4H_{10}$	$C_{4.0}O_{3.9}H_{10}$
p-Dimethylaminobenzaldehyde	$N_1C_9O_1H_{11}$	$N_{0.9}C_{8.8}O_{1.1}H_{11}$
Dimethylglyoxime	$N_2C_4O_2H_8$	$N_{1.9}C_{4.0}O_{2.1}H_8$
Diphenylglyoxime	$N_2C_{14}O_2H_{12}$	$N_{2.1}C_{14.0}O_{2.3}H_{12}$

a) Calculated from two runs for each sample.

analyzed. No difference between threonine and homoserine was found irrespective of their structural isomerism. Since S atom could not be determined, it was neglected in the composition of methionine. The method was applied to the compounds consisting of C and H as well as C, H, and N, satisfactory results being obtained (Table 6).

Discussion

Relative Correction Factors of CO_2, COS, and CS_2. Eqs. 1 and 2 for the reaction between CO and S were supported by Stock *et al.*[6,7] We found CO_2, COS, and CS_2 as the reaction products. The relative correction factors of CO_2, COS, and CS_2 were determined on the assumption that the reaction between CO and S proceeds in accordance with Eqs. 1 and 2, which were confirmed as follows: The N_2 gas containing 30—100 vol % CO was prepared by use of a N_2 bomb and a CO bomb equipped with a needle-valve and a flow-meter, respectively, and the mixed gas was sealed into a reaction tube containing 20 mg S, followed by heating at 950 °C and analysis of the gases produced (Fig. 10). The peak area ratios of CO, COS, and CS_2 to CO_2 were found to be constant irrespective of change of vol% CO. By taking it for granted that the reaction products are restricted to CO_2, COS, and CS_2, Eqs. 1 and 2 are concluded to hold for the reaction between CO, and S under the above conditions. Since CO_2 was produced as shown in Eq. 2, the reaction between CO_2 and S was examined, and the reaction mixture was found to contain the following: CO_2, COS, and sulfur dioxide(SO_2) as the major component, and CO and CS_2 as a trace component. Thus the reaction between CO_2 and S is supposed to proceed primarily as follows.

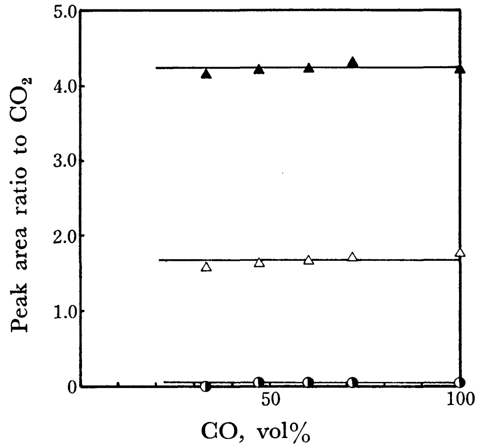

Fig. 10. Relationship between the amount of CO and the peak area ratios using a Yanagimoto GCG-5DH gas chromatograph. ◑: CO/CO_2, ▲: COS/CO_2, △: CS_2/CO_2.

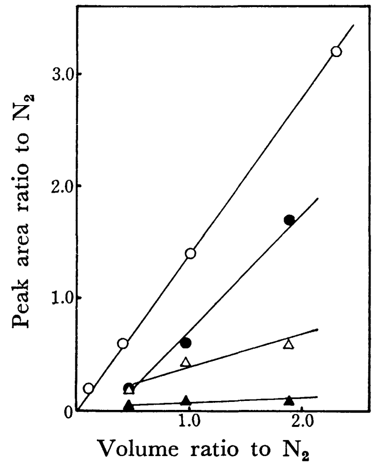

Fig. 11. Effect of CS_2* on the peak area ratios.
* CS_2 added by the quartz capillary. (○) Mixture of N_2 and SO_2, (●) mixture of N_2, SO_2 and CS_2, (△) produced CO_2, (▲) produced COS.

$$2CO_2 + \frac{3}{2}S_2 = 2COS + SO_2. \tag{9}$$

If we take Eqs. 2 and 9 into consideration, the formation of SO_2 is expected for the reaction between CO and S. However, no SO_2 was found. This is understandable if we accept the equation which was experimentally confirmed (Fig. 11).

$$CS_2 + SO_2 = CO_2 + \frac{3}{2}S_2. \tag{10}$$

The amount of SO_2 decreases by addition of CS_2 to SO_2, CO_2 and COS being simultaneously formed. Though the equation was also

$$3CS_2 + 2SO_2 = 2COS + CO_2 + S_2, \tag{11}$$

described for the formation of CO_2 and COS from CS_2 and SO_2, it was not acceptable since the amount of COS was confirmed experimentally to be about one-fifth that of CO_2, irrespective of the mole ratio of COS: CO_2=2 : 1. Assuming the conversions in Eqs. 2, 9, and 10 to be α, β, and γ, we have equilibrium fractions of each component based on a unit mass of COS as follows:

$$\begin{array}{ccccc} 2COS & = & CO_2 & + & CS_2, \\ 1-\alpha & & 0.5\alpha & & 0.5\alpha \end{array} \tag*{(2)′}$$

$$\begin{array}{ccccccc} 2CO_2 & + & \frac{3}{2}S_2 & = & 2COS & + & SO_2, \\ 0.5\alpha(1-\beta) & & & & 0.5\alpha\beta & & 0.25\alpha\beta \end{array} \tag*{(9)′}$$

$$\begin{array}{ccccccc} CS_2 & + & SO_2 & = & CO_2 & + & \frac{3}{2}S_2. \\ 0.5\alpha-0.25\alpha\beta\gamma & & 0.25\alpha\beta(1-\gamma) & & 0.25\alpha\beta\gamma & & \end{array} \tag*{(10)′}$$

From the values $K_{eq}=2.67\times10^4$ at 1200 K and $K_{eq}=2.24\times10^4$ at 1300 K for Eq. 10,[8] the value of γ becomes approximately equal to 1. The fraction of CS_2 is equal to $0.5\alpha-0.25\alpha\beta\gamma=0.5\alpha-0.25\alpha\beta$ and that of CO_2 to $0.5\alpha(1-\beta)+0.25\alpha\beta\gamma=0.5\alpha-0.25\alpha\beta$. This implies that Eq. 2 holds even in the introduction of Eqs. 9 and 10.

Adaptability of Calibration Curves. The space velocity of a reactant gas was very large in the high temperature range, and the reaction between a sample gas and S could not go to completion.[1] Pyridine derivatives in particular were less decomposable and much carbonaceous residue remained after the reaction. By the present method, pyridine and quinoline derivatives were easily decomposed, no carbonaceous residue remaining. The reaction seems to proceed completely and stoichiometrically (Tables 4, 5, and 6).

The calibration curves obtained from four compounds were applicable to various compounds. However, they cannot be applied to aromatic sulfonic acids and nitro compounds. SO_2 was formed in a batchwise apparatus and a flow-type apparatus,[9] but not by the present method. This seems to be due to the difference in the reaction conditions. SO_2 formed in the former case moves quickly to the low temperature zone with other gases, remaining unreacted, while that in the present case is made to react with CS_2 at 950 °C according to Eq. 10. This is reasonable if we take the relationship between $\Delta G°$ and TK into consideration (Fig. 12). Compounds deviated from the calibration curves are given in Table 7. Since the amounts of CO_2 and COS formed according to Eqs. 9 and 10 were considered in Eqs. 6 and 7, the deviation seems to arise from other reasons. The amount of H_2S formed was unexpectedly small and the formation of water(H_2O) was always observed in a sample for which analytical data deviated markedly from the calibration curves. Detection of H_2O was carried out under the following conditions: A 2.2 m Porapak-Q (80—100 mesh) column, initial temperature 60 °C, operated at the rate of 5 °C/min. H_2O was assumed to be formed by the reactions (Eqs. 12, 13, and 14) between SO_2 and H_2S or H_2 from the results of the following experiment. The reaction between SO_2 and H_2 in the presence of S was examined in a similar manner to that given before. The amount of SO_2 decreased with an increase in the amount of H_2 while that of H_2O increased in the opposite way.

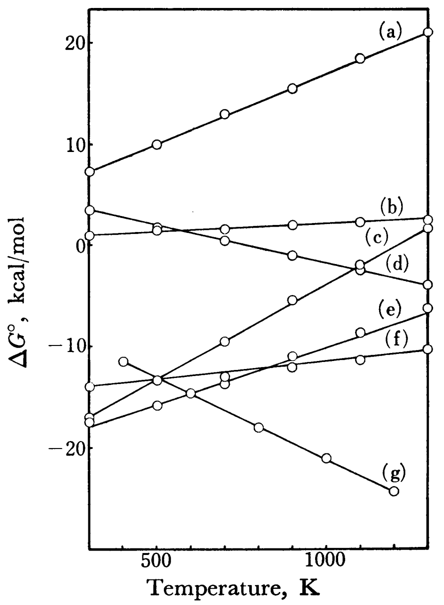

Fig. 12. Relationship between $\Delta G°$ and temperature. a: Eq. 9, b: Eq. 2, c: Eq. 1, d: Eq. 12, e: Eq. 13, f: Eq. 14, g: Eq. 10.

TABLE 7. COMPOUNDS DEVIATED FROM THE CALIBRATION CURVES

Compound	Formula	
	Theoretical	Found[a)]
2,6-Dimethylphenol	$C_8O_1H_{10}$	$C_{8.5}O_{1.2}H_{10}$
8-Quinolinol	$N_1C_9O_1H_7$	$N_{1.3}C_{9.6}O_{1.1}H_7$
m-Nitroaniline	$N_2C_6O_2H_6$	$N_{2.8}C_{6.4}O_{2.4}H_6$
Sodium 1-naphthalene-sulfonate	$C_{10}O_3S_1Na_1H_7$	$C_{9.0}O_{5.3}H_7$

a) Calculated from two runs for each sample.

$$H_2 + \frac{1}{2}S_2 = H_2S, \tag{12}$$

$$H_2S + \frac{1}{2}SO_2 = H_2O + \frac{3}{4}S_2, \tag{13}$$

$$H_2 + \frac{1}{2}SO_2 = H_2O + \frac{1}{4}S_2. \tag{14}$$

Since no correction was made for the formation of H_2O in the present method, the erroneous data of H and O in Eqs. 6, 7, and 8 seem to bring about the deviation from the calibration curves. Some phenols also produced H_2O, causing deviation from calibration curves. Two paths for the formation of H_2O were expected, one leading to Eq. 13 or 14 by way of Eq. 9 and the other based on a direct dehydration reaction instead of a decarbonylation reaction in the thermal decomposition of the sample. Since the conversion of Eq. 9 was found to be fairly low, the path involving Eq. 9 is less expected than that involving a dehydration reaction.

Comparison of the Present Method with Previous One. From a comparison with the method described previously, the characteristics of the present method are summarized as follows: 1) No carbonaceous residue was observed, 2) A large amount of COS was found, 3) No SO_2 was detected, 4) Weighing is unnecessary, 5) No information was obtained on the functional group. 1) and 5) indicate that the reaction is complete. All the compounds containing oxygen atom gave CO, CO_2, and COS, making the determination of atomic ratio complicated. We examined the catalytic disproportionation of COS[10] in the presence of a quartz powder with the intention of obtaining simple products, but no satisfactory results were obtained.

References

1) T. Hara and S. Ito, *Bull. Chem. Soc. Jpn.*, **44**, 2427 (1971).

2) R. F. Bacon and R. Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942).

3) J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, **39**, 275 (1963).

4) W. L. Thornsberry, Jr., *Anal. Chem.*, **43**, 452 (1971).

5) C. T. Hodges and R. F. Matson, *Anal. Chem.*, **37**, 1065 (1965).

6) A. Stock and P. Seeling, *Ber.*, **52**, 681 (1919).

7) A. Stock, W. Sieke, and E. Pohland, *Ber.*, **57**, 719 (1924).

8) I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances," Springer-Verlag, Berlin (1973), p. 162.

9) T. Hara and K. Fujinaga, unpublished.

10) J. R. Partington and H. H. Neville, *J. Chem. Soc.*, **1951**, 1230.