Pyrolytic Sulfurization Gas Chromatography. II.[1] Simple Determination of the Correction Factors Using Five Standard Compounds

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An improvement has been made in the pyrolytic sulfurization gas chromatographic method, by which the atomic ratio between C, H, O, and N in a sample can be simultaneously determined. Analysis was carried out by use of the correction factors instead of calibration curves. Correction factors were obtained by use of five standard compounds, naphthalene, thiourea, cyanoguanidine, sucrose, and amidosulfuric acid. The method is simple, accurate, and applicable to various compounds.

In order to establish a new elemental analysis method by which several elements can be simultaneously determined, a combustion technique in sulfur (S) vapor instead of the conventional one in oxygen (O) atmosphere was proposed.[1] The individual elements in a sample were converted as follows: carbon (C) to carbon dioxide (CO_2), carbonyl sulfide (COS), and carbon disulfide (CS_2), hydrogen (H) to hydrogen sulfide (H_2S), O to CO_2 and COS and nitrogen (N) to nitrogen molecule (N_2). The products were determined by gas chromatography. The chemical composition of the original compound was estimated by dividing each peak area of N_2, C-, and O-containing compounds by the peak area of H_2S, and by applying the calibration curves between H and C or O or N to the quotients. In order to find the sum of individual peak areas of C- and O-containing compounds, the relation between the peak areas of CO_2, COS, and CS_2 and their mole numbers was used, the correction factors of CO_2, COS, and CS_2 being obtained from the reaction between carbon monoxide (CO) and S.

Since the chemical composition was determined by the calibration curves obtained from four compounds and the correction factors obtained by the reaction between pure CO and S, the method was not always simple and convenient.

The present method is much more convenient as compared with the previous one. Five compounds, naphthalene, thiourea, cyanoguanidine, sucrose, and amidosulfuric acid were chosen as standard and the correction factors of the individual products to H_2S were obtained on the assumption that each peak area of the products corresponds to their mole numbers in the original compound. The method is characterized by obtaining all the correction factors by five times of analysis and by estimating the weight ratio of each atom by a simple calculation using the correction factors. The method is applicable to various compounds and reasonable results are obtained.

Experimental

Apparatus and Reagents. The sampler and displacement apparatus were similar to those previously used. A transparent quartz tube, 2.5 mm i.d., 3.5 mm o.d., and 110 mm long, was used after treatment similar to that in the previous procedure. Gas chromatograms were taken on Shimadzu GC-4B and GC-4C. Naphthalene, thiourea, sucrose, and cyanoguanidine were of reagent grade for elemental analysis, and the other reagents were of analytical grade.

Procedure. The procedure was similar to that given in the previous paper except for placing the sample in a reaction tube and keeping it in a desiccator overnight.

Detection of water as a product could not be carried out by combination of the silica gel column and the molecular sieve 5A column in the previous experiment. However, it could be achieved by connecting a 0.25 m Chromosorb 104 (80—100 mesh) column with a 1.75 m Porapak Q (80—100 mesh) column in series and by raising temperature at a rate of 20 °C/min over 80—185 °C. Under these conditions, N_2, CO_2, H_2S, COS, H_2O, SO_2, and CS_2 were separated satisfactorily. Though the separation of CO from N_2 was difficult, it was found that the amount of CO evolved was negligible.

Results and Discussion

Correction Factors. The relationship between the constituent atoms of standard compounds and the products by the reaction is as follows: Naphthalene (C, H) to CS_2 and H_2S; thiourea and cyanoguanidine (C, H, N) to CS_2, H_2S, and N_2; sucrose (C, H, O) to CS_2, H_2S, CO_2, and COS; amidosulfuric acid (N, H, O) to H_2S, N_2, H_2O, and SO_2. Assuming that each peak area of the compounds corresponds to their mole numbers in the original compound, we obtain

$$\left(\frac{\mathrm{C}}{\mathrm{H}}\right)_t = \frac{K(\mathrm{CS_2})A(\mathrm{CS_2})}{2K(\mathrm{H_2S})A(\mathrm{H_2S})} = \frac{K(\mathrm{CS_2})A(\mathrm{CS_2})}{2A(\mathrm{H_2S})}, \tag{1}$$

$$\left(\frac{\mathrm{N}}{\mathrm{H}}\right)_t = \frac{K(\mathrm{N_2})A(\mathrm{N_2})}{K(\mathrm{H_2S})A(\mathrm{H_2S})} = \frac{K(\mathrm{N_2})A(\mathrm{N_2})}{A(\mathrm{H_2S})}, \tag{2}$$

$$\left(\frac{\mathrm{C}}{\mathrm{H}}\right)_t = \frac{K(\mathrm{CO_2})A(\mathrm{CO_2})+K(\mathrm{COS})A(\mathrm{COS})+K(\mathrm{CS_2})A(\mathrm{CS_2})}{2K(\mathrm{H_2S})A(\mathrm{H_2S})}, \tag{3}$$

$$\left(\frac{\mathrm{O}}{\mathrm{H}}\right)_t = \frac{2K(\mathrm{CO_2})A(\mathrm{CO_2})+K(\mathrm{COS})A(\mathrm{COS})}{2K(\mathrm{H_2S})A(\mathrm{H_2S})}, \tag{4}$$

$$\left(\frac{\mathrm{N}}{\mathrm{H}}\right)_t = \frac{K(\mathrm{N_2})A(\mathrm{N_2})}{K(\mathrm{H_2S})A(\mathrm{H_2S})+K(\mathrm{H_2O})A(\mathrm{H_2O})}, \tag{5}$$

$$\left(\frac{\mathrm{O}}{\mathrm{H}}\right)_t = \frac{2K(\mathrm{SO_2})A(\mathrm{SO_2})+K(\mathrm{H_2O})A(\mathrm{H_2O})}{2[K(\mathrm{H_2S})A(\mathrm{H_2S})+K(\mathrm{H_2O})A(\mathrm{H_2O})]}, \tag{6}$$

where $A(\mathrm{CS_2})$, $A(\mathrm{H_2S})$, $A(\mathrm{N_2})$, $A(\mathrm{CO_2})$, $A(\mathrm{COS})$, $A(\mathrm{SO_2})$, and $A(\mathrm{H_2O})$ are referred to the individual peak area and $(\mathrm{C/H})_t$, $(\mathrm{N/H})_t$, and $(\mathrm{O/H})_t$ to the theoretical atomic ratios in individual compounds. Each correction factor was obtained on the basis of $K(\mathrm{H_2S})=1.00$.

Table 1. Correction factors

Standard compound	Correction factor						
	$K(N_2)$	$K(CO_2)$	$K(H_2S)$	$K(COS)$	$K(H_2O)$	$K(SO_2)$	$K(CS_2)$
Naphthalene			1.00				0.609
Thiourea	1.26		1.00				0.600
Cyanoguanidine	1.18		1.00				0.601
Sucrose		1.10	1.00	0.712			
Amidosulfuric acid			1.00		2.33	0.816	
Average	1.22	1.10	1.00	0.712	2.33	0.816	0.603

Table 2. Calculation of the content of C, H, O, and N

Element	Product	Mole ratio	Weight ratio	Content / %
N	N_2	$K(N_2)A(N_2)=1.22A(N_2)$	$M(N_2)K(N_2)A(N_2)=28.014[1.22A(N_2)]$	Obtained from Eq. 7
C	CO_2	$K(CO_2)A(CO_2)=1.10A(CO_2)$	$M(CO_2)K(CO_2)A(CO_2)=44.009[1.10A(CO_2)]$	Obtained from Eq. 8
	COS	$K(COS)A(COS)=0.712A(COS)$	$M(COS)K(COS)A(COS)=28.010[0.712A(COS)]$	
	CS_2	$K(CS_2)A(CS_2)=0.603A(CS_2)$	$M(CS_2)K(CS_2)A(CS_2)=12.011[0.603A(CS_2)]$	
H	H_2S	$K(H_2S)A(H_2S)=1.00A(H_2S)$	$M(H_2S)K(H_2S)A(H_2S)=2.016A(H_2S)$	Obtained from Eq. 9
	H_2O	$K(H_2O)A(H_2O)=2.33A(H_2O)$	$M(H_2O)K(H_2O)A(H_2O)=18.015[2.33A(H_2O)]$	
O	CO_2	$1.10A(CO_2)$	$44.009[1.10A(CO_2)]$	Obtained from Eq. 10
	COS	$0.712A(COS)$	$28.010[0.712A(COS)]$	
	H_2O	$2.33A(H_2O)$	$18.015[2.33A(H_2O)]$	
	SO_2	$K(SO_2)A(SO_2)=0.816A(SO_2)$	$M(SO_2)K(SO_2)A(SO_2)=31.998[0.816A(SO_2)]$	

The correction factor of CS_2, $K(CS_2)$, was calculated by Eq. 1 from the results of naphthalene, thiourea, and cyanoguanidine, and that of N_2 similarly by Eq. 2 from the results of thiourea and cyanoguanidine. $K(CO_2)$ and $K(COS)$ were obtained by Eqs. 3 and 4 from the results of sucrose, and $K(H_2O)$ and $K(SO_2)$ by Eqs. 5 and 6 from the results of amidosulfuric acid. All the correction factors (Table 1) were used in the following analysis.

Determination of the Atomic Ratio of Compounds. The atomic ratio between C, H, O, and N was calculated by use of the chromatogram data (Table 2). The mole ratios between the individual products were found by multiplying the correction factors by the peak areas. The weight ratios between the individual products were obtained by multiplying the above mole ratios by the molecular weights obtained by substracting the weight of S from the molecular weight of the products, the weight ratios of the individual products to all the products being found.

As seen from Eqs. 7—10, the weight ratios between the individual elements were obtained by multiplying the weight ratio of the desired element in the products by the weight ratios and by summing them up.

$$N_{wt\%}=\left[\frac{2E(N)}{M(N_2)}\,\frac{M(N_2)K(N_2)A(N_2)}{n}\right]\times 100=\left[28.014\frac{1.22A(N_2)}{n}\right]\times 100, \tag{7}$$

$$\begin{aligned}C_{wt\%}&=\left[\frac{E(C)}{M(CO_2)}\,\frac{M(CO_2)K(CO_2)A(CO_2)}{n}+\frac{E(C)}{M(COS)}\,\frac{M(COS)K(COS)A(COS)}{n}\right.\\&\quad\left.+\frac{E(C)}{M(CS_2)}\,\frac{M(CS_2)K(CS_2)A(CS_2)}{n}\right]\times 100\\&=\left[12.011\times\frac{1.10A(CO_2)+0.712A(COS)+0.603A(CS_2)}{n}\right]\times 100,\end{aligned} \tag{8}$$

$$\begin{aligned}H_{wt\%}&=\left[\frac{2E(H)}{M(H_2S)}\,\frac{M(H_2S)K(H_2S)A(H_2S)}{n}+\frac{2E(H)}{M(H_2O)}\,\frac{M(H_2O)K(H_2O)A(H_2O)}{n}\right]\times 100\\&=\left[2.016\times\frac{A(H_2S)+2.33A(H_2O)}{n}\right]\times 100,\end{aligned} \tag{9}$$

$$\begin{aligned}O_{wt\%}&=\left[\frac{2E(O)}{M(CO_2)}\,\frac{M(CO_2)K(CO_2)A(CO_2)}{n}+\frac{E(O)}{M(COS)}\,\frac{M(COS)K(COS)A(COS)}{n}\right.\\&\quad\left.+\frac{E(O)}{M(H_2O)}\,\frac{M(H_2O)K(H_2O)A(H_2O)}{n}+\frac{2E(O)}{M(SO_2)}\,\frac{M(SO_2)K(SO_2)A(SO_2)}{n}\right]\times 100\\&=\left[\frac{2[1.10A(CO_2)]+0.712A(COS)+2.33A(H_2O)+2[0.816A(SO_2)]}{n}\times 15.999\right]\times 100,\end{aligned} \tag{10}$$

Table 3. Analytical results of amino acids and carboxylic acids

Sample	C wt%			H wt%			O wt%			N wt%		
	Theor.	Exptl.	Error	Theor.	Exptl.	Erorr	Theor.	Exptl.	Error	Theor.	Exptl.	Error
Glycine	32.00	32.68	0.68	6.71	6.76	0.05	42.63	41.86	−0.77	18.66	18.70	0.04
γ-Aminobutyric acid	46.59	46.59	0	8.80	9.02	0.22	31.03	30.99	−0.04	13.58	13.40	−0.18
L-Phenylalanine	65.43	65.08	−0.35	6.71	6.71	0	19.37	19.58	0.19	8.48	8.63	0.15
L-Tryptophan	64.69	64.12	−0.57	5.92	5.63	−0.29	15.67	16.23	0.56	13.72	14.02	0.30
L-Citrulline	41.14	41.71	0.57	7.48	7.39	−0.09	27.40	27.18	−0.22	23.99	23.72	−0.27
L-Methionine a)	51.26	51.20	−0.06	9.46	9.41	−0.05	27.31	27.55	0.24	11.96	11.83	−0.13
L-Aspartic acid	36.10	36.12	0.02	5.30	5.19	−0.11	48.08	47.77	−0.31	10.52	10.92	0.40
L-Glutamic acid	40.82	41.10	0.28	6.17	5.93	−0.24	43.50	43.82	0.32	9.52	9.15	−0.37
L-Homoserine	40.33	40.73	0.40	7.62	7.42	−0.20	40.29	39.47	−0.82	11.76	12.38	0.62
Malonic acid	34.63	34.67	0.04	3.87	3.74	−0.13	61.50	61.59	0.09			
Fumaric acid	41.39	40.88	−0.51	3.47	3.43	−0.04	55.14	55.69	0.55			
Succinic acid	40.68	40.59	−0.09	5.12	4.98	−0.14	54.20	54.43	0.23			
Suberic acid	55.16	54.75	−0.41	8.10	8.13	0.03	36.74	37.12	0.38			
Lauric acid	71.95	71.98	0.03	12.08	12.05	−0.03	15.97	15.97	0			
Myristic acid	73.63	73.07	−0.56	12.36	12.64	0.28	14.01	14.28	0.27			
Palmitic acid	74.94	74.12	−0.82	12.58	12.73	0.15	12.48	13.14	0.66			
Stearic acid	75.99	75.14	−0.85	12.76	13.08	0.32	11.25	11.78	0.53			
Terephthalic acid	57.84	57.61	−0.23	3.64	3.52	−0.12	38.52	38.87	0.35			

a) Since S atom could not be determined, it was neglected in the composition of methionine.

where n is referred to the sum of the weight ratios, $M(N_2)$, $M(CO_2)$, $M(COS)$, $M(H_2S)$, $M(H_2O)$, $M(SO_2)$, and $M(CS_2)$ to the molecular weight of each compound, and $E(N)$, $E(C)$, $E(H)$, and $E(O)$ to the atomic weight of each element.

Analysis of Various Compounds. Various amino acids and carboxylic acids were analyzed (Table 3). The accuracy of the present method is similar to that of the former. However, an erroneous result is obtained when the carbon content is high. This seems to be due to the tailing phenomena with an increasing amount of CS_2 and the subsequent and incorrect reading of the chromatogram. The former method is applicable only to compounds containing H, but the present method is applicable even to H-free inorganic compounds.

Compounds other than amino acids and carboxylic acids were analyzed (Table 4). In the previous experiment, the compounds containing nitro group and phenols gave erratic results owing to the formation of water. However, in the present experiment, good results were obtained which agree with the theoretical values. This is due to the fact that no water is formed. It was concluded that the difference resulted from the different oxygen uptake of the two chromatographs, Shimadzu GC-4B and GC-4C, and the oxygen uptake by an apparatus from air took place during charge of the next sample after completion of analysis. It is remarkable in a new apparatus. The oxygen uptake by a new apparatus is minimized by treating a stainless steel tube with an aqueous solution of water glass or disodium

Table 4. Analytical results of the other compounds

Sample	C wt%			H wt%			N wt%			O wt%		
	Theor.	Exptl.	Error	Theor.	Exptl.	Error	Theor.	Exptl.	Error	Theor.	Exptl.	Error
meso-Erythritol	39.34	39.19	−0.15	8.25	8.44	0.19	52.41	52.37	−0.04			
Dimethylglyoxime	41.37	40.87	−0.50	6.94	6.92	−0.02	27.56	27.31	−0.25	24.13	24.89	0.76
Diphenylglyoxime	69.99	69.61	−0.38	5.03	5.28	0.25	13.32	13.34	0.02	11.66	11.77	0.11
p-Dimethylaminobenzaldehyde	72.46	71.67	−0.79	7.43	7.88	0.45	10.72	10.93	0.21	9.39	9.53	0.14
Benzophenone	85.69	84.80	−0.89	5.53	5.87	0.34	8.78	9.33	0.55			
Benzil	79.98	79.55	−0.43	4.80	4.79	−0.01	15.22	15.65	0.43			
2,2′-Bipyridine	76.90	76.11	−0.79	5.16	5.26	0.10				17.94	18.63	0.69
Myristyl alcohol	78.43	77.58	−0.85	14.11	14.91	0.80	7.46	7.51	0.05			
2,2′,3,3′,4,4′,5,5′,6-Nonamethyldiphenylmethane	89.73	89.11	−0.62	10.27	10.89	0.62						
2,6-Dimethylphenol	78.65	79.18	0.53	8.25	8.33	0.08	13.10	12.49	−0.61			
8-Quinolinol	74.47	73.71	−0.76	4.86	4.99	0.13	11.02	11.16	0.14	9.65	10.14	0.49
m-Nitroaniline	52.17	51.59	−0.58	4.38	4.42	0.04	23.17	23.29	0.12	20.28	20.71	0.43

TABLE 5. ANALYTICAL RESULTS OF ACETATES

Sample	Structural formula	C wt%			H wt%			O wt%		
		Theor.	Exptl.	Error	Theor.	Exptl.	Error	Theor.	Exptl.	Error
Sodium acetate	CH_3COONa	40.68	40.31	−0.37	5.12	5.02	−0.10	54.19	54.67	0.47
Potassium acetate	CH_3COOK	40.68	40.34	−0.34	5.12	5.23	0.11	54.19	54.43	0.24
Magnesium acetate	$Mg(CH_3COO)_2 4H_2O$	25.27	27.89	2.62	7.42	7.64	0.22	67.31	64.48	−2.83
Calcium acetate	$Ca(CH_3COO)_2 H_2O$	35.30	35.85	0.55	5.92	5.68	−0.24	58.78	58.47	−0.31
Strontium acetate	$Sr(CH_3COO)_2 1/2H_2O$	37.80	38.32	0.52	5.55	5.27	−0.28	56.65	56.41	−0.24
Barium acetate	$Ba(CH_3COO)_2$	40.68	40.86	0.18	5.12	5.02	−0.10	54.19	54.12	−0.07

hydrogenphosphate.

The analytical results of sodium 1-naphthalenesulfonate did not agree with the theoretical values as in the previous work. This is attributed to the purity of a sample judging from the results of gravimetric analysis of sodium and sulfur.

The accuracy in the determination of C, H, O, and N is shown by the following standard deviation: $\sigma_C=0.46$, $\sigma_H=0.24$, $\sigma_O=0.39$, and $\sigma_N=0.36\%$. Though five compounds were chosen as standard, they could be reduced to three if accuracy of the analysis including the reading of the chromatogram is improved.

Analysis of Acetates. The acetates of alkali and alkaline earth metal were analyzed (Table 5). No analysis could be carried out for lithium acetate since the reaction tube containing lithium acetate exploded during the course of reaction. Of the alkaline earth metal acetates, magnesium acetate gave a considerable error. This shows that magnesium, differing from other alkaline earth metals, has a larger affinity to oxygen than to sulfur. This is understandable if we take into consideration $\Delta G^\circ=49.16\text{kJ/mol}$ at 1200 K for the formation of magnesium sulfide.[2)]

References

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2) I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances," Springer-Verlag, Berlin (1973), p. 441.