Pyrolytic Sulfurization Gas Chromatography. III. Simultaneous Determination of the Atomic Ratio between C, H, O, and N in a Metallo-organic Compound

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Simultaneous determination of the atomic ratio between C, H, O, and N in a metallo-organic compound containing transition element is possible by the pyrolytic sulfurization gas chromatographic method, addition of reducing agent being unnecessary. Analytical results of metallo-organic compounds depend on the characteristics of their metal oxides. A few organophosphorus compounds were analyzed. The formation of water could be predicted from the atomic ratio of carbon to oxygen in a compound.

Simultaneous determination of the atomic ratio between C, H, O, and N in a sample can be achieved with the usual organic compounds[1] by pyrolytic sulfurization gas chromatography (PSGC).[2] The present study has been carried out to confirm whether PSGC can be applied to the analysis of various metallo-organic compounds containing transition elements. The affinity of metallic elements for oxygen is so strong that quantitative release of oxygen from their oxides is difficult. Simultaneous determination of oxygen with C, H, and N is impossible by the conventional methods. The oxygen in the metallo-organic compound has been determined either by subtracting the total amount of C, H, N, and metal oxide from the weight of a smple or by estimating the oxygen separately from the determination of C, H, and N. The former method is apt to introduce a relatively large error and is not applicable to samples containing molybdenum, cadmium, and so on, the oxides of which are volatile under the analytical conditions. The latter method has a disadvantage in that some reducing agent must be added to the sample in order to liberate oxygen from the combustion residues.

However, the present PSGC method based on a sulfur combustion technique, is characterized by converting the metal in a compound into sulfide, even in the case where the metal oxide is more stable than the corresponding sulfide since carbon atoms in the compound act as the reducing agent, releasing the whole oxygen in the sample. It is possible to determine the atomic ratio without a special procedure such as addition of reducing agent.

Experimental

Apparatus and Reagents. The reagents and apparatus used were the same as those reported[1] except that peak areas of the gas chromatogram were read out by use of a Shimadzu digital integrator EIA. A definite amount of sample was taken with a Shimadzu microbalance MDP-5.

Procedure. The preparation and reaction conditions of sample as well as conditions of gas chromatographic analysis are similar to those reported.[1]

Samples. The following samples were prepared by the methods found in literature for their gravimetric analyses: magnesium oxalate, $MgC_2O_4 \cdot 2H_2O$;[3] cobalt(II) oxalate, $CoC_2O_4 \cdot 2H_2O$;[3] copper(II) oxalate, CuC_2O_4;[4] cadmium oxalate, CdC_2O_4;[5] bis(8-quinolinolato)magnesium, $Mg(C_9H_6ON)_2$;[6] oxobis(8-quinolinolato)titanium(IV), $TiO(C_9H_6ON)_2$;[6] dioxobis(8-quinolinolato)molybdenum(VI), $MoO_2(C_9H_6ON)_2$;[6] dioxobis(8-quinolinolato)tungsten(VI), $WO_2(C_9H_6ON)_2$;[6] bis(8-quinolinolato)copper(II), $Cu(C_9H_6ON)_2$;[6] dioxo (8-quinolinol) bis (8-quinolinolato) uranium (VI), $UO_2(C_9H_6ON)_2(C_9H_7ON)$;[6] bis(8-quinolinolato)zinc(II), $Zn(C_9H_6ON)_2$;[6] bis(8-quinolinolato)manganese(II), $Mn(C_9H_6ON)_2 \cdot 2H_2O$;[6] tris(8-quinolinolato)iron(III), $Fe(C_9H_6ON)_3$;[6] bis(8-quinolinolato)cobalt(II), $Co(C_9H_6ON)_2 \cdot 2H_2O$;[6] bis(8-quinolinolato)nickel(II), $Ni(C_9H_6ON)_2$;[6] tris(8-quinolinolato) aluminium, $Al(C_9H_6ON)_3$;[6] tris(8-quinolinolato)lanthanum(III), $La(C_9H_6ON)_3$;[6] bis(8-quinolinolato)cadmium(II), $Cd(C_9H_6ON)_2 \cdot 2H_2O$;[6] tris(8-quinolionlato)chromium(III), $Cr(C_9H_6ON)_3$;[7] bis(2,3-butanedione dioximato)palladium(II), $Pd(C_4H_7O_2N_2)_2$;[8] bis(2,3-butanedione dioximato)nickel(II), $Ni(C_4H_7O_2N_2)_2$;[8] (benzoin oximato)copper(II), $Cu(C_{14}H_{11}O_2N)$;[8] bis(anthranilato)copper(II), $Cu(C_7H_6O_2N)_2$;[8] bis(anthranilato)zinc(II), $Zn(C_7H_6O_2N)_2$;[8] bis(anthranilato)nickel(II), $Ni(C_7H_6O_2N)_2$;[8] bis(anthranilato)manganese(II), $Mn(C_7H_6O_2N)_2$;[8] bis(anthranilato)cobalt(II), $Co(C_7H_6O_2N)_2$;[8] bis(anthranilato)cadmium(II), $Cd(C_7H_6O_2N)_2$;[8] bis(salicylaldehyde oximato)copper(II), $Cu(C_7H_6O_2N)_2$.[8] The composition and purity of samples were confirmed by the C and H analysis carried out in the Elemental Analysis Center of Pharmaceutical Department for Kyoto University (Table 1). The experimental results were in fair agreement with the theoretical values. Naphthalene, thiourea, sucrose, cyanoguanidine, bis(2,4-pentanedionato)magnesium, and tris(2,4-pentanedionato)iron(III) for elemental analysis were of reagent grade, the other reagents being commercial products. The metal oxides were of analytical grade and treated at 950 °C before use.

Results and Discussion

Reactivity of Metal Oxide. The reactivity between metal oxide and sulfur was investigated prior to the analysis of metallo-organic compounds. The reaction of silver nitrate ($AgNO_3$) as a reference substance seems to proceed completely in accordance with Eq. 1, since 1) a large, positive value of ΔG°_{1200K} in Eq. 1, 642.6 kJ·mol^{-1} was obtained from the thermodynamic data[9] by means of Ulich's approximate equation, 2) $AgNO_3$ produced only nitrogen molecule (N_2) and sulfur dioxide (SO_2) as reaction products, and 3) proportionality holds between the amount of $AgNO_3$ and the peak area of SO_2. The reactivity of metal oxide is expressed in terms of α, which refers to the mole ratio of SO_2 from the metal oxide, M_mO_n against that from

TABLE 1. ANALYTICAL RESULTS OF CARBON AND HYDROGEN IN METALLO-ORGANIC COMPOUNDS

Sample	Carbon wt %			Hydrogen wt %		
	Calcd	Found	Error	Calcd	Found	Error
Magnesium oxalate $MgC_2O_4 \cdot 2H_2O$	16.19	16.31	0.12	2.72	2.84	0.12
Bis(8-quinolinolato)magnesium $Mg(C_9H_6ON)_2$	69.15	68.94	−0.21	3.87	4.11	0.24
Tris(8-quinolinolato)lanthanum(III) $La(C_9H_6ON)_3$	56.76	56.06	−0.70	3.18	3.41	0.23
Dioxo(8-quinolinol)bis(8-quinolinolato)-uranium(VI) $UO_2(C_9H_6ON)_2(C_9H_7ON)$	46.10	45.87	−0.23	2.72	2.84	0.12
Oxobis(8-quinolinolato)titanium(IV) $TiO(C_9H_6ON)_2$	61.38	60.34	−1.04	3.43	3.36	−0.07
Tris(8-quinolinolato)chromium(III) $Cr(C_9H_6ON)_3$	66.94	67.14	0.20	3.75	3.98	0.23
Dioxobis(8-quinolinolato)molybdenum(VI) $MoO_2(C_9H_6ON)_2$	51.94	51.74	−0.19	2.91	3.09	0.18
Dioxobis(8-quinolinolato)tungsten(VI) $WO_2(C_9H_6ON)_2$	42.88	43.13	0.25	2.40	2.62	0.22
Bis(anthranilato)manganese(II) $Mn(C_7H_6O_2N)_2$	51.39	51.41	0.02	3.70	3.81	0.11
Tris(8-quinolinolato)iron(III) $Fe(C_9H_6ON)_3$	66.41	66.58	0.17	3.72	3.48	−0.24
Bis(anthranilato)cobalt(II) $Co(C_7H_6O_2N)_2$	50.77	49.81	−0.96	3.65	3.64	−0.01
Bis(2,3-butanedione dioximato)nickel(II) $Ni(C_4H_7O_2N_2)_2$	33.26	33.45	0.19	4.88	4.96	0.08
Bis(anthranilato)nickel(II) $Ni(C_7H_6O_2N)_2$	50.81	49.92	−0.89	3.65	4.07	0.42
Bis(8-quinolinolato)nickel(II) $Ni(C_9H_6ON)_2$	62.30	62.29	−0.01	3.49	3.23	−0.26
Bis(anthranilato)copper(II) $Cu(C_7H_6O_2N)_2$	50.07	50.18	0.11	3.60	3.74	0.14
Bis(salicylaldehyde oximato)copper(II) $Cu(C_7H_6O_2N)_2$	50.07	50.04	−0.03	3.48	3.61	0.13
(Benzoin oximato)copper(II) $Cu(C_{14}H_{11}O_2N)$	58.23	57.71	−0.52	3.84	4.21	0.37
Bis(8-quinolinolato)zinc $Zn(C_9H_6ON)_2$	61.13	60.95	−0.18	3.42	3.68	0.26
Bis(anthranilato)zinc $Zn(C_7H_6O_2N)_2$	49.80	49.70	−0.10	3.58	3.82	0.24
Bis(anthranilato)cadmium $Cd(C_7H_6O_2N)_2$	43.71	43.45	−0.26	3.14	3.29	0.15
Bis(8-quinolinolato)cadmium $Cd(C_9H_6ON)_2$	49.50	49.53	0.03	3.69	3.96	0.27
Tris(8-quinolinolato)alminium $Al(C_9H_6ON)_3$	70.59	70.39	−0.20	3.95	4.22	0.27

$AgNO_3$. Thus, the reactivity of metal oxide in Eq. 2 is approximately estimated by Eq. 3, where $A°(SO_2)$ and $A(SO_2)$ refer to the peak areas of SO_2 obtained with a mol of $AgNO_3$ and b mol of M_mO_n, respectively. The oxides of molybdeneum(VI),

$$AgNO_3 + S_2 = \frac{1}{2}Ag_2S + \frac{1}{2}N_2 + \frac{3}{2}SO_2 \qquad (1)$$

$$\frac{3}{2}a = A°(SO_2),$$

$$M_mO_n + xS_2 = M_mS_n + \frac{n}{2}SO_2 \qquad (2)$$

$$\frac{n}{2}b\alpha = A(SO_2),$$

TABLE 2. RELATIVE CONVERSIONS OF METAL OXIDES

Metal oxide	Relative conversion[a)] α	Metal oxide	Relative conversion α
MgO	0	Fe_2O_3	1.1
CaO	0.67	NiO	0.33
TiO_2	0	CuO	0.94
U_3O_8	0.13	ZnO	1.1
V_2O_5	0.40	Al_2O_3	0
MoO_3	1.0	SiO_2	0
WO_3	0.88	Bi_2O_3	1.0
Cr_2O_3	0.70	Mn_3O_4	0.96

a) Estimated by Eq. 3.

$$\alpha = \frac{A(SO_2)3a}{A^\circ(SO_2)nb}, \tag{3}$$

manganese(II, III), iron(III), copper(II), zinc(II), and bismuth(III) react quantitatively with sulfur (Table 2). The oxides of calcium(II), uranium(VI), vanadium(V), tungsten(VI), and nickel(II) react with sulfur to some extent, oxygen being liberated as SO_2. However, the oxides of magnesium(II), titanium(IV), aluminium(III), and silicon(III) are barely reduced by sulfur under the experimental conditions.

The value of $\Delta G^\circ_{1200\mathrm{K}}$ for Eq. 2 gives a measure of the reactivity of metal oxide with sulfur. The results shown

TABLE 3. EQUILIBRIUM BETWEEN THE OXIDE AND SULFIDE OF EACH METAL

Metal oxide	Reaction[a)]	$\Delta G^\circ_{1200\mathrm{K}}$ / kJ mol^{-1}
Na_2O	$Na_2O(s)+3/4S_2(g) \rightarrow Na_2S(s)+1/2SO_2(g)$	−169.12
MgO	$MgO(s)+3/4S_2(g) \rightarrow MgS(s)+1/2SO_2(g)$	49.16
CaO	$CaO(s)+3/4S_2(g) \rightarrow CaS(s)+1/2SO_2(g)$	−56.32[d)]
TiO_2[b)]	$TiO_2(s)+3/2S_2(g) \rightarrow TiS_2(s)+SO_2(g)$	182.84[d)]
MoO_3	$MoO_3(s)+9/4S_2(g) \rightarrow MoS_3(s)+3/2SO_2(g)$	−88.99[d)]
Mn_3O_4	$Mn_3O_4(s)+5/2S_2(g) \rightarrow 3MnS(s)+2SO_2(g)$	−177.49
Fe_2O_3	$Fe_2O_3(s)+7/4S_2(g) \rightarrow 2FeS(s)+3/2SO_2(g)$	−75.14
CuO	$CuO(s)+3/4S_2(g) \rightarrow CuS(s)+1/2SO_2(g)$	−108.20
ZnO	$ZnO(s)+3/4S_2(g) \rightarrow ZnS(s)+1/2SO_2(g)$	−59.91
CdO	$CdO(s)+3/4S_2(g) \rightarrow CdS(s)+1/2SO_2(g)$	−105.73
SiO_2	$SiO_2(s)+3/2S_2(g) \rightarrow SiS_2(s)+SO_2(g)$	287.19
Bi_2O_3	$Bi_2O_3(s)+9/4S_2(g) \rightarrow Bi_2S_3(s)+3/2SO_2(g)$	−202.09[d)]

a) (s): Solid phase, (g): gaseous phase. b) TiO_2: Rutile. c) SiO_2: Quartz.
d) ΔG° at 1000K.

TABLE 4. ANALYTICAL RESULTS OF METALLO-ORGANIC COMPOUNDS

Sample[a)]	Group	C wt % Theor	C wt % Exptl	C wt % Error	H wt % Theor	H wt % Exptl	H wt % Error	O wt % Theor	O wt % Exptl	O wt % Error	N wt % Theor	N wt % Exptl	N wt % Error
Tris(8-quinolinolato)-lanthanum(III) $La(C_9H_6ON)_3$	III A	74.99	74.77	−0.22	4.19	4.13	−0.06	11.10	10.85	−0.25	9.72	10.25	0.53
Uranyl(VI) acetate $UO_2(CH_3COO)_2 \cdot 2H_2O$	III A	25.81	30.83	5.02	5.41	6.20	0.79	68.77	62.96	−5.81			
Dioxo(8-quinolinol)-bis(8-quinolinolato)-uranium(VI) $UO_2(C_9H_6ON)_2 \cdot (C_9H_7ON)$	III A	69.67	71.60	1.93	4.11	4.32	0.21	17.19	15.13	−2.06	9.03	8.95	−0.08
Oxobis(8-quinolinolato)-titanium(IV) $TiO(C_9H_6ON)_2$	IV A	71.05	74.71	3.66	3.97	4.21	0.24	15.77	11.71	−4.06	9.21	9.36	0.15
Tris(8-quinolinolato)-chromium(III) $Cr(C_9H_6ON)_3$	VI A	74.99	74.48	−0.51	4.19	4.15	−0.04	11.10	11.34	0.24	9.72	10.02	0.30
Dioxobis(8-quinolinolato)-molybdenum(VI) $MoO_2(C_9H_6ON)_2$	VI A	67.50	66.85	−0.65	3.78	3.88	0.10	19.98	19.95	−0.03	8.75	9.32	0.57
Dioxobis(8-quinolinolato)-tungsten(VI) $WO_2(C_9H_6ON)_2$	VI A	67.50	67.34	−0.16	3.78	3.31	−0.47	19.98	20.08	0.10	8.75	9.26	0.51
Bis(8-quinolinolato)-manganese(II) $Mn(C_9H_6ON)_2 \cdot 2H_2O$	VII A	66.66	65.95	−0.71	4.97	4.92	−0.05	19.73	20.30	0.57	8.64	8.82	0.18
Bis(anthranilato)-manganese(II) $Mn(C_7H_6O_2N_2)$	VII A	61.76	62.16	0.40	4.44	4.15	−0.29	23.51	23.74	0.23	10.29	9.95	−0.34
Tris(2,4-pentanedionato)iron(III) $Fe(C_5H_7O_2)_3$	VIII	60.59	60.92	0.33	7.12	7.35	0.23	32.29	31.73	−0.56			

TABLE 4. (Continued)

Sample[a]	Group	C wt %			H wt %			O wt %			N wt %		
		Theor	Exptl	Error	Theor	Exptl	Error	Theor	Exptl	Error	Theor	Exptl	Error
Tris(8-quinolinolato)iron(III) $Fe(C_9H_6ON)_3$	VIII	74.99	74.93	−0.06	4.19	3.95	−0.24	11.10	11.42	0.32	9.72	9.70	−0.02
Cobalt(II) oxalate $CoC_2O_4\cdot 2H_2O$	VIII	19.37	19.10	−0.27	3.25	3.21	−0.04	77.38	77.69	0.31			
Bis(anthranilato)cobalt(II) $Co(C_7H_6O_2N)_2$	VIII	61.76	61.05	−0.71	4.44	4.51	0.07	23.51	23.99	0.48	10.29	10.44	0.15
Bis(8-quinolinolato)cobalt(II) $Co(C_9H_6ON)_2\cdot 2H_2O$	VIII	66.66	66.20	−0.46	4.97	4.92	−0.05	19.73	20.32	0.59	8.64	8.57	−0.07
Bis(2,3-butanedione dioximato)nickel(II) $Ni(C_4H_7O_2N_2)_2$	VIII	41.74	42.02	0.28	6.13	6.48	0.35	27.80	27.50	−0.30	24.34	24.00	−0.34
Bis(anthranilato)nickel(II) $Ni(C_7H_6O_2N)_2$	VIII	61.76	61.25	−0.51	4.44	4.58	0.14	23.51	23.33	−0.18	10.29	10.83	0.54
Bis(8-quinolinolato)nickel(II) $Ni(C_9H_6ON)_2$	VIII	74.99	74.62	−0.37	4.19	4.54	0.35	11.10	11.41	0.31	9.72	9.43	−0.29
Palladium(II) acetate $Pd(CH_3COO)_2$	VIII	40.68	40.15	−0.53	5.12	5.13	0.01	54.19	54.72	0.53			
Bis(2,3-butanedione dioximato)palladium(II) $Pd(C_4H_7O_2N_2)_2$	VIII	41.74	41.58	−0.16	6.13	6.15	0.02	27.80	27.41	−0.39	24.34	24.85	0.51
Copper(II) oxalate CuC_2O_4	VIII	27.29	27.20	−0.09				72.71	72.80	0.09			
Copper(II) acetate $Cu(CH_3COO)_2\cdot H_2O$	VIII	35.30	35.72	0.42	5.92	5.75	−0.17	58.78	58.53	−0.25			
(Benzoin oximato)copper(II) $Cu(C_{14}H_{11}O_2N)$	VIII	74.65	74.09	−0.56	4.92	5.13	0.21	14.21	14.60	0.39	6.23	6.18	−0.05
Bis(salicylaldehyde oximato)copper(II) $Cu(C_7H_6O_2N)_2$	VIII	61.76	61.15	−0.61	4.44	4.26	−0.18	23.51	23.87	0.36	10.29	10.72	0.43
Bis(anthranilato)copper(II) $Cu(C_7H_6O_2N)_2$	VIII	61.76	61.77	0.01	4.44	4.80	0.36	23.51	23.43	−0.08	10.29	10.00	−0.29
Bis(8-quinolinolato)copper(II) $Cu(C_9H_6ON)_2$	VIII	74.99	75.00	0.01	4.19	4.16	−0.03	11.10	10.80	−0.30	9.72	10.06	0.34
Silver(I) acetate CH_3COOAg	VIII	40.68	40.64	−0.04	5.12	4.73	−0.39	54.19	54.63	0.44			
Bis(anthranilato)zinc(II) $Zn(C_7H_6O_2N)_2$	II B	61.76	61.06	−0.70	4.44	4.41	−0.03	23.51	23.66	0.15	10.29	10.86	0.57
Bis(8-quinolinolato)zinc(II) $Zn(C_9H_6ON)_2$	II B	74.99	75.01	0.02	4.19	4.12	−0.07	11.10	10.99	−0.11	9.72	9.88	0.16
Cadmium(II) oxalate CdC_2O_4	II B	27.29	27.18	−0.11				72.71	72.82	0.11			
Bis(anthranilato)cadmium(II) $Cd(C_7H_6O_2N)_2$	II B	61.76	61.75	−0.01	4.44	4.48	0.04	23.51	22.80	−0.71	10.29	10.97	0.68
Bis(8-quinolinolato)cadmium(II) $Cd(C_9H_6ON)_2\cdot 2H_2O$	II B	66.66	66.28	−0.38	4.97	5.05	0.08	19.73	19.46	−0.27	8.64	9.22	0.58
Mercury(II) acetate $Hg(CH_3COO)_2$	II B	40.68	40.69	0.01	5.12	5.18	0.06	54.19	54.12	−0.07			
Tris(8-quinolinolato)aluminium(III) $Al(C_9H_6ON)_3$	II B	74.99	78.05	3.06	4.19	4.57	0.37	11.10	7.12	−3.98	9.72	10.26	0.54

a) Metal atoms were neglected in the composition of metallo-organic compounds since they could not be determined.

in Table 3 correspond fairly well to those in Table 2. Since the ΔG° value of magnesium(II) oxide, titanium(IV) oxide, and silicon(III) oxide among the metal oxides are positive and large, it is understandable that these metal oxides show no reactivity to sulfur.

Analysis of Various Metallo-organic Compounds. Various metallo-organic compounds containing transition elements were analyzed (Table 4). Almost all the complex salts gave satisfactory results, but the complex salts of Ti, U, and Al gave a fairly negative error in the oxygen value. Because of the high stability and the difficult reduction of the oxides of titanium(IV), aluminium(III), and uranium(VI), the oxygen atom in their complex salts seems to be partly transferred into the residues, giving rise to error.

Magnesium(II) oxide does not react with sulfur, but bis(8-quinolinolato)magnesium(II)reacts quantitatively with sulfur to give an exact oxygen value without producing magnesium(II) oxide. In order to clarify the difference in the two cases, study was carried out on a series of magnesium salts (Table 5). Bis(2,4-pentanedionato)magnesium(II) as well as bis(8-quinolinolato) magnesium(II) gave expected results, while oxalate and acetate of magnesium(II) gave fairly low oxygen values (Table 5). This can be attributed to the shortage of carbon atom necessary for the prevention of the formation of magnesium(II) oxide. In conclusion, the present method gives satisfactory oxygen values when the number of carbon atom exceeds that of oxygen atom in magnesium compound.

Analysis of Organophosphorus Compounds. Various organophosphorus compounds were analyzed (Table 6). Carbon-rich compounds such as triphenylphosphine oxide give satisfactory oxygen values, while carbon-poor compounds such as guanidine phosphate gives fairly low oxygen value, which may be ascribed to the formation of polyphosphoric acid. It seems that carbon atoms prevent oxygen atoms from the formation of polyphosphoric acid as in magnesium compounds. Inorganic phosphorus compounds did not react quantitatively with sulfur, the whole amount of oxygen not being liberated.

Decomposition of Water. By the present method, N_2, carbon dioxide, hydrogen sulfide, carbonyl sulfide, water, SO_2, and carbon disulfide can be determined simultaneously under the experimental conditions. Since the tailing phenomenon is observed on the water peak, it is desirable to avoid the formation of water for accurate determination. The formation of water was observed with magnesium(II) oxalate tetrahydrate, magnesium(II) acetate tetrahydrate, and cobalt(II) oxalate dihydrate but not with the other componds containing water of crystallization such as sodium citrate dihydrate and oxalic acid dihydrate. It seems that water is decomposed with an increasing number of carbon atom

Table 5. Analytical results of magnesium compounds

Sample[a]	C wt %			H wt %			O wt %			N wt %		
	Theor	Exptl	Error	Theor	Exptl	Error	Theor	Exptl	Error	Theor	Exptl	Error
Magnesium oxalate $MgC_2O_4\cdot 2H_2O$	19.37	21.88	2.51	3.25	3.69	0.44	77.38	74.43	−2.95			
Magnesium acetate $Mg(CH_3COO)_2\cdot 4H_2O$	25.27	27.89	2.62	7.42	7.64	0.22	67.31	64.48	−2.83			
Bis(2,4-pentanedionato)-magnesium $Mg(C_5H_7O_2)_2\cdot 2H_2O$	51.27	51.77	0.50	7.75	8.03	0.28	40.98	40.19	−0.79			
Bis(8-quinolonolato)-magnesium $Mg(C_9H_6ON)_2$	74.99	74.41	−0.58	4.19	4.54	0.35	11.10	11.23	0.13	9.72	9.81	0.09

a) Metal atoms were neglected in the composition of magnesium compound since they could not be determined.

Table 6. Analytical results of organophosphorus compounds

Sample[a]	C wt %			H wt %			O wt %			N wt %		
	Theor	Exptl	Error	Theor	Exptl	Error	Theor	Exptl	Error	Theor	Exptl	Error
Guanidine phosphate $(CH_5N_3)_2H_3PO_4$	12.97	15.25	2.28	7.08	8.15	1.07	34.54	21.31	−13.41	45.39	55.47	10.08
Di-*n*-octadecyl phosphate $(C_{18}H_{37}O)_2HPO_2$	75.59	75.77	0.18	13.22	13.28	0.06	11.19	10.95	−0.24			
Triphenylphosphine oxide $(C_6H_5)_3PO$	87.42	87.53	0.11	6.11	5.98	−0.13	6.47	6.49	0.02			
Tripenylphosphine $(C_6H_5)_3P$	93.46	93.51	0.05	6.54	6.49	−0.05						

a) Phosphorus atoms were neglected in the composition of organophosphorus compounds since they could not be determined.

TABLE 7. ANALYTICAL RESULTS OF ALKALI METAL COMPOUNDS

Sample[a)]	C wt % Theor	C wt % Exptl	C wt % Error	H wt % Theor	H wt % Exptl	H wt % Error	O wt % Theor	O wt % Exptl	O wt % Error	N wt % Theor	N wt % Exptl	N wt % Error
Sodium oxalate $Na_2C_2O_4$	27.29	27.57	0.28				72.71	72.43	−0.28			
Sodium formate HCOONa	26.68	26.91	0.23	2.24	2.24	0	71.08	70.85	−0.23			
Sodium tartrate $Na_2C_4H_4O_6 \cdot 2H_2O$	26.10	26.41	0.31	4.38	4.02	−0.36	69.52	69.57	0.05			
Sodium citrate $Na_3C_6H_5O_7 \cdot 2H_2O$	32.01	31.58	−0.43	4.03	3.79	−0.24	63.96	64.63	0.67			
Sodium glutamate $NaC_5H_8O_4N \cdot H_2O$	36.59	36.45	−0.14	6.14	6.23	0.09	48.74	48.36	−0.38	8.53	8.96	0.43
Potassium hydrogen tartrate KHC_4H_5O	32.23	31.60	−0.63	3.38	3.27	−0.11	64.39	65.13	0.74			
Potassium hydrogen phthalate $KHC_8H_4O_4$	58.19	58.05	−0.14	3.05	2.82	−0.23	38.76	39.13	0.37			

a) Metal atoms were neglected in the composition of alkali metal compounds since they could not be determined.

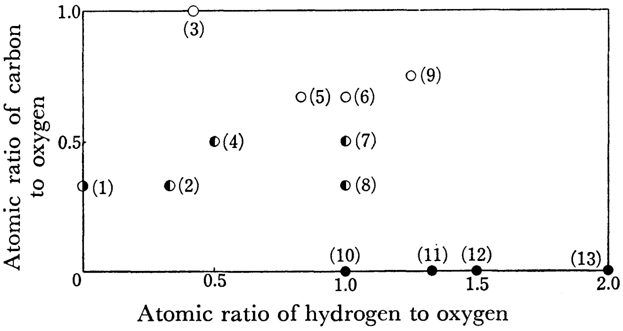

Fig. 1. Effect of the atomic ratio on the decomposition of water.

◐: H_2O produced, ◑: SO_2 produced, ●: both H_2O and SO_2 produced, ○: neither H_2O nor SO_2 produced. (1): $SrCO_3$, (2): $KHCO_3$, (3): $[C_6H_2(NO_2)_3]_2NH_{(2,4,6)}$, (4): HCOONa, (5): $KHC_4H_4O_6$, (6): $C_4H_6O_6$, (7): $Na_2C_4H_4O_6 \cdot 2H_2O$, (8) $(COOH)_2 \cdot 2H_2O$, (9): $C_6H_8O_7 \cdot H_2O$, (10): HSO_3NH_2, (11): NH_4NO_3, (12): $(NH_2)_2\text{-}H_2SO_4$, (13): $(NH_4)_2SO_4$.

in the compound to form hydrogen sulfide and carbonyl sulfide similarly as in magnesium compounds. As shown in Fig. 1, no water is formed when the atomic ratio of carbon to oxygen exceeds 0.5, while excess oxygen which is not consumed by carbon forms SO_2 when the above ratio is less than 0.5, followed by the reaction between SO_2 and hydrogen sulfide and by the formation of water. The formation of water from SO_2 and hydrogen sulfide can be easily understood from the previous results.[2)]

Analysis of Alkali Metal Compounds. It should be emphasized that organic alkali metal salts give satisfactory results. In the conventional elemental analysis using an oxygen combustion technique, alkali and alkaline earth metal compounds are apt to be converted into their carbonates. Vanadium(V) oxide has been added to prevent the formation of carbonate for the analysis of carbon. There are many alkali and alkaline earth metal compounds the analysis of which are of great importance. The present method provides a convenient tool for the elemental analysis, since no special procedure such as the addition of vanadium(V) oxide is necessary.

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