Pyrolytic Sulfurization Gas Chromatography. XIII. Simultaneous Determination of the Atomic Ratio between C, H, O, and N in a Metal Organic Chelate Compound

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In order to clarify the effect of the coexistent elements on the determination of the atomic ratio between C, H, O, and N by the pyrolytic sulfurization gas chromatography (PSGC), compounds containing 25 kinds of elements were investigated. Only 7 of these interfered the determination of the atomic ratio. Several organophosphorus, lithium-, and boron-containing compounds were also analyzed. The results obtained by the present work are summarized in the periodic table together with those from previous work.

In order to establish a new organic elemental analysis method by which several elements can be simultaneously determined, the authors have developed pyrolytic sulfurization gas chromatography (PSGC) based on a combustion technique in sulfur vapor instead of the conventional one in an oxygen atmosphere.[1] According to PSGC, the simultaneous determination of the atomic ratio between C, H, O, and N in a sample can be achieved with a usual organic compound,[2] a metal organic chelate compound,[3] a polymer,[4] and an organic halogen compound.[5]

In the field of elemental analysis, research concerning metal organic chelate compounds has not been carried out so much because of the fact that metallic elements show a strong affinity for oxygen and are apt to form oxides and carbonates. However, PSGC method is characterized by conversion of the metal in a compound into sulfide by means of a sulfur combustion technique and by simultaneously determining the atomic ratio between C, H, O, and N in a sample without using a special procedure such as addition of reducing agent. In the previous work,[3] this PSGC method was applied to the analysis of compounds containing 24 elements: Na, K, Mg, Ca, Sr, Ba, La, Ti, U, Cr, Mo, W, Mn, Fe, Co, Ni, Pd, Cu, Ag, Zn, Cd, Hg, Al, and P. But many elements still remain unsolved, so the present study has been carried out with the objective of estimating the atomic ratio between C, H, O, and N in compounds containing 25 metallic elements other than the previously reported ones: Li, Rb, Cs, Be, Ce, Pr, Eu, Th, Zr, Hf, V, Nb, Rh, Pt, Au, B, Ga, In, Tl, Si, Pb, As, Sb, Bi, and Se. Several organophosphorus compounds were also analyzed. The results obtained by the present work are summarized in the periodic table together with those obtained by the previous study. The PSGC method can be successfully applied to the analysis of the compounds containing 39 elements, but not to those containing 10 kinds of elements.

Experimental

Apparatus and Reagents. The reagents and apparatus used were the same as those reported.[2] The peak areas of the gas chromatogram were read out by the use of a Shimadzu digital integrator E1A. A definite amount of metal oxide was taken with a Shimadzu microbalance MDP-5.

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

Samples. The following samples were prepared by the methods found in the literature for their gravimetric analyses: bis(2-methyl-8-quinolinolato)beryllium(II), $Be(C_{10}H_8ON)_2$;[6] tetrakis(mandelato)zirconium(IV), $Zr(C_8H_8O_3)_4$;[7] tetrakis(mandelato)hafnium(IV), $Hf(C_8H_8O_3)_4$;[8] tetrakis(8-quinolinolato)hafnium(IV), $Hf(C_9H_6ON)_4$;[9] trioxotetrakis(8-quinolinolato)divanadium(V), $V_2O_3(C_9H_6ON)_4$;[9] oxotris(8-quinolinolato)niobium(V), $NbO(C_9H_6ON)_3$;[10] tris(8-quinolinolato)bismuth(III), $Bi(C_9H_6ON)_3$;[9] tris(8-quinolinolato)antimony(III), $Sb(C_9H_6ON)_3$;[11] tris(thionalidato)antimony(III), $Sb(C_{12}H_{10}ONS)_3$;[12] bis(thionalidato)mercury(II), $Hg(C_{12}H_{10}ONS)_2$;[12] tetrakis(8-quinolinolato)thorium(IV), $Th(C_9H_6ON)_4$;[13] triethanolammonium tetraphenylborate, $(HOH_2CH_2C)_3NHB(C_6H_5)_4$;[14] dibutylammonium tetraphenylborate, $(n\text{-}C_4H_9)_2NH_2B(C_6H_5)_4$;[14] benzylammonium tetraphenylborate, $C_6H_5NH_3B(C_6H_5)_4$;[14] 8-quinolinol-quinolinolium tetraphenylborate, $(C_9H_7ON)_2HB(C_6H_5)_4$;[15] gold(I) 2-mercaptoacetate, $AuSO_2H_3C_2$;[16] (2,2′,4,4′,6,6′-hexanitrodiphenylaminato)potassium, $KN[C_6H_2(NO_2)_3]_2$;[17] (2,2′,4,4′,6,6′-hexanitrodiphenylaminato)rubidium, $RbN[C_6H_2(NO_2)_3]_2$;[17] (2,2′,4,4′,6,6′-hexanitrodiphenylaminato)cesium, $CsN[C_6H_2(NO_2)_3]_2$;[17] tris(2,4-pentanedionato)rhodium(III), $[Rh(C_5H_7O_2)_3]$; bis(*N*,*N*′-disalicylideneethylenediaminato)cerium(IV), $[Ce(C_{16}H_{14}O_2N_2)_2]$, and bis(2,4-pentanedionato)platinum(II), $[Pt(C_5H_7O_2)_2]$ were prepared by the method found in the literature.[18] Lithium butanoate, lithium hexanoate, lithium octanoate, and lithium decanoate were obtained by allowing lithium hydoxide to react with the corresponding acid and by recrystallizing them repeatedly until the range of the melting point of each sample decreased to less than 1 °C. The other reagents were commercial products and were purified in a way similar to that used for the lithium salts. The composition and purity of the samples were confirmed by the CH and/or CHN analysis carried out in the Elemental Analysis Center of the Pharmaceutical Department of Kyoto University (Table 1). *p*-Aminophenylarsonic acid for elemental analysis, octaphenylcyclotetrasiloxane for atomic absorption spectroscopy, and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III) and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)praseodymium(III) for NMR spectroscopy were of reagent grade and were used without further purification. The metal oxides were of analytical grade and treated at 950 °C before use.

TABLE 1. ANALYTICAL RESULTS OF CARBON, HYDROGEN, AND NITROGEN IN A METAL ORGANIC CHELATE COMPOUND

Sample	C (wt%)			H (wt%)			N (wt%)		
	Calcd	Found	Error	Calcd	Found	Error	Calcd	Found	Error
Bis(2-methyl-8-quinolinolato)beryllium(II) $Be(C_{10}H_8ON)_2$	73.83	73.99	+0.16	4.96	5.20	+0.24	8.61	8.62	+0.01
Tetrakis(8-quinolinolato)thorium(IV) $Th(C_9H_6ON)_4$	53.47	53.20	−0.27	2.99	3.07	+0.08	6.93	6.83	−0.10
Tetrakis(8-quinolinolato)hafnium(IV) $Hf(C_9H_6ON)_4$	57.26	56.96	−0.30	3.20	2.98	−0.22	7.42	7.40	−0.02
Oxotris(8-quinolinolato)niobium(V) $NbO(C_9H_6ON)_3$	59.90	59.67	−0.23	3.35	3.24	−0.11	7.76	7.71	−0.05
Trioxotetrakis(8-quinolinolato)divanadium(V) $V_2O_3(C_9H_6ON)_4$	59.52	59.82	+0.30	3.33	3.21	−0.12	7.71	7.80	+0.09
Triethanolammonium tetraphenylborate $(HOH_2CH_2C)_3NHB(C_6H_5)_4$	76.92	77.19	+0.27	7.53	7.78	+0.25	2.99	2.97	−0.02
8-Quinolinol-8-quinolinolium tetraphenylborate $(C_9H_7ON)_2HB(C_6H_5)_4$	82.76	82.84	+0.08	5.62	5.80	+0.18	4.59	4.63	+0.04
Dibutylammonium tetraphenylborate $(n\text{-}C_4H_9)_2NH_2B(C_6H_5)_4$	85.51	85.30	−0.21	8.97	8.98	+0.01	3.12	3.14	+0.02
Benzylammonium tetraphenylborate $H_5C_6NH_2HB(C_6H_5)_4$	87.12	87.36	+0.24	7.07	6.96	−0.11	3.28	3.17	−0.11
Piperazinium dihydrogen phosphate monohydrate $C_4H_{10}N_2H_3PO_4 \cdot H_2O$	23.77	23.61	−0.16	7.48	7.60	+0.12	13.86	13.89	+0.03
Benzoguanamine phosphate $C_9H_9N_5 \cdot H_3PO_4$	37.90	37.97	+0.07	4.24	4.32	+0.08	24.56	24.72	+0.16
Benzidine phosphate $C_{12}H_{12}N_2 \cdot H_3PO_4$	51.07	51.03	−0.04	5.36	5.33	−0.03	9.93	10.01	+0.08
Lithium butanoate C_3H_7COOLi	51.09	51.25	+0.16	7.50	7.32	−0.18			
Lithium hexanoate $C_5H_{11}COOLi$	59.03	58.93	−0.10	9.08	8.88	−0.20			
Lithium octanoate $C_7H_{15}COOLi$	64.00	64.16	+0.16	10.07	10.04	−0.03			
Lithium decanoate $C_9H_{19}COOLi$	67.40	67.25	−0.15	10.75	10.88	+0.13			
(2,2′,4,4′,6,6′-Hexanitrodiphenylaminato)-potassium $KN[C_6H_2(NO_2)_3]_2$	30.20	30.34	+0.14	0.84	0.84	0			
(2,2′,4,4′,6,6′-Hexanitrodiphenylaminato)-cesium $CsN[C_6H_2(NO_2)_3]_2$	25.24	25.27	+0.03	0.71	0.64	−0.07			
Bis(*N*,*N*′-disalicylideneethylenediaminato)-cerium(IV) $[Ce(C_{16}H_{14}O_2N_2)_2]$	57.13	57.09	−0.04	4.19	4.43	+0.24			
Tetrakis(mandelato)zirconium(IV) $Zr(C_8H_8O_3)_4$	54.92	54.96	+0.04	4.61	4.76	+0.15			
Tetrakis(mandelato)hafnium(IV) $Hf(C_8H_8O_3)_4$	48.83	48.75	−0.08	4.10	3.70	−0.40			
Tris(2,4-pentanedionato)rhodium(III) $[Rh(C_5H_7O_2)_3]$	45.01	45.28	+0.27	5.29	5.31	+0.02			
Bis(2,4-pentanedionato)platinum(II) $[Pt(C_5H_7O_2)_2]$	30.54	30.47	−0.07	3.59	3.58	−0.01			
Gold(I) 2-mercaptoacetate $HSCH_2COOAu$	8.34	8.50	+0.16	1.05	1.21	+0.16			
Bis(8-quinolineselenolato)cadmium(II) $Cd(C_9H_6SeN)_2$	41.05	41.29	+0.24	2.30	2.54	+0.24			
Tris(8-quinolinolato)indium(III) $In(C_9H_6ON)_3$	59.26	59.18	−0.08	3.32	3.32	0			
Thallium(I) acetate CH_3COOTl	9.12	9.06	−0.06	1.15	1.15	0			
Bis(8-quinolinolato)lead(II) $Pb(C_9H_6ON)_2$	43.63	43.71	+0.08	2.44	2.30	−0.14			
Antimony potassium tartrate $SbOC_4H_4O_6K$	14.79	14.93	+0.14	1.24	1.23	−0.01			
Tris(8-quinolinolato)antimony(III) $Sb(C_9H_6ON)_3$	58.51	58.13	−0.38	3.27	3.46	+0.19			
Tris(8-quinolinolato)bismuth(III) $Bi(C_9H_6ON)_3$	50.56	50.56	0	2.83	3.06	+0.23			
Triphenyl phosphate $(C_6H_5O)_3PO$	66.26	66.16	−0.10	4.63	4.62	−0.01			

Results and Discussion

Reactivity of Metal Oxide. The reactivity between metal oxide and sulfur was investigated prior to the analysis of metal organic chelate compound. The reactivity of metal oxide is expressed in terms of α,

TABLE 2. RELATIVE CONVERSIONS OF METAL OXIDES

Metal oxide	Group	Relative conversion α	Metal oxide	Group	Relative conversion α
BeO	IIA	0	Nb_2O_5	VA	0.01
La_2O_3	IIIA	0.51	Ta_2O_5	VA	0.01
ThO_2	IIIA	0.01	B_2O_3	IIIB	0.17
ZrO_2	IVA	0.01	SiO_2	IVB	0
HfO_2	IVA	0.01	As_2O_3	VB	0.96
V_2O_5	VA	0.37	Bi_2O_3	VB	1.00

TABLE 3. ANALYTICAL RESULTS OF ORGANIC CHELATE COMPOUNDS

Sample	C (wt%)			H (wt%)			O (wt%)			N (wt%)		
	Calcd	Exptl	Error	Calcd	Exptl	Error	Calcd	Exptl	Error	Calcd	Exptl	Error
Lithium butanoate C_3H_7COOLi	55.16	55.08	−0.08	8.10	8.30	+0.20	36.74	36.62	−0.12			
Lithium hexanoate $C_5H_{11}COOLi$	62.58	62.63	+0.05	9.63	9.65	+0.02	27.79	27.72	−0.07			
Lithium octanoate $C_7H_{15}COOLi$	67.10	67.34	+0.24	10.56	10.23	−0.33	22.34	22.43	+0.09			
Lithium decanoate $C_9H_{19}COOLi$	70.18	70.13	−0.05	11.19	11.18	−0.01	18.63	18.68	+0.05			
(2,2′,4,4′,6,6′-Hexanitrodiphenylaminato)potassium $KN[C_6H_2(NO_2)_3]_2$	32.89	32.91	+0.02	0.92	1.00	+0.08	43.81	43.73	−0.08	22.37	22.36	−0.01
(2,2′,4,4′,6,6′-Hexanitrodiphenylaminato)rubidium $RbN[C_6H_2(NO_2)_3]_2$	32.89	32.99	+0.10	0.92	1.05	+0.13	43.81	43.67	−0.14	22.37	22.29	−0.08
(2,2′,4,4′,6,6′-Hexanitrodiphenylaminato)cesium $CsN[C_6H_2(NO_2)_3]_2$	32.89	32.98	+0.09	0.92	0.98	+0.06	43.81	43.63	−0.18	22.37	22.41	+0.04
Bis(2-methyl-8-quinolinolato)beryllium(II) $Be(C_{10}H_8ON)_2$	75.93	80.96	+5.03	5.10	4.81	−0.29	10.11	5.60	−4.51	8.85	8.63	−0.22
Bis(*N*,*N*′-disalicylideneethylenediaminato)cerium(IV) $[Ce(C_{16}H_{14}O_2N_2)_2]$	72.17	71.92	−0.25	5.30	5.33	+0.03	12.01	12.17	+0.16	10.52	10.58	+0.06
Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)praseodymium(III) $Pr(C_{11}H_{19}O_2)_3$	72.09	72.33	+0.24	10.45	10.30	−0.15	17.46	17.37	−0.09			
Tris(2,2,6,6-tetramethyl-3, 5-heptanedionato)europium(III) $Eu(C_{11}H_{19}O_2)_3$	72.09	72.05	−0.04	10.45	10.41	−0.04	17.46	17.54	+0.08			
Tetrakis(8-quinolinolato)thorium(IV) $Th(C_9H_6ON)_4$	74.99	77.56	+2.57	4.19	4.18	−0.01	11.10	9.02	−2.08	9.72	9.24	−0.48
Tetrakis(mandelato)zirconium(IV) $Zr(C_8H_8O_3)_4$	63.15	69.57	+6.42	5.30	4.62	−0.68	31.55	25.81	−5.74			
Tetrakis(mandelato)hafnium(IV) $Hf(C_8H_8O_3)_4$	63.15	69.21	+6.06	5.30	4.61	−0.69	31.55	26.18	−5.37			
Tetrakis(8-quinolinolato)hafnium(IV) $Hf(C_9H_6ON)_4$	74.99	80.53	+5.54	4.19	3.78	−0.41	11.10	6.25	−4.85	9.72	9.44	−0.28
Trioxotetrakis(8-quinolinolato)divanadium(V) $V_2O_3(C_9H_6ON)_4$	69.23	71.45	+2.22	3.87	3.52	−0.35	17.93	16.44	−1.49	8.97	8.58	−0.39
Oxotris(8-quinolinolato)niobium(V) $NbO(C_9H_6ON)_3$	72.31	72.02	−0.29	4.05	4.04	−0.01	14.27	14.28	+0.01	9.37	9.66	+0.29
Tris(2,4-pentanedionato)rhodium(III) $[Rh(C_5H_7O_2)_3]$	60.59	60.78	+0.19	7.12	7.01	−0.11	32.29	32.21	−0.08			

TABLE 3. (Continued).

Sample	C (wt%)			H (wt%)			O (wt%)			N (wt%)		
	Calcd	Exptl	Error	Calcd	Exptl	Error	Calcd	Exptl	Error	Calcd	Exptl	Error
Bis(2,4-pentanedionato)-platinum(II) $[Pt(C_5H_7O_2)_2]$	60.59	60.81	+0.22	7.12	7.13	+0.01	32.29	32.06	−0.23			
Bis(glycinato)platinum(II) $[Pt(NH_2CH_2COO)_2]$	32.44	32.36	−0.08	5.44	5.46	+0.02	43.21	43.03	−0.18	18.91	19.15	+0.24
Gold(I) 2-mercaptoacetate $HSCH_2COOAu$	40.69	40.57	−0.12	5.12	5.04	−0.08	54.19	54.39	+0.20			
Bis(8-quinolineselenolato)-cadmium(II) $Cd(C_9H_6SeN)_2$	84.35	84.38	+0.03	4.72	4.78	+0.06				10.93	10.84	−0.09
Bis(thionalidato)mercury-(II) $Hg(C_{12}H_{10}ONS)_2$	78.24	78.32	+0.08	5.47	5.29	−0.18	8.68	8.74	+0.06	7.60	7.65	+0.05
Sodium tetraphenylborate $NaB(C_6H_5)_4$	93.46	93.60	+0.14	6.54	6.40	−0.14						
Dibutylammonium tetraphenylborate $(n\text{-}C_4H_9)_2NH_2B(C_6H_5)_4$	87.62	90.67	+3.05	9.19	9.33	+0.14				3.19	0	−3.19
Benzylammonium tetraphenylborate $C_6H_5NH_2HB(C_6H_5)_4$	89.38	92.44	+3.06	7.26	7.55	+0.29				3.36	0	−3.36
Triethanolammonium tetraphenylborate $(HOH_2CH_2C)_3NHB(C_6H_5)_4$	78.74	81.92	+3.18	7.71	8.14	+0.43	10.49	8.28	−2.21	3.06	1.66	−1.40
8-Quinolinol-8-quinolinolium tetraphenylborate $(C_9H_7ON)_2HB(C_6H_5)_4$	84.11	88.66	+4.55	5.88	5.55	−0.33	5.33	4.34	−0.99	4.67	1.45	−3.22
Tris(8-quinolinolato)-gallium(III) $Ga(C_9H_7ON)_3$	74.99	74.96	−0.03	4.19	4.15	−0.04	11.10	11.30	+0.20	9.72	9.59	−0.13
Tris(8-quinolinolato)-indium(III) $In(C_9H_6ON)_3$	74.99	75.01	+0.02	4.19	4.20	+0.01	11.10	11.19	+0.09	9.72	9.61	−0.11
Thallium(I) acetate CH_3COOTl	40.68	40.54	−0.14	5.12	5.00	−0.12	54.19	54.46	+0.27			
Octaphenylcyclotetrasiloxane $Si_4C_{48}H_{40}O_4$	84.68	94.08	+9.40	5.92	5.92	0	9.40	0	−9.40			
Bis(8-quinolinolato)-lead(II) $Pb(C_9H_6ON)_2$	74.99	74.73	−0.26	4.19	4.20	+0.01	11.10	11.38	+0.28	9.72	9.69	−0.03
p-Aminophenylarsonic acid $H_2NC_6H_4AsO_3H_2$	50.70	50.95	+0.25	5.67	5.46	−0.21	33.77	33.53	−0.24	9.85	10.07	+0.22
Antimony potassium tartrate $SbOC_4H_4O_6K$	29.28	29.52	+0.24	2.46	2.43	−0.03	68.26	68.05	−0.21			
Tris(8-quinolinolato)-antimony(III) $Sb(C_9H_6ON)_3$	74.99	75.28	+0.29	4.19	4.02	−0.17	11.10	11.11	+0.01	9.72	9.59	−0.13
Tris(thionalidato)-antimony(III) $Sb(C_{12}H_{10}ONS)_3$	78.24	78.30	+0.06	5.47	5.25	−0.22	8.68	8.69	+0.01	7.60	7.76	+0.16
Tris(8-quinolinolato)-bismuth(III) $Bi(C_9H_6ON)_3$	74.99	74.72	−0.27	4.19	4.26	+0.07	11.10	11.38	+0.28	9.72	9.64	−0.08

which refers to the mole ratio of sulfur dioxide (SO_2) from the metal oxide against that from a reference substance, silver nitrate. The reactivity of metal oxide, a, is estimated approximately by the equation adopted in the previous paper (Table 2).[3] As can be seen from Table 2, the oxides of beryllium(II), thorium(IV), zirconium(IV), hafnium(IV), niobium(V), tantalum-(V), silicon(IV), and boron(III) are barely converted into the sulfides under the experimental conditions, while arsenic(III) and bismuth(III) oxide react quantitatively with sulfur.

Analysis of Various Organic Chelate Compounds. Various metal organic chelate compounds were analyzed (Table 3). The compounds containing four elements of the lanthanoids, La, Ce, Pr, and Eu gave fairly good results. Lanthanoids, especially light rare earths, resemble each other very closely in chemical properties, so it can be expected that PSGC is applicable to the compounds containing three light rare earth elements other than the investigated ones. Selenium was expected to form carbon diselenide and hydrogen selenide under the experimental conditions and to give an error in C and H values. Selenium did not, however, interfere with the determination of the atomic ratio and satisfactory results were obtained with (8-quinolineselenolato)-cadmium(II). Almost all the complexes gave satisfactory

TABLE 4. ANALYTICAL RESULTS OF ORGANOPHOSPHORUSCOMPOUNDS

Sample	C (wt%)			H (wt%)			O (wt%)			N (wt%)		
	Calcd	Exptl	Error	Calcd	Exptl	Error	Calcd	Exptl	Error	Calcd	Exptl	Error
Piperazinium dihydrogenphosphate monohydrate $C_4H_{10}N_2 \cdot H_3PO_4 \cdot H_2O$	28.07	33.55	+5.48	8.83	10.88	+2.05	46.73	37.24	−9.49	16.37	18.32	+1.95
Benzoguanamine phosphate $C_9H_9N_5 \cdot H_3PO_4$	42.52	45.71	+3.19	4.76	5.04	+0.28	25.17	20.59	−4.58	27.55	28.66	+1.11
Benzidine phosphate $C_{12}H_{12}N_2 \cdot H_3PO_4$	57.36	58.43	+1.07	6.02	5.94	−0.08	25.47	24.52	−0.95	11.15	11.11	−0.04
Triphenyl phosphate $(C_6H_5O)_3PO$	73.21	73.01	−0.20	5.12	5.12	0	21.67	21.87	+0.20			

results, but the complexes of Be, Th, Zr, Hf, V, B, and Si gave a negative error in the oxygen value. As can be seen from Table 2, the oxides of these seven elements were highly stable and were scarecely converted into their sulfides. Therefore, the oxygen atom in their complex salts is expected to remain more or less in the residues and this is consistent with the results shown in Table 3. Negative errors in both the oxygen and nitrogen values were obtained in several ammonium tetraphenylborates. Boron nitride was subjected to pyrolytic sulfurization under the experimental conditions, but no evolution of nitrogen was observed. From the above mentioned fact, the negative error in nitrogen values of ammonium tetraphenylborates seems to be ascribed to the formation of boron nitride.

Analysis could not be carried out for lithium acetate, CH_3COOLi, since the reaction tube containing lithium acetate, in which the atomic ratio of carbon to oxygen (C/O) is 1.0, exploded by itself during the course of sulfurization. With the objective of clarifying this phenomena, a series of lithium salts were investigated. Oxygen-rich compounds such as lithium lactate ($C_3H_5O_3Li$, C/O=1.0) and lithium citrate tetrahydrate ($C_6H_5O_7Li_3 \cdot 4H_2O$, C/O=0.55) could not be analyzed since the reaction tube exploded by itself similarly to the way it did in lithium acetate. Relatively oxygen-poor compounds such as lithium butanoate (C_3H_7COOLi, C/O=2.0), lithium hexanoate ($C_5H_{11}COOLi$, C/O=3.0), lithium octanoate ($C_7H_{15}COOLi$, C/O=4.0), and lithium decanoate ($C_9H_{19}COOLi$, C/O=5.0) could be subjected to sulfurization without any explosion. The satisfactory results are obtained when value of C/O exceeds 2.0. The above explosion seems to be ascribed to some lithium silicate, $xLi_2O\,ySiO_2$, which is formed by the reaction between SiO_2 and Li_2O.

Analysis of Organophosphorus Compounds. It was reported in the previous paper that carbon-rich compounds such as dioctadecyl hydrogenphosphate [$(n\text{-}C_{18}H_{37}O)_2HPO_2$, C/O=9.0] gave satisfactory results while carbon-poor compounds such as diguanidium hydrogenphosphate [$(CH_5N_3)_2H_3PO_4$, C/O=0.5] produced a low oxygen value. In order to clarify the difference between these two cases, further study was carried out on a series of organic phosphates in which the oxidation number of phosphorus is +5, that is, piperazinium dihydrogenphosphate monohydrate ($C_4C_{10}N_2 \cdot H_3PO_4 \cdot H_2O$, C/O=0.8), benzoguanamine phosphate ($C_9H_9N_5 \cdot H_3PO_4$, C/O=2.5), benzidine phosphate ($C_{12}H_{12}N_2 \cdot H_3PO_4$, C/O=3.0), and triphenyl phosphate [$(C_6H_5O)_3PO$, C/O=4.5]. As can be seen from Table 4, the present method gives satisfactory results when the value of C/O exceeds 4.5 but does not satisfactory results in C/O less than 3.0.

Interferences. As can be seen from the above-mentioned results, PSGC was applicable to various metal organic chelate compounds, and the atomic ratio between C, H, O, and N in a sample could be determined simultaneously. Some metals in their compounds took up the oxygen in a sample to form their oxides during pyrolytic sulfurization, and this brought about the most serious problems in the analyses of the compounds containing these metals. However, if one takes into account the difficulties in analysis of oxygen in a metal organic chelate compound by the conventional methods, the utility of PSGC in analysis of metal organic chelate compound is obvious even though the applicable elements are restricted.

On the basis of the results obtained with regard to the formation of oxides, the effect of the coexistent elements on the determination of the atomic ratio is summarized on the periodic table (Fig. 1). The amount of oxygen

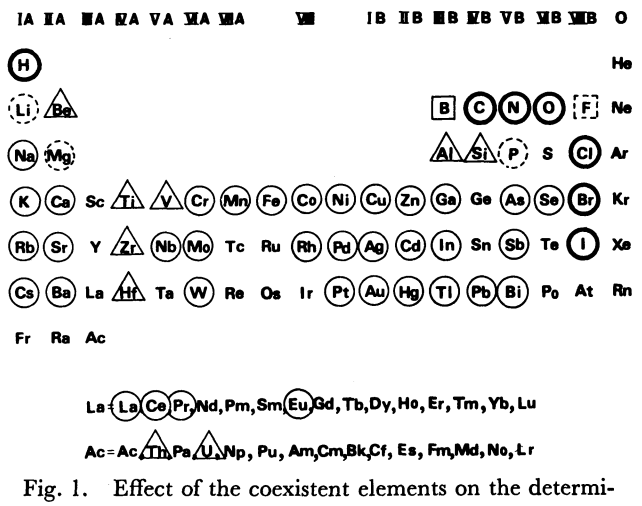

Fig. 1. Effect of the coexistent elements on the determination of the atomic ratio.
○: Harmless, △: form oxide and harmful, □: form both oxide and nitride and harmul, □: react with reaction tube also harmful, ○: can be determined simultaneously.

in an organic compound containing an oxygen atom and one of the following 39 kinds of elements can be satisfactorily estimated by PSGC : (Li), Na, K, Rb, Cs, (Mg), Ca, Sr, Ba, Nb, Cr, Mo, W, Mn, Fe, Co, Rh, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, Pb, (P), As, Sb, Bi, Se, La, Ce, Pr, and Eu. Since there is close resemblance in chemical properties between the elements of lanthanoids, more particularly between ones of light rare earths, it can be expected that PSGC is applicable to the compounds containing three other lanthanoids, *i.e.*, Nd, Pm, and Sm, and the number of applicable elements would rise to 42. Both magnesium- and lithium-containing samples gave satisfactory results only if the number of carbon atoms exceeds that of oxygen atoms in a sample. Organic phosphates gave satisfactory results when the value of C/O exceeded 4.5, but the quantitative details of other types of organophosphorus compounds is not still clear. The compound containing oxygen atoms and one of the following 10 elements, however, gave a low oxygen value: Be, Ti, Zr, Hf, Th, U, V, B, Al, and Si. Boron-containing compounds show a negative error in both oxygen and nitrogen values.

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