Contributions to the Interpretation of Mass Spectrum of Tetraethoxysilane (TEOS)

III. Accurate mass and M+1, M+2 isotopic effect measurements

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The aim of this article in continuation of Parts I [1] and II [2] is the interpretation of the TEOS mass spectrum as a precursor in the sol-gel process. In Part I [1] the primary fragmentation ions at masses 207, 193, 179 and 163 were obtained experimentally by B/E linked scan by radical induced fragmentation reactions. In Part II [2] eliminations of neutral fragments from the primary ions and the obtained ions by consecutive elimination reactions were evidenced experimentally by the B/E and B/E(1-E)$^{1/2}$ linked scans. In this third and final Part of interpretation of the TEOS mass spectrum, the separation of ions by mass spectrometry at high resolutions of 5000 and 6600, relative to standard resolution 1000, and measurements of the M+1 and M+2 isotopic effects at the resolution of 5000 are presented. The separation of the ions with nominal mass 105 at high resolution is detailed.

*Keywords**:** tetraethoxysilane, mass spectrum, accurate mass, M+1, M+2 isotopic effects*

The first purpose of the author's studies [3] was the separation and identification of molecular species obtained in sol-gel process by gas chromatography coupled with mass spectrometry (GC-MS).

The basic factors that influence sol-gel process have been studied systematically by GC-MS: the type of precursor alkoxide, the solvent nature, the water quantity used in hydrolysis, the reactant mixing order and the catalyst type. The results were published between 1994 and 2007 [4-10].

The second purpose of the author's studies was the development of a procedure for the interpretation of mass spectra [1-3, 11-19] of some silicon alkoxides and their transesters and oligomers obtained by the sol-gel process.

The relationship between the chemical structure of the molecules and their mass spectra has been highlighted by Lafferty [11]. According to his theory the relative intensity of fragmentation ions is determined by the stability of the reaction products and of the bond strength. A complementary theory has been developed by Djerassi [12]. According to this theory the charge and radical localization after ionization contribute to establish the initiation centers of the fragmentation reactions.

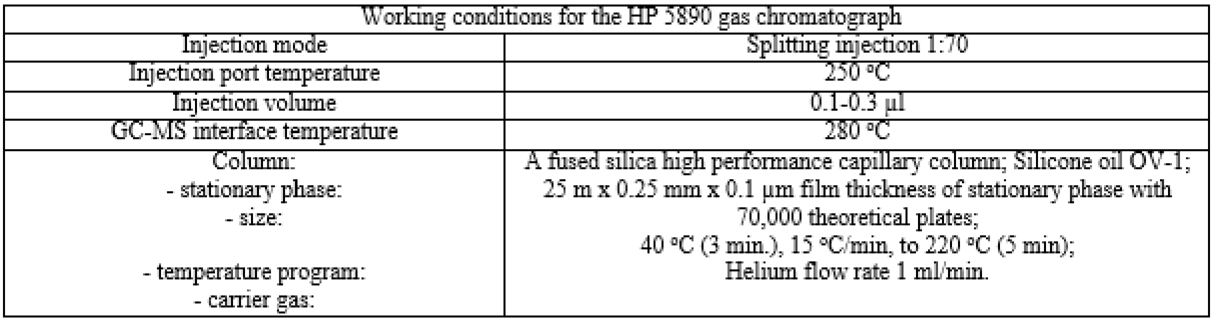
The double-focusing GC-MS tandem can establish the fragmentation pathways of the ions from the mass spectrum of an organic compound such as tetraethoxysilane directly through the B/E and B/E (1-E)$^{1/2}$ linked scans. Thus, the daughter ions and neutral molecule removals for a given ion in mass spectrum were determined [1-3]. This instrument can also separate at high resolutions the ions with the same nominal mass and which differ only by fractions of a whole mass. Thus we obtain the fine structure of a mass spectrum. The confirmation of the existence of ions obtained in mass spectrum of TEOS was achieved by measurements of M+1, M+2 isotopic effects and by calculation of double bond equivalents (DBE).

Experimental part

The development of GC-MS method for TEOS monomer determination in sol-gel processes consisted in establishing of the GC separation conditions of the analyzed components and in establishing of the optimal MS parameters. In this work the separation conditions of TEOS ions by mass spectrometry at high resolutions of 5000 and 6600, and measurements of the M+1 and M+2 isotopic effects at high resolution of 5000 are presented (Table 1).

Table 1

GC-MS METHOD AND OPTIMISATION PARAMETERS



Working conditions for the HP 5890 gas chromatograph	
Injection mode	Splitting injection 1:70
Injection port temperature	250 °C
Injection volume	0.1-0.3 µl
GC-MS interface temperature	280 °C
Column: - stationary phase: - size: - temperature program: - carrier gas:	A fused silica high performance capillary column; Silicone oil OV-1; 25 m x 0.25 mm x 0.1 µm film thickness of stationary phase with 70,000 theoretical plates; 40 °C (3 min.), 15 °C/min, to 220 °C (5 min); Helium flow rate 1 ml/min.

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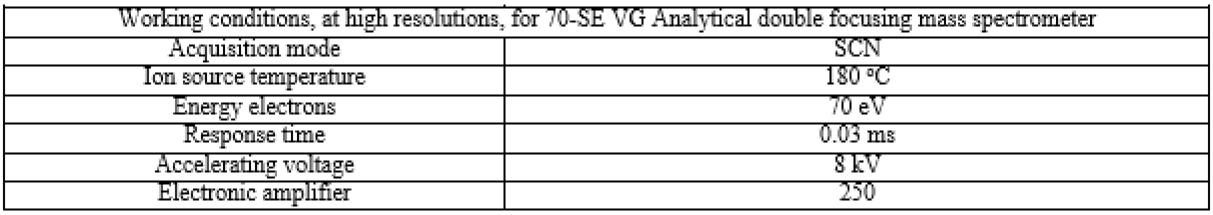


Working conditions, at high resolutions, for 70-SE VG Analytical double focusing mass spectrometer	
Acquisition mode	SCN
Ion source temperature	180 °C
Energy electrons	70 eV
Response time	0.03 ms
Accelerating voltage	8 kV
Electronic amplifier	250

Results and discussions

Contributions to the interpretation of mass spectrum of tetraethoxysilane (TEOS)

For this work has been achieved a library of the mass spectra obtained for TEOS in the different sol-gel reaction mixtures [3], analyzed by GC-MS at a resolution of R=1000 and presented in Figure 1. It shows the TEOS mass spectrum obtained by averaging the 12 TEOS mass spectra and contains the molecular ion at m/e 208 with adjacent isotopic ions at m/e 209 and m/e 210 together with 84 fragmentation ions.

An increased number (95) of TEOS fragmentation ions at high resolutions (R=5000 and R=6600) (Table 2) and also measurements of M+1, M+2 isotopic effects of 62 ions (Table 3) are presented.

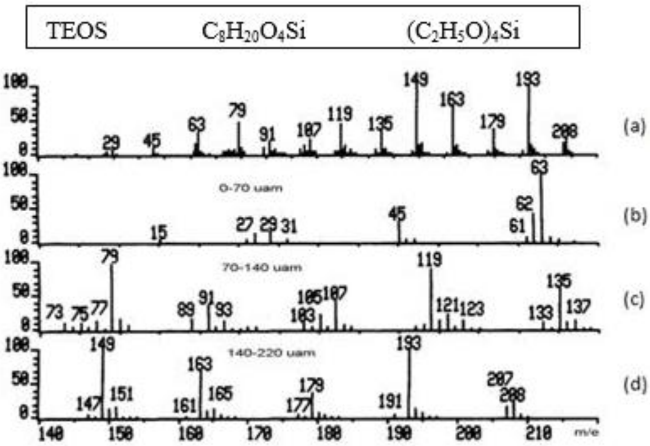


Fig. 1. Mass spectrum of tetraethoxysilane (TEOS) as an average of 12 mass spectra at resolution R=1000; (a) full, (b) 0-70 amu (c) 70-140 amu and (d) 140-220 amu.

The separation of ions by mass spectrometry at high resolutions

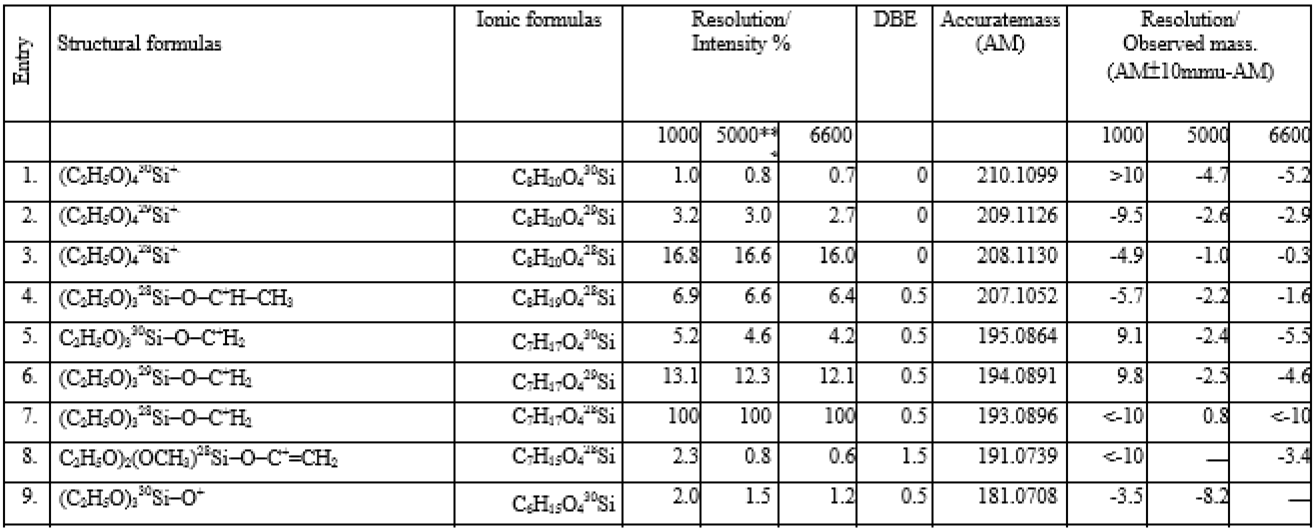
The power of resolution of a mass spectrometer is a measure of its capacity to separate ions with a defined mass difference. For two peaks of M_1 and M_2 masses the resolution is given by the expression $R=M_1/\Delta M$ where $\Delta M = M_2 - M_1$.

At low resolution (R=1000), the mass spectrum of TEOS in Fig. 1 consists in a series of peaks at whole m/e values.

The separation of ions with whole masses is relatively easy. Thus for the separation of the molecular ion of TEOS with m/e 208 and its M+1 isotop with m/e 209 is required a resolution R=208/1=208, accessible for any mass spectrometer. For the separation of ions which differ only by fractions of a whole mass, such as the ions with m/e 106.0367 and m/e 106.0003, is required a high resolution R=106/0.0364=2912 (Table 2).

Table 2

THE STRUCTURAL AND IONIC FORMULAS OF THE IONS IN THE TEOS MASS SPECTRUM. THE ACCURATE MASS MEASUREMENT OF IONS AT HIGH RESOLUTION AND THE DOUBLE BOND EQUIVALENT (DBE).



Entry	Structural formulas	Ionic formulas	Resolution/ Intensity %			DBE	Accuratemass (AM)	Resolution/ Observed mass. (AM±10mmu-AM)		
			1000	5000***	6600			1000	5000	6600
1.	$(C_2H_5O)_4{}^{30}Si^{+\cdot}$	$C_8H_{20}O_4{}^{30}Si$	1.0	0.8	0.7	0	210.1099	>10	-4.7	-5.2
2.	$(C_2H_5O)_4{}^{29}Si^{+\cdot}$	$C_8H_{20}O_4{}^{29}Si$	3.2	3.0	2.7	0	209.1126	-9.5	-2.6	-2.9
3.	$(C_2H_5O)_4{}^{28}Si^{+\cdot}$	$C_8H_{20}O_4{}^{28}Si$	16.8	16.6	16.0	0	208.1130	-4.9	-1.0	-0.3
4.	$(C_2H_5O)_3{}^{28}Si{-}O{-}C^+H{-}CH_3$	$C_8H_{19}O_4{}^{28}Si$	6.9	6.6	6.4	0.5	207.1052	-5.7	-2.2	-1.6
5.	$C_2H_5O)_3{}^{30}Si{-}O{-}C^+H_2$	$C_7H_{17}O_4{}^{30}Si$	5.2	4.6	4.2	0.5	195.0864	9.1	-2.4	-5.5
6.	$(C_2H_5O)_3{}^{29}Si{-}O{-}C^+H_2$	$C_7H_{17}O_4{}^{29}Si$	13.1	12.3	12.1	0.5	194.0891	9.8	-2.5	-4.6
7.	$(C_2H_5O)_3{}^{28}Si{-}O{-}C^+H_2$	$C_7H_{17}O_4{}^{28}Si$	100	100	100	0.5	193.0896	<-10	0.8	<-10
8.	$C_2H_5O)_2(OCH_3)^{28}Si{-}O{-}C^+{=}CH_2$	$C_7H_{15}O_4{}^{28}Si$	2.3	0.8	0.6	1.5	191.0739	<-10	—	-3.4
9.	$(C_2H_5O)_3{}^{30}Si{-}O^+$	$C_6H_{15}O_4{}^{30}Si$	2.0	1.5	1.2	0.5	181.0708	-3.5	-8.2	—

10.	$(C_2H_5O)_3{}^{29}Si{-}O^{+}$	$C_6H_{15}O_4{}^{29}Si$	4.3	3.7	3.2	0.5	180.0735	1.4	-4.9	4.9
11.	$(C_2H_5O)_3{}^{28}Si{-}O^{+}$	$C_6H_{15}O_4{}^{28}Si$	27.3	23.9	22.8	0.5	179.0739	-1.2	-2.3	7.8
12.	$(C_2H_5O)_2(OH)^{28}Si{-}O{-}C^{+}{=}CH_2$	$C_6H_{13}O_4{}^{28}Si$	1.6	1.4	1.1	1.5	177.0583	-1.3	0.5	5.9
13.	$(C_2H_5O)_2(OCH_3)^{30}Si{-}O^{+}$	$C_5H_{13}O_4{}^{30}Si$	1.1	0.9	0.7	0.5	167.0551	-1.0	0.9	8.8
14.	$(C_2H_5O)_2(OCH_3)^{29}Si{-}O^{+}$	$C_5H_{13}O_4{}^{29}Si$	1.2	0.8	0.5	0.5	166.0578	-5.9	-8.3	-3.6
15.	$(C_2H_5O)_2(OCH_3)^{28}Si{-}O^{+}$	$C_5H_{13}O_4{}^{28}Si$	8.8	6.6	5.6	0.5	165.0583	-5.5	-6.2	-6.1
16.	$(C_2H_5O)_3{}^{30}Si+$	$C_6H_{15}O_3{}^{30}Si$	↑+	↑+	↑+	0.5	165.0758	>10	—	—
17.	$(C_2H_5O)_3{}^{29}Si^{+}$	$C_6H_{15}O_3{}^{29}Si$	8.4	6.4	5.9	0.5	164.0786	-2.2	-4.7	-2.8
18.	$(C_2H_5O)_3{}^{28}Si^{+}$	$C_6H_{15}O_3{}^{28}Si$	62.6	56.6	55.2	0.5	163.0790	0.0	-1.4	0.4
19.	$(C_2H_5O)_2(H)^{28}Si{-}O{-}C^{+}{=}CH_2$	$C_6H_{13}O_3{}^{28}Si$	0.5	0.3	0.2	1.5	161.0633	5.8	-6.0	10.0
20.	$(C_2H_5O)_2(OH)^{30}Si{-}O^{+}$	$C_4H_{11}O_4{}^{30}Si$	0.8	0.6	0.5	0.5	153.0395	-3.9	4.0	0.1
21.	$(C_2H_5O)_2(OH)^{29}Si{-}O^{+}$	$C_4H_{11}O_4{}^{29}Si$	0.8	0.5	0.4	0.5	152.0422	-7.4	6.8	2.5
22.	$(C_2H_5O)_2(OH)^{28}Si{-}O^{+}$	$C_4H_{11}O_4{}^{28}Si$	8.5	5.8	4.9	0.5	151.0426	-5.9	—	-2.5
23.	$(C_2H_5O)(OCH_3)^{30}Si^{+}$	$C_5H_{13}O_3{}^{30}Si$	↑+	↑+	↑+	0.5	151.0602	2.3	-2.5	8.7
24.	$(C_2H_5O)(OCH_3)^{29}Si^{+}$	$C_5H_{13}O_3{}^{29}Si$	10.3	8.5	7.9	0.5	150.0626	2.3	-2.5	8.7
25.	$(C_2H_5O)(OCH_3)^{28}Si^{+}$	$C_5H_{13}O_3{}^{28}Si$	92.9	81.1	80.3	0.5	149.0633	4.8	0.6	3.6
26.	$C_2H_5O)(CH_3O)(H)^{28}Si{-}O{-}C^{+}{=}CH_2$	$C_5H_{11}O_3{}^{28}Si$	3.0	2.0	1.6	1.5	147.0477	6.9	-2.5	3.3
27.	$(C_2H_5O)(CH_3O)(OH)^{30}Si{-}O^{+}$	$C_3H_9O_4{}^{30}Si$	1.7	0.4	0.3	0.5	139.0238	4.3	4.4	>10
28.	$(C_2H_5O)(CH_3O)(OH)^{29}Si{-}O^{+}$	$C_3H_9O_4{}^{29}Si$	0.4	0.3	0.2	0.5	138.0265	-2.8	—	3.0
29.	$(C_2H_5O)(CH_3O)(OH)^{28}Si{-}O^{+}$	$C_3H_9O_4{}^{28}Si$	3.4	2.4	2.1	0.5	137.0270	-0.7	-6.8	-6.5
30.	$(C_2H_5O)_2(OH)^{30}S^{i+}$	$C_4H_{11}O_3{}^{30}Si$	↑+	↑+	↑+	0.5	137.0445	>10	—	—
31.	$(C_2H_5O)_2(OH)^{29}Si^{+}$	$C_4H_{11}O_3{}^{29}Si$	2.2	1.8	2.1	0.5	136.0473	3.9	-6.8	-1.7
32.	(C2H5O)2(OH)28Si^{+}	$C_4H_{11}O_3{}^{28}Si$	22.9	18.1	17.7	0.5	135.0477	6.0	-1.3	0.0
33.	$(C_2H_5O)(H)(OH)^{29}Si{-}O{-}C^{+}{=}CH_2$	$C_4H_9O_3{}^{29}Si$	0.6	0.4	0.3	1.5	134.0316	-4.1	-9.7	-8.5
34.	$(C_2H_5O)(H)(OH)^{28}Si{-}O{-}C^{+}{=}CH_2$	$C_4H_9O_3{}^{28}Si$	3.8	2.1	1.9	1.5	133.0321	-8.2	—	>10
35.	$(C_2H_5O)(HO)_2{}^{30}Si{-}O^{+}$	$C_2H_7O_4{}^{30}Si$	0.7	0.4	0.2	0.5	125.0082	-4.2	6.7	0.9
36.	$(C_2H_5O)(HO)_2{}^{29}Si{-}O^{+}$	$C_2H_7O_4{}^{29}Si$	0.4	0.3	0.2	0.5	124.0109	-0.3	—	>10
37.	$(C_2H_5O)(OH)_2{}^{28}Si{-}O^{+}$	$C_2H_7O_4{}^{28}Si$	4.7	3.4	3.2	0.5	123.0113	1.7	-3.4	-1.5
38.	$(C_2H_5O)(CH_3O)(OH)^{30}Si^{+}$	$C_3H_9O_3{}^{30}Si$	↑+	↑+	↑+	0.5	123.0289	>10	—	+↑
39.	$(C_2H_5O)(CH_3O)(OH)^{29}Si^{+}$	$C_3H_9O_3{}^{29}Si$	0.7	0.6	0.5	0.5	122.0316	0.1	-2.0	-6.8
40.	$(C_2H_5O)(CH_3O)(OH)^{28}Si^{+}$	$C_3H_9O_3{}^{28}Si$	7.1	4.6	3.7	0.5	121.0329	0.6	-5.0	-3.5
41.	$(C_2H_5O)_2(H)^{30}Si^{+}$	$C_4H_{11}O_2{}^{30}Si$	↑+	↑+	↑+	0.5	121.0496	>10	—	+↑
42.	$(C_2H_5O)_2(H)^{29}Si^{+}$	$C_4H_{11}O_2{}^{29}Si$	3.7	2.8	2.0	0.5	120.0524	5.0	-2.3	6.0
43.	$(C_2H_5O)_2(H)^{28}Si^{+}$	$C_4H_{11}O_2{}^{28}Si$	38.5	28.5	27.5	0.5	119.0528	6.8	1.9	0.7
44.	$(C_2H_5O)(H)_2{}^{29}Si{-}O{-}C^{+}{=}CH_2$	$C_4H_9O_2{}^{29}Si$	2.4	1.9	1.8	1.5	118.0367	-3.0	-8.9	-8.4
45.	$(C_2H_5O)(H)_2{}^{28}Si{-}O{-}C^{+}{=}CH_2$	$C_4H_9O_2{}^{28}Si$	1.9	1.4	1.3	1.5	117.0371	>10	4.1	>10
46.	$(CH_3O)(HO)_2{}^{29}Si{-}O^{+}$	$CH_5O_4{}^{29}Si$	—	—	—	0.5	109.9922	—	—	—
47.	$(CH_3O)(HO)_2{}^{28}Si{-}O^{+}$	$CH_5O_4{}^{28}Si$	1.9	1.0	0.9	0.5	108.9957	-7.7	—	>10
48.	$(C_2H_5O)(HO)_2{}^{30}Si^{+}$	$C_2H_7O_3{}^{30}Si$	↑+	↑+	↑+	0.5	109.0132	9.8	7.1	3.0
49.	$(C_2H_5O)(HO)_2{}^{29}Si^{+}$	$C_2H_7O_3{}^{29}Si$	1.2	1.0	0.8	0.5	108.0160	1.4	-1.7	-4.7
50.	$(C_2H_5O)(HO)_2{}^{28}Si^{+}$	$C_2H_7O_3{}^{28}Si$	16.9	12.3	11.9	0.5	107.0164	2.6	-0.6	-1.0
51.	$(C_2H_5O)(CH_3O)(H)^{30}Si^{+}$	$C_3H_9O_2{}^{30}Si$	↑+	↑+	↑+	0.5	107.0340	—	—	—
52.	$(C_2H_5O)(CH_3O)(H)^{29}Si^{+}$	$C_3H_9O_2{}^{29}Si$	0.8	0.5	0.3	0.5	106.0367	>10	-3.3	-6.0
53.	$(HO)_2(H)^{29}Si{-}O{-}C^{+}{=}CH_2$	$C_2H_5O_3{}^{29}Si$	↑+	↑+	0.3	1.5	106.0003	>10	<-10	<-10
54.	$(C_2H_5O)(CH_3O)(H)^{28}Si^{+}$	$C_3H_9O_2{}^{28}Si$	9.9	5.3	4.7	0.5	105.0372	>10	0.9	2.1
55.	$(HO)_2(H)^{28}Si{-}O{-}C^{+}{=}CH_2$	$C_2H_5O_3{}^{28}Si$	↑+	4.1	↑+	1.5	105.0008	>10	4.8	2.0
56.	$(CH_3O)(H)_2{}^{30}Si{-}O{-}C^{+}{=}CH_2$	$C_3H_7O_2{}^{30}Si$	↑+	↑+	↑+	1.5	105.0184	—	<-10	<-10

57.	$(CH_3O)(H)_2{}^{29}Si–O–C^+=CH_2$	$C_3H_7O_2{}^{29}Si$	1.2	0.8	0.6	1.5	104.0211	-1.5	-2.7	-7.8
58.	$(CH_3O)(H)_2{}^{28}Si–O–C^+=CH_2$	$C_3H_7O_2{}^{28}Si$	3.7	2.4	2.1	1.5	103.0215	4.0	0.0	-2.6
59.	$(HO)_3{}^{30}SiO^+$	$H_3O_4{}^{30}Si$	—	—	—	0.5	96.9769	<-10	<-10	—
60.	$(HO)_3{}^{29}SiO^+$	$H_3O_4{}^{29}Si$	0.6	0.4	0.3	0.5	95.9796	—	—	—
61.	$(HO)_3{}^{28}SiO^+$	$H_3O_4{}^{28}Si$	0.5	0.3	0.2	0.5	94.9800	<-16	<-10	-8.4
62.	$(CH_3O)(HO)_2{}^{29}Si^+$	$CH_5O_3{}^{29}Si$	0.5	0.3	0.2	0.5	94.0003	4.3	—	-7.8
63.	$(CH_3O)(HO)_2{}^{28}Si^+$	$CH_5O_3{}^{28}Si$	4.7	3.3	3.1	0.5	93.0007	5.6	5.6	5.6
64.	$(C_2H_5O)(OH)(H)^{30}Si^+$	$C_2H_7O_2{}^{30}Si$	↑+	↑+	↑+	0.5	93.0183	—	—	—
65.	$(C_2H_5O)(OH)(H)^{29}Si^+$	$C_2H_7O_2{}^{29}Si$	1.3	1.0	0.9	0.5	92.0211	>10	—	0.7
66.	$(C_2H_5O)(OH)(H)^{28}Si^+$	$C_2H_7O_2{}^{28}Si$	13.7	9.2	9.0	0.5	91.0215	>10	—	9.5
67.	$(HO)(H)_2{}^{30}Si–O–C^+=CH_2$	$C_2H_5O_2{}^{30}Si$	↑+	↑+	↑+	1.5	91.0027	-3.4	-3.6	-9.4
68.	$(HO)(H)_2{}^{29}Si–O–C^+=CH_2$	$C_2H_5O_2{}^{29}Si$	3.7	2.5	2.3	1.5	90.0054	-3.4	-3.6	-9.4
69.	$(HO)(H)_2{}^{28}Si–O–C^+=CH_2$	$C_2H_5O_2{}^{28}Si$	5.7	3.8	3.7	1.5	89.0058	-7.9	-7.9	<-10
70.	$(OH)_3{}^{30}Si^+$	$H_3O_3{}^{30}Si$	3.5	1.6	1.5	0.5	80.9819	-2.0	2.3	8.2
71.	$(OH)_3{}^{29}Si^+$	$H_3O_3{}^{29}Si$	2.8	2.0	1.8	0.5	79.9847	2.6	5.5	-9.1
72.	$(OH)_3{}^{28}Si^+$	$H_3O_3{}^{28}Si$	44.1	39.2	28.5	0.5	78.9851	2.5	5.2	-8.0
73.	$(CH_3O)(HO)(H)^{29}Si^+$	$CH_5O_2{}^{29}Si$	0.6	0.4	0.3	0.5	78.0054	>10	—	-2.8
74.	$(CH_3O)(HO)(H)^{28}Si^+$	$CH_5O_2{}^{28}Si$	4.9	3.7	3.1	0.5	77.0058	3.2	5.4	-6.5
75.	$(C_2H_5O)(H)_2{}^{29}Si^+$	$C_2H_7O^{29}Si$	1.1	0.9	0.8	0,5	76.0261	—	—	—
76.	$(C_2H_5O)(H)_2{}^{28}Si^+$	$C_2H_7O^{28}Si$	3.0	2.3	2.1	0.5	75.0266	>10	—	5.2
77.	$(H)_3{}^{29}Si–O–C^+=CH_2$	$C_2H_5O^{29}Si$	1.2	1.0	0.9	1.5	74.0105	-1.8	0.1	-7.2
78.	$(H)_3{}^{28}Si–O–C^+=CH_2$	$C_2H_5O^{28}Si$	3.3	2.5	2.2	1.5	73.0109	2.0	1.2	-3.3
79.	$(OH)_2(H)^{30}Si^+$	$H_3O_2{}^{30}Si$	1.4	0.9	0.6	0.5	64.9870	2.4	-0.1	-0.7
80.	$(OH)_2(H)^{29}Si^+$	$H_3O_2{}^{29}Si$	1.8	1.2	1.0	0.5	63.9898	5.7	-4.0	1.8
81.	$(OH)_2{}^{30}Si^{+\cdot}$	$H_2O_2{}^{30}Si$	↑+	↑+	↑+	0.5	63.9793	3.2	-4.6	-0.2
82.	$(OH)_2(H)^{28}Si^+$	$H_3O_2{}^{28}Si$	27.1	18.5	14.1	0.5	62.9902	3.6	-4.0	0.2
83.	$(OH)_2{}^{29}Si^{+\cdot}$	$H_2O_2{}^{29}Si$	↑+	↑+	0.4	0.5	62.9820	3.2	-4.6	-0.2
84.	$(OH)_2{}^{28}Si^{+\cdot}$	$H_2O_2{}^{28}Si$	12.7	8.5	7.0	0.5	61.9824	3.2	-4.7	-0.2
85.	$(CH_3O)(H)_2{}^{28}Si^+$	$CH_5O^{28}Si$	2.1	1.1	1.0	0.5	61.0109	—	-6.3	2.4
86.	$(OH)(H)_2{}^{29}Si^+$	$H_3O^{29}Si$	—	—	—	0.5	47.9948	—	—	—
87.	$(OH)(H)_2{}^{28}Si^+$	$H_3O^{28}Si$	1.2	0.7	0.8	0.5	46.9953	>10	6.4	-0.3
88.	$(OH)^{30}Si^+$	$HO^{30}Si$	↑+	0.5	0.3		46.9765	-8.0	6.6	—
89.	$(OH)^{29}Si^+$	$HO^{29}Si$	0.9	0.7	0.5		45.9792	1.5	-4.7	—
90.	$(OH)^{28}Si^+$	$HO^{28}Si$	10.5	9.0	6.5		44.9796	5.2	1.2	—
91.	$H_3{}^{29}Si^+$	$H_3{}^{29}Si$	—	—	—		31.9999	—	—	—
92.	$H_3{}^{28}Si^+$	$H_3{}^{28}Si$	1.3	0.5	0.4		31.0004	<-10	—	—
93.	$H^{29}Si^+$	$H^{29}Si$	0.4	0.2	—		29.9843	—	—	—
94.	$H^{28}Si^+$	$H^{28}Si$	9.8	6.6	0.9		28.9847	<-10	—	—
95.	$C_2H_5{}^+$	C_2H_5	—	1.3	1.1	0.5	29.0391	0.3	-3.3	—

Legend: * the average of six determinations; > 10 mmu and <-10mmu outside of the accepted error; — absent ion from the spectrum.
↑ +summation with previous ion

As the resolution increases the sensitive of the mass spectrometer decreases. The resolutions of 5000-6000 (Table 2) are optimal for a tandem GC-MS as the one used for the determinations of this work. In this way they can get sufficiently intense ions at a high resolution at which the error of measurement of their mass does not exceed ±10 mmu (atomic mass milliunits).

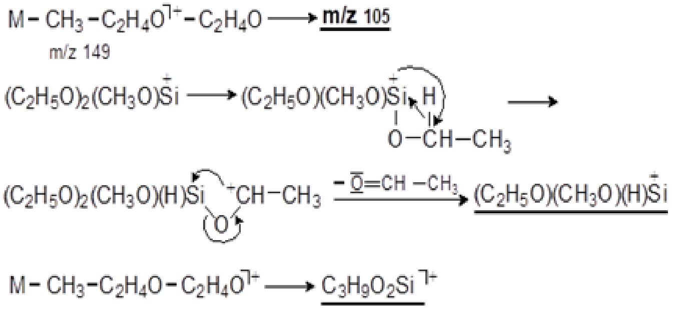
The most difficult to separate are the TEOS ions with the same nominal mass and which differ only by fractions of a whole mass, e.g. the ions with the order numbers: 15-16, 22-23, 29-30, 37-38, 40-41, 47-48, 50-51, 52-53, 54-56, 63-64, 66-67, 80-81, 82-83, 87-88 and 94-95, with the nominal masses 165, 151, 137, 123, 121, 109, 107, 106, 105, 93, 91, 64, 63, 47 and 29 respectively (Table 2 in the gray background).

In the Table 2 are shown the structural and ionic formulas of the ions obtained at high resolutions. An argument concerning the existence of these ions is the accurate mass measure with the specified error (±10 mmu) at high resolution: 5000, 6600 toward the standard resolution 1000. Another argument for the existence of ions is the double bond equivalent encoded as DBE.

The separation of the ions with nominal mass 105 at high resolution

An example of separating at high resolution is that of the ions with nominal mass 105 with the ordinal number 54-56 in Table 2. The ion $C_3H_9O_2{}^{28}Si^+$ obtained on the reaction pathway B.1.2.1. (Table 4), according to Equation (1) has the exact mass M=105,0372. It is separated from the ion $C_2H_5O_3{}^{28}Si^+$ obtained on the reaction pathway B.4.7. (Table 4), according to Equation (2), and which has the exact mass M=105,0008.

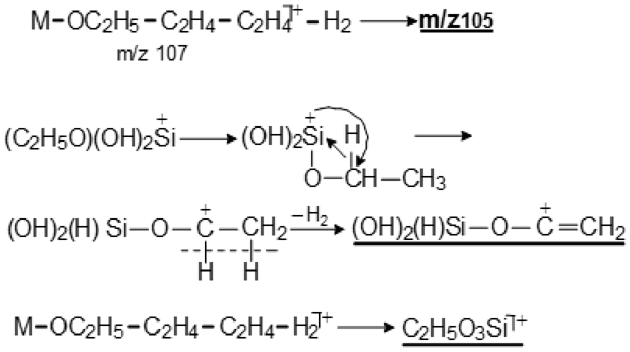
B.1.2.1. $M - CH_3 - C_2H_4O - C_2H_4O]^{+}$ m/z 105 I = 5.3 %



(1)

M_{ELE} =105.0372 M_{OBS} =105.0363 ΔM = 0.8 mmu DBE=0.5

B.4.7 $M - OC_2H_5 - C_2H_4O - H_2]^{+}$ m/z 105 I = 4.0 %



(2)

M_{ELE} =105.0008 M_{OBS} =104.9960 ΔM = 4.8 mmu DBE=1.5

The minimum resolution required for the separation of the ions with nominal mass 105 is R=105/0,0371=2830. At the resolution R=1000 the three ions with nominal mass 105 have total intensity 9,9 % (Table 2, the positions 54-56). At the optimum resolution R=5000, between resolution power and sensitivity of mass spectrometer, the ions $C_3H_9O_2{}^{28}Si^+$ and $C_2H_5O_3{}^{28}Si^+$ were separated having the intensities 5.3% and 4.1% respectively (Table 2, the positions 54-55), according to the reaction pathways B.1.2.1. and B.4.7. in Table 4.

Figure 2 shows the mass spectrum of TEOS in the range m/e 104-106 with the separation of these two ions at a resolution R=5000. The observed masses 104.9960 and 105.0363 respectively fall into the preset error of ±10 mmu.

The ion $C_3H_7O_2{}^{30}Si^+$ with exact mass 105.0184 obtained through M+2 isotope effect can be separated from each of the two ions with nominal mass 105 discussed above at a resolution of about 6,000, but this ion can not be revealed because of its low intensity.

Accurately measuring the ion masses is a strong argument for confirming the reaction pathways in mass spectrum. This argument of the existence of ions must be confirmed by other arguments as the isotopic effects, the equivalent of double bonds, etc.

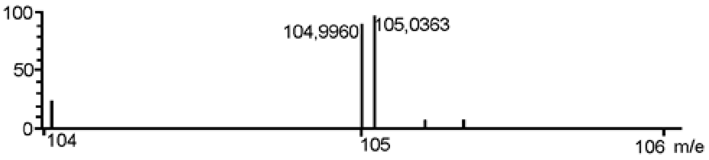


Fig. 2. The separation of the fragmentation ions $C_3H_9O_2\,^{28}Si^+$ with mass 105.0372 and $C_2H_5O_3\,^{28}Si^+$ with mass105.0008 at high resolution (R=5000) with preset error of ± 10 mmu

Isotopic effects of ions in the TEOS mass spectrum

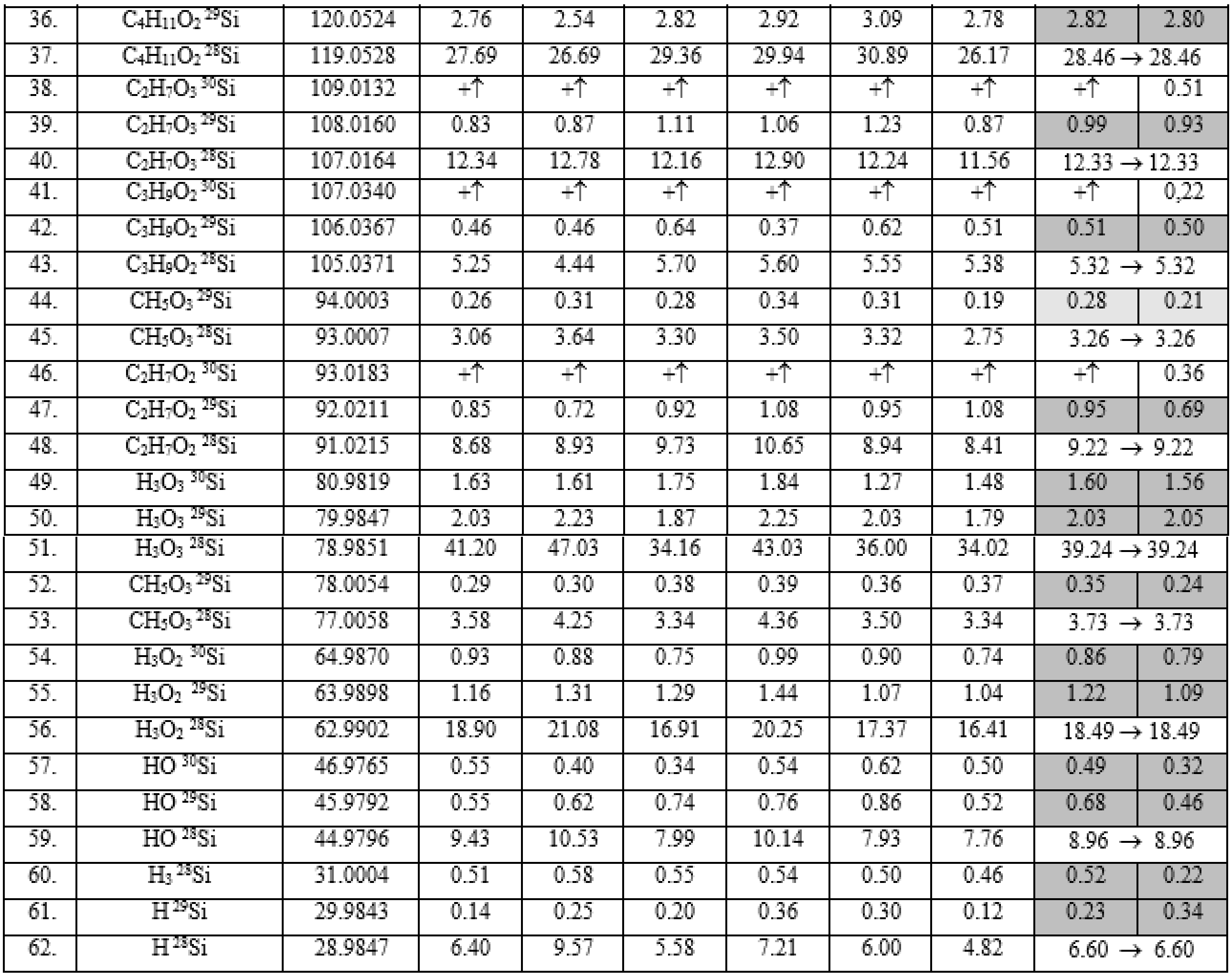
According to the isotopic distributions of the atoms that compose an silicon alkoxide as TEOS, the strongest M+1 and M+2 isotopic effects are due to silicon atom (4.67 and 3.10%) followed by the M+1 isotopic effect of carbon atom (1.1%). The M+2 isotopic effect of the silicon atom is selective in the case of silicon alkoxides and substituted alkoxides without halogen atoms [1-3, 17].

In Table 3 are presented the measurements of M+1 and M+2 isotopic effects at optimal resolution (R=5000).

Table 3

THE M+1 AND M+2 ISOTOPIC EFFECTS (GRAY BACKGROUND CELLS) FOR IONS FROM THE TEOS MASS SPECTRUM AT THE HIGH RESOLUTION (R=5000)

Entry	Ionic formulas	Accurate mass	The ion intensity from the TEOS mass spectrum at the high resolution (R=5000)						I_A %	I_C %
			1	2	3	4	5	6		
1.	$C_8H_{20}O_4\,^{30}Si$	210.1099	0.85	0.68	0.86	0.93	0.80	0.73	0.81	0.84
2.	$C_8H_{20}O_4\,^{29}Si$	209.1126	2.65	3.19	2.92	3.45	2.75	2.92	2.98	2.42
3.	$C_8H_{20}O_4\,^{28}Si$	208.1130	15.19	16.48	17.25	17.18	17.67	15.95	16.62 → 16.62	
4.	$C_7H_{17}O_4\,^{30}Si$	195.0864	4.07	3.97	5.51	4.96	4.96	4.22	4.62	4.91
5.	$C_7H_{17}O_4\,^{29}Si$	194.0891	11.56	12.28	12.31	12.91	12.38	12.57	12.34	13.41
6.	$C_7H_{17}O_4\,^{28}Si$	193.0896	100.0	100.0	100.0	100.0	100.0	100.0	100.0→ 100.0	
7.	$C_6H_{15}O_4\,^{30}Si$	181.0708	1.34	1.33	2.02	1.44	1.65	1.42	1.53	1.14
8.	$\mathbf{C_6H_{15}O_4\,^{29}Si}$	**180.0735**	**3.33**	**3.39**	**4.00**	**3.61**	**4.19**	**3.59**	3.69	2.92
9.	$C_6H_{15}O_4\,^{28}Si$	179.0739	23.22	24.77	24.16	23.42	24.48	23.10	23.86 → 23.86	
10.	$C_5H_{13}O_4\,^{30}Si$	167.0551	0.46	0.31	0.77	0.72	0.62	0.56	0.57	0.31
11.	$C_5H_{13}O_4\,^{29}Si$	166.0578	0.63	0,49	1.01	0.79	0.86	0.74	0.75	0.78
12.	$C_5H_{13}O_4\,^{28}Si$	165.0583	6.82	5.49	7.71	5.93	6.99	6.68	6.60 → 6.60	
13.	$C_6H_{15}O_3\,^{30}Si$	165.0758	+↑	+↑	+↑	+↑	+↑	+↑	+↑	2.56
14.	$C_6H_{15}O_3\,^{29}Si$	164.0786	6.49	6.67	6.47	6.22	6.58	6.20	6.44	6.84
15.	$C_6H_{15}O_3\,^{28}Si$	163.0790	57.85	56.90	56.23	56.66	56.80	55.24	56.61→ 56.61	
16.	$C_4H_{11}O_4\,^{30}Si$	153.0395	0.42	0.38	0.74	0.72	0.62	0.44	0.55	0.26
17.	$C_4H_{11}O_4\,^{29}Si$	152.0422	0.54	0.46	0.45	0.45	0.41	0.51	0.47	0.58
18.	$C_4H_{11}O_4\,^{28}Si$	151.0426	5.63	5.11	6.62	5.92	6.17	5.55	5.84 → 5.84	
19.	$C_5H_{13}O_3\,^{29}Si$	150.0626	8.33	7.94	9.17	9.00	8.72	7.62	8.46	8.96
20.	$C_5H_{13}O_3\,^{28}Si$	149.0633	79.75	78.82	83.5	82.82	83.91	78.32	81.11 → 81.11	
21.	$C_3H_9O_3\,^{30}Si$	139.0238	0.33	0.31	0.53	0.32	0.42	0.50	0.40	0.11
22.	$C_3H_9O_4\,^{29}Si$	138.0265	0.16	0.23	0.30	0.39	0.36	0.21	0.28	0.21
23.	$C_3H_9O_4\,^{28}Si$	137.0270	2.23	1.86	2.96	2.41	2.67	2.37	2.42 → 2.42	
24.	$C_4H_{11}O_3\,^{30}Si$	137.0445	+↑	+↑	+↑	+↑	+↑	+↑	+↑	0.78
25.	$C_4H_{11}O_3\,^{29}Si$	136.0473	1.70	1.81	1.84	1.61	2.06	1.60	1.77	1.78
26.	$C_4H_{11}O_3\,^{28}Si$	135.0477	18.14	18.69	18.59	18.96	17.90	16.04	18.05 → 18.05	
27.	$C_4H_9O_3\,^{29}Si$	134.0316	0.28	0.31	0.46	0.43	0.41	0.37	0.38	0.20
28.	$C_4H_9O_3\,^{28}Si$	133.0321	1.70	1.75	2.48	2.23	1.95	2.17	2.05 → 2.05	
29.	$C_2H_7O_4\,^{30}Si$	125.0082	0.28	0.23	0.55	0.58	0.41	0.31	0.39	0.15
30.	$C_2H_7O_4\,^{29}Si$	124.0109	0.14	0.19	0.37	0.54	0.41	0.26	0.32	0.26
31.	$C_2H_7O_4\,^{28}Si$	123.0113	3.29	2.89	3.68	3.62	4.11	3.01	3.43 → 3.43	
32.	$C_3H_9O_3\,^{30}Si$	123.0289	+↑	+↑	+↑	+↑	+↑	+↑	+↑	0.19
33.	$C_3H_9O_3\,^{29}Si$	122.0316	0.45	0.38	0.74	0.54	0.84	0.38	0.56	0.40
34.	$C_3H_9O_3\,^{28}Si$	121.0329	4.01	4.30	5.59	4.78	4.53	4.08	4.55 → 4.55	
35.	$C_4H_{11}O_2\,^{30}Si$	121.0496	+↑	+↑	+↑	+↑	+↑	+↑	+↑	1.17



36.	$C_4H_{11}O_2\,^{29}Si$	120.0524	2.76	2.54	2.82	2.92	3.09	2.78	2.82	2.80
37.	$C_4H_{11}O_2\,^{28}Si$	119.0528	27.69	26.69	29.36	29.94	30.89	26.17	28.46 → 28.46	
38.	$C_2H_7O_3\,^{30}Si$	109.0132	+↑	+↑	+↑	+↑	+↑	+↑	+↑	0.51
39.	$C_2H_7O_3\,^{29}Si$	108.0160	0.83	0.87	1.11	1.06	1.23	0.87	0.99	0.93
40.	$C_2H_7O_3\,^{28}Si$	107.0164	12.34	12.78	12.16	12.90	12.24	11.56	12.33 → 12.33	
41.	$C_3H_9O_2\,^{30}Si$	107.0340	+↑	+↑	+↑	+↑	+↑	+↑	+↑	0,22
42.	$C_3H_9O_2\,^{29}Si$	106.0367	0.46	0.46	0.64	0.37	0.62	0.51	0.51	0.50
43.	$C_3H_9O_2\,^{28}Si$	105.0371	5.25	4.44	5.70	5.60	5.55	5.38	5.32 → 5.32	
44.	$CH_5O_3\,^{29}Si$	94.0003	0.26	0.31	0.28	0.34	0.31	0.19	0.28	0.21
45.	$CH_5O_3\,^{28}Si$	93.0007	3.06	3.64	3.30	3.50	3.32	2.75	3.26 → 3.26	
46.	$C_2H_7O_2\,^{30}Si$	93.0183	+↑	+↑	+↑	+↑	+↑	+↑	+↑	0.36
47.	$C_2H_7O_2\,^{29}Si$	92.0211	0.85	0.72	0.92	1.08	0.95	1.08	0.95	0.69
48.	$C_2H_7O_2\,^{28}Si$	91.0215	8.68	8.93	9.73	10.65	8.94	8.41	9.22 → 9.22	
49.	$H_3O_3\,^{30}Si$	80.9819	1.63	1.61	1.75	1.84	1.27	1.48	1.60	1.56
50.	$H_3O_3\,^{29}Si$	79.9847	2.03	2.23	1.87	2.25	2.03	1.79	2.03	2.05
51.	$H_3O_3\,^{28}Si$	78.9851	41.20	47.03	34.16	43.03	36.00	34.02	39.24 → 39.24	
52.	$CH_5O_3\,^{29}Si$	78.0054	0.29	0.30	0.38	0.39	0.36	0.37	0.35	0.24
53.	$CH_5O_3\,^{28}Si$	77.0058	3.58	4.25	3.34	4.36	3.50	3.34	3.73 → 3.73	
54.	$H_3O_2\,^{30}Si$	64.9870	0.93	0.88	0.75	0.99	0.90	0.74	0.86	0.79
55.	$H_3O_2\,^{29}Si$	63.9898	1.16	1.31	1.29	1.44	1.07	1.04	1.22	1.09
56.	$H_3O_2\,^{28}Si$	62.9902	18.90	21.08	16.91	20.25	17.37	16.41	18.49 → 18.49	
57.	$HO\,^{30}Si$	46.9765	0.55	0.40	0.34	0.54	0.62	0.50	0.49	0.32
58.	$HO\,^{29}Si$	45.9792	0.55	0.62	0.74	0.76	0.86	0.52	0.68	0.46
59.	$HO\,^{28}Si$	44.9796	9.43	10.53	7.99	10.14	7.93	7.76	8.96 → 8.96	
60.	$H_3\,^{28}Si$	31.0004	0.51	0.58	0.55	0.54	0.50	0.46	0.52	0.22
61.	$H\,^{29}Si$	29.9843	0.14	0.25	0.20	0.36	0.30	0.12	0.23	0.34
62.	$H\,^{28}Si$	28.9847	6.40	9.57	5.58	7.21	6.00	4.82	6.60 → 6.60	

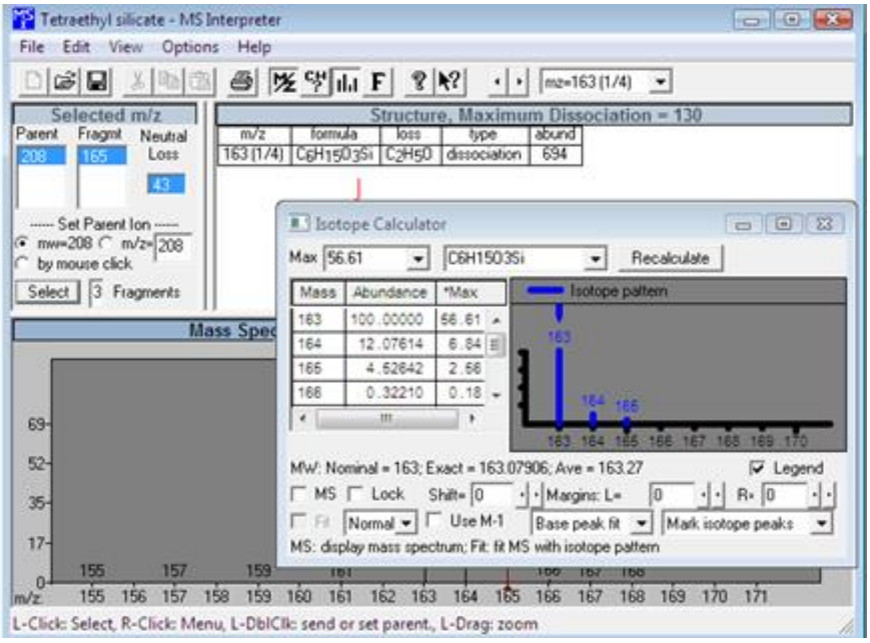
Legend: I_A: The average of six intensities obtained experimentally; I_C: The M+1 and M+2 intensities calculated based on the M experimental values (the ions with ^{28}Si) indicated by symbol →.

To calculate more precisely the M+1, M+2 isotopic effects, the ion intensity was measured on a statistical basis at high resolution (R=5000). The average intensity of each ion in the mass spectrum was obtained with a Merck standard of tetraethoxysilane by GC-MS analysis repeated six times; the average value of an ion intensity was encoded I_A. Theoretical isotopic effects (I_T) calculated by an ISO dedicated program [17] were compared with these experimental average values. The basis for calculation of the theoretical isotopic effects was the experimental average value of the intensities of ions with the isotope 28 of the silicon atom, indicated in Table 1, with the side arrow. The values of experimental and theoretical M+1and M+2 isotopic effects are shown in the same table in cells on gray background.

There is a good agreement between the experimental M+1 and M+2 isotopic effects and those calculated theoretically for the most of ions in the TEOS mass spectrum.

Sometimes it is necessary to correct the occurring interferences. Thus the ion $C_6H_{15}O_3\,^{30}Si$ with the ionic mass 165.0758 obtained as M+2 isotope effect of the ion $C_6H_{15}O_3\,^{28}Si$ with the ionic mass 163.0790 (Table 3) overlaps the ion $C_5H_{13}O_4\,^{28}Si$ with the ionic mass 165.0583. The resolution R=5000 is insufficient in this case to that required R=9429, at the mass difference between the two ions of only 0.0175. The calculated M+2 isotope effect of the ion $C_6H_{15}O_3\,^{28}Si$ (Table 3, the position 12) is 2.56% (Fig. 3) and is different from the 6.60% average intensity of the ion $C_5H_{13}O_4\,^{28}Si$, which is actually a sum of intensities of the two unseparated mentioned ions. These deviations from the calculated isotopic effects often indicate new fragmentation pathways that can be highlighted for example by operating at a higher resolution.

The ions of TEOS mass spectrum were obtained experimentally by the B/E and B/E(1-E)$^{1/2}$ linked scans presented in Part I and Part II [1-2] and by accurate mass meassurements at high resolutions in present work. Thus, there can be written the 38 fragmentation pathways for the primary events and eliminations of neutral molecules, only for the ions with ^{28}Si isotope (Table 4).



Structure, Maximum Dissociation = 130

m/z	formula	loss	type	abund
163 (1/4)	$C_6H_{15}O_3Si$	C_2H_5O	dissociation	694

● mw=208 ○ m/z= 208

3 Fragments

Max 56.61 C6H15O3Si

Mass	Abundance	*Max
163	100.00000	56.61
164	12.07614	6.84
165	4.52642	2.56
166	0.32210	0.18

MW: Nominal = 163; Exact = 163.07906; Ave = 163.27

☑ Legend

☐ MS ☐ Lock Shift= 0 Margins: L= 0 R= 0

☐ Fit Normal ☐ Use M-1 Base peak fit Mark isotope peaks

MS: display mass spectrum; Fit: fit MS with isotope pattern

Fig. 3. The M+2 isotopic effect (2.56 %) of the ion $C_6H_{15}O_3{}^{28}Si$ with accurate mass 163.0790 and the average intensity in TEOS mass spectrum (56.61%) at high resolution 5000.

Table 4
THE MASS SPECTRUM OF TETRAETHOXYSILANE. FRAGMENTATION PATHWAYS BY LINKED SCANS AND ACCURATE MASSES

TEOS	$C_8H_{20}O_4Si$	$(C_2H_5O)_4Si$	M=208,1130

I. The ionisation process

$M - e \longrightarrow M^{+\cdot}$	$208 - e \longrightarrow 208.1100^{+\cdot}$

II. Fragmentation pathways

A.Primary events: cleavage of σ bonds and radical eliminations

A.1.	$M^{+\cdot} - H^{\bullet +}$	$\rightarrow$ 207.1036^{+}	$\leftarrow 208^{+\cdot} - 1^{\bullet +}$
A.2.	$M^{+\cdot} - CH_3{}^{\bullet +}$	$\rightarrow$ 193.0888^{+}	$\leftarrow 208^{+\cdot} - 15^{\bullet +}$
A.3.	$M^{+\cdot} - C_2H_5{}^{\bullet +}$	$\rightarrow$ 179.0716^{+}	$\leftarrow 208^{+\cdot} - 29^{\bullet +}$
A.4.	$M^{+\cdot} - OC_2H_5{}^{\bullet +}$	$\rightarrow$ 163.0794^{+}	$\leftarrow 208^{+\cdot} - 45^{\bullet +}$

B. Eliminations of neutral molecules

B.1. Elimination of acetaldehide: CH_3CHO M=44 44		**B.2. Elimination of ethylene: $CH_2 = CH_2$ M= 28**	
B.1.1.1.	$207^{+} - 44 \longrightarrow 163.0794^{+}$	**B.2.1.1.**	$207^{+} - 28 \longrightarrow 179.0746^{+}$
2.	$193^{+} - 44 \longrightarrow 149.0639^{+}$	**2.**	$193^{+} - 28 \longrightarrow 165.0522^{+}$
3.	$179^{+} - 44 \longrightarrow 135.0477^{+}$	**3.**	$179^{+} - 28 \longrightarrow 151.0401^{+}$
4.	$163^{+} - 44 \longrightarrow 119.0535^{+}$	**4.**	$163^{+} - 28 \longrightarrow 135.0477^{+}$
B.1.2.1.	$149^{+} - 44 \longrightarrow 105.0363^{+}$	**B.2.2.1.**	$165^{+} - 28 \longrightarrow 137.0205^{+}$
2.	$135^{+} - 44 \longrightarrow 91.0310^{+}$	**2.**	$151^{+} - 28 \longrightarrow 123.0088^{+}$
3.	$119^{+} - 44 \longrightarrow 75.0318^{+}$	**3.**	$135^{+} - 28 \longrightarrow 107.0158^{+}$
B.1.3.1.	$105^{+} - 44 \longrightarrow 61.0133^{+}$	**B.2.3.1.**	$137^{+} - 28 \longrightarrow 108.9880^{+}$
2.	$91^{+} - 44 \longrightarrow 46.9977^{+}$	**2.**	$123^{+} - 28 \longrightarrow 94.9716^{+}$
3.	$75^{+} - 44 \longrightarrow 31.0016^{+}$	**3.**	$107^{+} - 28 \longrightarrow 78.9903^{+}$

B.3. Mixt elimination of acetaldehide and ethylene			
B.3.1.	$M^{+\cdot} - CH_3{}^{\bullet} - C_2H_4 - C_2H_4O$	$\longrightarrow$	121.0294^{+}
B.3.2.	$M^{+\cdot} - CH_3{}^{\bullet} - C_2H_4O - C_2H_4 - C_2H_4$	$\longrightarrow$	92.9951^{+}
B.3.3.	$M^{+\cdot} - CH_3{}^{\bullet} - C_2H_4O - C_2H_4O - C_2H_4$	$\longrightarrow$	77.0112^{+}
B.3.4.	$M^{+\cdot} - OC_2H_5{}^{\bullet} - C_2H_4O - C_2H_4 - C_2H_4O$	$\longrightarrow$	62.9904^{+}

B.4. Elimination of hydrogen molecule	
(1) $193^{+} - 2 \longrightarrow 191.0705^{+}$	(6) $119^{+} - 2 \longrightarrow 117.0412^{+}$
(2) $179^{+} - 2 \longrightarrow 177.0588^{+}$	(7) $107^{+} - 2 \longrightarrow 104.9960^{+}$
(3) $163^{+} - 2 \longrightarrow 161.0573^{+}$	(8) $105^{+} - 2 \longrightarrow 103.0215^{+}$
(4) $149^{+} - 2 \longrightarrow 147.0452^{+}$	(9) $91^{+} - 2 \longrightarrow 88.9979^{+}$
(5) $135^{+} - 2 \longrightarrow 133.0239^{+}$	(10) $75^{+} - 2 \longrightarrow 73.0211^{+}$

Conclusions

The aim of these tree articles (Part I-III) was the interpretation of tetraethoxysilane (TEOS) mass spectrum, as a precursor in the sol-gel process.

The procedure for the interpretation of mass spectra for alcoxysilanes presented in Part I [1] was applied for tetraethoxysilane (TEOS). This procedure has a practical importance for the identification of unknown chemical compounds when it is possible the application of double focusing GC-MS method and linked scans.

In this third and final Part, the arguments for the existence of 95 ions in TEOS mass spectrum (Table 2) are presented by experimental accurate mass measurements at high resolutions (5000 and 6600), and calculate the double bonds equivalent (DBE). A detailed example is presented: the separation of the ion $C_3H_9O_2\,{}^{28}Si^+$ with mass 105.0372 and the ion $C_2H_5O_3\,{}^{28}Si^+$ with mass 105.0008 at high resolution (R=5000).

There are also presented experimental measurements of the M+1 and M+2 isotopic effects at high resolution (5000) for the most intense 22 ions of TEOS mass spectrum (Table 3).

The ions of TEOS mass spectrum were obtained experimentally by the B/E and $B/E(1-E)^{1/2}$ linked scans presented in Part I and Part II [1-2] and by accurate mass meassurements at high resolutions in present work. Thus, there can be written the 38 fragmentation pathways for the primary events and eliminations of neutral molecules, only for the ions with ^{28}Si isotope (Table 4).

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