

TEOS Oligomers and Transesters Identified by GC-MS in the sol-gel Process. Operational Mass Spectral Libraries

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Abstract. The aim of this article is the presentation of new user mass spectral libraries created based on unambiguous assigning of the mass spectra of the tetraethoxysilane (TEOS) oligomers and transesters obtained in the sol-gel process. Gas-chromatography coupled with mass spectrometry (GC-MS) was used to unambiguous identification the TEOS oligomers and transesters obtained in the hydrolysis, condensation and transesterification, reactions of tetraethoxysilane in parental solvent (EtOH) and nonparental solvents (MeOH and n-PrOH). The author's procedure for the interpretation of mass spectra of silicon alkoxides was applied for TEOS, TEOS dimer, methoxy-transesters, and TEOS cyclic tetramer. GC and MS arguments for unambiguous assigning of TEOS oligomers and transesters in the sol-gel process were presented. Experimental B/E and B/E(1-E)^{1/2} linked scans, accurate mass at high resolution and M+1, M+2 isotopic effects, applied in previous works, were used as MS arguments. The NBS mass spectral library run under the RSX-11-PLUS operating system was used to create new mass spectral libraries. In this article are presented three user mass spectral libraries codified: TRANSME0 for methoxy-transesters, PROPOXY1 for propoxy-transesters in the histogram plot and tabular format and ICECHIM6 (first 12 entries in histogram plot format) for TEOS oligomers in the parental solvent.

Keywords: TEOS oligomers and transesters, sol-gel process, GC-MS arguments, user mass spectral libraries

1. Introduction

The basic factors that influence the sol-gel process have been studied systematically by GC-MS [1]: type of precursor alkoxide (ethanol in Table 1), the solvent nature (equation 1-11), the water quantity used in hydrolysis, the reactant mixing order and the catalyst type. The results were published between 1994 and 2007 [3-9].

 Table 1. TEOS as precursor alkoxide. The initial HCl

catalyzed reaction mixtures	
<u>Si(</u> OC ₂ H ₅) ₄ : H ₂ O : C ₂ H ₅ OH	(1)
<u>Si(</u> OC ₂ H ₅) ₄ : H ₂ O : CH ₃ OH	(2)
$Si(OC_2H_5)_4$: H ₂ O : C ₃ H ₇ OH	(3)
In the ratios 1:1:1.75 (mol/mol)	

Equation 1-11 Types of chemical reactions in the sol-gel process: The solvent nature.

A. HYDROLYSIS - CONDENSATION REACTIONS

 $\begin{array}{l} (C_{2}H_{5}O)_{4}Si + H_{2}O \rightleftharpoons (C_{2}H_{5}O)_{3}Si(OH) + C_{2}H_{5}OH \\ (1) \\ 2(C_{2}H_{5}O)_{3}Si(OH) \rightleftharpoons (C_{2}H_{5}O)_{3}Si - O - Si(OC_{2}H_{5})_{3} + H_{2}O \\ (C_{2}H_{5}O)_{3}Si(OH) + (C_{2}H_{5}O)_{4}Si \rightleftharpoons (C_{2}H_{5}O)_{3}Si - O - Si(OC_{2}H_{5})_{3} + C_{2}H_{5}OH \\ etc. \end{array}$

B. TRANSESTERIFICATION REACTIONS

(1) ETHOXY \rightarrow METHOXY (C₂H₅O)₄Si + CH₃OH \rightleftharpoons (CH₃O)Si(OC₂H₅)₃ + C₂H₅OH (4) (CH₃O)Si(OC₂H₅)₃ + CH₃OH \rightleftharpoons (CH₃O)₂Si(OC₂H₅)₂ + C₂H₅OH (5) etc.

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(2) ETHOXY \rightarrow PROPOXY	
$(C_2H_5O)_4Si + C_3H_7OH \rightleftharpoons (C_3H_7O)Si(OC_2H_5)_3 + C_2H_5OH$	(6)
$(C_{3}H_{7}O)Si(OC_{2}H_{5})_{3} + C_{3}H_{7}OH \rightleftharpoons (C_{3}H_{7}O)_{2}Si(OC_{2}H_{5})_{2} + C_{2}H_{5}OH$	(7)
etc.	
HYDROLYSIS OF TRANSESTERS	
(1) METHOXY	
$(CH_3O)Si(OC_2H_5)_3 + H_2O \rightleftharpoons (CH_3O)(C_2H_5O)_2Si(OH) + C_2H_5OH$	(8)
$(CH_3O)_2Si(OC_2H_5)_2 + H_2O \rightleftharpoons (CH_3O)_2(C_2H_5O)Si(OH) + C_2H_5OH$	(9)
etc.	
(2) PROPOXY	
$(C_3H_7O)Si(OC_2H_5)_3 + H_2O \rightleftharpoons (C_3H_7O)(C_2H_5O)_2Si(OH) + C_2H_5OH$	(10)
$(C_{3}H_{7}O)_{2}Si(OC_{2}H_{5})_{2} + H_{2}O \rightleftharpoons (C_{3}H_{7}O)_{2}(C_{2}H_{5}O)Si(OH) + C_{2}H_{5}OH$	(11)
etc.	
	(2) ETHOXY \rightarrow PROPOXY (C ₂ H ₅ O) ₄ Si + C ₃ H ₇ OH \rightleftharpoons (C ₃ H ₇ O)Si(OC ₂ H ₅) ₃ + C ₂ H ₅ OH (C ₃ H ₇ O)Si(OC ₂ H ₅) ₃ + C ₃ H ₇ OH \rightleftharpoons (C ₃ H ₇ O) ₂ Si(OC ₂ H ₅) ₂ + C ₂ H ₅ OH etc. HYDROLYSIS OF TRANSESTERS (1) METHOXY (CH ₃ O)Si(OC ₂ H ₅) ₃ + H ₂ O \rightleftharpoons (CH ₃ O)(C ₂ H ₅ O) ₂ Si(OH) + C ₂ H ₅ OH (CH ₃ O) ₂ Si(OC ₂ H ₅) ₂ + H ₂ O \rightleftharpoons (CH ₃ O) ₂ (C ₂ H ₅ O)Si(OH) + C ₂ H ₅ OH etc. (2) PROPOXY (C ₃ H ₇ O)Si(OC ₂ H ₅) ₃ + H ₂ O \rightleftharpoons (C ₃ H ₇ O)(C ₂ H ₅ O) ₂ Si(OH) + C ₂ H ₅ OH (C ₃ H ₇ O)Si(OC ₂ H ₅) ₂ + H ₂ O \rightleftharpoons (C ₃ H ₇ O) ₂ (C ₂ H ₅ O)Si(OH) + C ₂ H ₅ OH (C ₃ H ₇ O) ₂ Si(OC ₂ H ₅) ₂ + H ₂ O \rightleftharpoons (C ₃ H ₇ O) ₂ (C ₂ H ₅ O)Si(OH) + C ₂ H ₅ OH (C ₃ H ₇ O) ₂ Si(OC ₂ H ₅) ₂ + H ₂ O \rightleftharpoons (C ₃ H ₇ O) ₂ (C ₂ H ₅ O)Si(OH) + C ₂ H ₅ OH (C ₃ H ₇ O) ₂ Si(OC ₂ H ₅) ₂ + H ₂ O \rightleftharpoons (C ₃ H ₇ O) ₂ (C ₂ H ₅ O)Si(OH) + C ₂ H ₅ OH

The first purpose of the author's thesis [1] was the separation and identification of molecular species obtained in the sol-gel process by gas chromatography coupled with mass spectrometry (GC-MS). An important reference for the application of GC-MS in the sol-gel process was Wheeler's thesis [2].

TEOS oligomers and transesters obtained by reactions (1) - (11) under the restrictive conditions (Table 1) were separated by gas chromatography (Figure 1) and identified by their mass spectra for propoxy-transesters (Figure 2); the mass spectra of methoxy-transesters are presented in a previous work [16] and for oligomers in the author's thesis [1].

The second purpose of the author's thesis [1] was the development of a procedure for the interpretation of mass spectra of some silicon alkoxides and their oligomers and transesters obtained by the sol-gel process [12]. We mention McLafferty's book [10] regarding the interpretation of mass spectra. A general procedure for the interpretation of mass spectra is presented in reference [11].

The author's procedure for the interpretation of mass spectra of silicon alkoxides [1,12] was applied for TEOS [12,13,15], TEOS dimer [14], methoxy-transesters [16] and TEOS cyclic tetramer [17].



Figure 1. The chromatograms for (a) mixture with parental solvent, (b) the mixture with lower nonparental solvent (MeOH), and (c) the mixture with higher nonparental solvent (PrOH)



Figure 2a-f. The mass spectra of TEOS propoxy-transesters: (a) TEOS, (b) PTR1M, (c) PTR2M, (d) PTR3M, (e) PTR4M (TPOS) from reaction mixture (3) in Table 1, (f) PTR4M (TPOS) from the NBS spectrum library

2. Materials and methods

GC-MS method and optimisation parameters used to obtain user mass spectra are presented in previous work [16] and in the author's thesis [1].

The NBS mass spectral library was used by the GC-MS tandem (the HP 5890 gas chromatograph and 70-SE, VG Analytical double-focusing mass spectrometer) under the RSX-11M-PLUS operating system. Because there were no mass spectra in this library for products resulting from the sol-gel process, except for the TEOS monomer, it was necessary to create mass spectral libraries for TEOS oligomers and transesters identified in the sol-gel process, taking into account GC retention times and mass spectrum interpretations through MS experiments for unequivocal assignations. By means of a standard procedure were introduced from the keyboard at each input of a newly created library of data pairs mass per charge (m/z), intensity for each fragment of the tabulated mass spectrum, name, formula and molecular weight (MW) of a molecular species [18].

The TurboMass software procedure for the NIST mass spectral library can also be used to create new mass spectral libraries [19].

3. Results and discussions

In addition to the libraries available (NBS, NIST, etc.), we create "user" libraries, based on the NBS mass spectral library under the RSX-11M-PLUS operating system [18], that contain mass spectra from data files obtained by the GC-MS method.

Molecular species obtained by reactions (1) - (11) under the restrictive conditions from the initial mixtures (Table 1) and at different times after the start were characterized by the GC-MS method.

- GC and MS arguments from previous works [3-9, 12-17] for the unambiguous identification of TEOS oligomers and transesters in the sol-gel process are presented.

3.1. The GC arguments

- The retention time of the methoxy-transesters is shorter than the retention time of TEOS [16].

- Similarly, the retention time of the monohydroxylated methoxy-transesters is shorter than the retention time of TEOS silanol.



- The retention time of TEOS silanol is longer than the retention time of TEOS since the first one forms a hydrogen bonding with the stationary phase (methyl silicone).

- The retention times of the propoxy-transesters are longer than the retention times of TEOS (Figure 2).

- Similarly, the retention times of the monohydroxylated propoxy-transesters are longer than the retention time of TEOS silanol.

3.2. The MS arguments

- The mass spectra of TEOS were obtained from a Merck etalon, NBS library and Wheeler thesis [2].

- Primary fragmentation reactions (broken σ bonds) and neutral molecules eliminations (formaldehyde, acetaldehyde, ethylene, molecular hydrogen) were written on the basis of information obtained experimentally by the B/E and B/E (1-E)1/2 linked scans [1, 12-14, 16-17].

- The strong arguments for the existence of ions of TEOS oligomers and transesters were based on high-resolution measurements (R = 5000) of their accurate masses, and M+1 and M+2 isotope effects measurements [1, 14-17].

- The author's procedure for the interpretation of mass spectra of silicon alkoxides [1,12] was applied for TEOS [12,13,15], TEOS dimer [14] methoxy-transesters [16] and TEOS cyclic tetramer [17].

- The mass spectra of the methoxy-transesters are similar to that of TEOS but contain molecular and fragmentation ions with 14 units less which correspond to the difference between the mass of the CH_3 - and C_2H_5 - groups [16]. The scrambling degree was complete. Similar considerations are valid in the case of the corresponding monohydroxylated methoxy-transesters.

- The mass spectra of the propoxy-transesters are similar to that of TEOS but contain molecular and fragmentation ions with 14 units higher which correspond to the difference between the mass of the C_2H_5 - and C_3H_7 groups (Figure 2a-f). Similar considerations are valid in the case of the corresponding monohydroxylated propoxy-transesters.

- The mass spectra of TEOS transesters exhibit the molecular ions which permit an easier identification. Accurate mass measurements and the M+1 and M+2 isotopic effects for the molecular ions of methoxy-transesters were used to confirm their identification [16,1].

3.3. Supplementary arguments

- The MOPAC program was used by calculating the net atomic charges as an additional theoretical argument for assigning structures for these molecular species [1,12,14].

- Double bond equivalent (DBE) or level of unsaturation present in an organic molecule was calculated using the following equation: DBE = C-(H/2)+(N/2)+1, where: C = number of carbon atoms, H = number of hydrogen and halogen atoms, and N = number of nitrogen atoms; details in [1,13,15,16].

By unambiguous assigning the mass spectra for the precursor alkoxides and for the hydrolysis, transesterification and condensation products from the sol-gel process, based on the above-mentioned arguments, new mass spectral libraries were realized. These mass spectral libraries were stored in the memory of the data acquisition and processing system of the double focus GC-MS tandem type 70-SE.

Table 2. Operational mass spectral noraries created in Analytical Department reperiment			
Reaction systems	Mass spectral library name code	Number of entries	Observations
TEOS : H ₂ O : EtOH	ICECHIM0 to ICECHIM9	10-33	TEOS oligomers
TEOS : H ₂ O : MeOH	TRANSME0	35	TEOS methoxy-transesters
TEOS : H ₂ O : PrOH	TRANSPR1	18	TEOS propoxy-transesters

Table 2. Operational mass spectral libraries created in Analytical Department ICECHIM

We presented the mass spectral library with 12 entries, coded ICECHIM6. This library was created based on the molecular species obtained from the reaction mixture with the parent solvent at 96 h after the start. The chromatogram with the separation of these species is presented in Figure 1a, and the mass



spectra of the 12 entries of the ICECHIM6 library from monomers to cyclic tetramers of TEOS are presented in Figure 3.1-3.12.



Figure 3.1-3.12. The mass spectra of TEOS oligomers from monomers to tetramers in the ICECHIM6 library

The mass spectral library with 35 entries, coded TRANSME0, was created based on the molecular species obtained from the start reaction mixture with lower nonparental solvent (MeOH). The chromatogram with the separation of these species is presented in Figure 1b and the mass spectra of the 35 entries of the TRANSME0 library from monomers to trimers of TEOS transesters are presented in Figure 4.1-4.35 in the histogram plot format. The mass spectra of these 35 entries are shown in the tubular form in Figure 5.0-5.34.

The numbering of the mass spectra in the histogram plot format from 1 to 35 corresponds to the numbering of the mass spectra from 0 to 34 in the tabular form.

The mass spectral library with 18 entries, coded TRANSPR1, was created based on the species obtained with the reaction mixture with higher nonparental solvent (PrOH) at 24 h after the start.

The chromatogram with the separation of these species is presented in Figure 1c, and the mass spectra of the 18 entries of the TRANSME0 library from monomers to dimers of TEOS transesters are presented in Figure 6.1-6.18. The mass spectra of these 18 entries are presented in the tabular form in Figure 7.0-1.18.

The numbering of the mass spectra in the histogram plot format from 1 to 18 corresponds to the numbering of the mass spectra from 0 to 17 in the tabular form.







Figure 4.1-4.35. Mass spectra of TEOS methoxy-transesters from monomers to trimers in the TRANSME0 library.



IN TRINCTHONYETHONYETHONYETHONYETHONYETHONYETHONYETHONYETHONYETHONYETHONYETHONYETHONYETHONYETHONYETHONYETHONYET	IIII : DIRETHONDIETHONSILANE (TR2ID	INTERNAL DIMETHORYETHORYSILAHOL (TR2NO)
ELC = C ₀ H ₄₄ O ₄ SLRTH = 8-80-8	ELC : C ₆ H ₁₅ O ₄ SL RFN : 8-80-8	ELC : C ₄ H ₁₂ O ₄ SL 8FN : 0-80-0
NUT: LIG NF IF DF CF 2 000000 LMD 0 NNS NM NS	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	NUT 152 NF IF Cf 909090 LUD 2 1N5 1N1 185 1N1 185 1N1 185 1N1 13 26 4/6 11 51 37 127 9/4 14 14/4 47 83 32 211 130 262 15 16/6 61 49 57 68 133 262 17 3 82 83 105 22 113 26 19 62 84 105 22 140 32 22 13 24 62 219 166 32 211 126 37 20 20 20 44 107 1109 123 43 24 55 123 43 24 144 32 13 265 133 43 25 13 43 25 14 14 16 111
IIII : HET-KKYTRIET-KKKYSILIA-E (TRUK)	NEER : METHIOXYDIETHONYSILAROL (TRIMO	III : TETPRETHIOYSILAJE (ID
ELC : C ₇ H ₁₈ O ₄ SL RFN : 8-00-0	ELC : C ₈ H ₁₄ Q,8L RFN : 0-00-0	ELC : C ₀ H ₂₀ O ₄ SL RFN : 0-00-0
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	RMT 195 RF IF F 06080 UBs : 4 R65 111 44 45 45 68 50 92 20 111 81 116 118	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $
HAR + TRIETHONYSILANDL (ND)	NAM : PENTMETROMETROMOISILOWNE CIRSO	NRM = TETRHETHOMODIETHOMODISILOWHE (TRAD)
C_GH_12Q_SL RFN : 0-00-0	ELC : CyH2o0ySi2 RFN : 8-08-0	ELC : C ₀ H ₂ QC/SL ₂ RFN : 0-60-0
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NAM : TRINETHONYTRIETHONYDISILONNE (TRAD)	NHR = DIRETNKKYTETARETNKKYDUSILONNE (TRED)	NEW : OINETHOXYTRIETHONYDISILORHWL (TR2DO)
ELC : CyH210,Si2	ELC : C ₁₀ H ₂₆ O ₇ Si ₂ RFN : 0-08-0	ELC : C ₈ H ₂₂ C ₉ SL ₂ BFN : 0-68-0
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	NIT: 314 RF NIT: NIT NIT <td></td>	





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Figure 5.0-5.34. Mass spectra of TEOS methoxy-transesters from monomers to trimers from the TRANSME0 library in the tabular form







Figure 6.1-6.18. The mass spectra of TEOS propoxy-transesters from monomers to dimers in the TRANSPR1 library

NRM : TRIETHOXYSILANOL (MO)	NAM : PROPONYDIETHOWYSILOXANOL (PTRIMO)	NRM : TETRRETHOWYSILANE (TEOS)
ELC : RFN : 0-20-0	ELC : RFN : 0-08-0	ELC : RFN : 8-98-9
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $



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NAM : DIPROPOXYTETRAETHOXYDISILOXANE (PTR2D)	NRM : TETREPROPOXYETHOXYDISILOXANIOL (PTR400) NRM : TRIPROPOXYTRIETHOXYDISILOXANE (PTR30	0)
ELC : R7N : 8-88-8	ELC : R7N : 0-00-0 ELC :	RFN : 0-80-0
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	NUT: 378 NF: NUT: 378 NF: NUT: 378 NF: NUT: 378 NT NS: NT NS: </td <td>CF 0000000 LM0 117 R5 JMT MRS JMT MRS JMT 283 4 257 6 262 238 223 223 223 223 223 223 223 223 223 223 223 233 223 233 223 233 223 233 223 233 223 233 223 233</td>	CF 0000000 LM0 117 R5 JMT MRS JMT MRS JMT 283 4 257 6 262 238 223 223 223 223 223 223 223 223 223 223 223 233 223 233 223 233 223 233 223 233 223 233 223 233

Figure 7.0-7.17. The mass spectra of TEOS propoxy-transesters from monomers to dimers from the TRANSPR1 library in the tabular form

4. Conclusions

Mass spectral libraries were created based on unambiguous assigning of the mass spectra of the identified TEOS oligomers and transesters in the sol-gel process.

Gas-chromatography coupled with mass spectrometry (GC-MS) was used to unambiguous identify the molecular species obtained in the hydrolysis, transesterification and condensation reactions of tetraethoxysilane in parental (TEOS) and nonparental solvents (MeOH and n-PrOH).

GC and MS arguments for unambiguous identify the TEOS oligomers and transesters in the sol-gel process were presented; details in [1, 3-9, 12-17].

The author's procedure [12] for the interpretation of mass spectra of silicon alkoxides was applied for TEOS, TEOS dimer, TEOS methoxy-transesters and TEOS cyclic tetramer.

A few mass spectral libraries made on the basis of some reaction mixtures with parental and nonparental solvent were realized with the NBS mass spectral library run under the RSX-11-PLUS operating system.

The mass spectral library with the first 12 entries, coded ICECHIM6 created based on the molecular species obtained from the TEOS reaction in the parent solvent (ethanol) is presented.

The TRANSME0 and TRANSPR1 operational mass spectral libraries, in nonparental solvents, with 35 entries and 18 entries respectively, in histogram plot and tabular forms, are presented.

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