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Separation and Identification of Molecular Species by GC-MS for the Reaction Mixture with Methyltrimethoxysilane (MTMOS)

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Abstract. *This article aimed to separate and identify molecular species obtained in the sol-gel process by gas chromatography coupled with mass spectrometry (GC-MS), for the reaction mixture with methyltrimethoxysilane (MTMOS). In the presence of an unhydrolyzed methyl group, the molecular species starting with the cyclic trimers, a series of geometric isomers were separated and identified due to the position of the methyl groups in relation to the ring plane of each siloxane molecule; in addition, for the hydrolyzed products, isomers with different relative positions of the hydroxyl groups to the methyl and methoxy groups were separated and identified. The reactivity of the new molecular species formed determines subsequent stages of the sol-gel process.*

Keywords*: methyltrimethoxysilane (MTMOS), mass spectra, sol-gel process*

1. Introduction

The first purpose of my thesis "The Reactivity of Alcoxides Studied by Ionic Processes in Gas Phase. Romanian Academy, Institute of Physical Chemistry "IG Murgulescu",1998 [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]. The TEOS:EtOH:H_2O reaction mixture was studied by Wheeler in acid catalysis at 90 minutes after preparation.

The GC separations obtained in this work are much improved compared to those achieved in the mentioned study due to the use of high-performance and chemically inert fused silica capillary column. Also, due to the higher sensitivity of the double-focusing mass spectrometer, compared to the one with quadrupole in the mentioned study, more complete mass spectra were obtained, especially in the molecular ion area, necessary for the attribution of the structures of the separate molecular species

The basic factors that influence the sol-gel process have been studied systematically by GC-MS: the type of precursor alkoxide, tetraethoxysilane **(**TEOS), methyltrimethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS), methyltrimethoxysilane (**MTMOS**), the type of solvent **(**EtOH, **MeOH**, PrOH), the amount of water for hydrolysis (sub-stoichiometric or without water), the order of introducing the reactants and the type of catalyst (**HCl**, HF, CH_3COOH, NH_3). The results were published between 1994 and 2007 [3-9].

The second objective of my thesis [1] was the study of the fragmentation reactions initiated by electronic impact in the ionization chamber of the mass spectrometer, of some alkoxides, transesters and oligomers with silicon obtained in the sol-gel process by means of a procedure for interpreting of the mass spectra [10-13] for the molecular species from the reaction mixtures analyzed by GC-MS. The author's procedure was applied for TEOS and TEOS dimer, for methoxy transesters of TEOS, and for TEOS cyclic tetramer. The results were published between 2014 and 2022 [14-21].

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2. Materials and methods

The HP 5890 gas chromatograph with a fused silica high-performance capillary column with 75,000 theoretical plates, and 70-SE VG-Analytical double focusing mass spectrometer with electrostatic and magnetic sectors were used.

Table 1. GC-MS method and optimization parameters

Working conditions for the HP 5890 gas chromatograph	
Injection mode	Splitting injection 1:70
Injection port temperature	250ºC
Injection volume	0.1-0.3 µL
GC-MS interface temperature	280ºC
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 75,000 theoretical plates 40ºC (3 min.), 15ºC/min, to 220ºC (5 min) Helium, flow rate 1 mL/min.
Working conditions for 70-SE, VG Analytical double focusing mass spectrometer	
Acquisition mode	SCN
Ion source temperature	180ºC
Electron energy	70 eV
Response time	0.03 ms
Accelerating voltage	8 kV
Electronic amplifier	250

3. Results and discussions

3.1.Identification of molecular species by GC-MS for the reaction mixture with methyl-trimethoxysilane (MTMOS)

The starting reaction mixture (1) had the composition:

$$\text{MTMOS: } H_2O\text{: MeOH 1:1:1,75 (mol / mol) (HCl } p\text{H = 3.5)} \quad (1)$$

The reaction mixture (1) with MTMOS was used at 96 h after preparation to identify molecular species by GC-MS; under the working conditions specified in subheading 2, the chromatogram of the mixture (1) represented in Figure 1 was obtained.

Equations 2 -5 are materialized for the reaction mixture with MTMOS where R = CH_3 and R' = CH_3 as follows:

$$(CH_3)Si(OCH_3)_3 + H_2O \underset{\text{esterification}}{\overset{\text{hydrolysis}}{\longleftrightarrow}} HO\text{-}Si(CH_3)(OCH_3)_2 + CH_3OH \quad (2)$$

$$HO\text{-}Si(CH_3)(OCH_3)_2 + H_2O \underset{\text{esterification}}{\overset{\text{hydrolysis}}{\longleftrightarrow}} (OH)_2Si(CH_3)(OCH_3) + CH_3OH \quad (3)$$

etc.

$$(CH_3)Si(OCH_3)_3 + HO\text{-}Si(CH_3)(OCH_3)_2 \underset{\text{alcoholize}}{\overset{\text{condensation}}{\longleftrightarrow}} (CH_3)(OCH_3)_2Si\text{-}O\text{-}Si(CH_3)(OCH_3)_2 + CH_3OH \quad (4)$$

$$(CH_3)(OCH_3)_2Si\text{-}OH + HO\text{-}Si(CH_3)(OCH_3)_2 \underset{\text{hydrolysis}}{\overset{\text{condensation}}{\longleftrightarrow}} (CH_3)(OCH_3)_2Si\text{-}O\text{-}Si(CH_3)(OCH_3)_2 + HOH \quad (5)$$

etc.

According to equations (2)-(5) it is possible to identify the hydrolysis and condensation products of MTMOS. At the same time, since the methyl group does not hydrolyze, it is expected that for the molecular species starting with the cyclic trimers, a series of geometric isomers will be highlighted due to the position of the methyl groups in relation to the ring plane of each siloxane molecule; in addition, for the hydrolyzed products, isomers with different relative positions of the hydroxyl groups to the methyl and methoxy groups are possible. Partial chromatograms of the whole chromatogram in Figure 1.b are shown in Figure 2 a-i with the molecular species peaks identified from monomers to octamers.

Methyltrimethoxysilane (MTMOS), as a precursor in the reaction mixture with scan number #103, in the partial chromatogram from Figure 2a, was identified by the NBS mass spectral library (Figure 3) and verified by analysis of a Merck company MTMOS standard.

The mass spectra of the separated molecular species by gas-chromatography (Figures 1b, 2a-i) are presented in Figures 3-10, and the results compared with the theoretically possible structures are summarized in Table 1.

Monomers. The mass spectrum of MTMOS shows the molecular ion of low intensity at m/e 136 (Figure 3 and Figure 4a). Cleavage of a methyl radical is the dominant primary event, thus the ion obtained with m/e 121 is the base ion of the spectrum.

Other primary event in the MTMOS mass spectrum are the elimination of a methoxy radical (m/e 105). Formaldehyde is successively removed from the primary ions with m/e 121, 105 and 135 until the methoxy groups are exhausted so that ions with mass differences of 30 amu are present in the spectrum.

The hydrolysis product of MTMOS at #133 (Figure 2a) has the mass spectrum in Figure 4b. The molecular ion at m/e 122 is 14 amu smaller than TMOS by replacing a methoxy group with a hydroxy group; the same difference of 14 amu is also observed for the other major ions in the spectrum. The elimination of methyl groups from the molecular ion and the loss of formaldehyde also explain this mass spectrum.

Figure 4c shows the mass spectrum of dihydrolyzed MTMOS with the molecular ion at m/e 108. It was obtained from the mixture (1) injected at 3 h.

Dimers. The first condensation reaction according to equations (4, 5) of the reaction mixture (1) is highlighted by the presence of the dimer at # 271 (Figure 1 and Figure 2b). Its mass spectrum is shown in Figure 4d has the molecular ion at m/e 226. The loss of methyl, methoxy, and methanol groups (m/e 211, 195, 194) from the molecular ion and the successive elimination of formaldehyde explain the mass spectrum of the dimer MTMOS.

The hydrolysis product of the dimer (# 286) has a molecular ion at m/e 212 with 14 amu lower than the unhydrolyzed dimer (Figure 4e). Besides the cleavage of methyl and methoxy groups from the molecular ion, a primary event occurs here: the elimination of water (m/e 194). The diol dimer with the mass spectrum in Figure 4f has the molecular ion at m/e 198 with 14 amu lower than that of the silanol dimer and 28 amu lower than that of the dimer. This mass spectrum was obtained from the reaction system (1) and analyzed by GC-MS after 3 h.

Structure formulas for monomers and dimers MTMOS with mass spectra in Figure 4 are presented in Table 1 together with the codes and names of structures and molecular masses.

Trimers. The chromatogram in Figure 1 follows the group of peaks of MTMOS trimers between scan numbers #309-393. The partial chromatogram in Figure 3c details these peaks. The identification mass spectra of cyclic and linear trimers are represented in Figure 5a-d. In Table 1 two isomers of the MTMOS trimer and three hydrolyzed isomers of it were highlighted.

According to the structural codes of the cyclic trimers of MTMOS from Table 1, two geometric isomers are possible, one with all methyl groups above the plane of the ring and the second with two methyl groups above the ring and one below. These two geometric isomers correspond to the coded mass spectra #309 and #312 respectively from Figure 5a. The fused silica chromatographic column with methyl siloxane as the stationary phase can separate the two isomers, but the mass spectra are almost identical.

The molecular ions of the two MTMOS trimers are at m/e 270. The cleavage of methyl groups and the successive elimination of formaldehyde largely explain the mass spectra of these trimers.

Geometric isomerism is also manifested for the monohydrolyzed products at #334, and #336 from the chomatogram 1a, with the mass spectra in Figure 5b obtained for the starting reaction mixture (1).

In Table 1, it can be seen that, in addition to the relative positions of the methyl groups to the ring, their relative position to the OH group also intervenes.

The two identified isomeric monohydrolyzed trimers show molecular ions at m/e 256 14 amu lower than those of the unhydrolyzed trimers. Next is the ion with m/e 241 obtained by losing a methyl group (base ion). The ion with m/e 211 is obtained by the loss of formaldehyde from the ion with m/e 241.

Geometric isomerism of the type mentioned above can be demonstrated by high-performance GC-MS instrumentation of the type used for this mixture.

In the case of the linear trimer (#373), there can be no geometric isomerism. Its mass spectrum is given in Figure 5c with the molecular ion at m/e 316, as a function of the molecular mass given along with the structural formula in Table 1.

Cleavage of the methyl group and elimination of methanol produces very intense m/e 301 and m/e 284 ions. Another intense primary event is the cleavage of a methoxy group (m/e 285). Successive formaldehyde removal follows with 30 amu differences between consecutive ions.

We have in this case two positional isomers at #377 and #380 for the hydrolyzed MTMOS linear trimer. The isomer with the OH group in position 1 (#380) is more retained by the GC column compared to the one with the OH group in position 2 due to the interaction through more accessible hydrogen bridges with the oxygen atoms of the siloxane chain of the stationary phase. Both positional isomers have molecular ions at m/e 302 14 amu lower than that of the unhydrolyzed trimer. The spectra can be interpreted by the same types of fragmentation reactions as for the linear trimer. Figure 5d also shows the MTMOS linear trimer diol from the mixture (1) after 3 h. It has a molecular mass of 288. The first ion in the spectrum corresponds to m/e 273 by the loss of a methyl group. The ion with m/e 273 eliminates of a methanol molecule, giving the base ion in the spectrum at m/e 241.

Tetramers. The group of tetramers between #393 and #454 (Figure 1 and Figure 2d) is located according to the chromatogram from 96 h in the center of the MTMOS oligomer distribution.

The subgroups of tetramers are: bicyclic with a molecular weight of 314, cyclic and branched cyclic with a molecular weight of 360, branched acyclic, and the linear tetramer with a molecular weight of 406.

The hydrolysis products of these subgroups have molecular weights of 300, 346, and 392, respectively.

Due to the large differences between the molecular masses of the subgroups, correlated with the presence of molecular ions, the identification of these subgroups is clear. Thus, the mass spectra in Figure 6 represent (a-b) the subgroup of cyclic tetramers; (c) the subgroup of hydrolyzed cyclic tetramers; (d) the subgroup of branched acyclic tetramers and the linear tetramer together with their monohydrolyzed species.

According to the structure codes in Table 1 for cyclic tetramers, there are three geometric isomers (4.0), (3.1), and (2.2) regarding the positions relative to the ring of the methyl groups. Similar mass spectra from #393, #396, and #405 in Figure 6a-b with molecular ions at m/e 360 correspond to these isomers. The last isomer (#405) is obtained in the reaction mixture (1) at 3 h (Figure 6b). The loss of methyl and methoxy groups and the elimination of formaldehyde explain most of the fragmentation ions in their mass spectra.

Two monohydrolyzed positional isomers of the cyclic tetramer are separated by GC at #402 and #406, respectively. In this case, the cleavage of a methyl radical and the elimination of methanol give the fragmentation ion at m/e 331 and respectively the base ion at m/e 299 (Figure 6c).

For the branched acyclic tetramer there is only one possible structure because in this case the geometric isomerism relative to the methyl groups cannot be produced due to their free rotation; a single structure is also possible for the hydrolyzed branched tetramer. The OH group can only be positioned at

the edge of silicon atoms. Only one non-hydrolysable CH_3 group remained at the central silicon atom. The peaks from #446 and #448 with molecular ions at m/e 406 and m/e 392 respectively correspond to the branched acyclic tetramer and the monohydrolyzed one (Figure 6d).

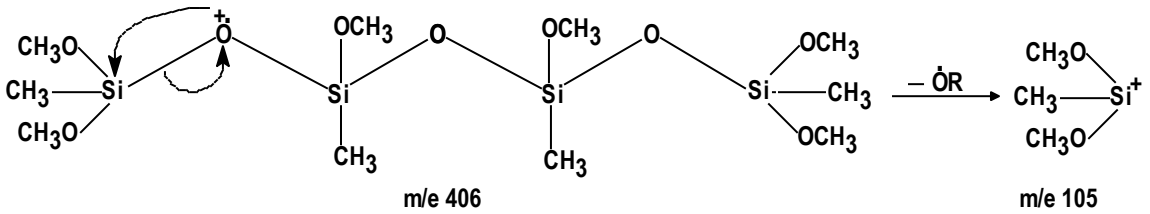
The linear tetramer is separated by GC at #451, and one of the two possible monohydrolyzed isomers (Table 1) appears at #454; molecular ions are present at m/e 406 and m/e 392 respectively.

For the non-hydrolyzed species of BTET and LTET, the primary events are the loss of methyl and methoxy groups (m/e 391 and 375) followed by successive eliminations of formaldehyde.

For the monohydrolyzed products, the cleavage of the radical is followed by the elimination of methanol (M-15-32) with the obtaining of the base ion in the spectrum from m/e 345 through this reaction path.

Both the branched tetramer (BTET) and the linear one (LTET) present in their mass spectra an intense fragmentation ion at m/e 105. In the case of MTMOS oligomers, the shielding by the methoxy groups of the Si-O-Si siloxane bond is small compared to that of the ethoxy groups in TEOS oligomers. That is why it is possible to ionize oxygen atoms from the siloxane chain and therefore to have the possibility of splitting this bond. These cleavages of siloxane bonds are more likely for acyclic oligomers compared to cyclic ones with a more compact structure.

Returning to the ion with m/e 105, it is obtained by the cleavage of the siloxane chain of the MTMOS tetramer (LTET) according to the reaction:



(6)

Pentamers. The group of MTMOS pentamers (Figure 1 and Figure 2e) has the mass spectra represented in Figure 7. According to Table 1, the subgroups of pentamers are: cyclic at #463, #465, #468, branched cyclic at #477 and #479 (from mixture (1) at 3 h) a branched acyclic at #513 and the linear pentamer at #518.

Cyclic pentamers remove a methyl radical from the molecular ion at m/e 450, obtaining the base ion from the spectrum at m/e 435. It also eliminates a methanol molecule (m/e 418). Successive losses of formaldehyde and methane follow (Figure 7a-b).

Acyclic pentamers (Figure 7c) fragment in the same way, with the difference that the elimination of a methyl radical leads to a less intense fragmentation ion (m/e 481).

The fragment ion at m/e 435 is the most intense common fragment ion of MTMOS pentamers and can be used for their identification.

In the case of linear pentamers, fragmentation ions are also obtained by cleavage of the siloxane bond. According to equation (6) by cleaving an MTMOS acyclic oligomer at the first oxygen atom of the siloxane chain, an ion with m/e 105 is obtained. If the siloxane bond is cleaved at the second oxygen atom, then we will obtain the fragmentation ion with m/e 195 with the following structural formula: $(CH_3)(CH_3O)_2Si\text{-}O\text{-}Si(CH_3)(OCH_3)^{]+}$ i.e. a summation between the mass of the ion 105 and the mass 90 of the structural unit of the MTMOS oligomers: [-O-Si(CH_3)(OCH_3)]. Indeed, in the mass spectra of oligomers B1LP (#513) and LP (#510) from Figure 7c, appear fragmentation ions with m/e 105 and m/e 195 respectively. Hydrolysis products of MTMOS pentamers were not highlighted (Table 1).

Hexamers. Starting with the MTMOS hexamer group, bicyclic molecular species were highlighted at #475 and #484 with molecular ions m/e 494. These oligomers have chromatographic retention times between cyclic and branched acyclic pentamers (Figure 2e). The mass spectra of the bicyclic hexamers are represented in Figure 8a together with cyclic and acyclic hexamers (Figure 8b-c). A series of fragmentation ions with m/e 343, 389, 433, and 479 are common to MTMOS hexamers, and the very

intense m/e 525 ion is common to cyclic and acyclic hexamers. The theoretical possibilities of geometric isomerism for hexamers are shown in Table 1. The fragmentation pattern is already known: cleavage of methyl and methoxy groups, elimination of methanol, and successive elimination of formaldehyde and methane.

Important events are also cleavage of the siloxane bond, especially for acyclic hexamers. In addition to the ions with m/e 105 and 195 already discussed, the ion with m/e 285 is also obtained by a reaction according to equation (6), but the cleavage takes place at the third oxygen atom of the siloxane bond; so two structural units (90x2)=180 are added to the m/e 105 ion, obtaining the ion with the structural formula: $(CH_3)(CH_3O)_2Si\text{-}O(CH_3)(CH_3O)_2Si\text{-}O\text{-}(CH_3)(CH_3O)^{+}$ at m/e 285.

Heptamers. The next group is heptamers between # 538 and # 664 with subgroups: bicyclic with molecular mass 584 (Table 1), cyclic (M=630), and acyclic (M=676). The bicyclic heptamers are eluted from the chromatographic column after the cyclic and before the acyclic hexamers (Figure 2f).

Identification mass spectra of MTMOS heptamers are shown in Figure 9a-c. A number of common fragmentation ions can be used to identify the group of heptamers. Among these more intense are ions with m/e 433, 477, 523, and 569. GC separated five cyclic heptamers with scan numbers #583, 587, 589, 593, and 595 (Figure 9b) as geometric isomers, two-branched acyclic heptamers (#651, 656) and the linear heptamer at #664 (Figure 9c).

Octamers. The last group in the chromatogram presented in Figure 1 is that of the octamers between #669 and #1088. The geometric isomerism due to the position of the methyl and methoxy groups relative to the ring is well illustrated for the cyclic octamers of molecular weight 720 (Table 1). These isomers are the most numerous group in the chromatogram of Figure 1 and are represented in detail in Figure 2h.

The mass spectra are, as expected, very similar and are shown in Figure 10a. The cluster of common fragment ions in the molecular ion region with m/e 705, 659, 613, and 567 (the latter base ion) is characteristic of cyclic MTMOS octamers.

Also, are identified two branched cyclic octamers at #796 and #811, a branched acyclic MTMOS octamer (#1058) with m/e 766 and the linear octamer at #1088 (Figure 10b), two branched cyclic octamers at #796 and #811, a branched acyclic MTMOS octamer (#1058) with m/e 766 and the linear octamer at #1088 (Figure 10b).

As for the heptamers, the MTMOS octamers (especially the acyclic ones) show fragmentation ions of the siloxane chain at m/e 105, 195, and 285.

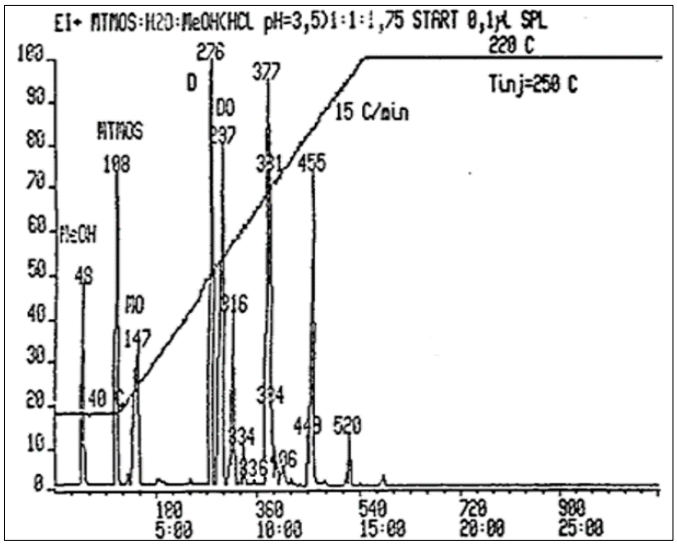


Figure 1a. The chromatogram of reaction mixture MTMOS:H_2O:MeOH 1:1:1.75 HCl *p*H=3.5 at the start. The two unhydrolized trimers at the scans #334 and #336 are separated

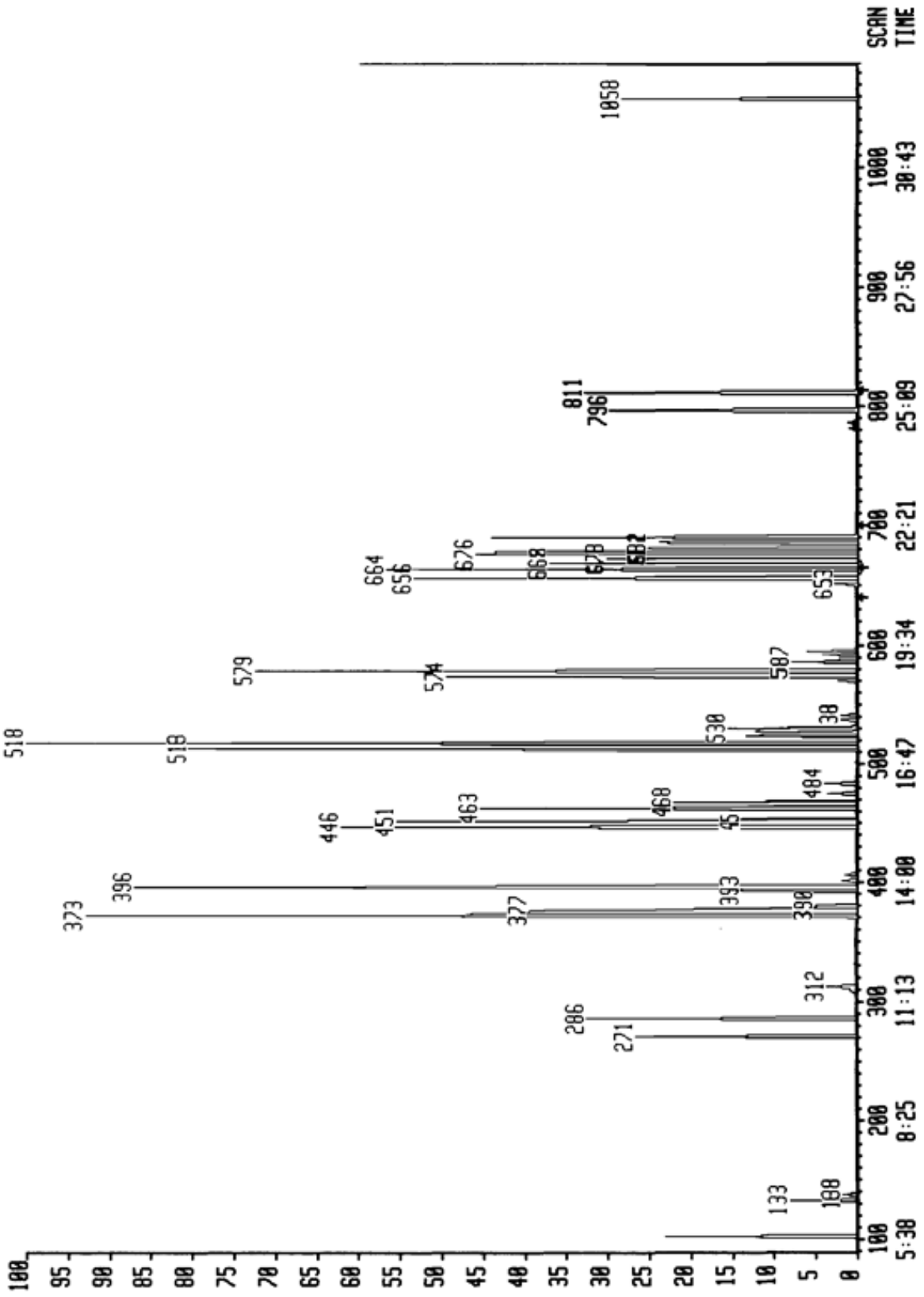


Figure 1b. The chromatogram of reaction mixture MTMOS:H_2O:MeOH 1:1:1.75 HCl *p*H=3.5 at 96 h

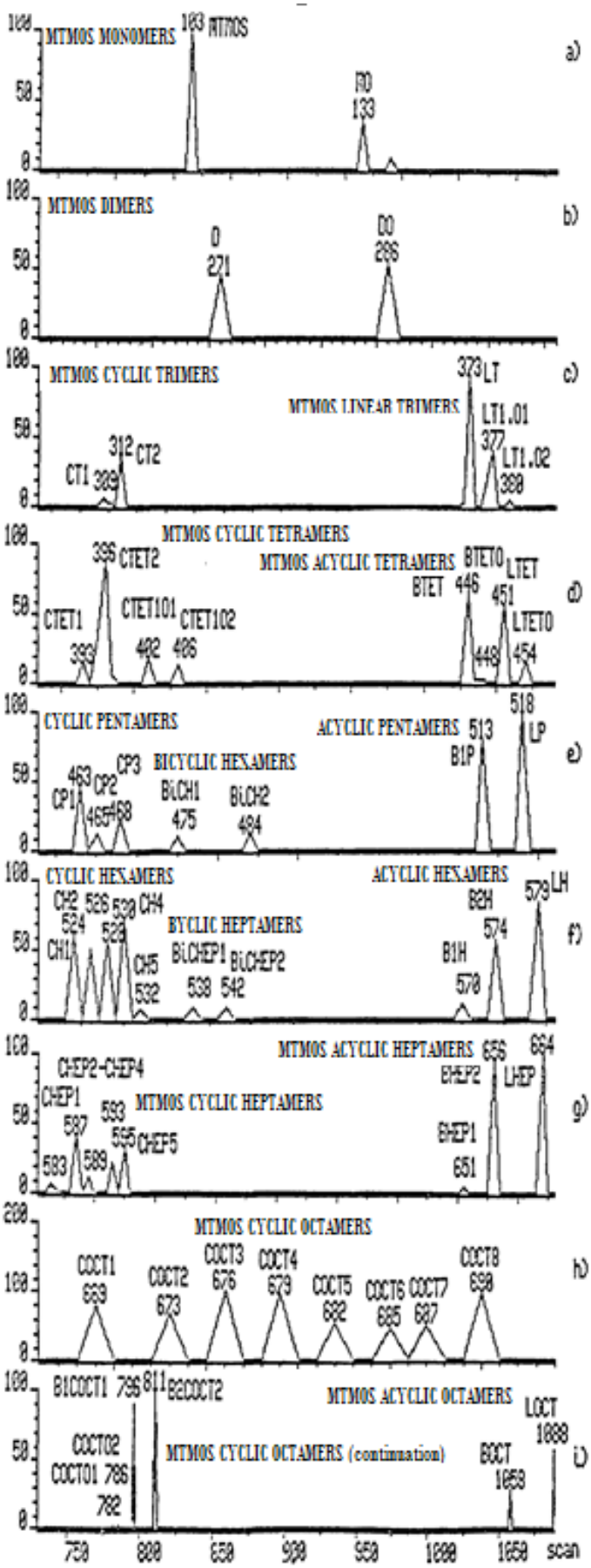


Figure 2a-i. Partial chromatograms from monomers to octamers of the chromatogram in Figure 1

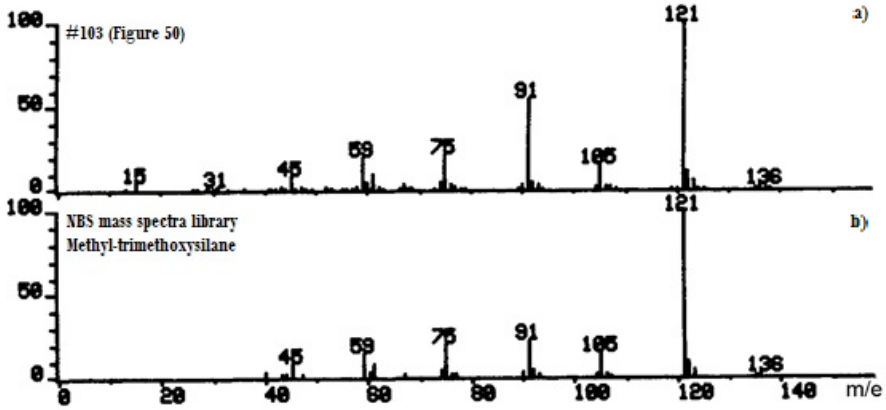


Figure 3a-b. MTMOS mass spectrum of the reaction mixture (1) compared with the NBS library.

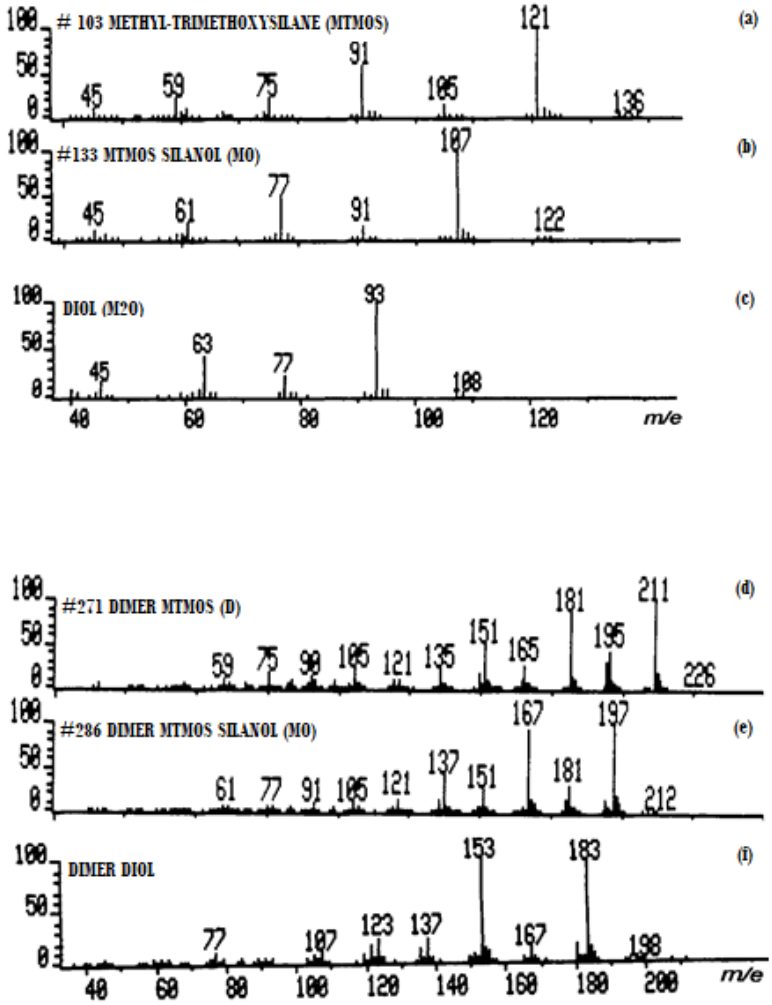
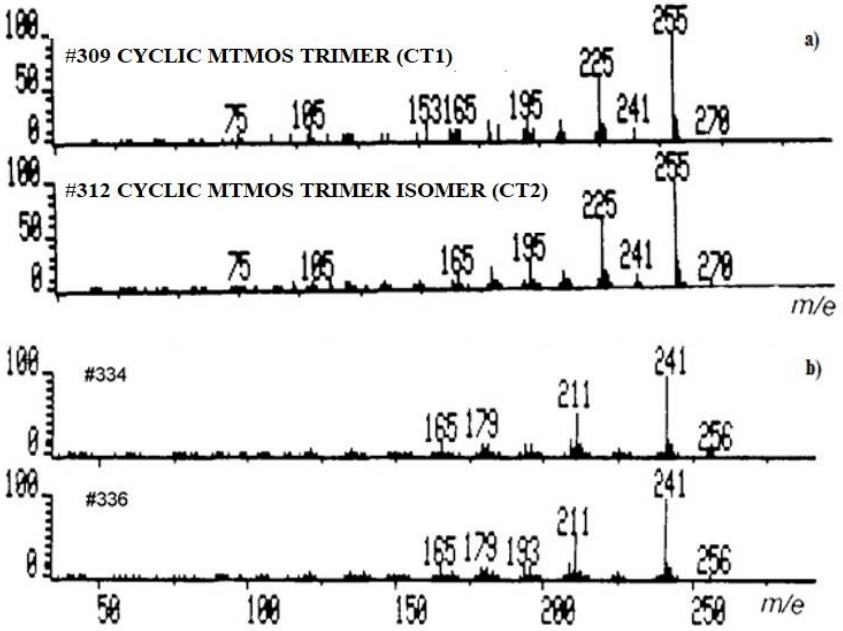


Figure 4a-d. Mass spectra for (a- c) monomer and (d-f) MTMOS dimers



The mass spectra in Figure 5b obtained for the reaction mixture MTMOS:H_2O:MeOH at the start (the chromatogram presented in Figure 1a).

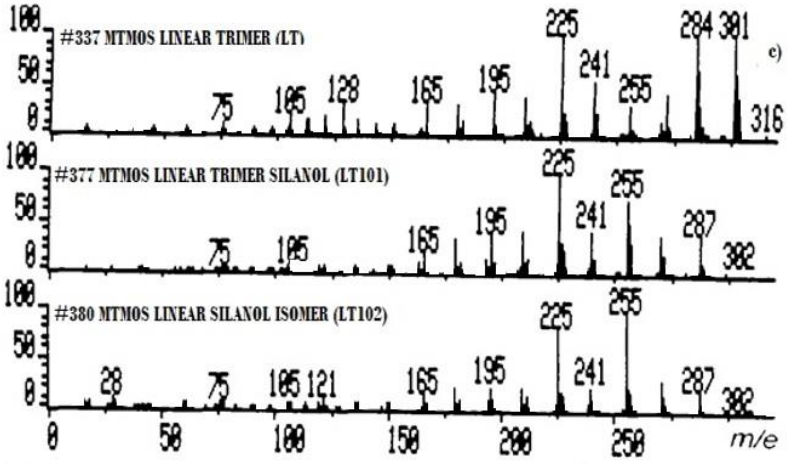


Figure 5a-c. Mass spectra for (a) - (b) cyclic trimers and (c) linear trimers

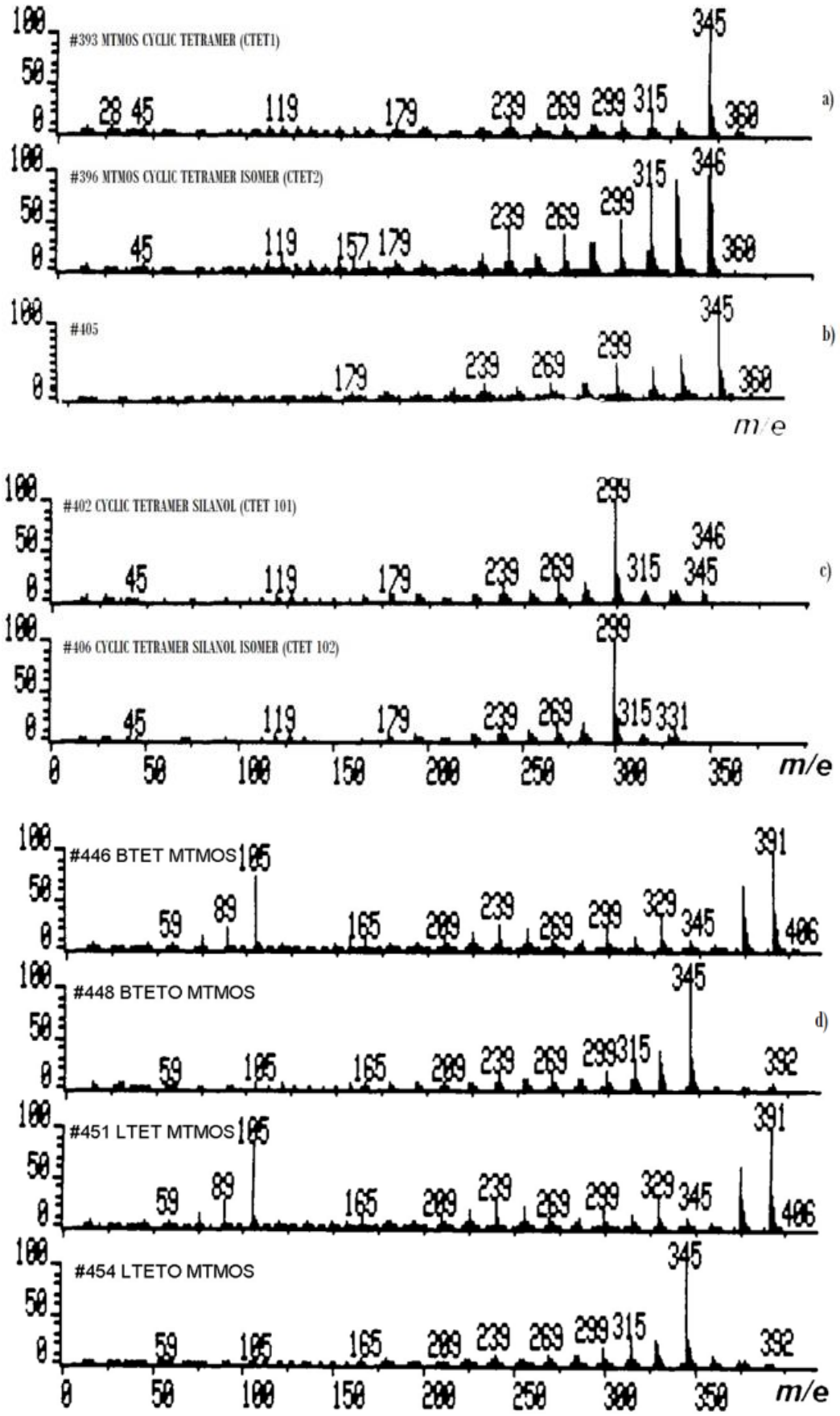


Figure 6a-d. Mass spectra for cyclic tetramers (a) - (c) and (d) acyclic tetramers

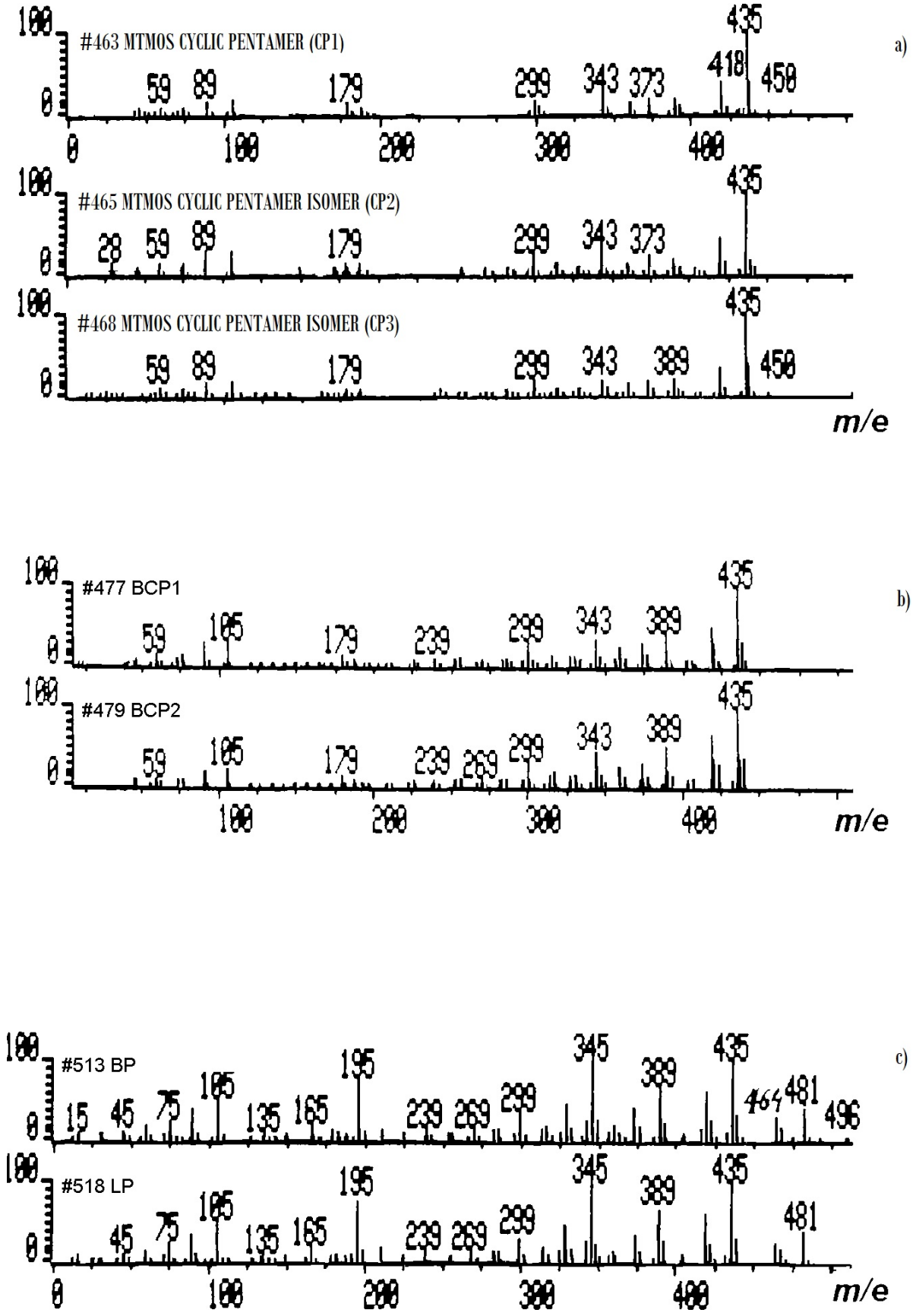


Figure 7a-c. Mass spectra for cyclic pentamers (a - b) and (c) acyclic pentamers

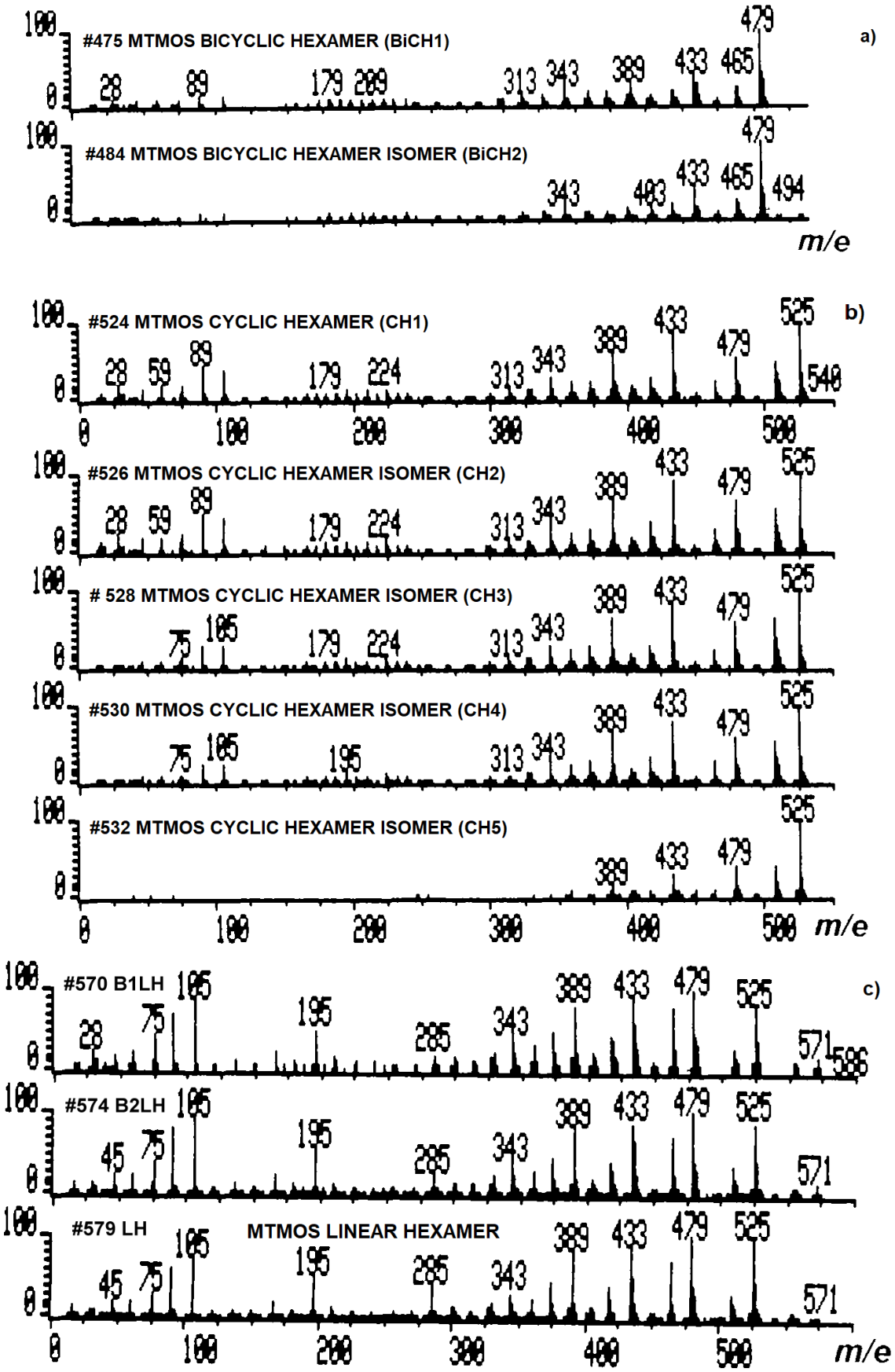


Figure 8a-c. Mass spectra for (a) bicyclic hexamers, (b) cyclic hexamers and (c) acyclic hexamers

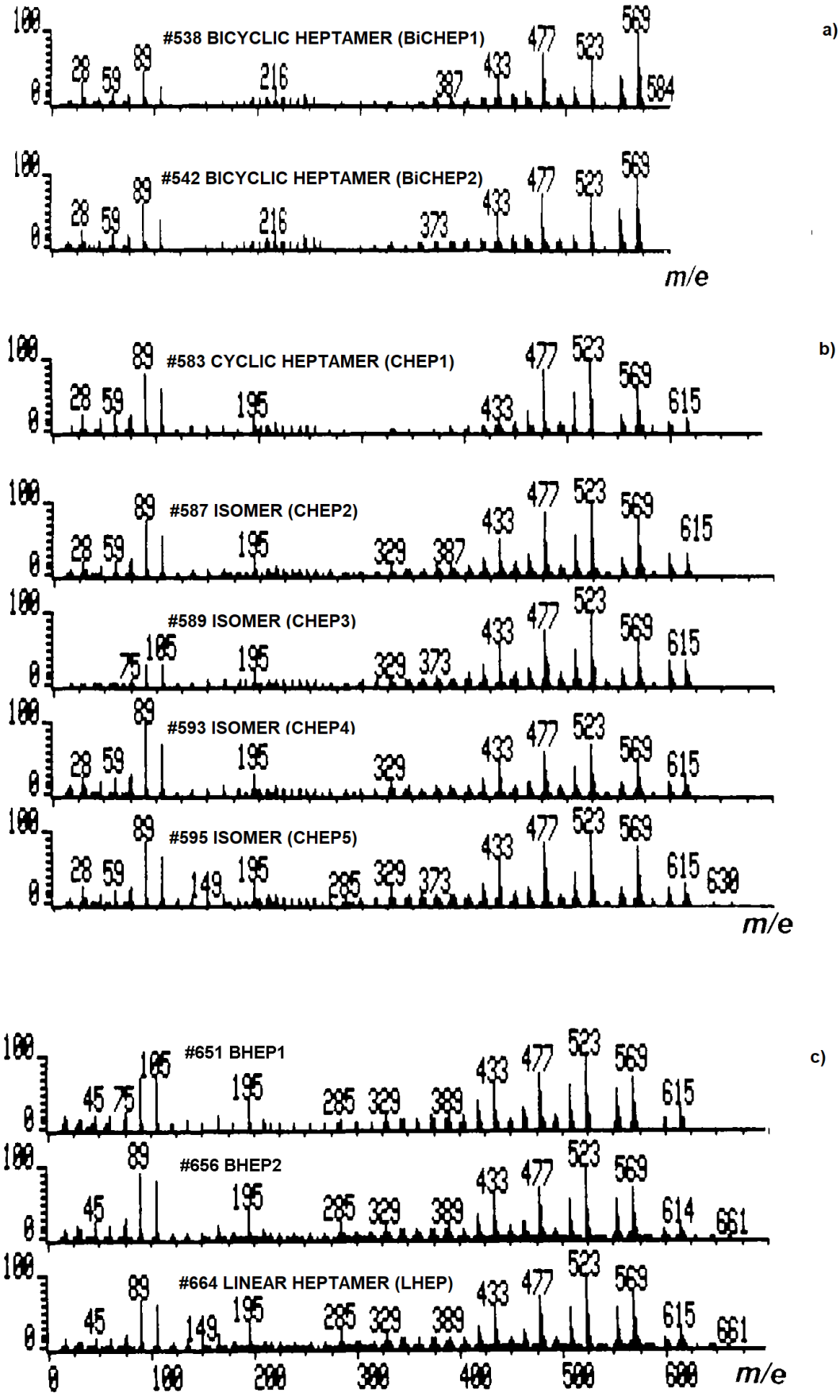


Figure 9a-c. Mass spectra for (a) bicyclic heptamers, (b) cyclic heptamers and (c) acyclic heptamers

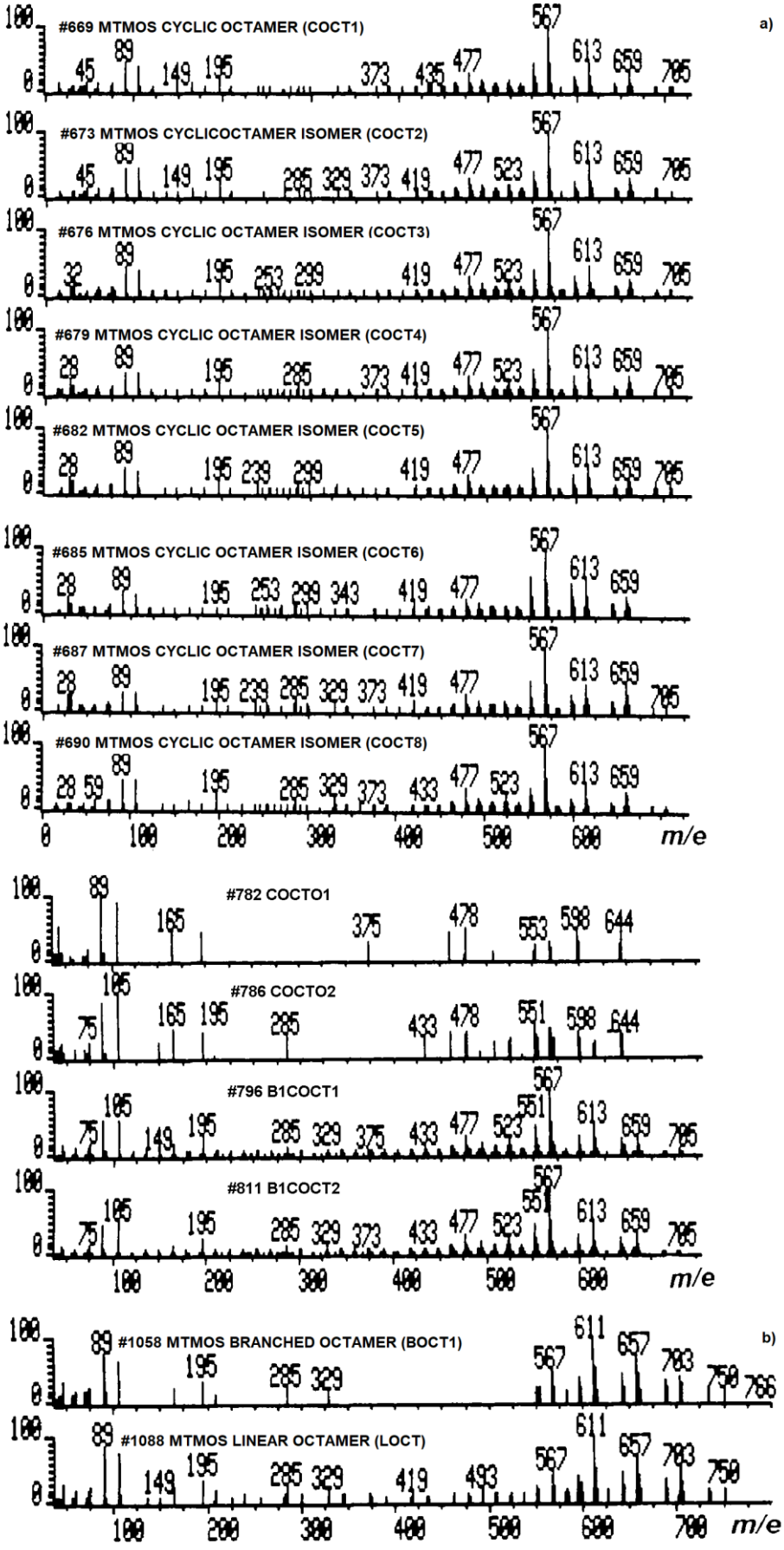
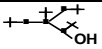
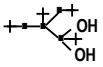
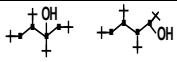
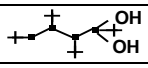
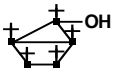
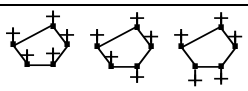
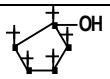
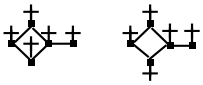
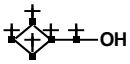
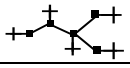
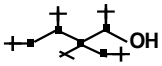
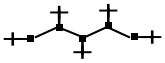
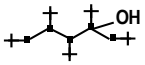
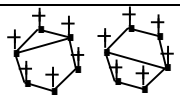
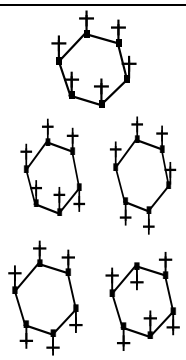
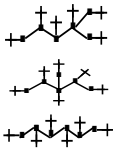
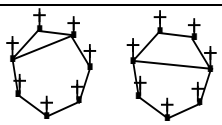
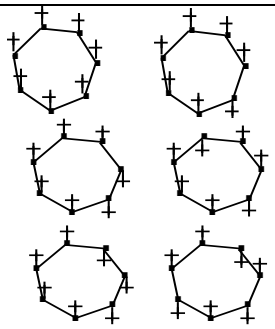
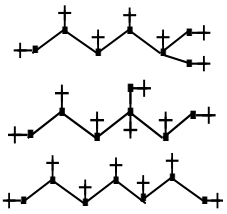
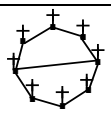
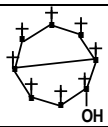


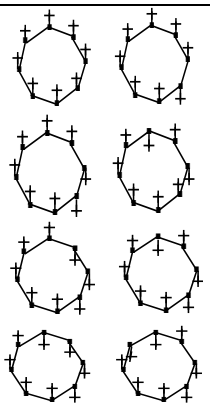
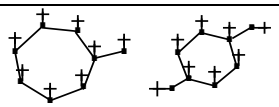
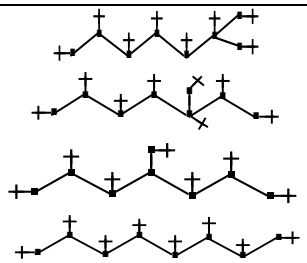
Figure 10a-b. Mass spectra for (a) cyclic octamers and (b) acyclic octamers

Table 1. Identified molecular species by mass spectrometry for the reaction mixture: MTMOS: H_2O: MeOH: 1: 1: 1.75 (HCl *p*H = 3.5) with chromatograms of separate species in Figure 1 and Figure 2a-i. The symbol • encode Si atom; the symbol •–• encode Si-O-Si bond, and the symbol •–+ encode bond Si– CH_3^+

No. scan	Structural formula	Structure code	Molecular mass	Code name
MTMOS MONOMERS				
103	$(CH_3)Si(OCH_3)_3$		136	MTMOS (M)
133	$(CH_3)Si(OH)(OCH_3)_2$		122	MO
180	$(CH_3)Si(OH)_2(OCH_3)$		108	M2O
MTMOS DIMERS				
271	$Si_2O(CH_3)_2(OCH_3)_4$		226	D
286	$Si_2O(CH_3)_2(OH)(OCH_3)_3$		212	DO
	$Si_2O(CH_3)_2(OH)_2(OCH_3)_2$		198	D2O1
	1,2 isomer			D2O2
MTMOS TRIMERS				
	MTMOS cyclic trimers			
309	$Si_3O_3(CH_3)_3(OCH_3)_3$ (*cis* isomer)		270	CT1
312	2,1 isomer			CT2
334 336	$Si_3O_3(CH_3)_3(OH)(OCH_3)_2$		256	CT1O1 CT1O2 CT1O3
	MTMOS linear trimers			
373	$Si_3O_2(CH_3)_3(OCH_3)_5$		316	LT
377	$Si_3O_2(CH_3)_3(OH)(OCH_3)_4$		302	LT1O1
380	1 isomer			LT1O2
393	$Si_3O_2(CH_3)_3(OH)_2(OCH_3)_3$		288	LT2O1
	1,2 and 1,3 isomers			LT2O2, LT2O3
MTMOS TETRAMERS				
	MTMOS bicyclic tetramers			
	$Si_4O_5(CH_3)_4(OCH_3)_2$		314	BICTET
	$Si_4O_5(CH_3)_4(OH)(OCH_3)$		300	BICTET1O
	MTMOS cyclic tetramers			
393 396 405	$Si_4O_4(CH_3)_4(OCH_3)_4$		360	CTET1 CTET2 CTET3
402 406	$Si_4O_4(CH_3)_4(OH)(OCH_3)_3$		346	CTET1O1 CTET1O2 CTET1O3 CTET1O4
MTMOS TETRAMERS				
	MTMOS cyclic tetramers			
	$Si_4O_4(CH_3)_4(OCH_3)_4$		360	BCTET1

	$Si_4O_4(CH_3)_4(OH)(OCH_3)_3$		346	BCTET101
	MTMOS branched acyclic tetramers			
446	$Si_4O_3(CH_3)_4(OCH_3)_6$		406	BTET
448	$Si_4O_3(CH_3)_4(OH)(OCH_3)_5$		392	BTET0
	$Si_4O_3(CH_3)_4(OH)_2(OCH_3)_4$		378	BTET201
	MTMOS linear acyclic tetramers			
451	$Si_4O_3(CH_3)_4(OCH_3)_6$		406	LTET
454	$Si_4O_3(CH_3)_4(OH)(OCH_3)_5$		39	LTET101 LTET102
	$Si_4O_3(CH_3)_4(OH)_2(OCH_3)_4$		378	LTET2O1
	MTMOS PENTAMERS			
	MTMOS bicyclic pentamers			
	$Si_5O_6(CH_3)_5(OCH_3)_3$		404	BICP1
	$Si_5O_6(CH_3)_5(OH)(OCH_3)_2$		390	BICPO1
	MTMOS cyclic pentamers			
463 465 468	$Si_5O_5(CH_3)_5(OCH_3)_5$		450	CP1 CP2 CP3
	$Si_5O_5(CH_3)_5(OH)(OCH_3)_4$		436	CP01
477 479	$Si_5O_5(CH_3)_5(OCH_3)_5$		450	BCP1 BCP2
	$Si_5O_5(CH_3)_5(OH)(OCH_3)_4$		436	BCP101
	MTMOS acyclic pentamers			
513	$Si_5O_4(CH_3)_5(OCH_3)_7$		496	BP
	$Si_5O_4(CH_3)_5(OH)(OCH_3)_6$		482	BP01
518	$Si_5O_4(CH_3)_5(OCH_3)_7$		496	LP
	$Si_5O_4(CH_3)_5(OH)(OCH_3)_6$		482	LPO1
	MTMOS HEXAMERS			
	MTMOS bicyclic hexamers			
475 484	$Si_6O_7(CH_3)_6(OCH_3)_4$		494	BiCH1 BiCH2

	MTMOS cyclic hexamers			
524 526 528 530 532	$Si_6O_6(CH_3)_6(OCH_3)_6$		540	CH1 CH2 CH3 CH4 CH5
	MTMOS acyclic hexamers			
570 574 579	$Si_6O_5(CH_3)_6(OCH_3)_8$		586	B1H B2H LH
	MTMOS HEPTAMERS			
	MTMOS bicyclic heptamers			
538 542	$Si_7O_8(CH_3)_7(OCH_3)_5$		584	BiCHEP1 BiCHEP2
	MTMOS cyclic heptamers			
583 587 589 593 595	$Si_7O_7(CH_3)_7(OCH_3)_7$		630	CHEP1 CHEP2 CHEP3 CHEP4 CHEP5
	MTMOS acyclic heptamers			
651 656 664	$Si_7O_6(CH_3)_7(OCH_3)_9$		676	B1HEP B2HEP LHEP
	OCTAMERI MTMOS			
	MTMOS bicyclic octamers			
	$Si_8O_9(CH_3)_8(OCH_3)_6$		674	BiOCT
	$Si_8O_9(CH_3)_8(OH)(OCH_3)_5$		660	BiOCT0

	MTMOS cyclic octamers			
669 673 676 679 682 685 687 690	$Si_8O_8(CH_3)_8(OCH_3)_8$		720	COCT1 COCT2 COCT3 COCT4 COCT5 COCT6 COCT7 COCT8
782 786	cyclic octamer in traces cyclic octamer in traces			
796 811	$Si_8O_8(CH_3)_8(OCH_3)_8$ (MTMOS branched cyclic octamers)		720	B1COCT1 B2COCT1
	MTMOS acyclic octamers			
1058 1088	$Si_8O_7(CH_3)_8(OCH_3)_{10}$		766	B1OCT1 B2OCT2 B3OCT3 LOCT

4. Conclusions

Identification by GC-MS of 65 molecular species (Table 1, column 1) from 85 theoretical structures (Table 1, column 3 and 5) was performed for the reaction mixture with alkoxide precursor methyl-trimethoxysilane (MTMOS) in parental solvent (MeOH) and acid catalyze (HCl). The mass spectra of identified species from monomers to octamers are presented in Figure 3-10.

In the presence of an unhydrolyzed methyl group, the molecular species starting with the cyclic trimers, a series of 47 geometric isomers were identified due to the position of the methyl groups in relation to the ring plane of each siloxane molecule; in addition, for the hydrolyzed products, 4 isomers with different relative positions of the hydroxyl groups to the methyl and methoxy groups were identified.

The subsequent stages of the sol-gel process are essentially determined by the reactivity of the new molecular species formed in the sol stage for different alkoxides, including in the case of reactions with MTMOS.

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