Proceeding Paper

The Molecular Species Identified by GS-MS in Sol-Gel Process. Operational Mass Spectrum 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.

Keywords: molecular species; sol-gel process; GC and MS arguments; user mass spectrum libraries

1. Introduction

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

GC arguments were: The restrictive conditions imposed on the initial reaction mixtures and the retention times in the gas chromatogram of molecular species obtained by hydrolysis, trans-esterification reactions and condensation in the sol-gel process [1–5].

The MS arguments were: Linked scans, accurate mass measurements and M+1, M+2 isotopic effects [6–10]. The mass spectra of the methoxy-transesters are similar to that of TEOS esters 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. The mass spectra of the propoxy transesters are similar to that of TEOS esters 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 [10].

An additional theoretical argument for assigning structures for these molecular species are complex quantum calculations with the ALCHEMY, MOPAC, HYPERCHEM programs, among which the distribution of net charges on fragmentation ion atoms is very important for the interpretation of mass spectra [6,10].

2. Materials and Methods

The experimental data for this paper were obtained on a GC-MS tandem produced by VG-Analytical. The HP 5890 Hewlett Packard gas chromatograph with a fused silica high-performance capillary column with 70,000 theoretical plates; stationary phase Silicone oil OV-1. VG Analytical double-focusing mass spectrometer: Acquisition mode SCN at standard and high resolution; B/E and (B/E) (1-E)1/2 linked scans. TurboMass Software

procedure was used to create mass spectrum libraries [11]. Run the Spectrum application and select the first spectrum that we want to add to the user library. Enter the name of the new library. Using the TurboMass Spectrum application, select spectra one at a time to put into the user library. In the Library application, set up the text data for each entry. Create the Presearch file for the new user library. Once we have created a user library, we can add new spectra to it at any time by repeating these steps [11].
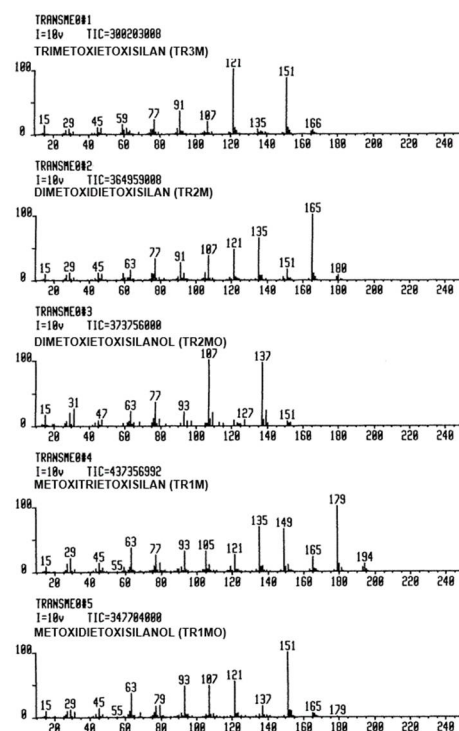
3. Results

In addition to the libraries available (NIST, NBS etc.), we created "user" libraries that contain user spectra from raw data files obtained by the GC-MS method. By unambiguously 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, mass spectrum libraries were realized. These mass spectrum libraries were stored in the memory of the data acquisition and processing system of the double focus GC-MS tandem type 70-SE. Table 1 present a few mass spectrum libraries created on the basis of some reaction mixtures with parental and nonparental solvents.

Table 1. Operational mass spectrum libraries created in Analytical Department.

Reaction Systems	Mass Spectrum Library Name Code	Number of Entries	Observations
TEOS: H_2O: EtOH	ICECHIM0 to ICECHIM9	10–33	start mixture to 9 days
TEOS: H_2O: MeOH	TRANSME0	35	methoxy transesters
TEOS: H_2O: PrOH	TRANSPR1	19	propoxy transesters

In Figures 1 and 2 are presented the first five and the last five entries of the operational mass spectrum library TRANSME0 with 35 entries.

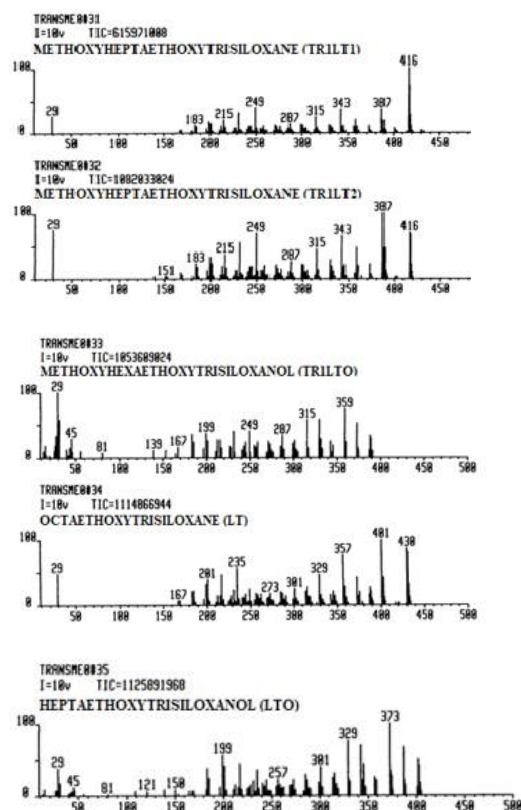**Figure 1.** TRANSME0 Mass spectrum library. Entries 1–5.

Figure 2. TRANSME0 Mass spectrum library. Entries 30–35.

4. Conclusions

Mass spectrum libraries were created based on unambiguous assigning of the mass spectra of the identified molecular species 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 (TEOS) in nonparental solvents (MeOH and n-PrOH).

GC and MS arguments for unambiguous identification of the molecular species in the sol-gel process were presented. Quantum calculations programs were used as an additional theoretical argument for assigning structures for these molecular species.

A few mass spectrum libraries made on the basis of some reaction mixtures with parental and nonparental solvent were realized with TurboMass Software.

The first five and the last five entries of the operational mass spectrum library TRANSME0 with 35 entries are presented.

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