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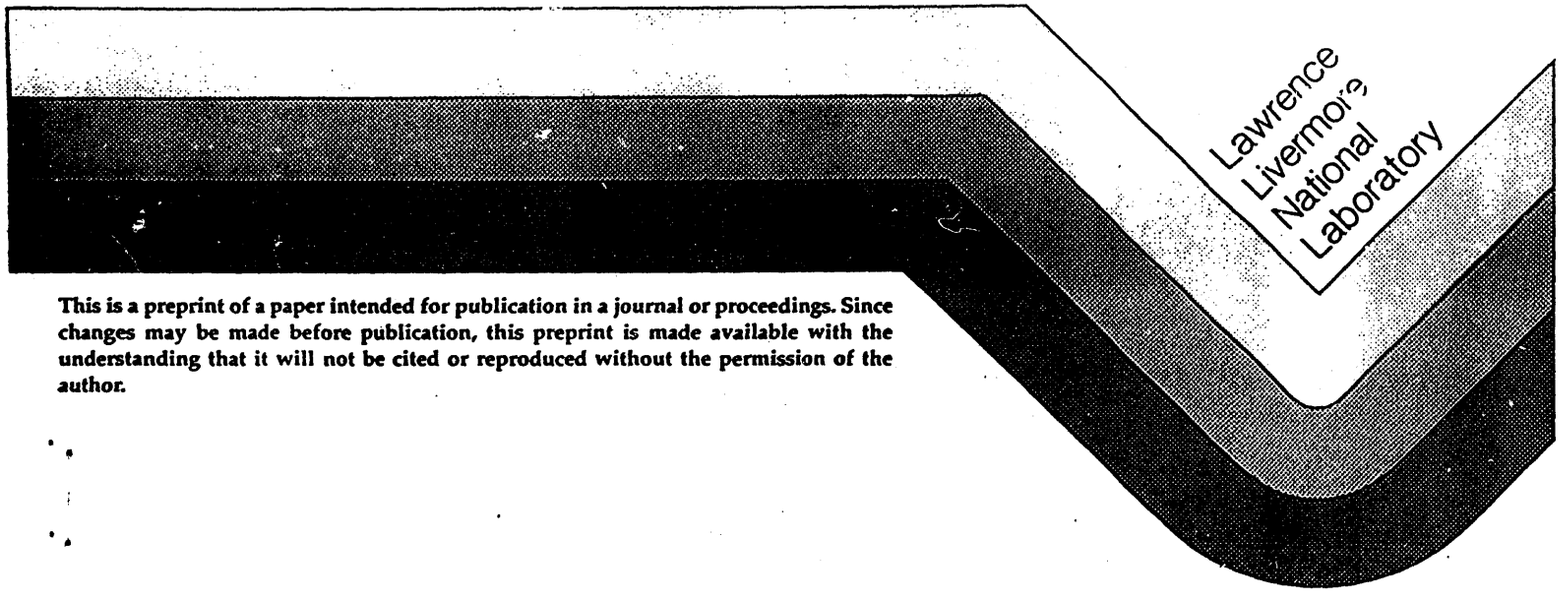

DISCLAIMER

TRANSPARENT ULTRALOW-DENSITY SILICA AEROGELS PREPARED BY A TWO-STEP SOL-GEL PROCESS*

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ABSTRACT

Interest in lowering aerogel densities for applications involving high energy charged particle detection via the Cherenkov effect has led to the development of a two-step sol-gel method for preparing ultralow-density aerogels. This method has been used in our laboratories to produce uncracked, transparent aerogel tiles with densities from .003 to .080 gms/cc. In this paper, we will give a detailed description of this method. Comparative characterization of conventional single-step base catalyzed aerogels to aerogels prepared by this two-step approach will be presented. Results indicate that the aerogel microstructure for the two-step approach differs from the bead-like structure proposed for single-step base catalyzed TMOS aerogels. TEM micrographs of aerogels prepared by the two-step method shown an interlinked polymer chain-like structure with an average chain diameter of 2-3nm and an average chain length of approximately 15nm. UV-VIS spectrophotometry shows the transmittance over the visible spectrum (400-800nm) to be significantly improved for the two-step aerogels by as much as 30%. Other measurements of the ultralow-density aerogels include BET surface area, and compressive modulus.

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INTRODUCTION

Interest in silica aerogels began at Lawrence Livermore National Laboratory in 1985 for use as a target component in inertial confinement fusion experiments. However, organic aerogels with very similiar microstructures and material properties but with lower atomic numbers have become the preferred material for these experiments [1]. Work continued in lowering silica aerogel densities for applications involving high energy charged particle detection via the Cerenkov effect and as a micrometeroid capture medium for NASA space shuttle missions.

Conventional silica sol-gel chemistry is limited for the production of transparent ultralow-density aerogels because (1) gelation is either slow or unachievable, and (2) even when gelation is achieved, the large pore sizes result in loss of transparency for aerogels <.020 g/cc. We have developed a two-step sol-gel process that circumvents the limitations of the conventional process and allows the formation of ultralow-density gels in a matter of hours. We have found that the gel time is dependent on the catalyst concentration. After supercrtical extraction, the aerogels are transparent, uncracked tiles with densities as low as .003 g/cc.

The classical sol-gel process for preparing aerogels involves the hydrolysis and condensation of silicon alkoxides according to the reactions:

$$nSi(OR)_4 + 4nH_2O \rightleftharpoons nSi(OH)_4 + 4nROH \qquad \text{(Hydrolysis)}$$

$$nSi(OH)_4 \rightleftharpoons nSiO_2 + 2nH_2O \qquad \text{(Condensation)}$$

This is typically done in a single-step procedure where tetralkoxysilane, water, catalyst, and a predetermined amount of alcohol for density control are mixed together. Hydrolysis begins and both reactions proceed simultaneously with condensation reactions involving the silanol groups forming siloxane bonds plus the by-products alcohol or water according to the following reactions:

$$\equiv Si - OR + H_2O \rightleftharpoons \equiv Si - OH + ROH \quad \text{(Hydrolysis)}$$

$$\equiv Si - OR + HO - Si \equiv \rightleftharpoons \equiv Si - O - Si \equiv + ROH \quad \text{(Alcohol condensation)}$$

$$\equiv Si-OH + HO - Si \equiv \rightleftharpoons \equiv Si - O - Si \equiv + H_2O \quad \text{(Water condensation)}$$

Solution viscosity rises, gelation occurs, and aging along with syneresis continue to strengthen the gel structure. Using the single-step method to prepare ultralow-density aerogels requires adding large quantities of excess solvent to the mixture to dilute the silica concentration. If alcohol is used as a diluent , as is generally the case, the backward hydrolysis reactions can become favored and prevent gel formation. Even when gelation is achieved after high dilution by this method, the gel time is extremely long and can result in loss of transparency for the resulting aerogels.

A way to bypass the above limitation to make transparent ultralow-density aerogel tiles is to use a two-step approach. The first step is to form a partially hydrolysed, partially condensed silica precursor (CS) by reacting tetralkoxy-silane with a sub-stoichiometric amount of water. This precursor is then further processed to a gel in the second step. An important part of the procedure is removing the reaction-generated alcohol in the first step and replacing it with a non-alcohol solvent. This approach has been used to make uncracked aerogel tiles ranging in density from .003 to .650 g/cc. Another important result of this chemistry is that the microstructure of the resulting aerogels is different from that of single-step aerogels.

EXPERIMENTAL

Preparation of CS

The first step in the procedure for preparing ultralow-density aerogels involves the formation of a condensed silica oil , as described previously [2]. Although the most transparent aerogels have been made with tetramethoxysilane (TMOS), the following procedure works equally well with tetraethoxysilane (TEOS) and ethanol as the solvent. TMOS supplied by Petrarch Systems, Inc. was used as the starting material, but, in order to have consistent and reproducible results *purification of the alkoxide is essential.* This is done by fractional distillation using a four foot silvered, vacuum jacketed fractionating column filled with glass beads under a N_2 purge. The purified TMOS is then mixed with methanol and a sub-stoichiometric amount of water and refluxed under acidic conditions for 16.0 hours. This

mixture is prepared by the sequential addition of TMOS, methanol, water, and hydrochloric acid in the molar ratio 1 TMOS: 2.4 MeOH: 1.3 H_2O: 10^{-5} HCl. The additional methanol is added to keep the reacting mixture single phase. The amount of water can be varied up to 1.6 moles of water per mole of alkoxide without gelation during refluxing. After refluxing, all alcohol produced by reaction and that initially added to keep the mixture single phase, is distilled off and the CS oil collected. The product is diluted with a non-alcholic solvent (eg. acetone, ether, or acetonitrile) and can be stored indefinitely for later use. The non-alcohol solvent inhibits the reverse equilibrium reactions and stabilizes the oligomeric silica mixture against reactions leading to gelation.

Preparation of Aerogels

Using CS as the precursor, the ultralow-density gel is made by reactions which complete the hydrolysis under basic conditions with a large excess of a non-alcohol solvent. This is typically done by mixing the CS with 2.7 moles of water per mole equivalent of the original TMOS, sufficient non-alcohol solvent (typically acetonitrile or acetone) to achieve targeted density, and 2 ml of ammonium hydroxide catalyst per liter of solution. The mixture is then stirred and poured into glass molds where gelation and aging occur at room temperature. Depending on catalyst concentration, a .010 g/cc alcogel can be made in a .5 hour.

Conversion of the alcogel to the aerogel is done by placing the glass molds directly in an autoclave for supercritical extraction of the solvent. The temperature is ramped to 300°C at a rate of 20°C/hr, while holding pressure generated by the solvent vapor at approximately 136 bars. The vessel is then depressurized at a rate of 20 bars/hr and the aerogel is allowed to slowly cool while the vessel is purged with dry N_2 gas.

Ultralow-density aerogels prepared in this manner are hydrophobic and stable when exposed to atmospheric conditions. Ultralow-density aerogels produced by low temperature carbon dioxide supercritcal drying are hydrophilic and have been observed to shrink badly when exposed to air.

Comparative characterization is with TMOS aerogels made by single-step base catalysis. Care is taken to use the same amount of water in both approaches with the molar ratio fixed at 4 H_2O: 1 TMOS.

Characterization Methods

The analytical techniques used to characterize the structure of the ultralow-density aerogels were transmission electron microscopy (TEM) and nuclear magnetic resonance spectrometry (NMR). Other techniques included BET nitrogen adsorption for surface area and UV-VIS spectrophotometry for

transmissivity measurements. To determine the composition of the CS precursor NMR, GC/MS and viscosity measurements were done.

The NMR data were obtained on a Bruker Model 300MSL Spectrometer operating at 59.62 MHz for the ^{29}Si nucleus. To study the CS precursor the experimental parameters were a 5-μs observed pulse width, a 1.10-sec acquisition time, a 4-sec recycle delay, and a 32k transform size. Gated decoupling was used to suppress the nuclear Overhauser effect. A "WALTZ-16" program was used to decouple protons[3]. Chromium(III) acetylacetonate [$Cr(acac)_3$, .015M] was needed as a paramagnetic relaxing agent.

A Hewlett-Packard 5985 GC/MS was used to analyse the CS. A 30 meter, DB1 capillary column with a dimethysiloxane coating was used in the gas chromatograph. The initial temperature was 70°C with a temperature ramp of 10°C/min. The CS was diluted with methylene chloride prior to analysis. The mass spectra data were obtained at 70ev ionization and a source temperature of 200°C.

The modulus (stiffness) of the aerogels was determined in uniaxial compression at an initial strain rate of 0.1%/sec. The measurments were done at ambient conditions. The relative humidity was generally 50-70% during testing and no special precautions were taken to prevent moisture adsorption by the aerogels. Great care was taken to ensure that the end faces of the test specimens were smooth and plane parallel. The compressive modulus was determined from the linear region of the load-displacement curve.

A JEOL model 200CX scanning transmission microscope (STEM) was used to obtain micrographs of aerogels. The aerogels were examined uncoated. Although charging from the electron beam can be a problem, we have found that the coating obscures the actual microstructure.

RESULTS AND DISCUSSION

Analysis of CS

The condensed silica precursor was analysed by NMR and GC/MS to determine the type and distribution of oligomers [4]. A typical ^{29}Si NMR spectrum with assignments is shown in figure 1. Assignments from the published literature [5,6] have been used to associate peaks with denoted structures. The Q notation used to describe the silicic acid ester structures is that of Engelhardt [7] where the superscript refers to the number of bridged silica atoms to the one under consideration. The schematic representation of the species shows the silicon atoms as dots with the oxygen atoms in the lines coupling the dots. The spectrum shows that condensation has proceeded to the formation of small linear chains and cyclic trimers and tetramers. Only trace amounts of fully linked (Q^4) species are present. Line broadening within

a peak assignment indicates a distribution of molecular weights.

NMR analysis also demonstrates that the condensed silica re-esterifies in the presence of methanol as shown in figure 2. In the Q^2 region, the singularly hydroxalated linear oligomer decreases with a concurrent increase of the fully esterifed species. The same tendency holds for the Q^1 region as well. Condensed silica stored in non-alcohol solvents do not show a significant change with this type of analysis. NMR analysis of CS stored in a sealed vessel for 1.5 years showed no significant change from the as prepared CS.

A typical GC/MS profile for the condensed silica is shown in figure 3. The data suggest the formation of small linear chains and cyclic trimers and tetramers and are in agreement with the NMR results. Determination of the relative peak areas show the cyclic tetramer and the cyclic trimer with one additional siloxane linkage to be the most abundant oligomeric species present. Subsequent addition of siloxane linkages leads to the next most abuntant species and eventually results in ring closure yielding a double trimer or tetramer (ladder-like). Linear species with greater than four siloxane linkages were not detected. GC/MS analysis, however, is limited to the low molecular weight species due to the non-volatility of the higher molecular weight oligomers.

Viscosity of the condensed silica was determined to be 480 centipoise by the falling ball method. This indicates molecular weights in the 10,000-15,000 range. Attempts to separate these high molecular weight oligomers by spinning band distillation and gel-permeation chromatography have been made without success. The refractive index of the condensed silica oil is 1.4063. The density is 1.328 g/cc.

Characterization of Aerogels

The transmittance of aerogels prepared by both methods is shown in figure 4. The data compare transmittance for equivalent density aerogels prepared by the two different approaches as well as an ultralow-density aerogel made by the two-step approach. Care was taken to use aerogels of the same thickness. The transmittance of the two-step aerogels is considerably higher than conventional aerogels for all wavelengths between 200 and 800 nm. What is surprising is the extent of increased uv transmittance of the ultralow-density aerogel. As the density is lowered and the porosity increased, one would expect increased extinction at all uv-vis wavelengths due to scattering from larger pores. These ultralow-density aerogels either have smaller than expected pores or very uniform pore sizes. To date we have not been able to accurately measure either.

Compressive modulus data for the single- and two-step methods are shown plotted in figure 5. The data for aerogel densities less than .08 g/cc shown in the plot have considerable scatter due to difficulty in these measurements but they are consistent with sound velocity data reported by Gross et al [9] for evacuated ultralow-density aerogels. Both their data and ours show a different power law slope for the ultralow density aerogels compared to the silica aerogels with higher densities.

The TEM micrographs of aerogels prepared by both methods are shown in figure 6. Conventional single-step base catalysed TMOS aerogels show strings of spheroidal particles linked together with minimal necking. The spheroidal particles have an average diameter of approximately 12 nm.The aerogels made by the two-step method, however, have a chainlike microstructure. The average width of the chains is approximately 2 nm and many chains are as long as 20 nm between connections. Recent high resolution transmission electron microscopy (HRTEM) using a replication process shows the two-step aerogel to be composed of many fine filaments which indicates a polymeric network [10]. Previous HRTEM showed the single-step aerogel consisted of spherical particles or beads ranging in size from 9-13 nm with an average diameter of 11 nm which is indicative of a colloidal microstructure [11].

The BET surface area measurements for the two-step aerogels from .003 to .100 g/cc are in the range of 550 to 675 m^2/g. These results are anomolously low compared to conventionally prepared aerogels which give values of 700 to 750 m^2/g and two-step aerogels of higher density with values of 850 to 950 m^2/g. It is possible that the ultralow-density aerogels have a number of pores too small for the nitrogen molecule to fill, thereby resulting in low BET measured values for the surface area. We are now attempting these measurements with argon and helium. The measured skeletal density by helium pycnometry for the two-step method is 1.81 g/cm^3, compared with 2.09 g/cm^3 for the single-step derived aerogels.

SUMMARY

A two-step method for preparing ultralow-density aerogels has been described. Results suggest that the microstructure for this two-step method is different from the bead-like structure proposed for single-step, base-catalysed TMOS aerogels. The data presented here suggests that the two-step method results in a polymer-chainlike structure with an average chain diameter of 2-3 nm and an average chain length >15 nm.

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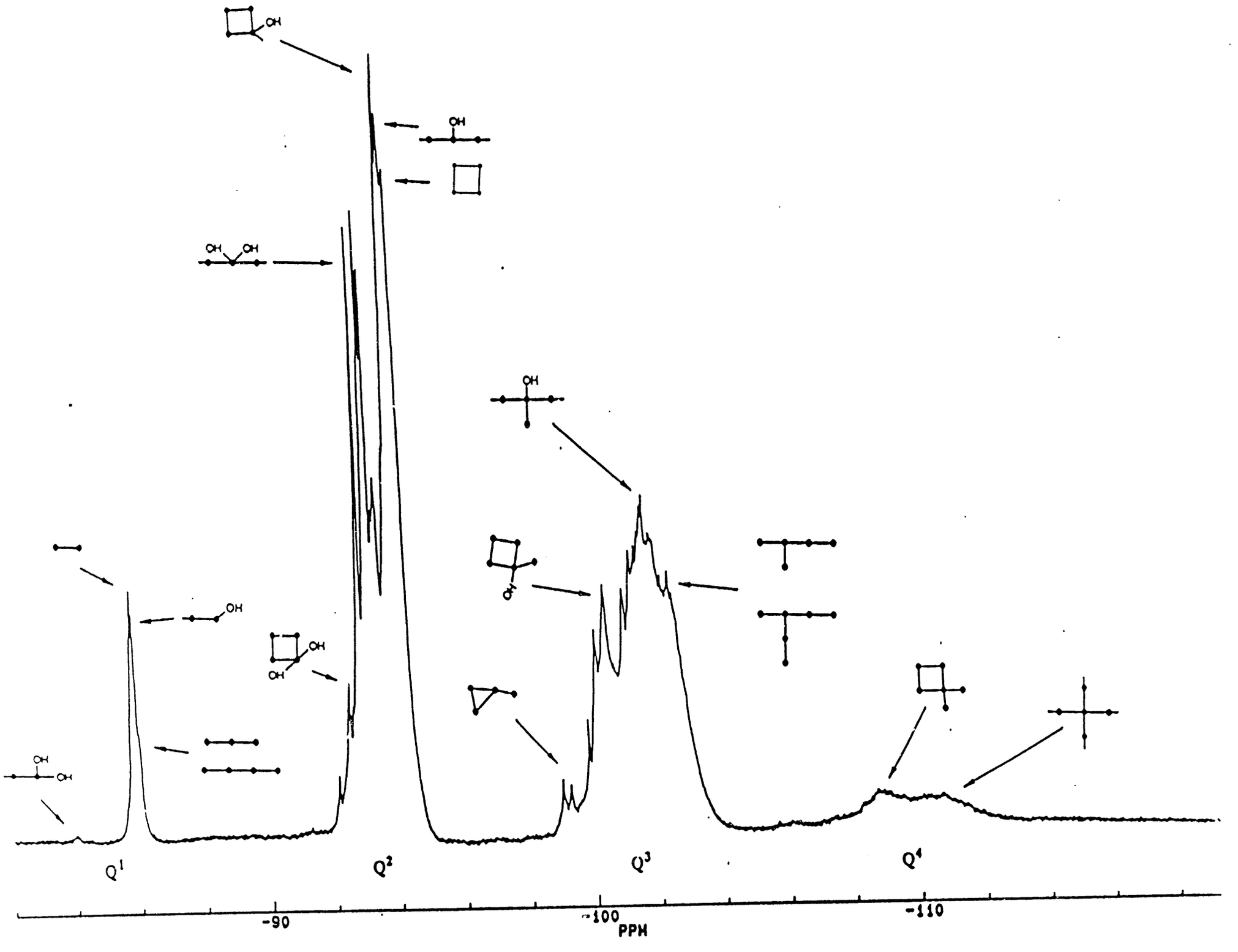
Figures :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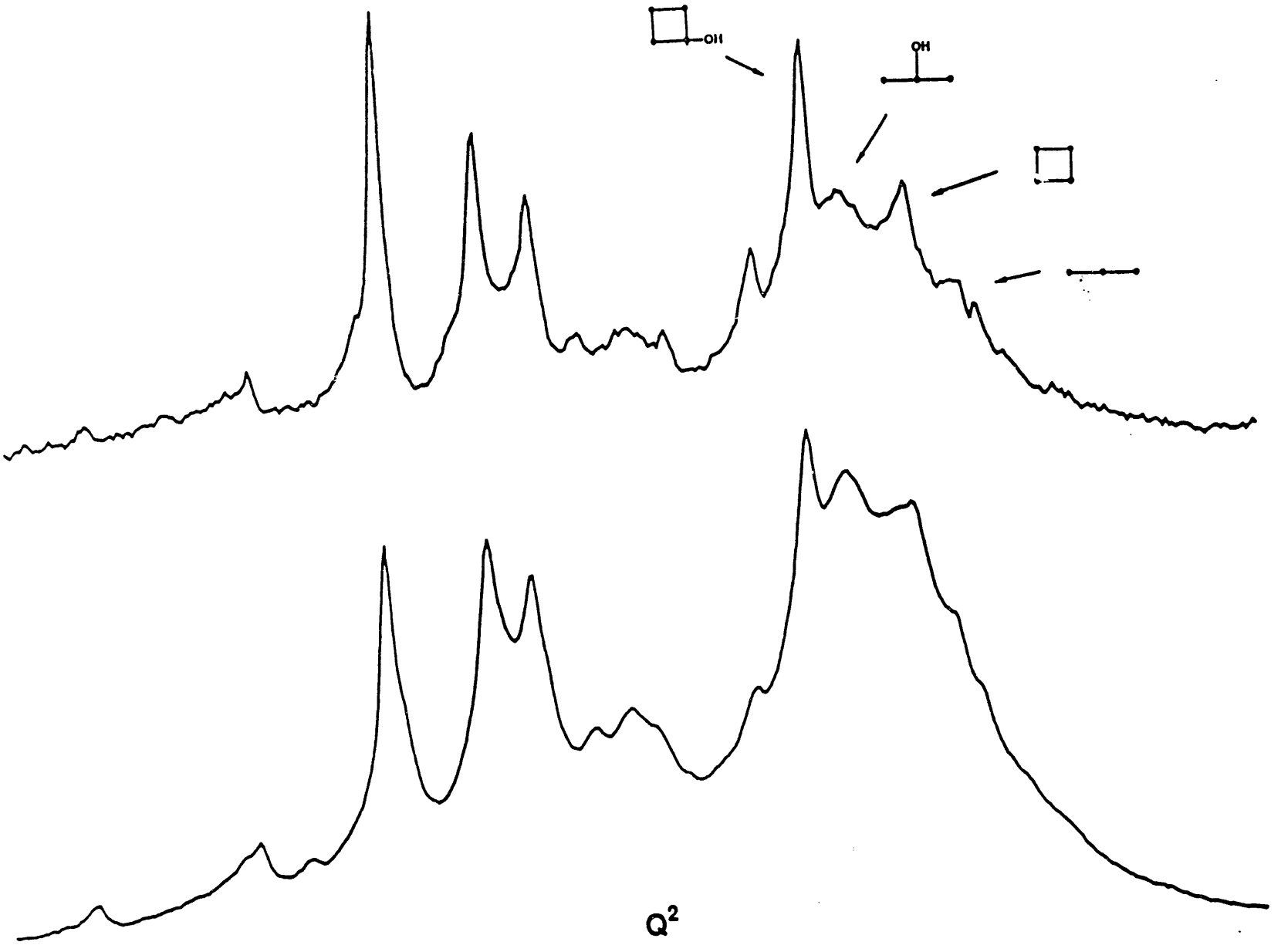
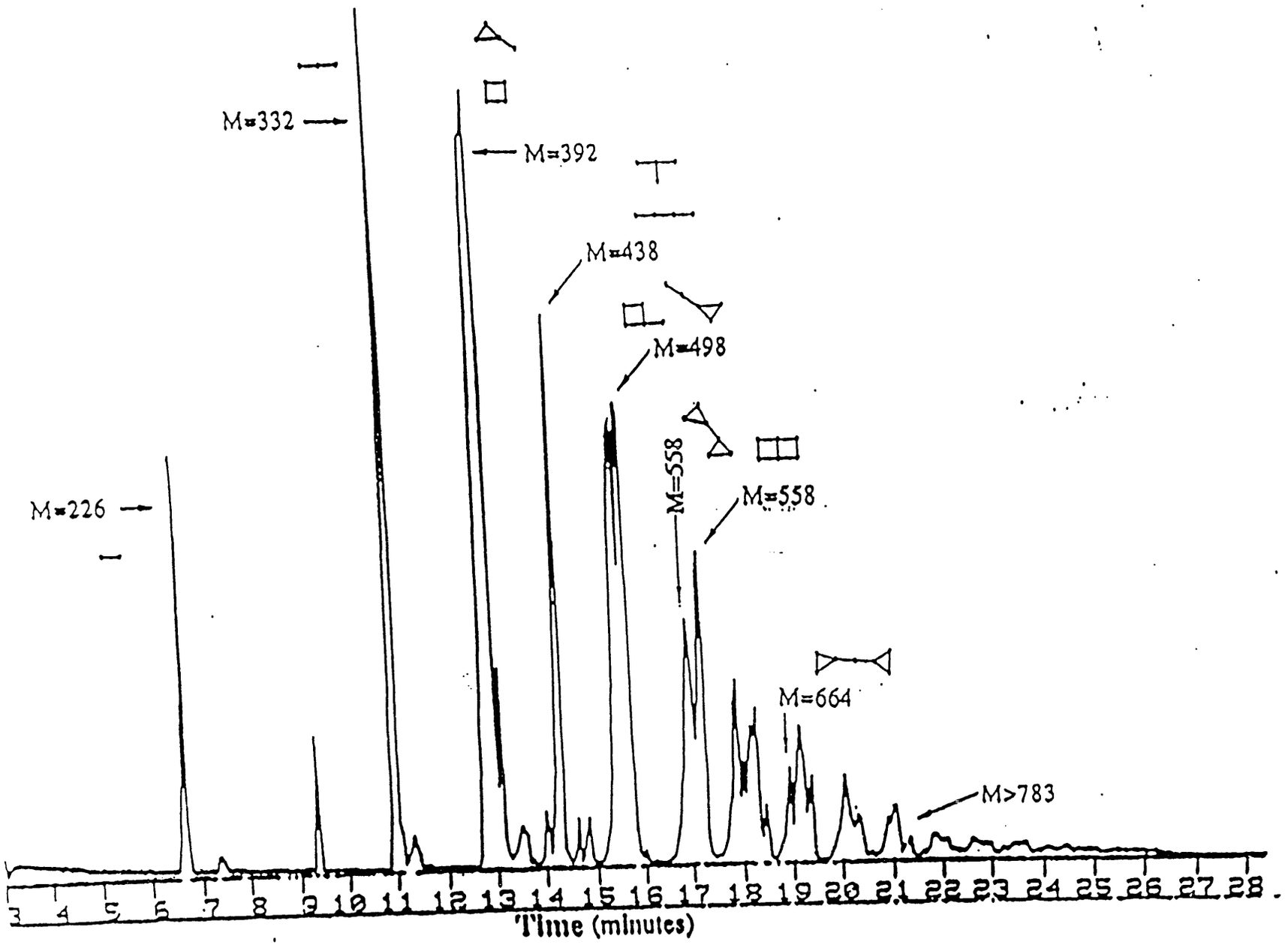
Q2
Q3
Q4
-90
-100
-110
PPH


OH
OH
Q²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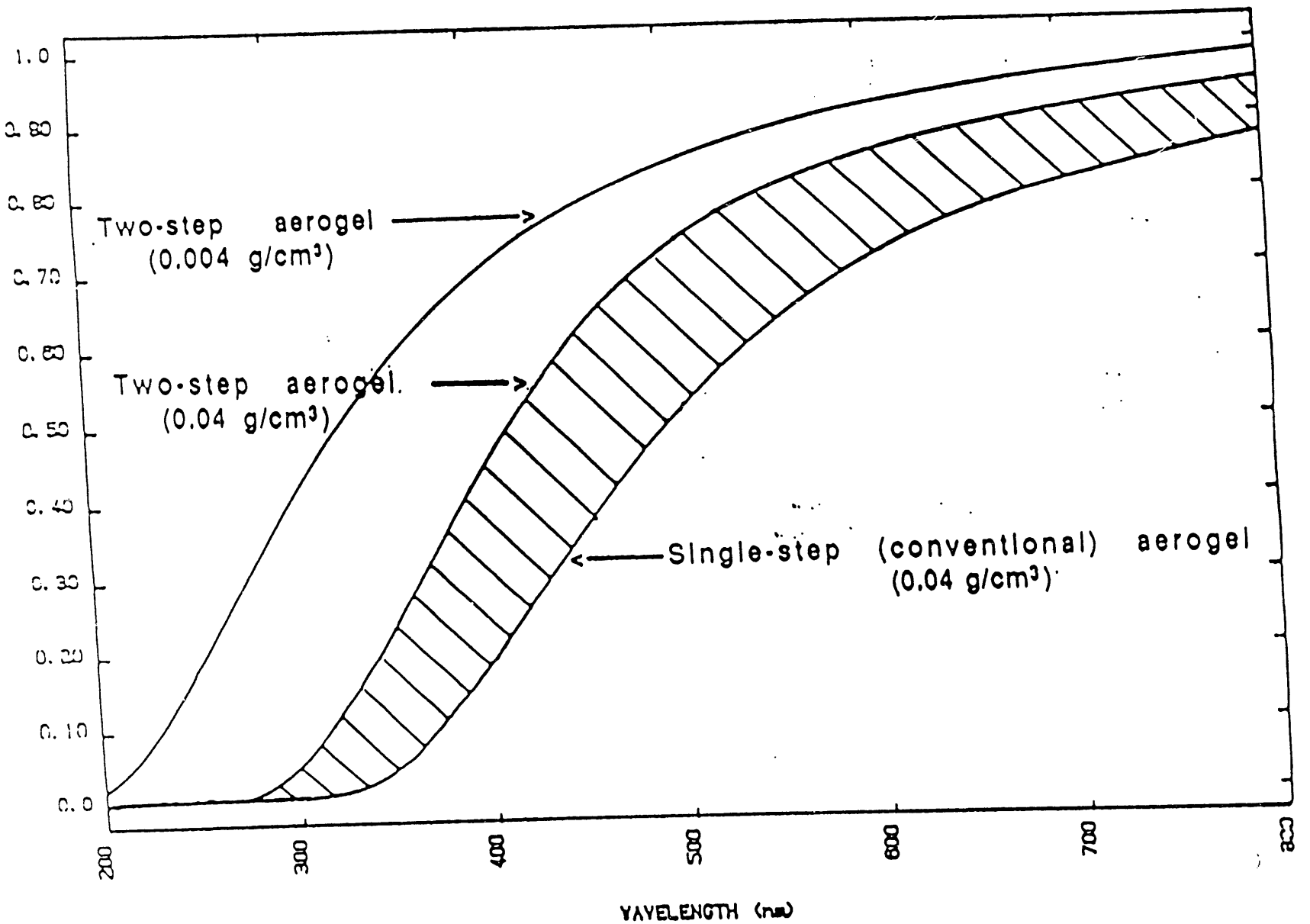
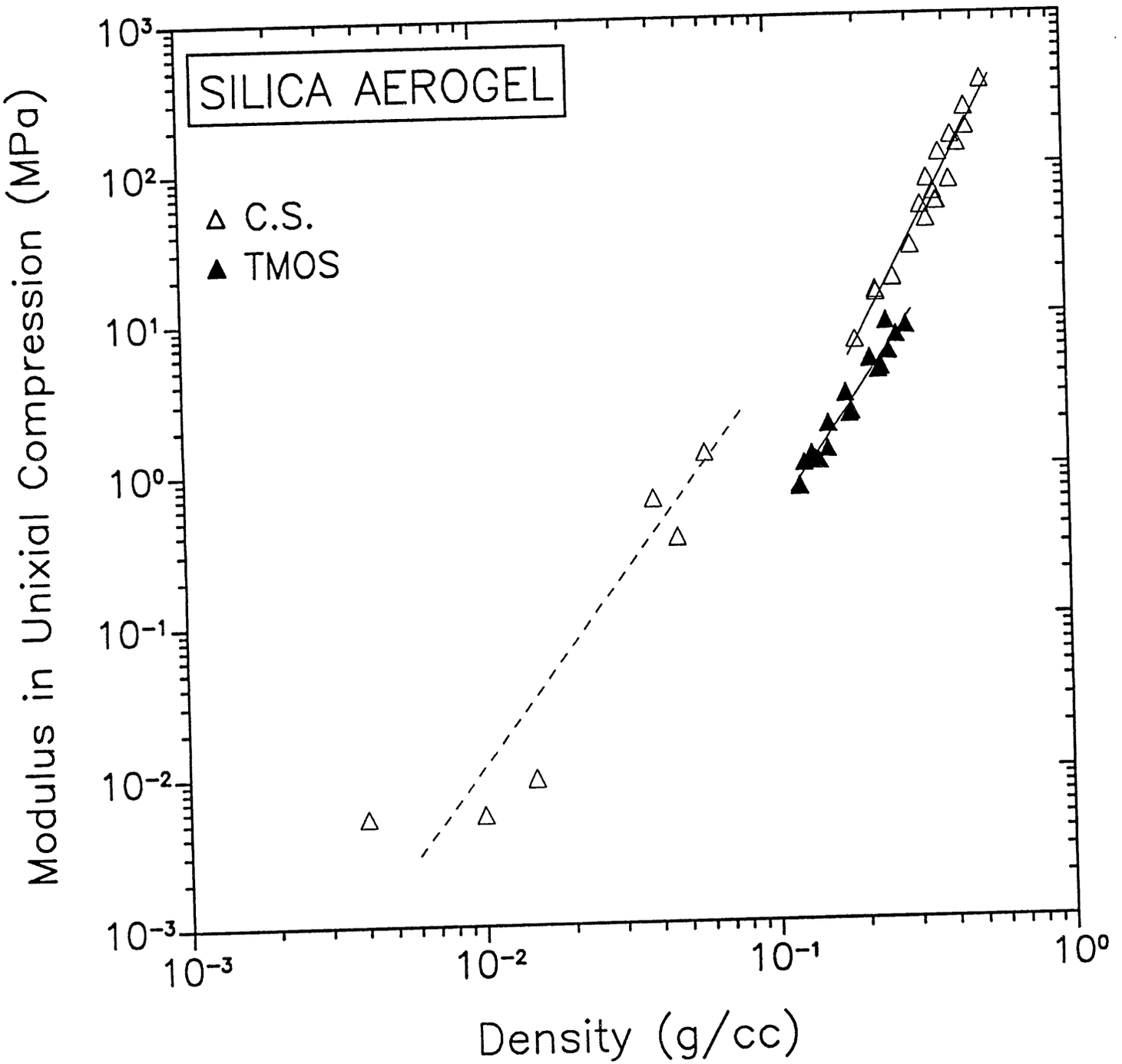
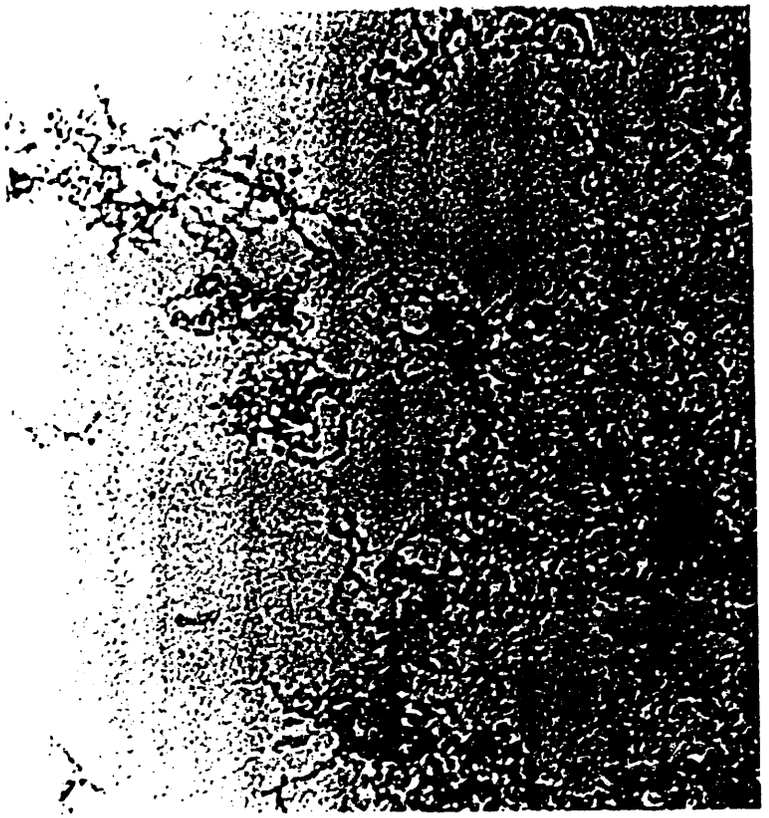
Time (minutes)


1.0
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.0
TRANSMITTANCE
200
300
400
500
600
700
800
WAVELENGTH (nm)
Two-step aerogel
(0.004 g/cm³)
Two-step aerogel
(0.04 g/cm³)
Single-step (conventional) aerogel
(0.04 g/cm³)


SILICA AEROGEL
△ C.S.
▲ TMOS
Modulus in Unixial Compression (MPa)
Density (g/cc)
10³
10²
10¹
10⁰
10⁻¹
10⁻²
10⁻³
10⁻³
10⁻²
10⁻¹
10⁰



TEM of ULD aerogel (0.008 g/cm^3)

200Å

TEM of CONV aerogel (0.04g/cm^3)

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