ANALYSIS OF GUMS USED IN INKS
AND FOUNTAIN SOLUTIONS

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ABSTRACT:

An analytical method was developed using
gas chromatography (GC) and gas chromatography
/mass spectrometry (GC/MS) to characterize some
common types of polysaccharides used in litho
fountain solutions and as additives to printing
ink binders.

Results of the analysis of Gum Arabic,
Carboxy methyl cellulose (CMC), Ethyl hydroxy
cellulose (EHEC), and Hydroxy ethyl cellulose
(HEC) are shown.

Examples will also be given showing how the
technique was used to identify the type and
amount of gum in fountain solutions. Also the
presence of EHEC in yellow Publication Gravure
inks was detected and the type of cellulosic
particle seen in plate and blanket contamination
characterized.

EXPERIMENTAL:

Samples of the Gum Arabic, CMC, EHEC,
and HEC model materials were hydrolyzed by
weighing out 10-15 mg of each sample combined
with 2ml of 0.5m trifluoro acetic acid (TFAA) in
water and placed on a hot plate with stirring at
120 C . The propose of the hydrolysis was to
break the more labile ether bond between each
saccharide to form monosaccharides.

The TFAA reagent was chosen due to its
universal effectiveness to cleave the ether
linkages between each sugar as compared to
other hydrolysis reagents that have been used.

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The hydrolysate was then evaporated to dryness. To the dried hydrolysate was added a solution of trimethyl silyl imidazole (TMSI) in pyridine. This in turn reacted with the hydroxyl groups on the monosaccharides and formed silyl derivatives.

This allowed a more conventional analysis using splitless capillary gas chromatography /mass spectrometry (GC/MS).

RESULTS:

The initial hydrolysis GC/MS results of these four materials are shown below;
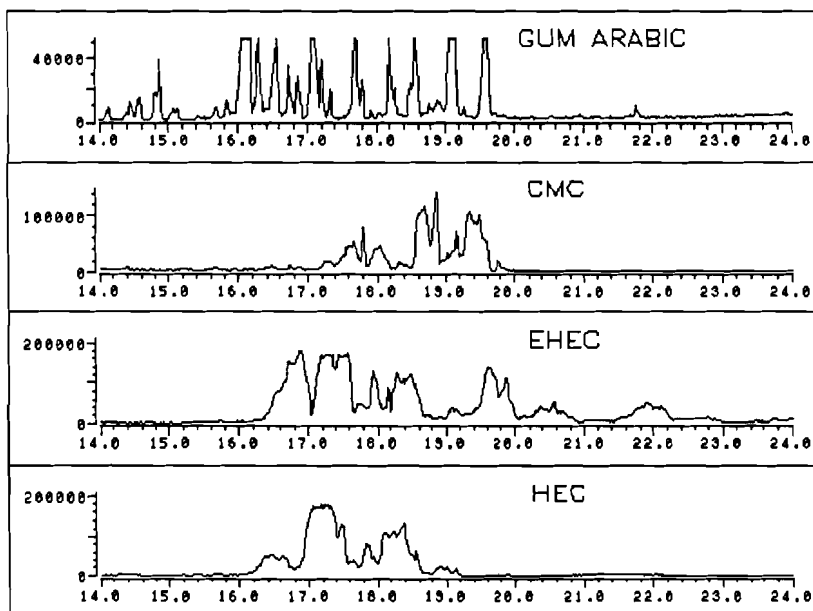
The data clearly revealed that the pattern of peaks of the hydrolysis products for these samples were completely different from each other. Therefore a study was started to determine the structure of these hydrolysis products that were seen on the GC/MS.

Here we see in the figure below one of the typical electron impact (EI) MS data obtained for the Gum Arabic sample. The bottom portion is a library reference spectrum of a sily-lated monosaccharide. You can see they correlated very well.
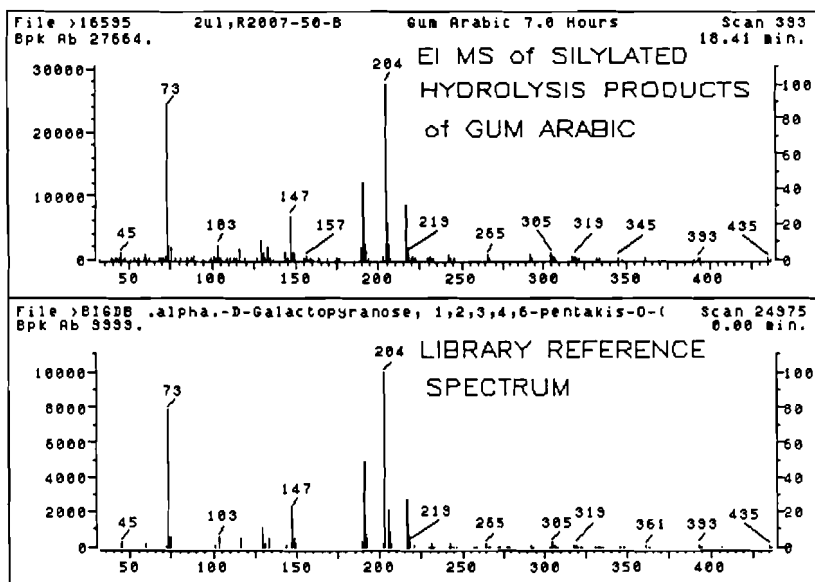

The EI MS data indicated no clear evidence of an ion indicative of the molecular weight of the monosaccharides detected. This means that the peaks could not be further characterize in this hydrolysis mixture as being one of the three major classes types of monosaccharides. These major classes are pentoses, deoxyhexoses and hexoses.

Therefore the technique of chemical ioniza-tion (CI) MS was done on these samples to try to solve this problem. CI MS is a milder form of ionization that produces a much simpler spectrum usually containing information about a compounds molecular weight.

CI MS is usually done in the presence of a
reagent gas. It is the selection of the proper
reagent gas that is necessary to obtain proper
molecular weight information.

Here we see an example of the CI MS data
from the analysis of the Gum Arabic sample.
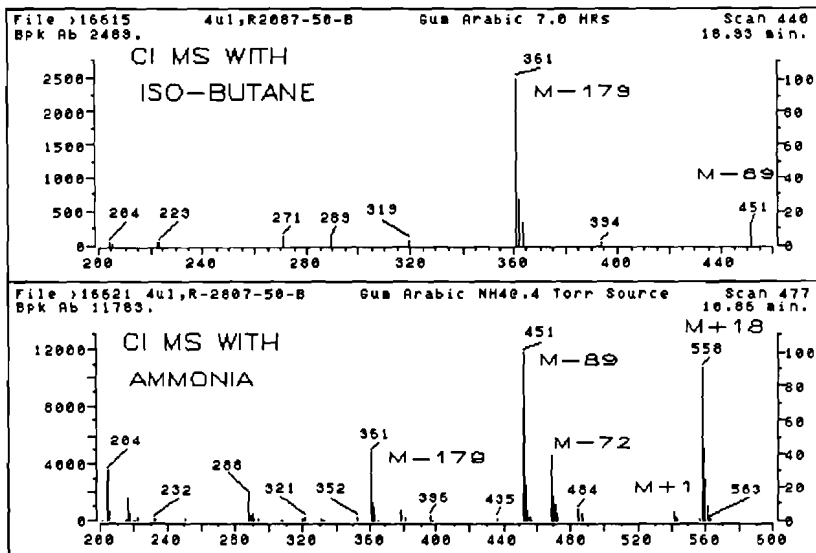
The use of iso butane as a CI reactant gas
did not yield the common M+1 (where M is the
molecular wieght) ions for these TMS sugars.
What was seen as the largest ion was a M-89
for the molecular weight minus an O-TMS Group.

The use of ammonia CI was found to yield a
M+18 ion that could be used to determine
the actual molecular weight of the monosac-
charides.   It should be noted the addition of
18 amu with the use of ammonia is common and
represents the addition of ammonia in the CI
MS reaction process.

With an actual molecular weight of 540 amu
means that this peak found in Gum Arabic
is a Pentakis TMS derivative of a hexose.

The GC/MS was now used in an attempt to determine the relative distribution of these various major classes of monosaccharides in the Gum Arabic sample. In the next figure we see the results for the Gum Arabic sample.

SILYLATED HYDROLYSIS PRODUCTS of GUM ARABIC
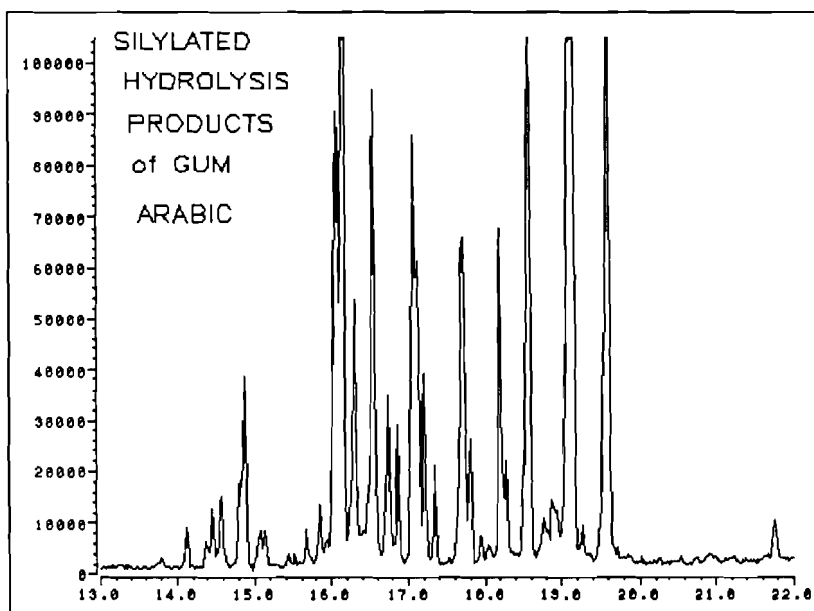
Based on the CI-MS analysis it indicated that the hydrolysis /silylation products seen here were identified as being pentoses (in which arabinose is also a pentose) with a retention time of 15.5 to 17 min. The balance being the deoxyhexoses from 17.0 to 18.5 min and hexoses from 18.5 to 20.0 min.

The data from the CMC sample indicated that all the peaks were based on hexoses. There was no GC/MS data from the silylated hydrolysis mixture that indicated materials with any acid functionality which should be present.

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This could be due to the lack of silylation and/or inability of these types of materials from eluting from the chromatographic column. It may also be due to lack of optimum hydrolysis time. Therefore a study was done to determine the best time for hydrolysis.

In the next figure we see the hydrolysis time study results for Gum Arabic.

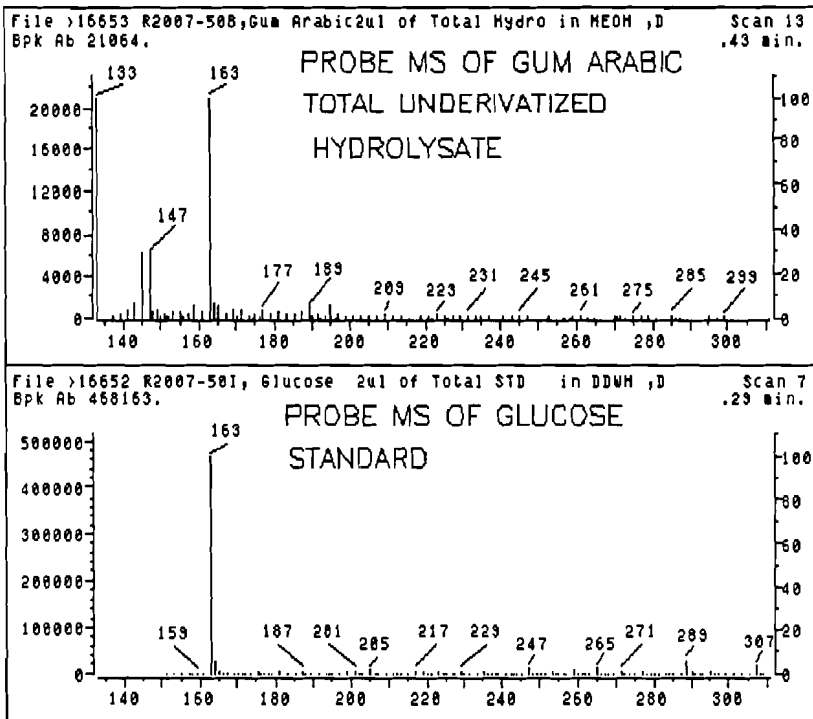ACID HYDROLYSIS OF GUM ARABIC
Total Mono Saccharides vs Time
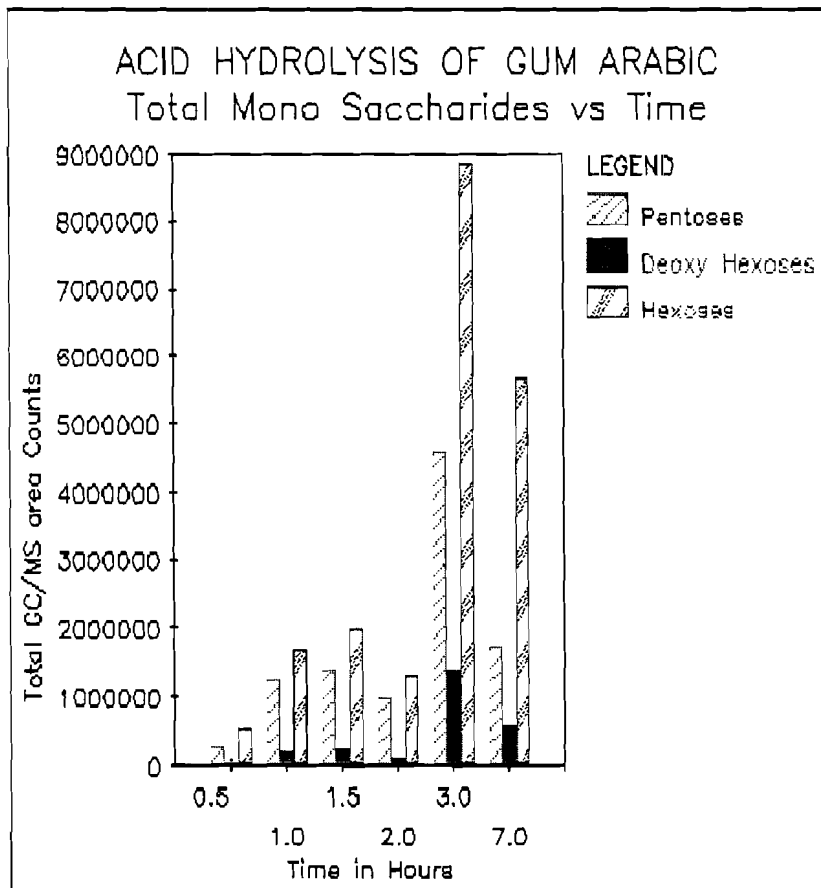
You can see from the data the the optimum hydrolysis time for the Gum Arabic is 3 hours. In the next figure we see the hydrolysis time study for the other model systems.

ACID HYDROLYSIS of MODIFIED GUMS
Total Products vs Time

LEGEND
CMC
HEC
EHEC

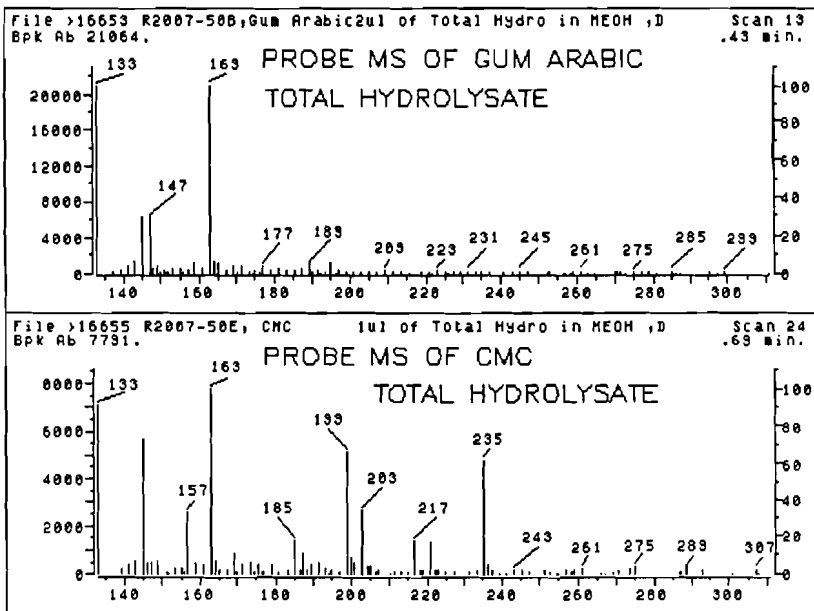Total GC/MS area Counts

Time In Hours
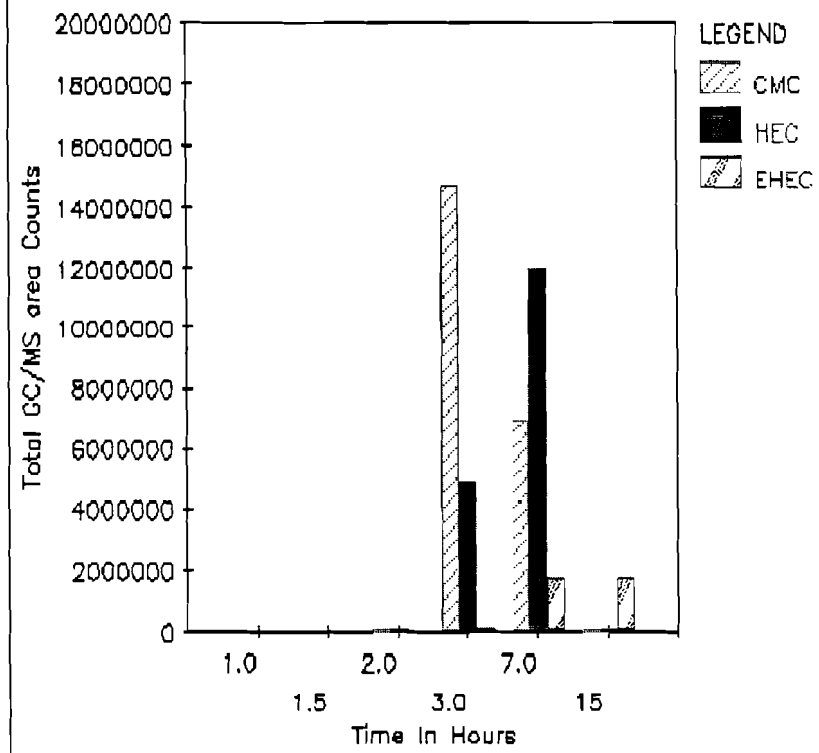
You can see from this data that the best time for CMC was 3 hrs while HEC and EHEC was found to be 7 hours.

This type of time data does not tell you if the total samples has been hydrolyzed. We wanted to know more specifically if the whole sample was truly attacked by the reagent. So the samples were placed directly into the MS without dervatization in CI mode using isobutane as the reagent gas to obtain this information. In the next figure we see the Gum Arabic hydrolysate as compared to a glucose standard.

File >16653 R2007-50B,Gum Arabic2ul of Total Hydro in MEOH ,D   Scan 13
Bpk Ab 21064.   .43 min.

PROBE MS OF GUM ARABIC
TOTAL UNDERIVATIZED
HYDROLYSATE

File >16652 R2007-50I, Glucose 2ul of Total STD in DDWH ,D   Scan 7
Bpk Ab 468163.   .29 min.

PROBE MS OF GLUCOSE
STANDARD

The probe examination of the glucose standard indicated a 163 ion for this compound with a molecular weight of 180 amu. The represents a loss of 17 amu from the molecular ion (ie. M-17) for loss of one of the hydroxyl groups. The Gum Arabic sample indicated the 133,147 and 163 as the major ions present. These are the M-17 ions for pentose, deoxyhexose and hexose. Note the absence of any higher mass ions and thus is proof that the hydrolysis is complete since no other higher molecular weight ions were detected.

The next figure is the MS data for Gum Arabic as compared to the CMC sample which seemed to indicated from the GC/MS analysis of the TMS derivatives the presence of only hexoses.

PROBE MS OF GUM ARABIC

TOTAL HYDROLYSATE

133 163 147 177 189 203 223 231 245 261 275 285 299

140 160 180 200 220 240 260 280 300

PROBE MS OF CMC

TOTAL HYDROLYSATE

133 163 157 185 199 203 217 235 243 261 275 289 307

140 160 180 200 220 240 260 280 300

significant amount of 133,147 and 163 ions for the M-17 of monosaccharides. Also detected were a series of other higher mass ions that seemed to shown apparent losses of 58 amu (M+1-59) for loss of an acid group (HO-CO-CH2). There was noted differences of 72 amu (M+1-73) for a possible methyl acid group (HO-CO-CH2-O).

Therefore probe MS analysis of the total undervatized hydrolysate combined with GC/MS analysis of the silylated hydrolysis products can differentiate Gum Arabic versus CMC and thus the technique can be used to characterize the these major types of gums used in fountain solutions.

The technique of fourier transformed based infrared red spectrometry (FT-IR) has been most notability used lately in the area of general characterizing of particles obtained from tape pulls. The limitation of the technique is it can not determine the exact type or source of a cellulosic material if detected in a particle .

The hydrolysis technique was applied to a
variety of other common cellulosic materials
that may be found in such particles to see if
they can be differentiated from each other and
to also establised a data base. In the next
figure we see some common types of materials.
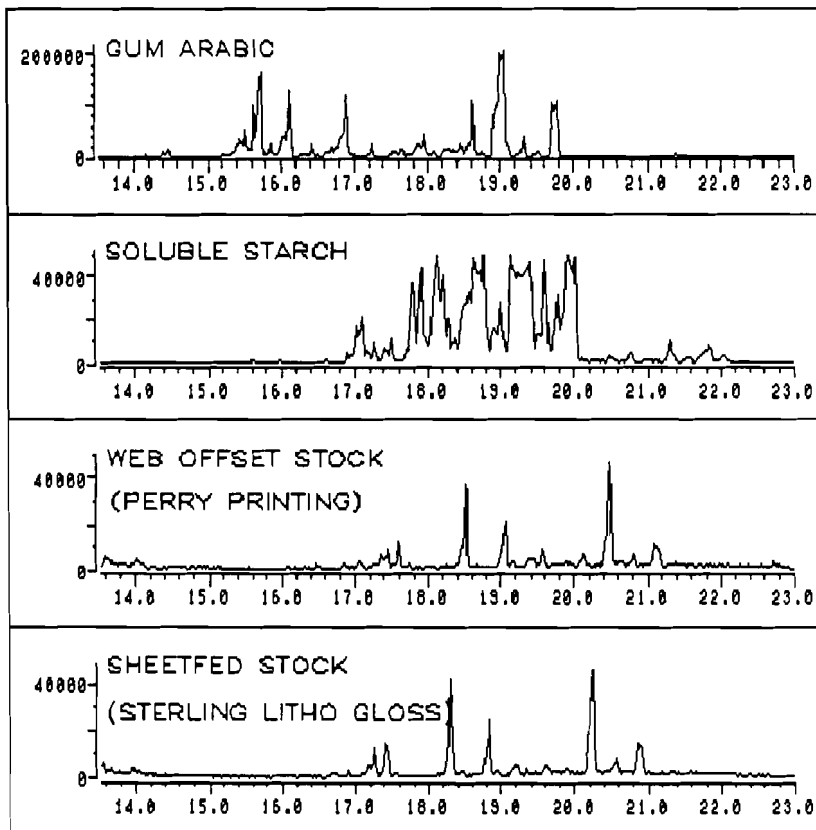
The data indicates that the pattern of
silylated monosaccharides is essentially differ-
ent in the above four samples with the exception
of the Web offset and Sheetfed stock samples.
The next figure are some more standards that
were examined.

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NEWS INK STOCK (HELLER-USDAN)

COTTON RAG

PAPER TOWEL
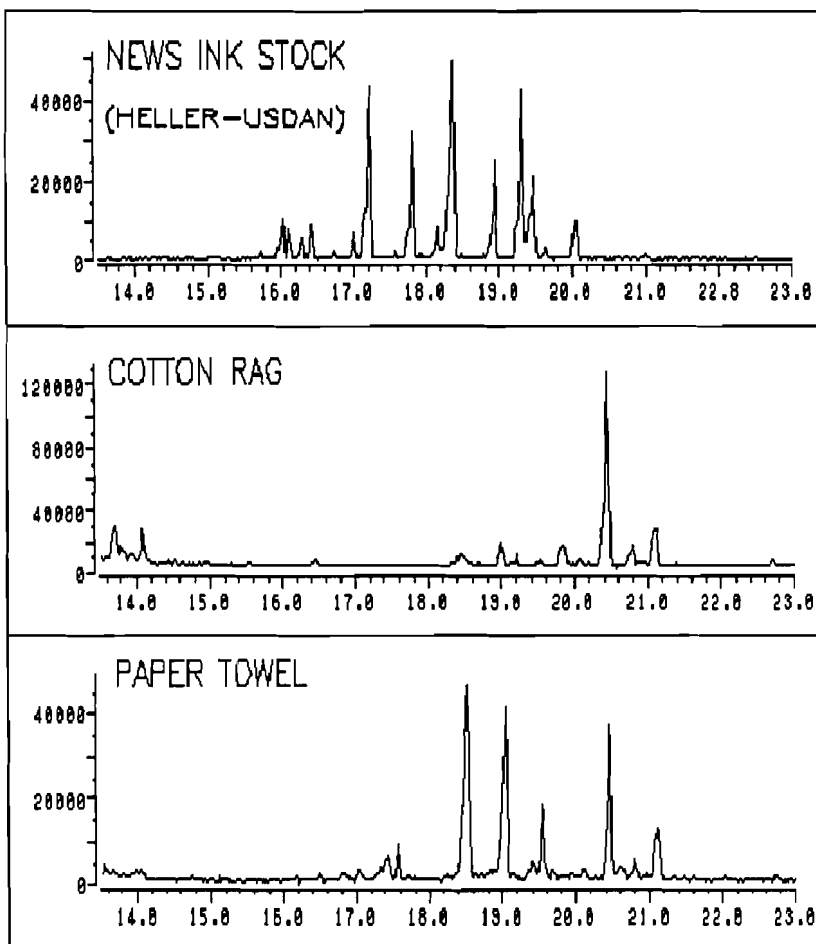
This data also indicates that the pattern of silylated monosaccharides is essentially unique for each of the samples examined.

Here we see in the next figure the micro acid hydrolysis /silylation GC/MS results of a tape pull particle of about 20um in size. Previous FT-IR analysis revealed it was based on some type of cellulosic material but could not be more definitive.
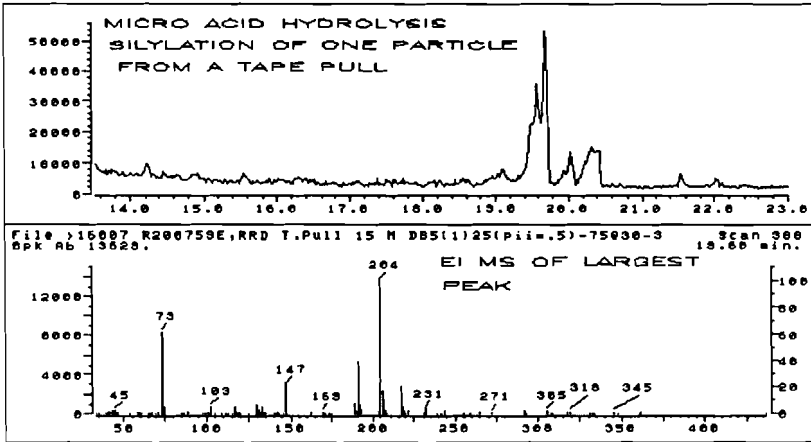
The GC/MS analysis indicated that it close-
ly matches a cotton rag. You can also see in
the bottom portion of the figure the mass spec-
trum of the largest peak, which matches the mass
spectrum seen in the Gum Arabic sample. This
technique could be very valuable in relation to
potential claims.

Now we will turn our attention back to the
EHEC and HEC model samples. In the next figure
we see the EI MS data from one of the peaks in
the acid hydrolysis/silylation of EHEC.
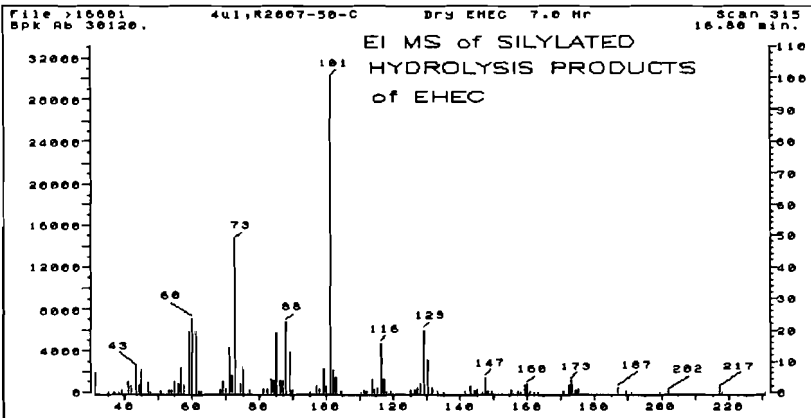
Note the absence of the 191,204 and 217 ions seen in the Gum Arabic & CMC case. What we see are ions at 85-129,129-173,173-217 that differ by 44amu for a O-C2H4 group. The EI MS data for HEC also revealed the same type of mass spectral data.

Again ,like in the Gum Arabic case, there was no ion indactive on the molecular weight of these moieties. Therefore CI MS was done on these samples. In the next figure we see the CI MS with isobutane and ammonia.
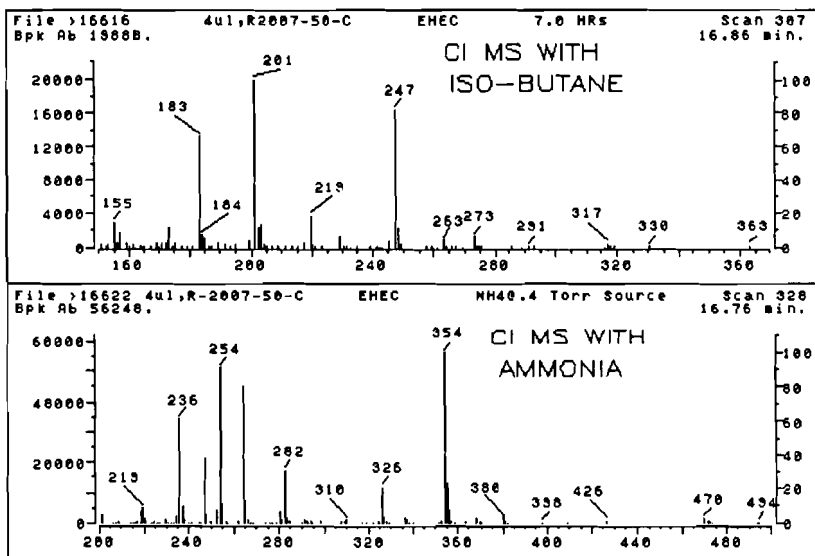

The CI MS data did show evidence of fragmentations for losses of 18 amu (H2O+), 44 amu (for C2H4O+), and 72 amu (for C2H4-O-C2H4+). This CI MS data suggested that molecular ions did not form for these compounds.

It is apparent that TMS derivatives of these species would be up into the 700+ amu range. It has been shown that TMS of sugars with molecular weights of 540 amu (like in the case of Gum Arabic) have varying molecular ion ranging from 5 to 100%.

Having molecular weights greater than this would probably result in no M+1 production and would especially be difficult when additional C2H5 and/or (O-C2H4) groups are considered.

Therefore the total underivatized hydrolysate was examined by the probe MS technique. The next figure shows these results.
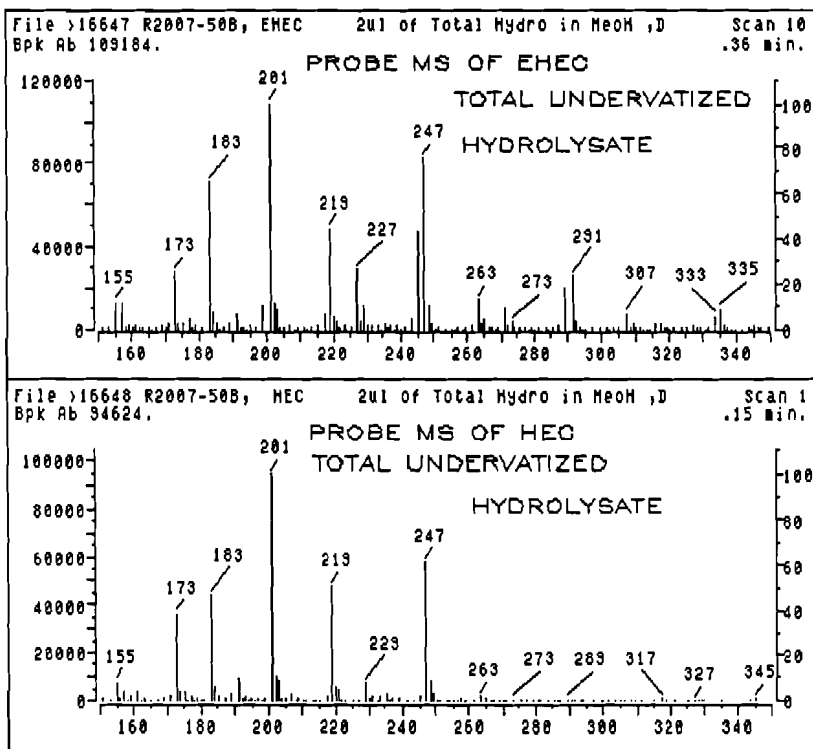
The data revealed many fragments that might be either molecular ions or M-17 ions as seen in the case of the Gum Arabic probe MS analysis. The probe MS results did reveal many ion series with losses of 28 amu (for C2H4) and 44 amu (for O- C2H4). Below in Table I are some of the possible structures associated with the probe MS data.

TABLE I - POSSIBLE STRUCTURES from the
PROBE MS DATA from EHEC & HEC SAMPLES

ION	STRUCTURE	ION	STRUCTURE
155		229	(2M+1 for TFAA)
157		245	(P+4ET-17)
173		247	(DH+3ET+1ETO-17),
			(H+4ET-17)
183		263	(P+4ET+1),
			(DH+2ET+2ETO-17),
			(H+3ET+1ETO-17)
191	(DH+1ETO-17)	271	
199		289	(P+4ET+1EO-17)
201		291	(P+5ET+1),
			(DH+3ET+2EO-17),
			(H+4ET+1ETO-17)
217	(P+3ET-17)	307	(DH+2ET+3ETO-17),
			(H+3ET+2ETO-17)
219		315	
227		333	(P+4ET+2EO-17)
		335	(P+5ET+1ETO+1),
			(DH+3ET+3EO-17),
			(H+4ET+2ETO-17)

Note:

183-227-271-315 is an unkown ion series based
on ETO

155-199-243 is an unkown ion series also based
on ETO

Where:

M= molecular ion   ET= ethyl group (C2H5)
P= pentose   ETO= ethylene oxide group
                        (C2H4O)
DH= deoxyhexose   -17 = is loss of an OH
H= hexose   TFAA= triflouro acetic acid
                        (reagent)

The last application in which this method was used was to try to detect the presence of these types of cellulosic materials present in a total ink sample.

A sample of yellow publication gravure ink was examined. The next figure shows the results of this analysis.
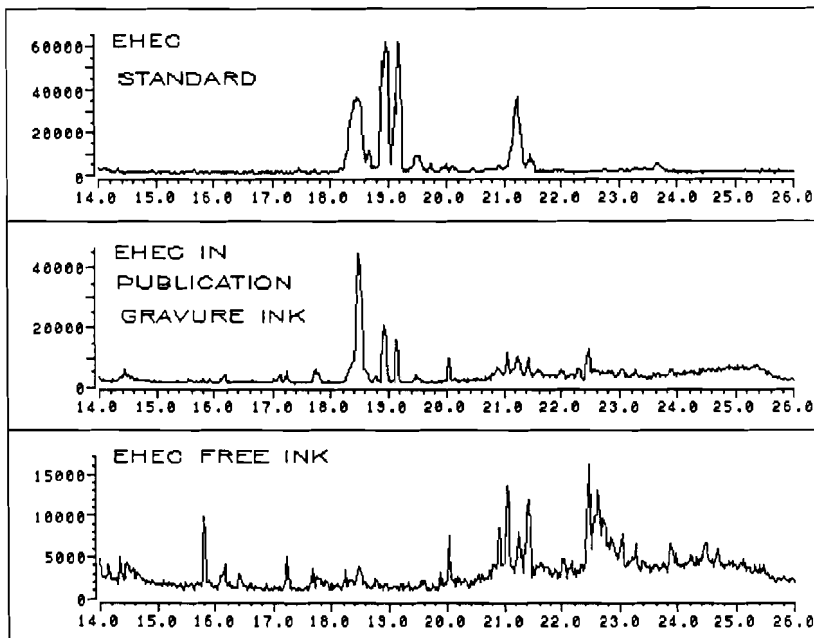
In the first experiment above we seen the examination of a 0.7 % EHEC standard that was subjected to acid hydrolysis/ silylation with analysis by GC/MS. The next experiment shows the analysis results of an ink that contained a similar amount of EHEC. The last experiment was an analysis of an ink that was free of any EHEC or any other cellulosic material. The data clearly revealed that there were no significant amount of interferences from the ink sample that would not allow the detection of these types of materials if they were present in ink samples.