Frontier Analysis, Ltd.

TECHNICAL SERVICE RESPONSE NO.: UT008

Subject: Analysis of "Angel Hair" Deposited in Burlington West Virginia (September 19, 2000)

Date: October 19, 2000

Requested By: Retha Rutherford
Burlington, West Virginia

Reported By: P. A. Budinger
Analytical Scientist

Background/Objective: On the morning of September 21, 2000 Retha Rutherford found white fibrous "spider-web" like material in her yard. It did not look like the usual webs. She took several pictures and her husband sampled the material. Mrs. Rutherford reports, "When trying to collect the samples of the stuff it turned to a clear goo somewhat like the slimy stuff you see when you cut okra." On the previous night at approximately 7:00 p.m. she heard a loud "droning" sound similar to that from a large airplane. This sound lasted about an hour. Yet the source of the sound was not visually obvious. Subsequent to the droning sound the dog became ill and vomited. Mrs. Rutherford also experienced a severe sinus attack. It is the objective of this analysis to identify this material in hopes it will provide a clue as to the source.

Following are three photographs (selected from ca. a dozen) that Mrs. Rutherford took of the material.

Conclusions:

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A white fibrous material and small amounts of other components were identified in the sample. Following are the identifications and some of the conclusions based on their analyses.

1) The white fibrous material is identified as a polymer containing protein amide type linkages, i.e. protein. Therefore, it is suspected that a biological source is involved in its manufacture. However, as this point the specific source remains unidentified. The data do show the fiber is close to that of silk made by insects and caterpillars. Also coating the fiber are droplets commonly noted in insect silks.

2) Other components attributed to the sample include a variety of fatty acid amides. The following are specifically "suggested": 4-methyl-pentamide; hexadecanamide; dodecanamide; N-tetradecanoic acid amide. It should be noted that this particular "angel hair" sample is unique in that it is the first time fatty acid amides have been detected. Trace amounts of heavier hydrocarbons such as eicosane ($C_{20}H_{42}$) and 2-methyl hexadecane are indicated. Eicosane has been found in a previous sample[1]. It is suspected these components are part of the purported gelatinous material (goo) noted by the witness. Perhaps they are final degradation products. Any lighter

[1] Frontier Analysis, Ltd. TSR No.: UT003

volatiles, if present, were probably lost during sample transferal and the failure of Ziploc® bag containers to adequately confine them.

3) The fibrous material compares to that from “angel hair” falls in Los Gatos, California (October 19-20, 1977)[2], Sacramento, California (November 11, 1999)[3], and Burns, Oregon (November 4, 1999)[4] which were also analyzed by this laboratory.

4) Research is being done to more accurately pinpoint the source of the “angel hair” and other materials. It should be noted that the suggestion that the material is from a biological origin does not rule out a possible “intelligent” influence. The “jury is still out” on the specific source of this material until further research is completed.

Procedure:

Sample: The material was gathered with rubber gloves and placed in a paper towel. The gloves were removed and in the process turned inside out. The glove, paper towel, and sample contents were placed inside a Ziploc® bag. The bag in turn was placed in another Ziploc® bag. On receipt of the sample only small amounts of white fibrous material was visually obvious.

Headspace GC-MS analysis was first done for any volatiles that may have survived the sample transferal. Five GC-MS runs were made which include: a blank (for system check); two runs of the volatiles inside the outer Ziploc® bag; one run of volatiles of the inner Ziploc® bag; one run of the volatiles inside the glove. Once the volatiles were analyzed, the bags were completely opened and infrared spectra were obtained of fibers observed in the sample using the Harrick SplitPea® cell on the Nicolet Avatar 360 spectrometer. Microscope photographs were obtained using the Leika GZ6 stereomicroscope interfaced to a Kodak Digital Science MDS 120 camera.

[2] Frontier Analysis, Ltd. TSR No.: UT002
[3] Ref. 1
[4] Frontier Analysis, Ltd. TSR No.: UT004

Results:

The results of the individual tests done on the three samples follow. These results are summarized in the conclusions section on the first page of this report.

Headspace GC-MS Analysis

The detailed results of the headspace GC-MS analysis can be found in the Appendix. These include a table that shows the best MS search results for each GC peak of all the runs, i.e. a blank (for system check), two runs of the volatiles inside the outer Ziploc® bag, one run of volatiles of the inner Ziploc® bag, and one run of the volatiles inside the glove. Also included are the GC chromatograms from each run with each peak labeled as to the best MS search "hit".

The data expectedly show more volatiles on the inside of the inner Ziploc® bag and glove rather than the exterior Ziploc® bag. The data in the table can be summarized as follows. There are a number of various components (in black font) that are attributed to the system blank or considered unrelated to the sample. There are also components (in blue font) that contain silicon and are due to contaminants which are most likely from the glove. (They are most concentrated in the run from inside the glove.) Other components (in red font) appear to be related to the sample. These are identified as primarily a mixture of fatty acid amides. Some closest "hits" in the MS search files specifically "suggest" the following amide type components: 4-methyl-pentamide; hexadecanamide; dodecanamide; N-tetradecanoic acid amide. Also detected at much lower levels were some heavier hydrocarbons such as eicosane ($C_{20}H_{42}$) and 2-methyl hexadecane. The eicosane has been detected by GC-MS analysis in a previous angel hair drop[5].

All of the components detected are higher molecular weight materials which are solid at room temperature, though with a enough vapor pressure to be detected by GC-MS. It is suspected many of the lighter materials (if present) were lost in the sample transferal and the fact that Ziploc® bags would not be expected to confine volatiles for very long[6]. It is speculated that the amides and hydrocarbons may be part of the purported gelatinous material. Perhaps they are final degradation products.

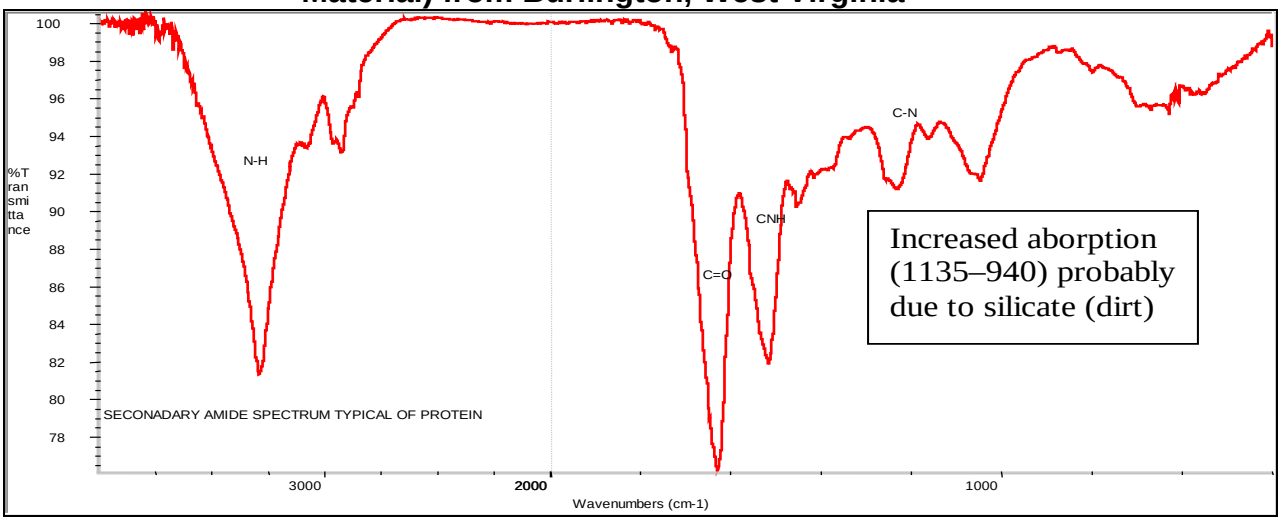
FT-IR Analysis

Several FT-IR spectra were obtained of the fibrous material. Prominent absorption bands due to N-H (3700 - 3000 cm^{-1}) and secondary amide C=O (1650 -1600 cm^{-1}) and CNH (1580 - 1470 cm^{-1}), as well as other weak to moderate bands identify the strands as a protein material. The spectra are very similar to that of spider silk, tent caterpillar silk, and silk (from processed silk, i.e. silk scarf). It suggests that the sample source is from a biological origin, i.e. animal, which may include webs from

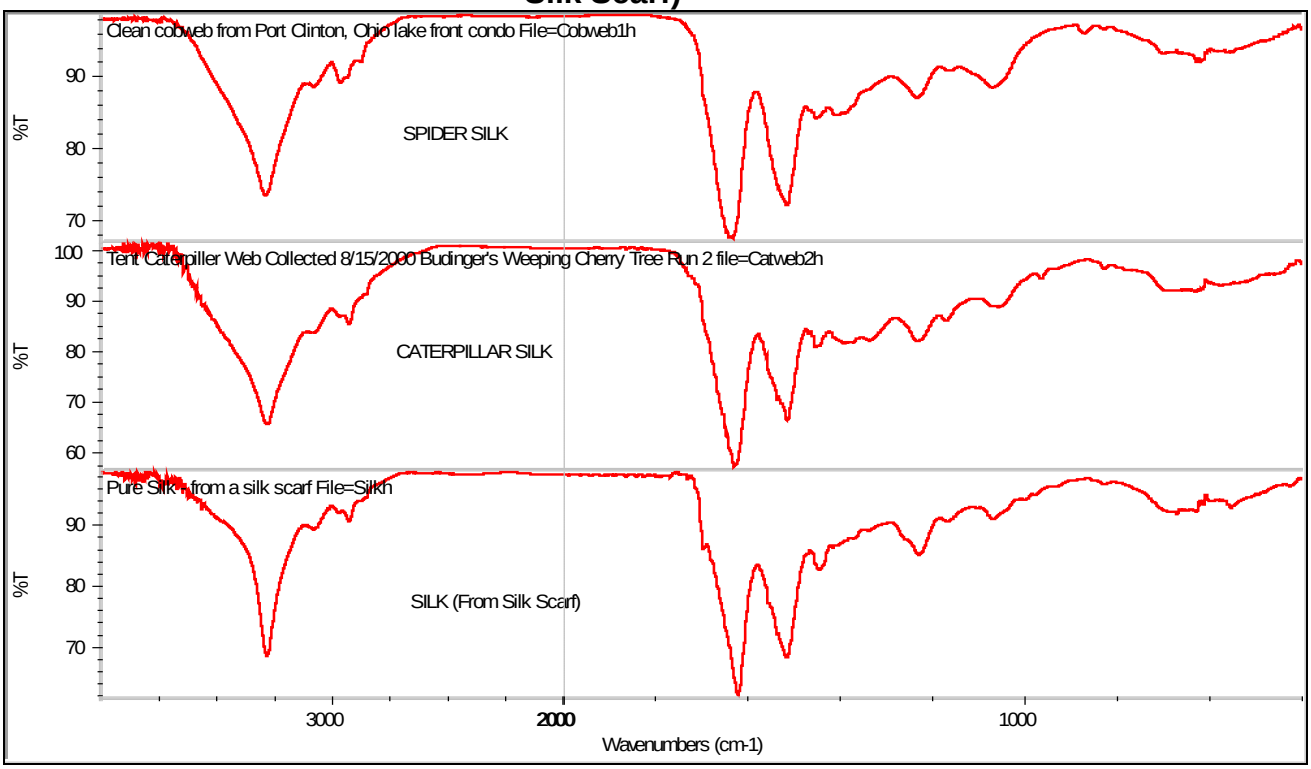
[5] Ref.: 1
[6] A tightly sealed glass jar would have been a more desirable container.

insects and caterpillars[7]. The spectra of the fibers from this drop are also similar to those obtained from other "angel hair" drops. It is also noted that in this current sample there is slightly more absorption between 1135 - 940 cm^{-1} compared to the references and angel hair from other drops. This additional absorption may suggest some silicate (dirt) is adhering to the sticky material. Following are all the above mentioned spectral data.

Most Representative Infrared Spectrum of "Angel Hair" (White Fibrous Material) from Burlington, West Virginia

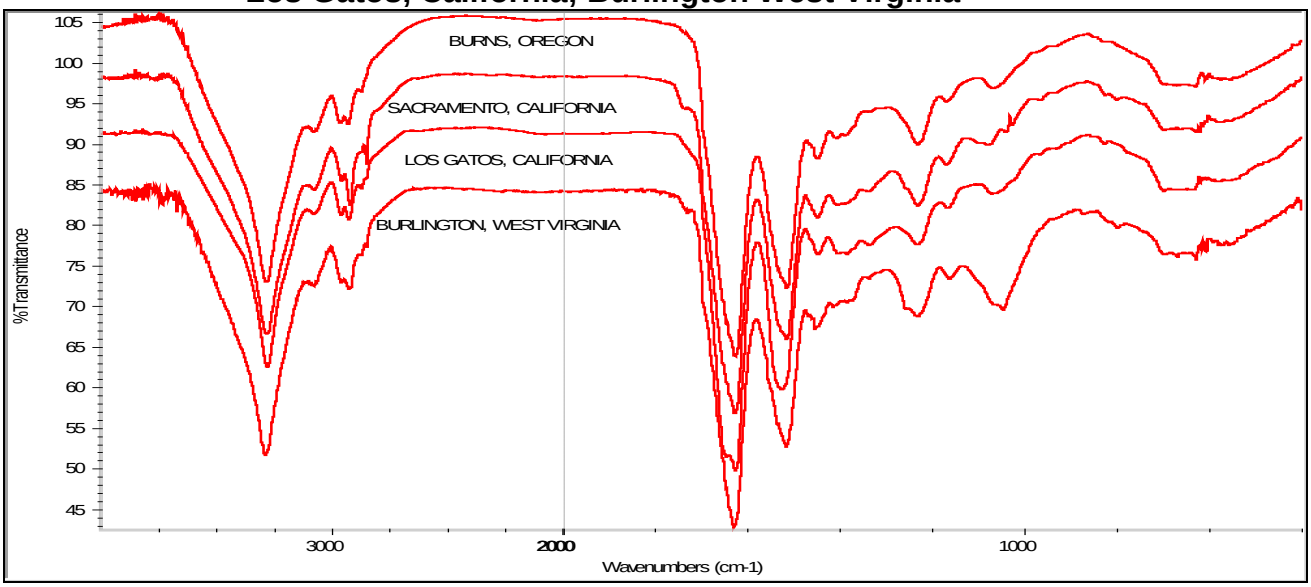


Reference Infrared Spectra of Spider Silk, Tent Caterpillar Silk, and Silk (from Silk Scarf)



[7] More research is needed to confirm these observations.

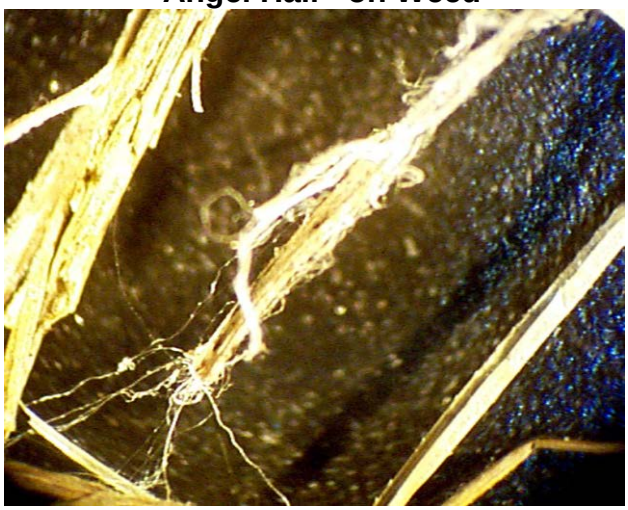
Infrared Spectra of "Angel Hair" from: Burns, Oregon; Sacramento, California; Los Gatos, California; Burlington West Virginia



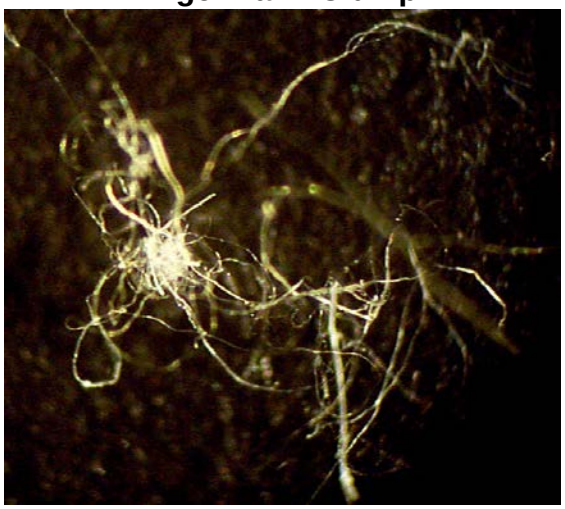
Microscopic Analysis

Microscope photographs of the fibrous material show they are extremely fine [8] and tend to bundle. The photos also show very tiny droplets on the fibers that are similar to the droplets observed on silk derived from insects or caterpillars. These were taken at 60x magnification.

"Angel Hair" on Weed



"Angel Hair" Clump



[8] SEM microscope analysis of Ref. 2 samples show the thickness of "angel hair" fibers are < 1 micron (0.17 – 0.27μ).

Acknowledgment: The author wishes to acknowledge and thank Richard L. Wilson who performed the Headspace GC/MS analysis.

File: UT008.DOC

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Phyllis A. Budinger

Distribution:

Brian Boldman
Ted Phillips
Nancy Talbott

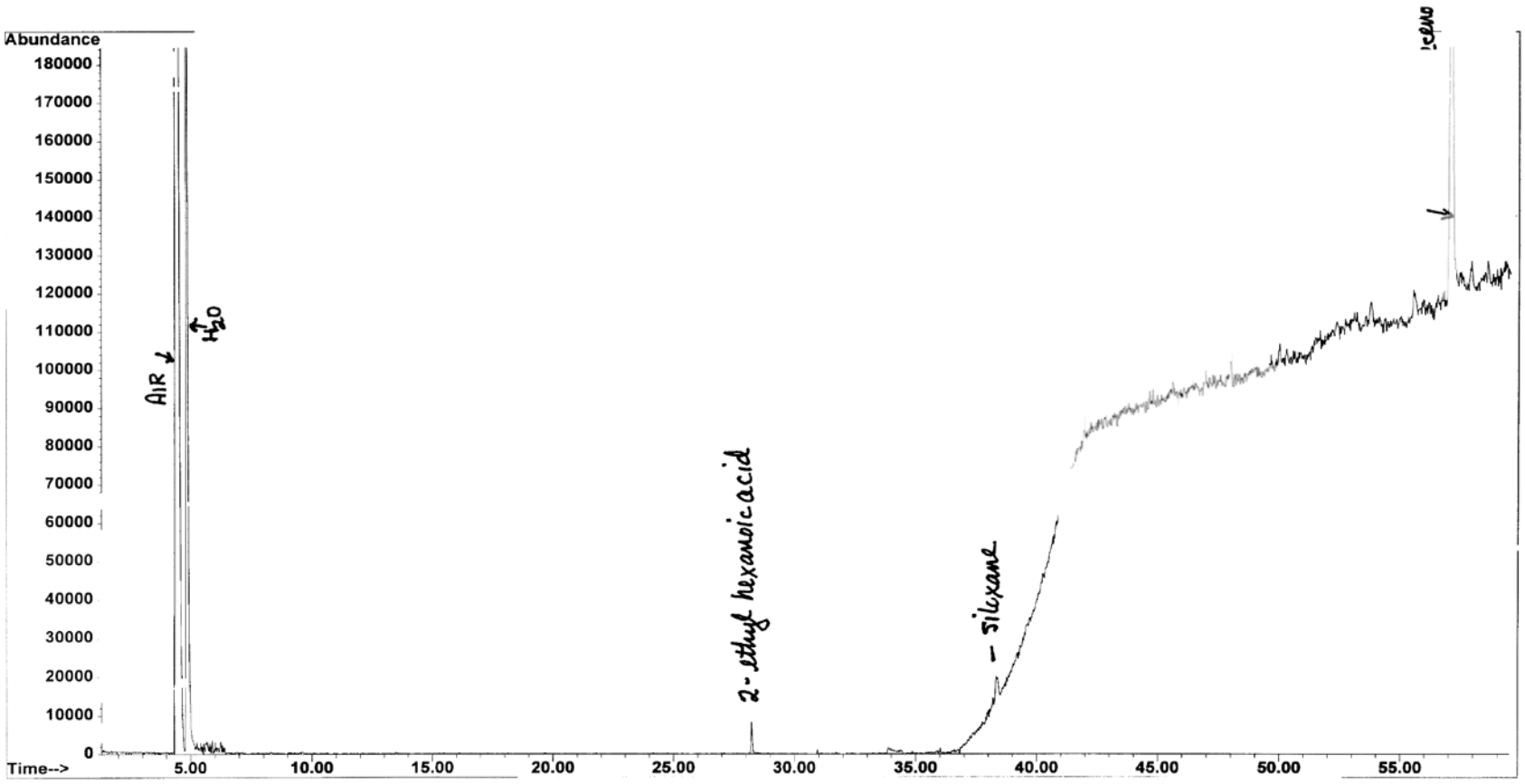
APPENDIX

GC-MS Search Results

Retention Time (min.)	Qual	Blank System Check	Qual	Inside First Bag (1st Run)	Qual	Inside First Bag (2nd Run)	Qual	Inside 2nd Bag	Qual	Inside Glove
4.5		Air		Air		Air		Air		Air
4.9		Water		Water		Water		Water		Water
19.7			83	siloxane (Hexamethyl-cyclotrisiloxane)	83	Siloxane (Hexamethyl-cyclotrisiloxane)	83	siloxane (Hexamethyl-cyclotrisiloxane)	83	siloxane (Hexamethyl-cyclotrisiloxane)
24.2									9	N,N'-bis(N-butyl) ethylenediamine
25.4							12	methyltripropoxy -silane		
28.2							50	nonanal?	38	1-ethyl-2-pentyl-cyclopropane?
28.22	80	2-ethyl-hexanoic acid	64	2-ethyl-hexanoic acid						
29.8									9	7-trimethylsilyl methylene-bicyclo [3,3,0]octan-2-one
30							9	trimethyl-3-penten -2-yl-silane		
34.4							39	trimethylsilyloxime (trimethylsilyl ester derivative of 3,5-dioxo octanedioic acid)	40	trimethylsilyloxime (trimethylsilyl ester derivative of 3,5-dioxo octanedioic acid)
38.3		siloxane								in blank - siloxane
42.4					50	4-methyl-pentamide	43	hexadecanamide	50	dodecanamide
42.8					59	Hexadecanamide	37	hexadecanamide	59	dodecanamide
43.5			30	eicosane C20H42					59	N-tetradecanoic acid amide
44.3			16	2-methyl-hexadecane					64	N-tetradecanoic acid amide
44.4					86	Dodecanamide	80	hexadecanamide		
55.8			86	hexadecanamide C16H33NO	86	Hexadecanamide	72	N-tetradecanoic acid amide		
57	14	9-octadecenoic acid m/z 239, 56		in blank (m/z 239, 56)		in blank (m/z 239, 56)				

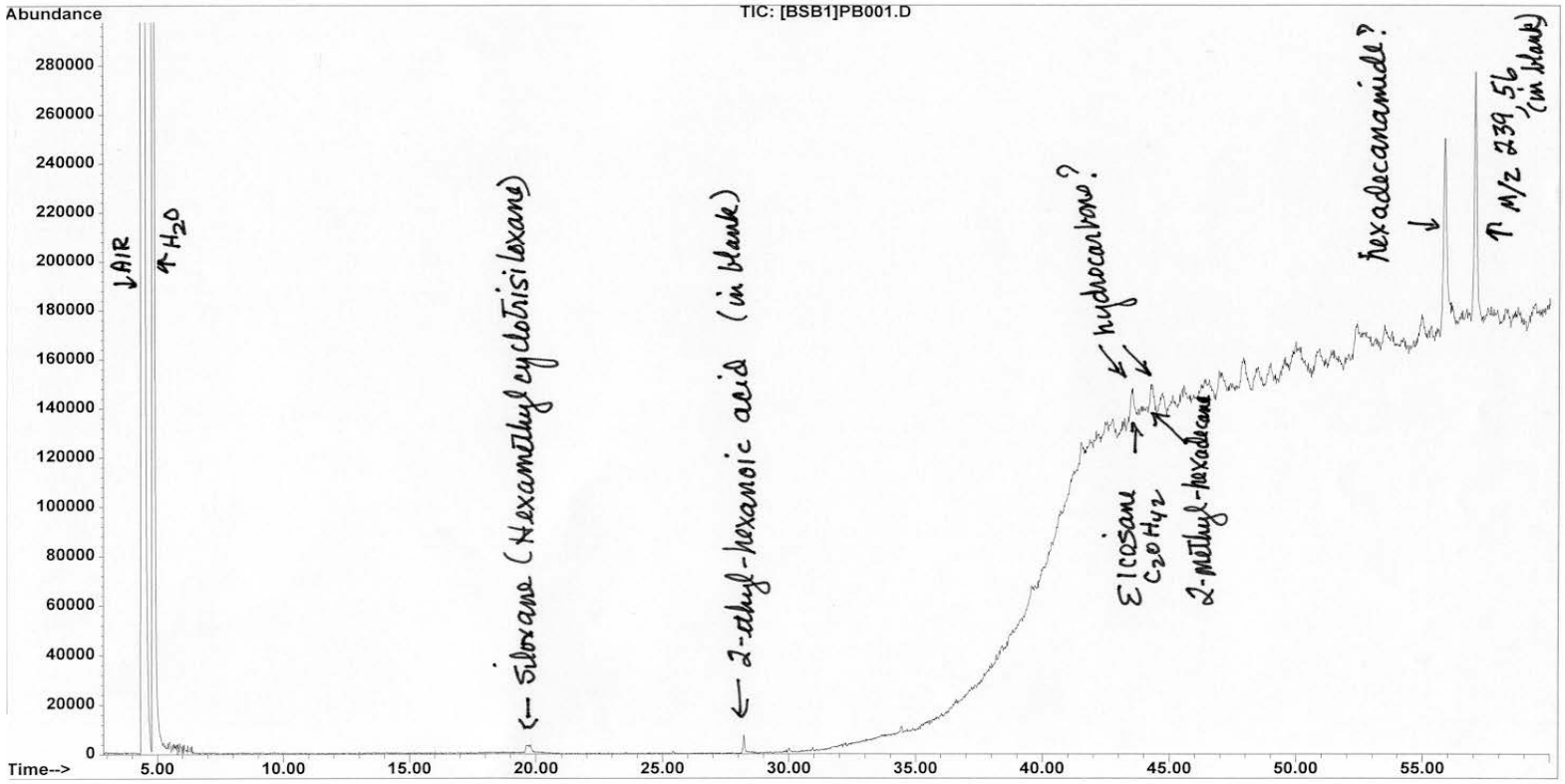
Qual = quality of the search [0 → 100 (best)]. Color Code: black for materials attributed to the blank or unrelated to the sample; blue for suspected contaminants from the packaging (most likely the glove); red for materials related to the sample.

File : C:\HPCHEM\4\DATA\BSB\PBBLK01.D
Operator : [BSB2]RLW 10/5/00
Acquired : 5 Oct 2000 5:12 using AcqMethod HSDB1
Instrument : GC/MS #4
Sample Name: HS Blank 10/5/00
Misc Info : HS 0.1 mL Split 5 40C/6 (6) 250C/19
Vial Number: 1



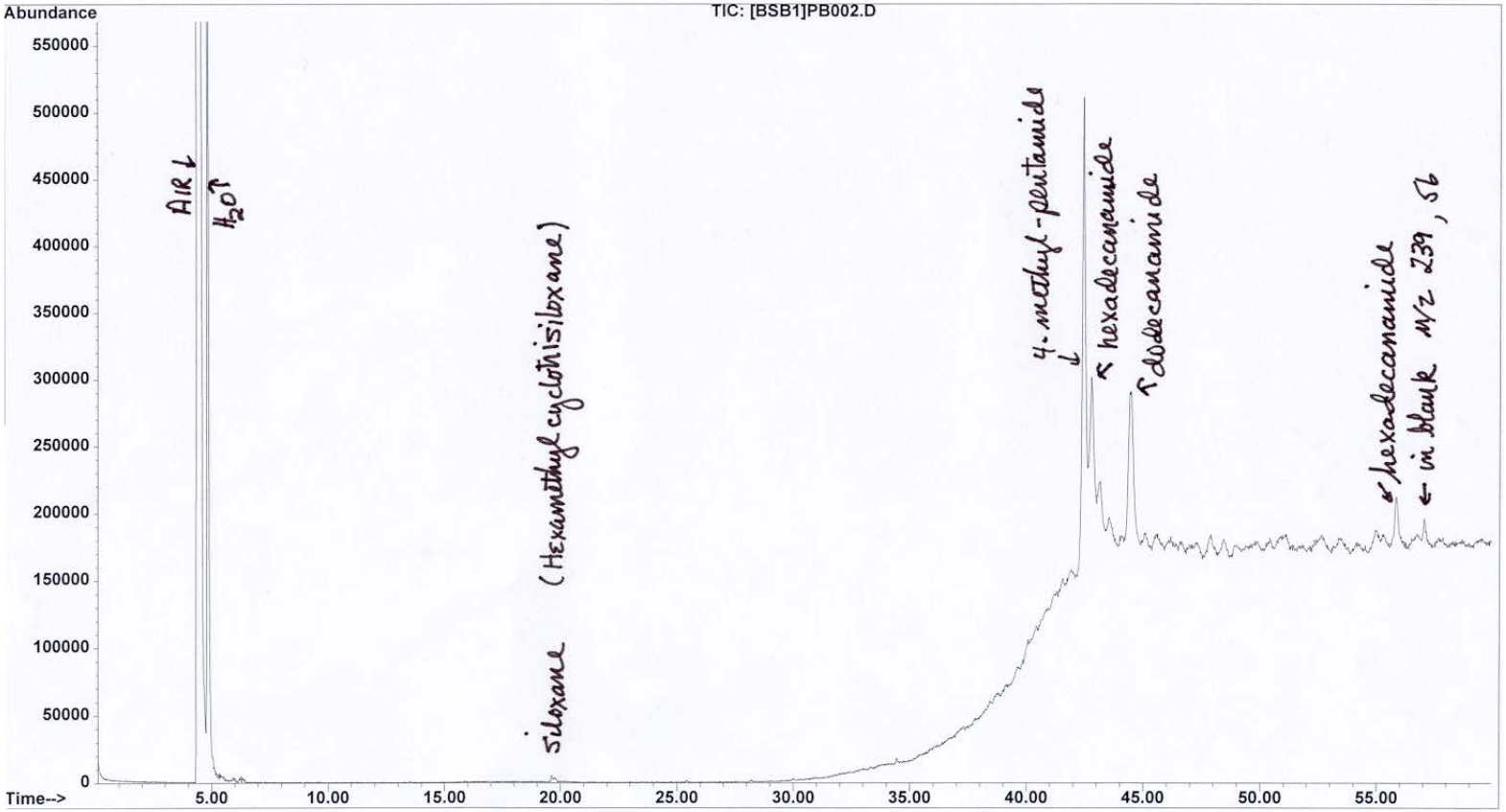
AIR BLANK (SYSTEM CHECK)
GC CHROMATOGRAM

```
File        : C:\HPCHEM\4\DATA\BSB\PB001.D
Operator    : [BSB1]RLW 10/5/00
Acquired    :  5 Oct 2000   7:11      using AcqMethod HSDB1
Instrument :   GC/MS #4
Sample Name: HS Inside Storage Bag 10/5/00
Misc Info   : HS 0.1 mL Split 5  40C/6 (6) 250C/19
Vial Number: 1
```



INSIDE FIRST STORAGE BAG (First Run)
GC CHROMATOGRAM

```
File        : C:\HPCHEM\4\DATA\BSB\PB002.D
Operator    : [BSB1]RLW 10/5/00
Acquired    :  5 Oct 2000   8:52     using AcqMethod HSDB1
Instrument :   GC/MS #4
Sample Name: HS Inside Storage Bag (2nd run)10/5/00
Misc Info   : HS 0.1 mL Split 5  40C/6 (6) 250C/19
Vial Number: 1
```



INSIDE FIRST STORAGE BAG (Second Run)
GC CHROMATOGRAM

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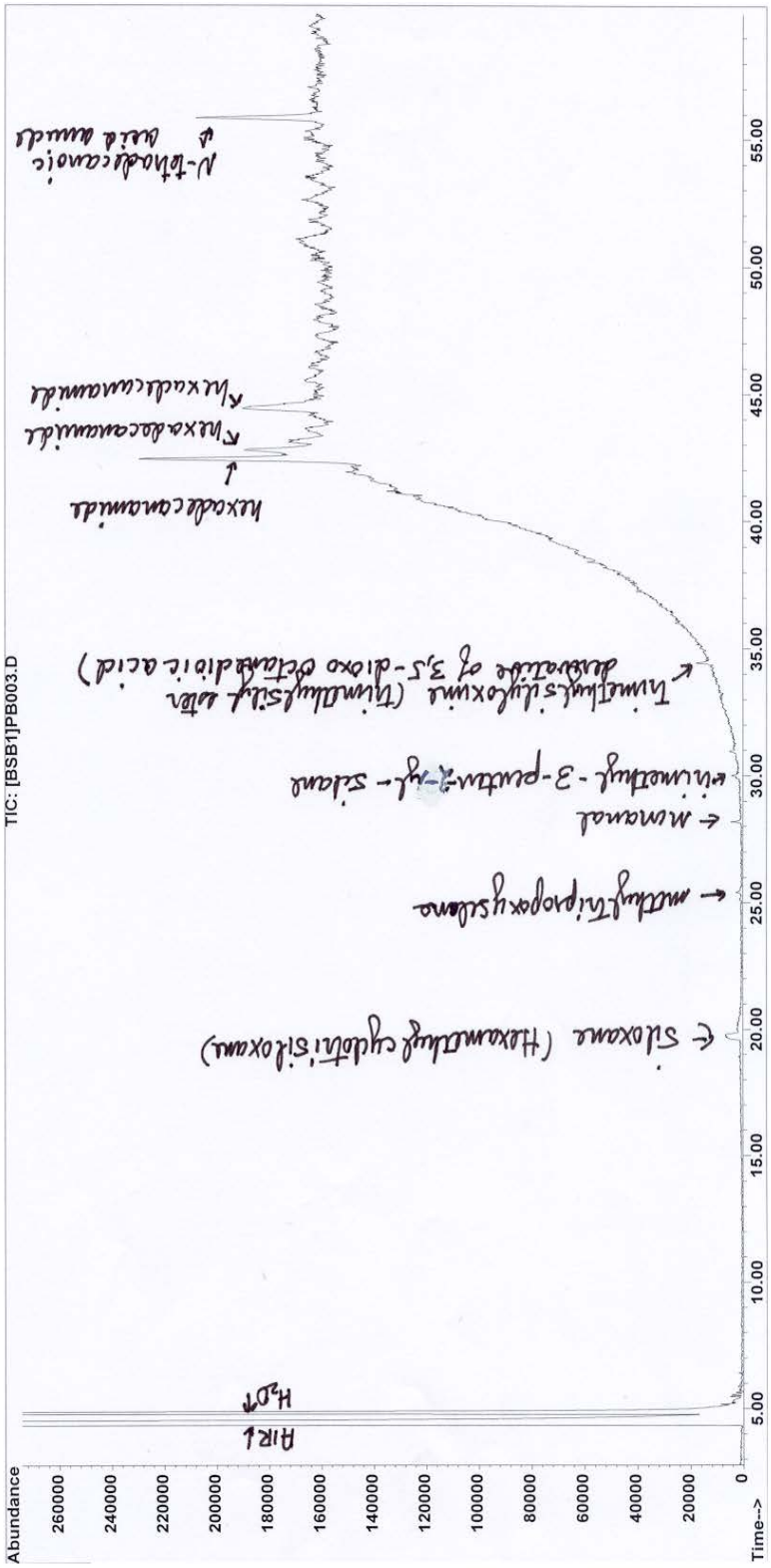
File        : C:\HPCHEM\4\DATA\BSB\PB003.D
Operator    : [BSB1]RLW 10/5/00
Acquired    : 5 Oct 2000  10:34     using AcqMethod HSDB1
Instrument  :   GC/MS #4
Sample Name: HS Inside 2nd Bag (1st run) 10/5/00
Misc Info   : HS 0.1 mL Split 5  40C/6 (6) 250C/19
Vial Number: 1
```



INSIDE SECOND BAG
GC CHROMATOGRAM

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File        : C:\HPCHEM\4\DATA\BSB\PB004.D
Operator    : [BSB1]RLW 10/5/00
Acquired    : 5 Oct 2000  13:37     using AcqMethod HSDB1
Instrument  :   GC/MS #4
Sample Name: HS Inside Glove (1st run) 10/5/00
Misc Info   : HS 0.1 mL Split 5  40C/6 (6) 250C/19
Vial Number: 1
```

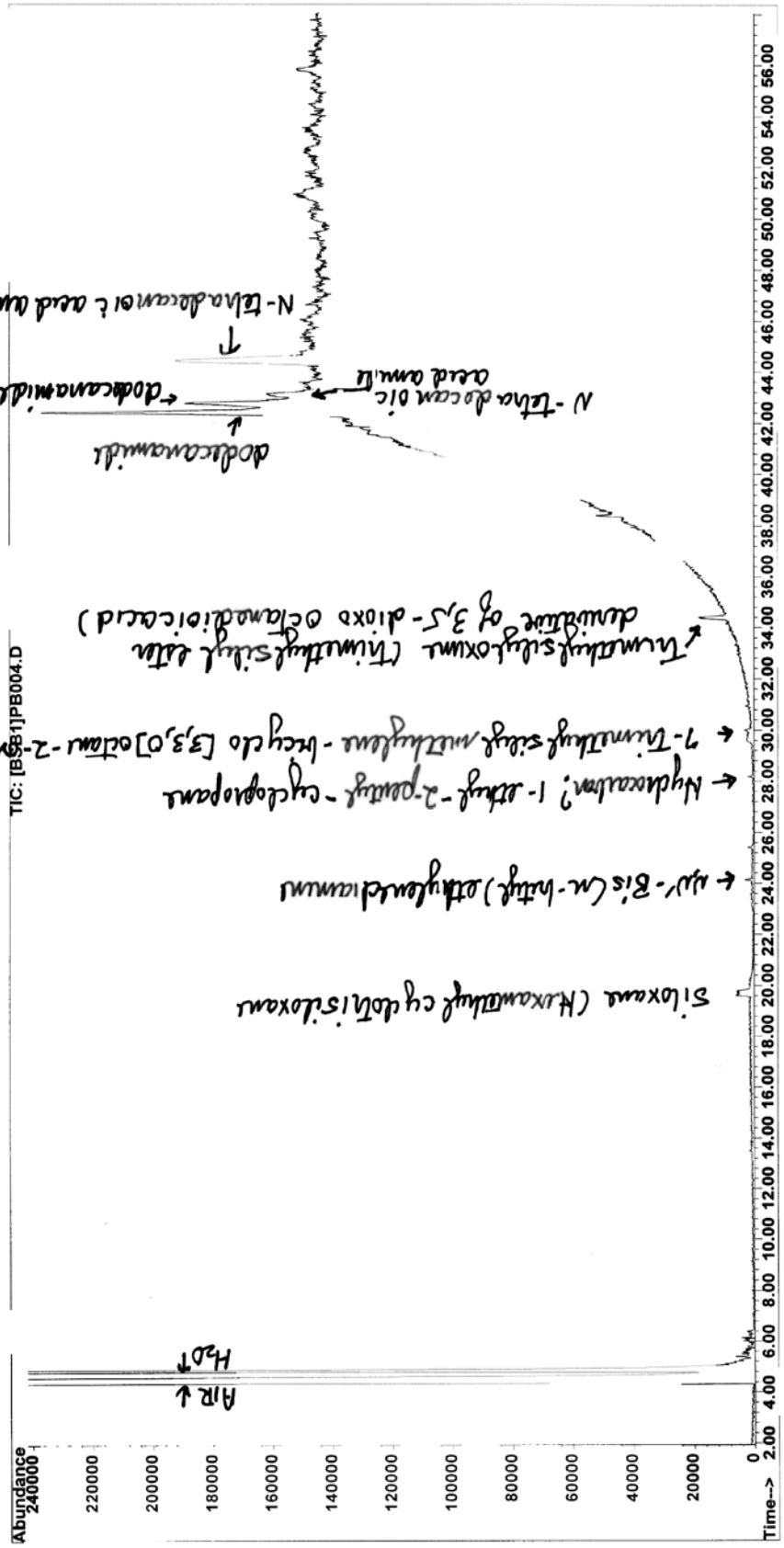

INSIDE GLOVE
GC CHROMATOGRAM