

NIST Mass Spectral Libraries in Forensic Trace Analysis

Trace Evidence Data Workshop

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William E. Wallace

NIST Mass Spectrometry Data Center

Biomolecular Measurement Division

Material Measurement Laboratory

MS Applied to Forensic Trace Analysis

- Toxicology/cause of death
 - urine, blood
 - hair, saliva, sweat
- Profiling
 - determination of sample origin
- Explosive/gun shot residues
 - Linking residues to people
- Arson investigation
 - Determination of accelerants
- Paints/inks/dyes/colorants
- Pharmaceutical adulterants
 - Especially in the developing world
- ...

... a (very) partial list



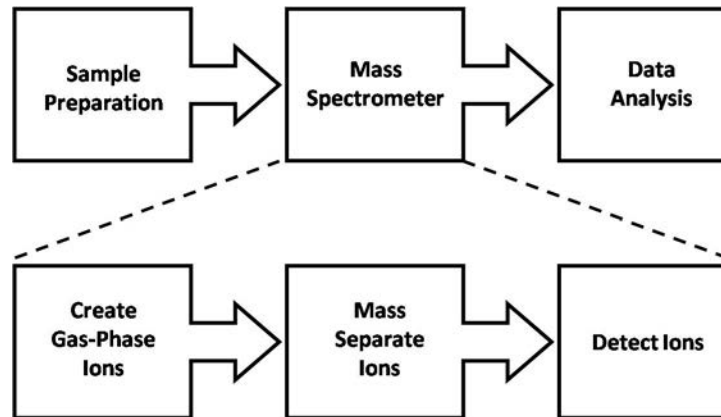
a NIST MSDC mass spectrometry lab

Why Mass Spectrometry?

Mass spectrometry is developing rapidly in the areas of sensitivity, specificity, and analytical throughput

- Handling of small volumes
- Clean up of complex samples
 - solid phase extraction

- Development of new software tools
- Sophisticated new algorithms



- New ionization methods
 - DART
- Greater efficiency in ionization

- Increased mass resolution
- Increased ion throughput

- Improved signal to noise
- New signal processing approaches

The NIST Mass Spectrometry Data Center rests on a central tenet—

Libraries are a necessity in identifying compounds from mass spectra

- Why?
- There is no comprehensive theory accurate enough to predict mass spectra for the purpose of compound identification
 - Although theory is useful for interpretation
- Consequently, library creation by systematic, comprehensive measurement has a long history in mass spectrometry...

... particularly at the National Bureau of Standards

- Brewer & Dibeler, *Journal of Research of the National Bureau of Standards*, 1945
- “The ratios in which the fragments occur are the same over a wide pressure range for each molecular species but are never the same for different species”

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

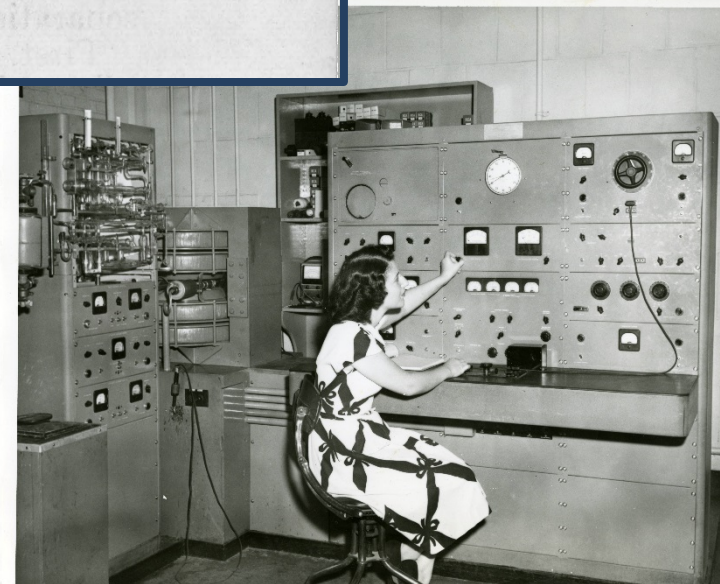
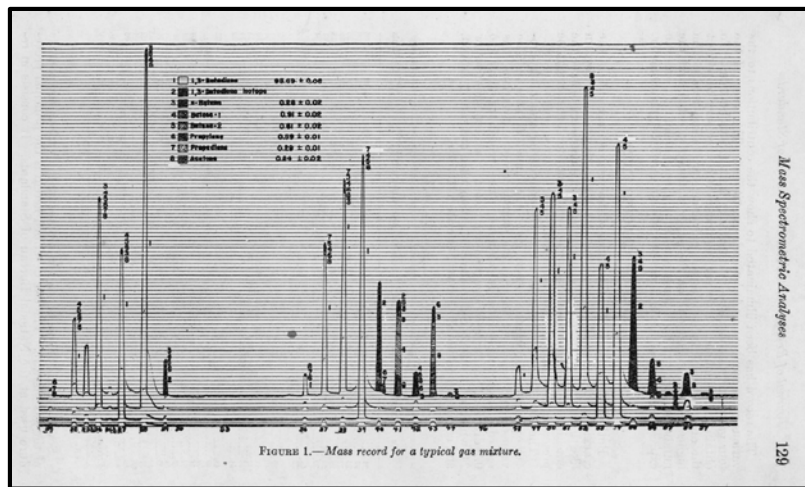
RESEARCH PAPER RP1664

Part of *Journal of Research of the National Bureau of Standards*, Volume 35,
August 1945

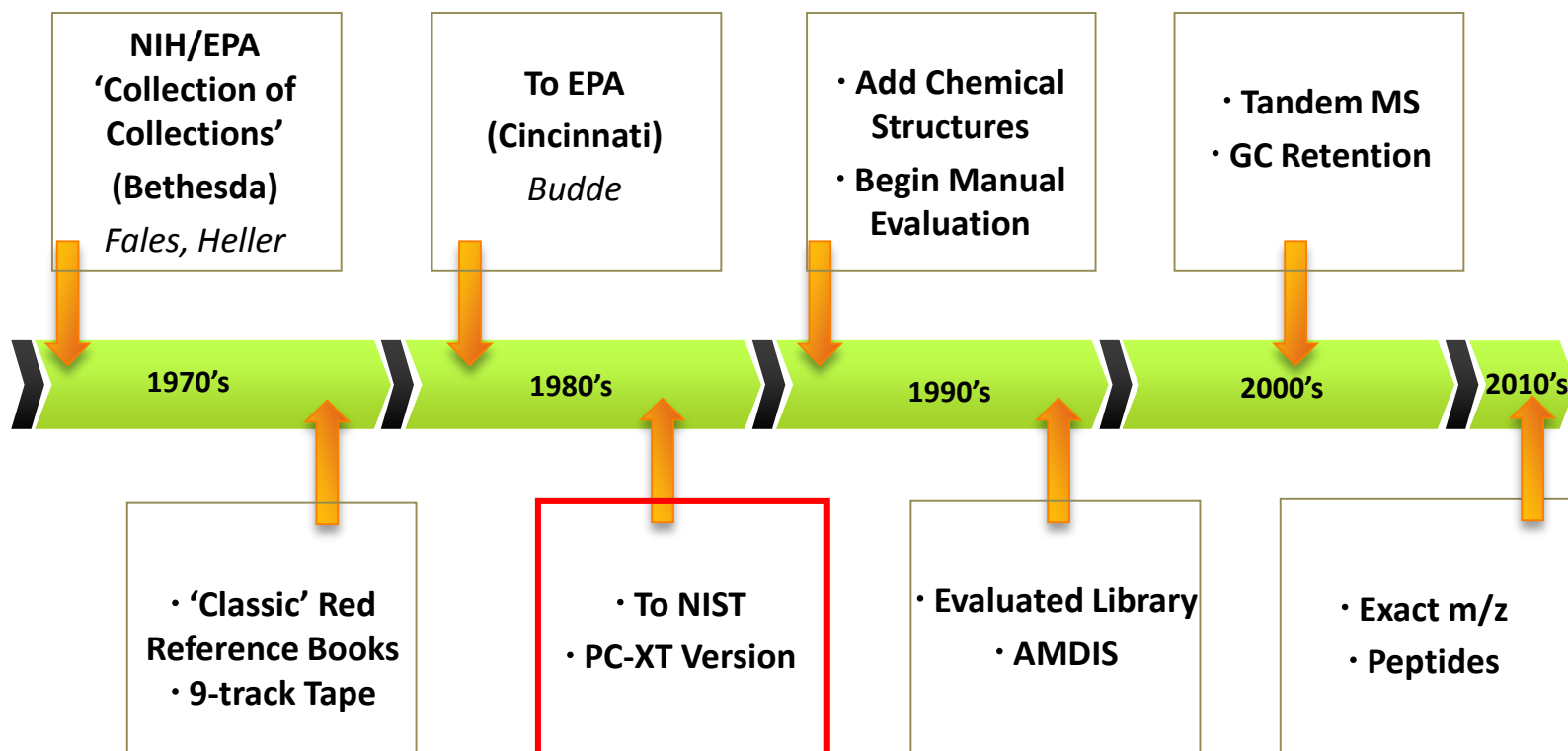
MASS SPECTROMETRIC ANALYSES OF HYDROCARBON
AND GAS MIXTURES¹

By A. Keith Brewer and Vernon H. Dibeler

NIST Archives photo
dated Sept. 29, 1948



Evolution of the NIST MS Library

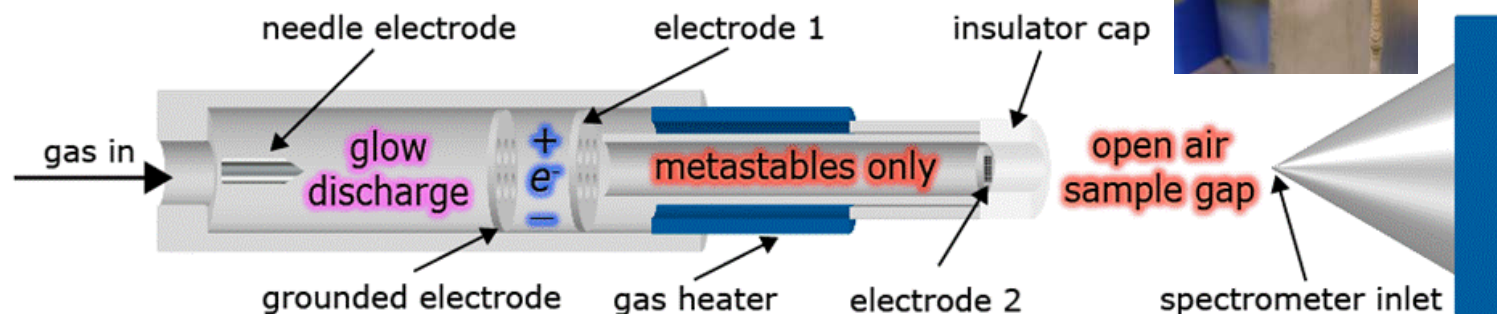


NIST Mass Spectral Libraries in Trace Analysis

- NIST/EPA/NIH Mass Spectral Database
 - Electron-impact ionization mass spectra typical of GC-MS analysis
- NIST Tandem MS Database
 - Electrospray ionization mass spectra typical of LC-MS analysis
- DART Forensics Library
 - For analysis directly from surfaces
 - An example of a 'targeted' library

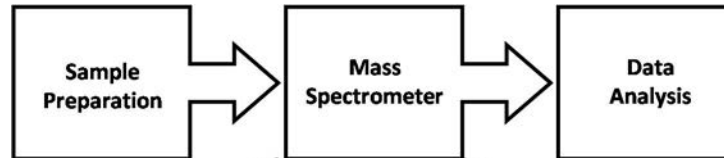


DART— direct analysis in real time



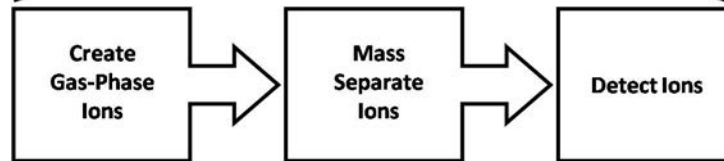
NIST MSDC Software Tools

- Handling of small volumes
- Clean up of complex samples
 - solid phase extraction



- Development of new software tools
- Testing new algorithms

- New ionization methods
 - DART
- Greater efficiency in ionization



- Increased mass resolution
- Increased ion throughput

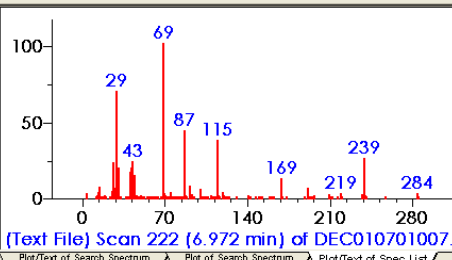
- Improved signal to noise
- New signal processing approaches

NIST GC-MS Library Search

Search List

#	S...	Name
4	A	Scan 1339 (26.715 min) of JAN21
5	A	Scan 1889 (36.437 min) of JAN2E
6	A	Scan 1108 (22.633 min) of JAN2E
7	A	Scan 222 (6.972 min) of DEC010;
8	A	Scan 815 (17.453 min) of DEC07
9	A	Scan 741 (16.144 min) of DEC10
10	A	Average of 38.980 to 39.086 min
11	A	Scan 1038 (21.397 min) of MAR0

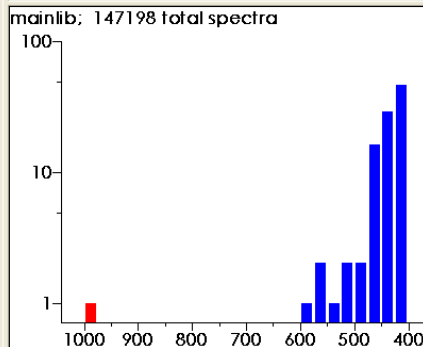
Query Spectrum



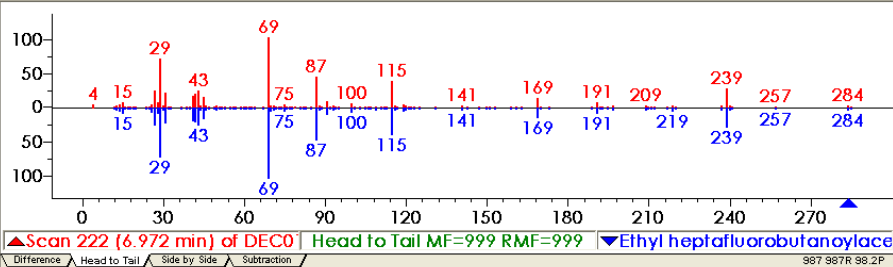
Name: Scan 222 (6.972 min) of DEC010701007.d 9906
 MW: N/A ID#: 625 DB: Text File
 120 m/z Values and Intensities:

4	32	12	5	13	20
14	39	15	70	16	4
17	2	18	4	19	14
20	4	24	2	25	9
26	45	27	232	28	67
29	685	30	29	31	197
32	5	33	7	37	3

Score Histogram



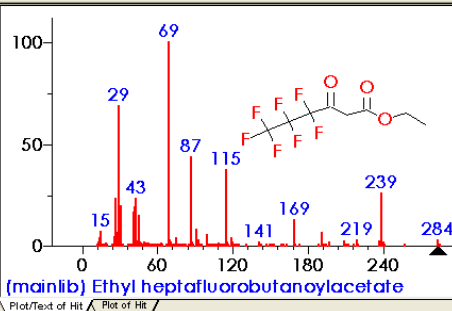
Compare Spectra



Hit List

...	Li...	Ma...	R.Mat...	Prob...	Name
1	M	987	987	98.2	Ethyl hept
2	M	600	720	0.98	Ethyl pent
3	M	567	576	0.25	4,6-Nonan
4	M	554	615	0.16	1,1,1,5,5,6
5	M	543	641	0.11	Butanoic c
6	M	504	690	0.02	1,3-Dioxar
7	M	502	683	0.02	1,3-Dioxar
8	M	499	683	0.02	1,3-Dioxar

Library Spectrum

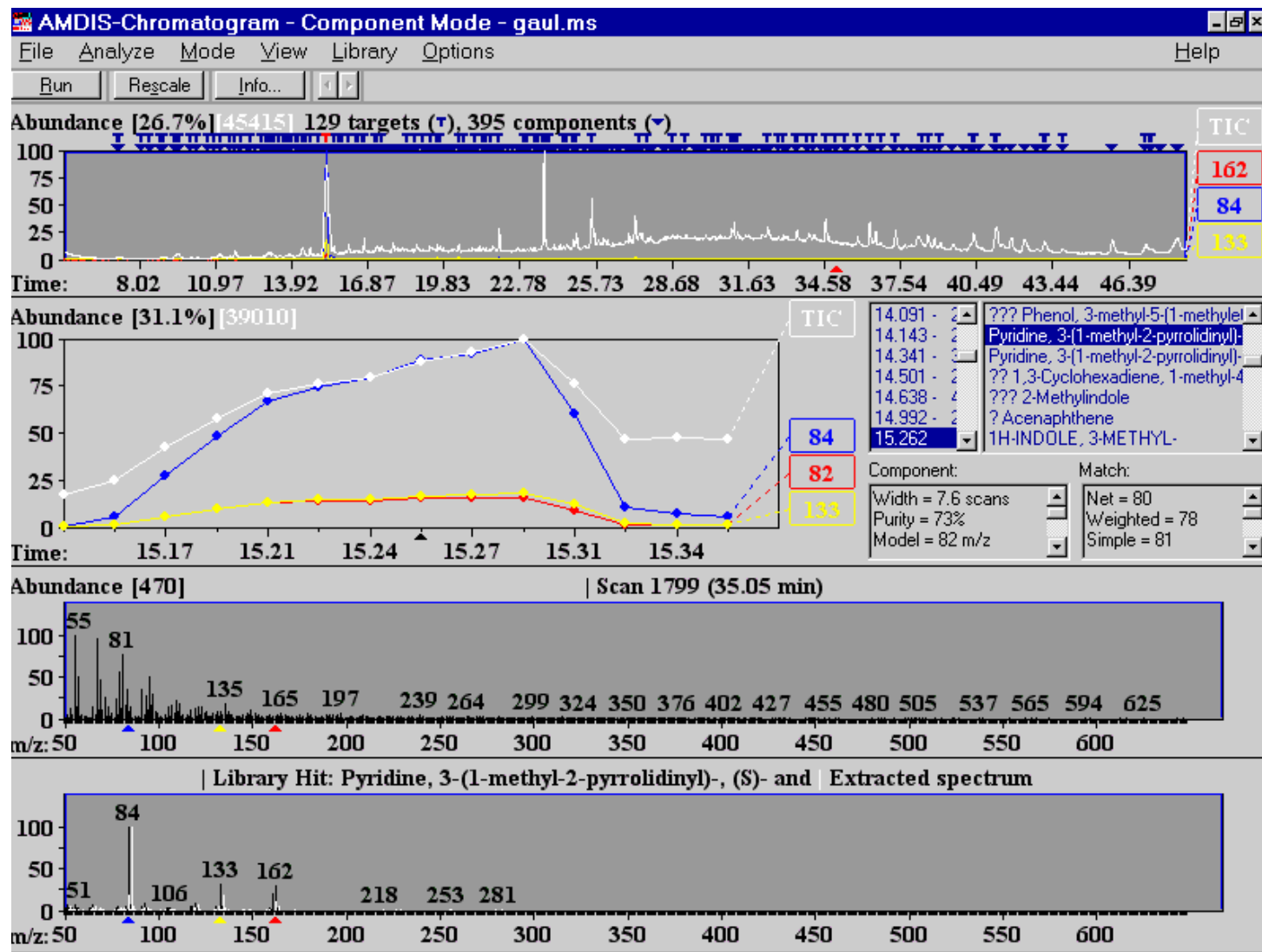


Name: Ethyl heptafluorobutanoylacetate
 Formula: C₈H₇F₇O₃
 MW: 284 CAS#: 336-62-9 NIST#: 135929
 ID#: 26564 DB: mainlib
 Other DBs: None
 Contributor: NIST Mass Spectrometry Data Center, 1994
 119 m/z Values and Intensities:

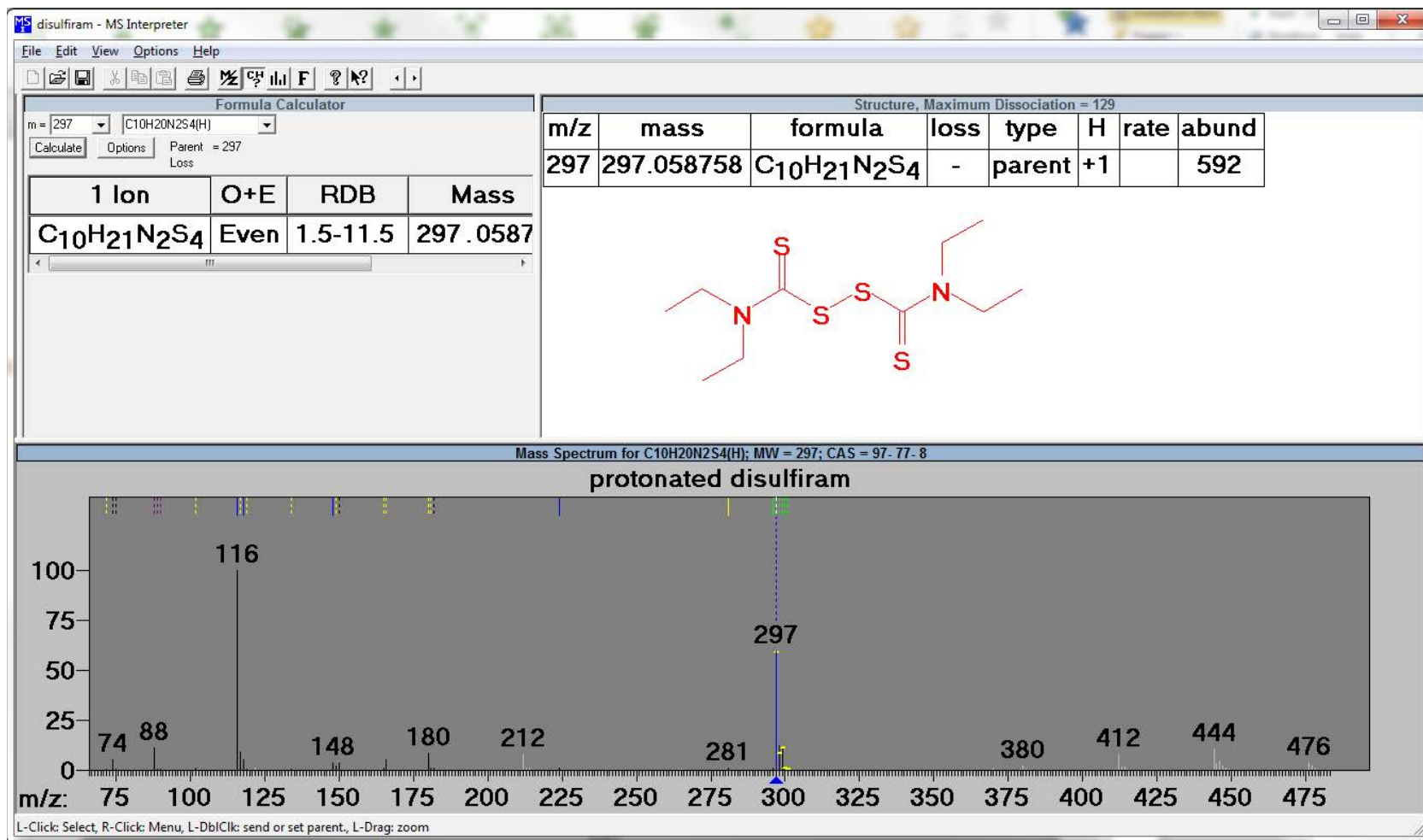
12	5	13	20	14	39
15	70	16	4	17	2
18	4	19	14	20	4
24	1	25	9	26	45
27	232	28	67	29	686
30	29	31	197	32	5

AMDIS

Automated Mass Spectral Deconvolution and Identification System



NIST MS Interpreter



What does the NIST MSDC need from the forensics community?

- What are the emerging trends that you are seeing in your labs?
- What compounds do they involve?
- How may NIST obtain certified samples?
 - purchase
 - synthesis
 - isolation from original matrix
- What can the NIST MSDC do to help build the community?
 - an interlaboratory round robin?
 - training on library searching?
 - guidance on uncertainty/false discovery rates?



MSDC staff meeting with customers at our trade show booth

Questions?

