Evaluation of the NIST Library Matching Quality of Mass Spectra Generated by the GC-HR-TOFMS with Multi-Mode Ionization Source

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Introduction

Comparison of electron ionization spectra against standardized libraries is a staple approach to compound identification in non-targeted GC-MS analysis. High-quality matches are central to the pace of, and confidence in, such analyses. Recent developments in gas chromatography high resolution mass spectrometry have progressed non-targeted analysis applications to a wide variety of studies. However, modern ion-optical design principles which allow gains in sensitivity and resolving power may inadvertently alter fragmentation patterns, which may in turn affect the reliability of automated comparisons against standard libraries. Thus, thorough evaluation and validation of the high-quality spectra matching to the standard libraries, like NIST, is necessary for comprehensive assessment of the promised benefits of new technologies.

Methods

LECO's novel Multi-mode Source™ (MMS™), coupled with multi-reflecting HR-TOFMS (Figure 1) was developed for GC-MS and GCxGC-MS non-targeted analysis of complex mixtures. To evaluate the matching quality of the EI spectra generated by the *MMS*, we collected data from 207 analytes across seven standards purchased from Restek (Table 1). The automatic peak finding, spectra deconvolution, and library search on the data were performed by LECO ChromaTOF® software. In this presentation, we summarize the outcomes from matching that peak data against the NIST23 library and evaluate the spectral quality of the data from HR-TOFMS with *MMS*. Two extracted samples were each spiked with one Multiresidue Pesticide Standard (MRPS). Mean library matching scores are assessed in total, by sample type, and by prominent moieties.

Table 1: Acquisition List.

Name	Restek Catalog #/Description
Florida TPH Standard	31266
EPA Method 8061A Phthalate Esters Mixture	33227
8270 MegaMix Standard (with Internal Standard)	31850
GC Multiresidue Pesticide Standard #2	32564/Organochlorine
GC Multiresidue Pesticide Standard #3	32565/Organonitrogen
GC Multiresidue Pesticide Standard #8	32570/Organophosphorous
GC Multiresidue Pesticide Standard #9	32571/Organophosphorous
Sample #1	Pu'er Tea Spiked With MRPS #2
Sample #2	Dietary Supplement Spiked with MRPS #8

Table 2: Instrument Parameters.

Pegasus® GC-HRT 4D			
Comprehensive Two-Dimensional Gas Chromatography			
Primary Column	Rxi-5 ms 30 m x 0.25 mm x 0.25 µm		
Secondary Column	Rxi-17Sil MS 2 m x 0.25 mm x 0.25 µm		
Temperature Program	1.00 min at 40 °C, 12.00 °C/min to 280 °C, 5.00 °C/min to 320 °C, and hold 15.00 min		
He Flow (mL/min) – All	1.0	**Inlet Temperature (°C)**	300
Modulation (s) – All	2nd Dimension Period = 1.5, Hot Pulse = 0.45, Cool Time = 0.30		
High Resolution Time-of-Flight Mass Spectrometer, R=25,000, MA<1ppm			
Transferline Temperature (°C)	320	**Acquisition Rate (sp/s)**	200
Ionization Source Temperature (°C)	250	**Mass Range, M/Z**	15–1500

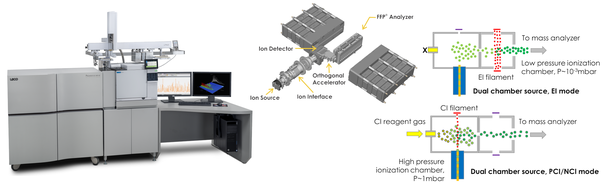

Figure 1: A Pegasus GC-HRT+ 4D with Analyzer and Source Illustrations.

Results

Table 3: Library Match Scores by Standard and Sample Type.

Acquisition			Mean Library Match Score	Std. Dev.
Standards	Alkanes, # Analytes = 16		920	28.3
	SVOCs, # Analytes = 80		934	28.9
	MRPS #2, # Analytes = 40		941	24.3
	MRPS #3, # Analytes = 25		938	13.8
	MRPS #8, # Analytes = 27		935	14.5
	MRPS #9, # Analytes = 8		932	18.2
	Phthalates, # Analytes = 15		939	13.1
Samples	Sample 1	# Std. Matches = 39	905	39.4
	Sample 2	# Std. Matches = 27	921	28.1

Table 4: Moiety Stratified Match Scores. Standards only. Each analyte was tagged with each moiety it contains and then mean values were generated using every molecule associated with each tag. Sulfamoyls, sulfates, sulfenamides, sulfite esters, sulfonate esters, and sulfones were condensed into one category (S-O/N). Any other tag with less than 3 entries was omitted.

Moiety	# in Set	Mean Library Match Score	Std. Dev.
Alkane	16	920	28.8
Amine	22	931	26.5
Aromatic	130	939	18.2
Brominated	7	936	13.6
Chlorinated	95	939	20.1
Cycloalkane	9	940	17.1
Deuterated	6	896	16.3
Epoxide	3	939	3.9
Ester	26	938	12.2
Ether	20	929	28.1
Fluorinated	9	933	11.5
Halogenated	101	939	19.8
Heterocycle	3	937	14.2
Hydroxy	16	945	13.1
Ketone	3	951	12.7
Nitrile	3	948	11.9
Nitro	28	928	22.9
Olefin	31	935	17.8
Phosphate	7	929	16.1
Phthalate	22	940	11.0
Polyaromatic	26	926	33.8
Polycyclic	17	939	13.2
S-O/N	9	942	18.6
Thioether	12	936	17.1
Thiophosphate	26	936	13.4

Results

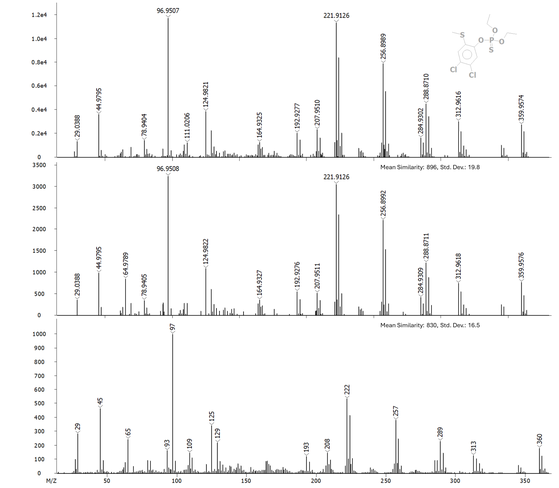

Figure 2: Chlorthiophos II Spectra from (Top) MRPS #8, (Mid) Sample #2, and (Bottom) NIST.

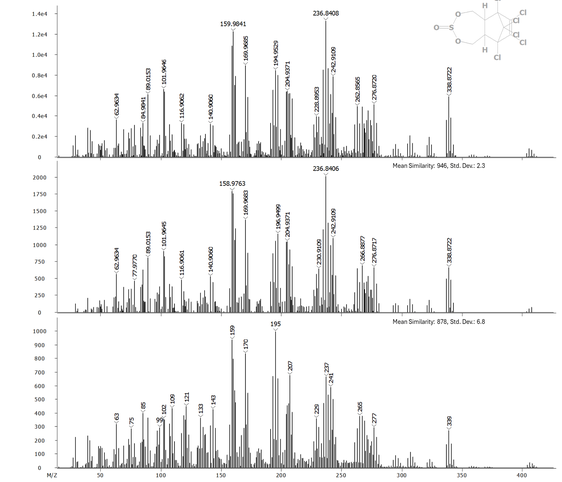

Figure 3: Endosulfan II Spectra from (Top) MRPS #2, (Mid) Sample #1, and (Bot) NIST.

Results

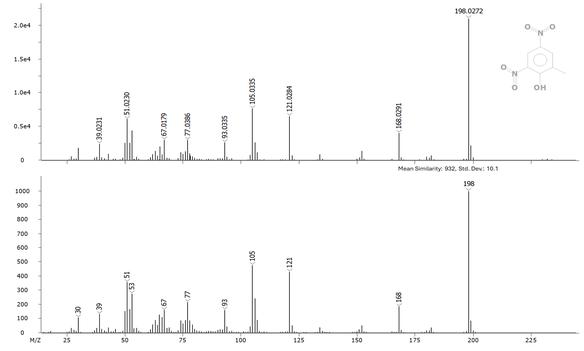

Figure 4: 2-methyl-4,6-dinitrophenol Spectra from (Top) 8270 MegaMix and (Bottom) NIST.

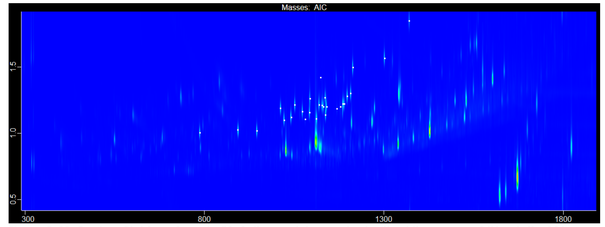

Figure 5: 2D Contour Plot from Sample #2. Spike analytes marked with white squares. S/N cutoff = 100. Siloxane/blank peaks filtered.

Conclusions

This multi-mode ionization source, as assessed using these 207 diverse analytes, generates fragmentation patterns which align very well with the NIST spectral library. Across all analytes in standard solutions, the mean library match score was 935 and the standard deviation for this value was 24.2. Mean match scores were agreeable regardless of moieties present. Percent differences for MRPS #2 spiked into a Pu'er Tea and MRPS #8 spiked into a dietary supplement were - 3.75 % and -1.44 %, illustrating how the system can easily maintain spectral confidence even in complex matrices. Overall, this study suggests the electron ionization mode of this multi-mode ion source, in combination with its high-resolution time of flight mass analyzer, yields spectra in excellent agreement with the quadrupole dominated NIST library.

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Conflict of Interest Disclosure

All authors are employed by LECO Corporation, manufacturer of GCxGC-HR-TOFMS and MMS.