Utilization of Hydrogen Carrier Gas on a High Resolution GC-TOFMS System: An Application Compendium

Joe Binkley; David Alonso | LECO Corporation, St. Joseph, MI USA

Background

Both the costs associated with a dwindling helium supply and the need for high sample throughput have fueled the desire to develop fast gas chromatography methods using hydrogen as a carrier gas. This poster demonstrates the ability to utilize hydrogen carrier gas on a high resolution GC-TOFMS system, the Pegasus® GC-HRT. Methods and data from multiple application markets, including specialty chemicals, forensics, and metabolomics, will be displayed. Various polymer additives were used to represent the specialty chemical market, drugs of abuse were used to demonstrate capabilities in the forensic market, and a derivatized metabolite mixture designed for metabolomics research was used for the metabolomics market.

GC-HRT methods utilizing hydrogen carrier gas were developed for analysis of representative specialty chemical, forensic, and metabolomic markets.

- Polymer additives were dissolved in chloroform prior to analysis.
- Drugs of abuse were dissolved in organic solvents and analyzed underivatized.
- Metabolites were derivatized prior to GC-HRT analysis using an optimized two-step procedure: 1) Treatment with methoxylamine hydrochloride and 2) MSTFA.

Helium

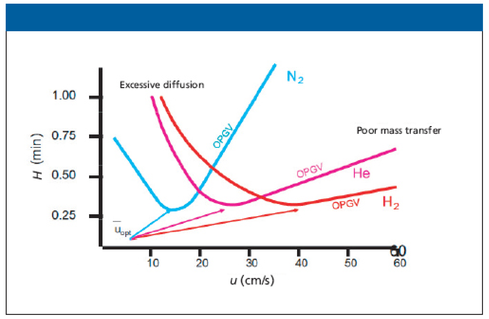

Figure 1. Van Deemter curves for He, N_2, and H_2.
OPGV = Optimum practical gas velocity.

Instrumentation

Figure 2. Pegasus GC-HRT High Resolution TOFMS.

Pegasus GC-HRT Capabilities

- High Resolution (Up to R=50,000)
- Mass Accuracy (< 1 ppm)
- Fast Acquisition Rates (Up to 200 spectra/second
- High Resolution Deconvolution™ (HRD™)
- **H_2 Carrier Gas Compatible**

Experimental

GC-HRT Methods (Polymer Additives)

GC Conditions

Column: Rxi-1ms 20 m x 0.1 8 mm x 0.18 micron film (Restek)
Carrier: Hydrogen @ 0.8 mL/min
Injection: 1 µL, split 20:1 @ 300°C
Oven: 50°C (0.5 min) to 300°C @ 50°C/min
Tr. Line: 300°C

HRT Conditions

Resolution: High (25k)
Mass Range: 40-700 m/z
Ionization: EI

GC-HRT Methods (Drugs of Abuse)

GC Conditions

Column: Rxi-1ms 20 m x 0.18 mm x 0.18 micron film (Restek)
Carrier: Hydrogen @ 0.8 mL/min
Injection: 1 µL, split 50:1 @ 280°C
Oven: 40°C (2 min) to 300°C @ 30°C/min
Tr. Line: 300°C

HRT Conditions

Resolution: High (25k)
Mass Range: 40-400 m/z
Ionization: EI

GC-HRT Methods (Metabolomics)

GC Conditions

Column: Rxi-1ms 20 m x 0.18 mm x 0.18 micron film (Restek)
Carrier: Hydrogen @ 0.8 mL/min
Injection: 1 µL, split 10:1 @ 250°C
Oven: 80°C to 300°C @ 40°C/min
Tr. Line: 300°C

HRT Conditions

Resolution: High (25k)
Mass Range: 50-600 m/z
Ionization: EI

Results

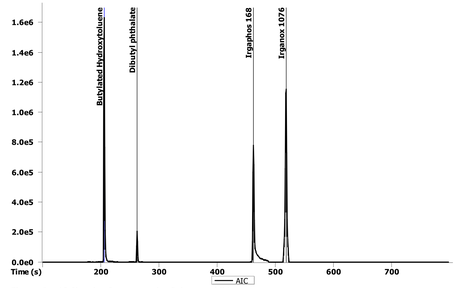

Figure 3. AIC Showing Representative Polymer Additives.

Table I. Tabular Data for Polymer Additives

Name	Quantity	Expected Ion m/z	Observed Ion m/z	Mass Accuracy (ppm)	Formula
Butylated Hydroxytoluene	853	220.1822	220.1824	1.2	$C_{15}H_{24}O$
Dibutyl phthalate	875	278.1513	NA	NA	$C_{16}H_{22}O_4$
Irgaphos 168	688	646.4699	646.4651	0.33	$C_{42}H_{63}O_3P$
Irganox 1076	564	530.4699	530.4696	0.49	$C_{35}H_{62}O_3$

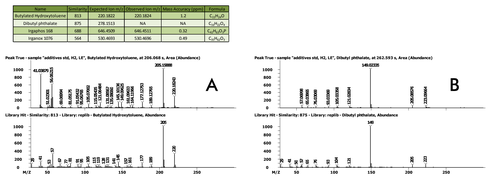

Figure 4. Deconvoluted (Peak True) and Library Hit Spectra for Butylated Hydroxytoluene (A) and Dibutyl Phthalate (B).

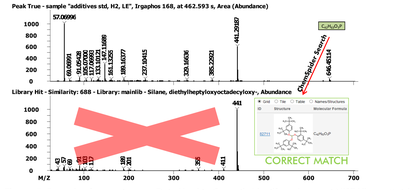

Figure 5. Example of Accurate Mass Data Used to Correctly Identify an Incorrect NIST Library Match.

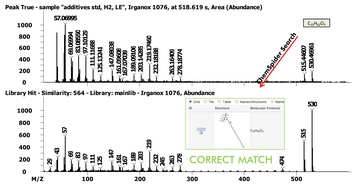

Figure 6. Example of Accurate Mass Data Used to Confirm a NIST Library Match.

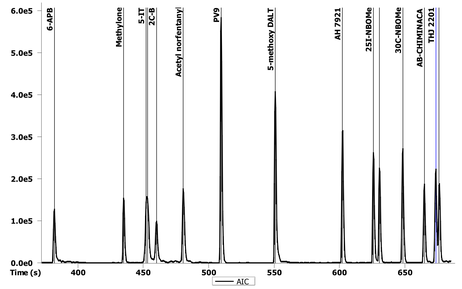

Figure 7. AIC Showing Representative Drugs of Abuse.

Table II. Tabular Data for Drugs of Abuse

Drug Compound	Quantity	Expected Ion m/z	Observed Ion m/z	Mass Accuracy (ppm)	Formula
6-APB	662	175.0952	175.0951	-0.59	$C_{11}H_{13}NO$
Methylone	780	207.089	NA	NA	$C_{11}H_{13}NO_3$
5-IT	719	174.1151	174.1155	2.26	$C_{13}H_{15}N$
N,N-DMT	566	188.1308	188.1307	-0.27	$C_{12}H_{17}N_2$
2C-B	674	259.0202	259.0205	0.95	$C_{10}H_{13}BrNO_2$
Acetyl norfentanyl	759	218.1414	218.1416	1.2	$C_{13}H_{18}N_2O$
PV9	809	273.2087	NA	NA	$C_{18}H_{27}NO$
5-methoxy DALT	763	270.1727	270.172	-2.3	$C_{17}H_{23}N_2O$
AH 7921	761	328.1104	NA	NA	$C_{16}H_{22}Cl_2N_2O$
25I-NBOMe	799	427.0639	NA	NA	$C_{18}H_{22}INO_3$
MT-45	762	348.256	NA	NA	$C_{24}H_{32}N_2$
30C-NBOMe	462	NA	NA	NA	$C_{19}H_{24}ClNO_3$
AB-CHMINACA	384	NA	NA	NA	$C_{20}H_{28}N_4O_2$
THJ 2201	737	360.1632	360.1627	-1.5	$C_{21}H_{21}FN_2O$
AM2201 benzimidazole analog	857	360.1632	360.162	-3.34	$C_{21}H_{21}FN_2O$

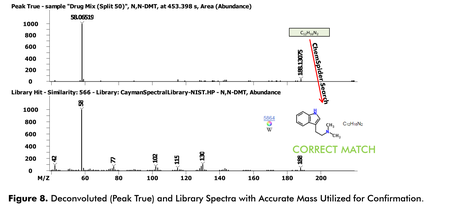

Figure 8. Deconvoluted (Peak True) and Library Spectra with Accurate Mass Utilized for Confirmation.

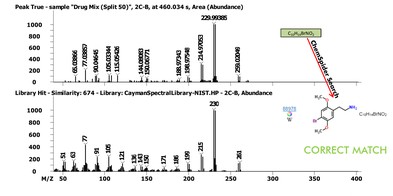

Figure 9. Deconvoluted (Peak True) and Library Spectra with Accurate Mass Utilized for Confirmation.

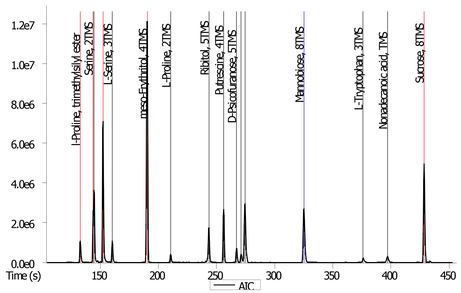

Figure 10. AIC Showing Representative Metabolites.

Table III. Tabular Data for TMS Derivatized Metabolites

Metabolite	Quantity	Expected Ion m/z	Observed Ion m/z	Mass Accuracy (ppm)	Formula
I-Proline, trimethylsilyl ester	775	187.10231	187.10231	0.034	$C_8H_{17}NO_2Si$
Serine, 2TMS	761	249.1211	NA	NA	$C_9H_{23}NO_3Si_2$
Silanol, trimethyl-, phosphate (3:1)	898	314.09493	314.0953	1.172	$C_9H_{27}O_4PSi_3$
Glycine, 3TMS	826	291.15006	291.14989	-0.588	$C_{11}H_{29}NO_2Si_3$
L-Serine, 3TMS	835	321.16062	NA	NA	$C_{12}H_{31}NO_3Si_3$
meso-Erythritol, 4TMS	864	410.21547	NA	NA	$C_{16}H_{42}O_4Si_4$
L-Proline, 2TMS	747	273.1311	NA	NA	$C_{11}H_{23}NO_2Si_2$
Ribitol, 5TMS	886	512.26556	NA	NA	$C_{17}H_{44}O_5Si_5$
Putrescine, 4TMS	899	376.25761	376.25611	-3.971	$C_{16}H_{40}N_2Si_4$
D-Psicofuranose, 5TMS	836	540.26047	NA	NA	$C_{17}H_{44}O_6Si_5$
D-(-)-Fructopyranose, 5TMS	781	540.26047	NA	NA	$C_{17}H_{44}O_6Si_5$
CITRIC ACID, 4TMS	848	480.18456	NA	NA	$C_{18}H_{36}O_7Si_4$
3-b-Mannobiose, 8TMS	765	918.43188	NA	NA	$C_{36}H_{86}O_{11}Si_8$
L-tryptophan, 3TMS	726	420.20791	NA	NA	$C_{20}H_{34}N_2O_2Si_3$
Nonadecanoic acid, TMS	760	370.32816	NA	NA	$C_{22}H_{46}O_2Si$
Sucrose, 8TMS	806	918.43188	NA	NA	$C_{36}H_{86}O_{11}Si_8$

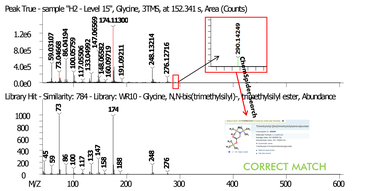

Figure 11. Deconvoluted (Peak True) and Library Spectra with Accurate Mass Utilized for Confirmation.

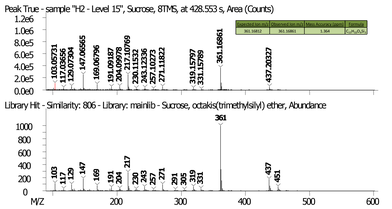

Figure 12. Deconvoluted (Peak True) and Library Spectra for Sucrose. Accurate Mass Measurement of m/z 361.16861 Confirms Chemical Formula of $C_{15}H_{33}O_6Si_3$ Which is Part of the Sucrose Structure.