

# Determination of Hydrocarbon Components in Petroleum Naphthas

LECO Corporation; Saint Joseph, Michigan USA

Key Words: GC-TOFMS, Petrochemical, Naphtha, Deconvolution, Retention Index

## 1. Introduction

The determination of hydrocarbon components in petroleum naphthas is of great importance to the Petrochemical industry. A knowledge of the composition in naphthas, reformates, or alkylates is useful in characterization of crude oils, reforming process control, and product quality assessment, as well as for regulatory purposes. Detailed hydrocarbon composition is also used as input in the mathematical modeling of refinery processes. A number of ASTM chromatographic methods have been developed to address these issues. Usually these methods require strict adherence to the parameters specified in order to avoid interferences from coelutions or analyte identification issues, thus resulting in methods that require long analysis times.

Mass spectrometers are usually used as a confirmation tool only, perhaps because a mass spectrometer is perceived to require a higher degree of analytical skill. In addition, most mass spectrometers also require good chromatographic separation to avoid misinterpretation of the spectrum generated. A typical mass spectrometer acquires data at a rate of 1 to 5 spectra per second. This presents a problem when one tries to enhance the speed of the chromatographic methods and narrow or coeluting peaks are obtained. The LECO Pegasus® GC-TOFMS offers several advantages over other types of GC-MS systems, one of which is that it provides fast data acquisition rates of up to 500 spectra/sec. This allows accurate definition of the narrowest GC peaks. In addition, the ion ratios for a spectrum in a TOF system do not change across the chromatographic peak; this means that each spectrum across the peak gives an accurate representation of the ion ratios for that particular analyte. Or in other words, the spectra obtained are not skewed. This is known as "spectral continuity".

Fast data acquisition rates, as well as spectral continuity across peaks, allow the development of algorithms that can be used to deconvolute complex chromatographic coelutions and extract the spectrum of each analyte. The deconvoluted spectra can then be used for library identification. Thus, it is possible to analyze complex samples such as naphthas using faster chromatographic methods without losing analytical information.

## 2. Experimental Conditions

A PIANO Standard and two naphtha process samples were analyzed using the LECO Pegasus GC-TOFMS system in order to characterize and quantify the analytes present in these samples. Method ASTM D5134 was implemented and modified to analyze these samples using faster chromatographic conditions without losing analytical resolution.

Method ASTM D5134 typically requires an analysis time of 122.5 minutes. By using a shorter column, acquiring data at 25 spectra per second, and implementing a faster GC oven temperature program the analysis time was reduced to 25 minutes—a 5-fold reduction in analysis time.

### GC-Parameters—Agilent® 6890 (EPC Mode)

#### Column:

Supelco® SPB-1; 30 m x 0.25 mm x 0.25 µm film

Injector Temperature: 225°C

Split Ratio: 400:1

#### Oven Program:

40°C for 2 minutes to 250°C at 10°C/minute,  
hold 2 minutes

#### Flow Rate:

Constant flow at 1.8 ml/minute

### MS-Parameters—Pegasus II GC-TOFMS (EI Mode)

Mass Range: 45 to 450 amu

Acquisition Rate: 25 spectra/seconds

Ion Source Temperature: 200°C

Total Acquisition Time: 25 minutes

## 3. Results and Discussion

Method ASTM D5134 specifies that quantifications be determined by area percentage calculations along with retention index calculations. When a mass spectrometer is used as the detector, the areas for each peak will be determined by the ionization efficiency of the analytes. In other words, even if two peaks have the same concentration, their areas may not be the same due to differences in their ionization efficiencies. This is why response factors are needed for each analyte present in the sample. Furthermore, it becomes very difficult to obtain accurate areas of closely eluting or coeluting peaks, since peaks will have area contribution from more than one component. This is why method D5134 uses a long column with a very slow temperature program. Most of these problems can be resolved by the Pegasus hardware/software without resorting to long columns or extended run times, as will be demonstrated in the following figures and tables.

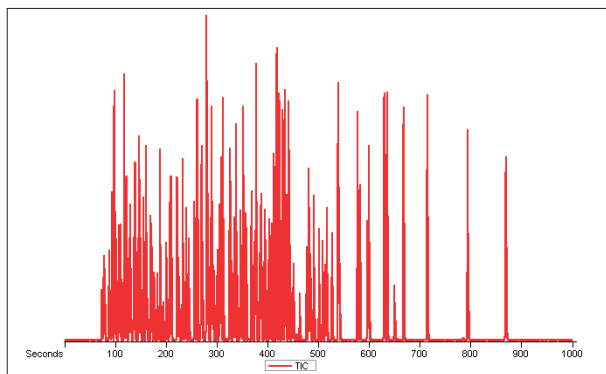


Figure 1. Total Ion Chromatogram (TIC) of a PIANO standard mix.

Figure 1 shows the Total Ion Chromatogram (TIC) for a PIANO standard with known composition (139 components). A number of peaks in this sample were not fully resolved chromatographically. Figure 2 illustrates one coelution. Most mass spectrometers cannot deconvolute such a close coelution mainly because they have low acquisition rates.

A Time-of-Flight (TOF) mass spectrometer, on the other hand, allows fast acquisition rates. The LECO Pegasus can acquire data at speeds up to 500 full mass spectra per second. In addition, the ion ratios do not change across a peak; meaning that the spectrum across the peak gives an accurate representation of the ion ratios for that particular analyte.

Fast data acquisition rates, combined with spectral continuity across peaks, has allowed the development of algorithms that can be used to locate peaks (Peak Find) and deconvolute complex chromatographic coelutions to extract the spectrum of each analyte for easy library identification. This is illustrated in Figure 2 where the TIC only shows one peak, but the Peak Find algorithm finds two peaks and deconvolutes them to obtain library searchable spectra. By plotting "unique" masses, ( $m/z$  91 and 69) it is evident that there are two peaks.

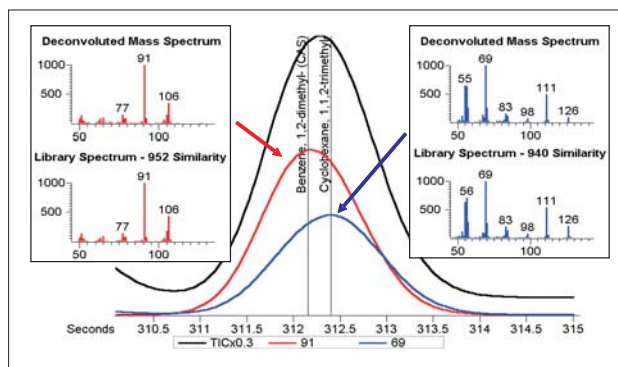


Figure 2. Automatic Peak Find and deconvolution of coeluting peaks in a PIANO standard mix.

One of the most difficult questions to answer is "What is the area contributed by each peak in the coelution"? The Pegasus software can answer this question by computing the area based on the spectral continuity of the peak. Since the ion ratios remain constant across a peak, it is possible to calculate accurate areas as illustrated in Figure 3.

This algorithm even works when coeluting peaks contain shared masses. This is illustrated in Figure 4 where  $m/z$  134 is shared by the two coeluting analytes. The Deconvolution algorithm correctly calculates the contribution of the shared masses for each spectrum as shown in Figure 5.

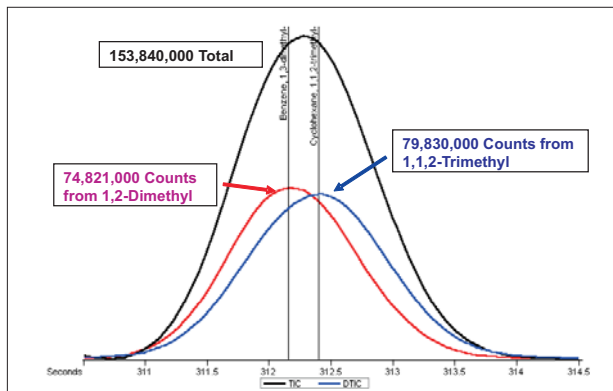


Figure 3. Calculated areas for coeluting peaks.

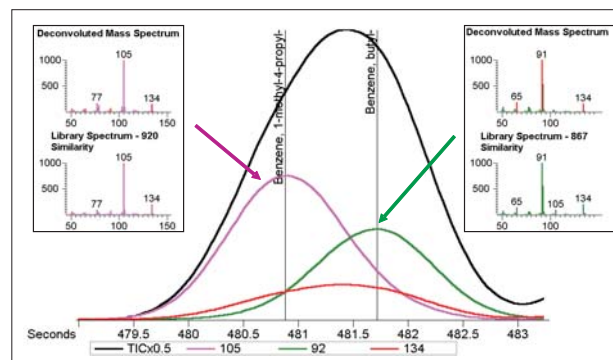


Figure 4. Deconvolution of coeluting peaks with shared masses ( $m/z$  65, 91 and 134 are shared).

By specifying a plot of mass 134, and deconvoluted mass 134 (d134), one can visually see the contribution of mass 134 to each of the peaks in the coelution. In the same manner, by specifying in the quantification masses a DTIC, one can obtain the area contribution of each coeluting peak. This same principle can be applied to the entire chromatogram so that total areas can be calculated for all peaks and thus obtain an area percentage calculation. Table 1 is a partial list of area percentage for the PIANO standard. Once an area percentage has been calculated, the results can be corrected by multiplying by a response factor to obtain weight percentage results.

Table 1. Partial Table of Area percentage and Weight percentage for PIANO Standard.

Analyte	Type	RT (sec)	Area	Area %	Weight %
1-Butene, 3-methyl-	Olefin	73.92	14,285,000	0.152	0.355
Butane, 2-methyl- (CAS)	Iso-Paraffin	75.52	8,351,200	0.089	0.414
1-Pentene	Olefin	76.96	23,348,000	0.249	0.755
1-Butene, 2-methyl-	Olefin	77.68	14,241,000	0.152	0.264
Pentane (CAS)	Paraffin	78.28	10,627,000	0.113	1.785
1,3-Butadiene, 2-methyl-	Olefin	78.88	17,310,000	0.184	0.437
2-Pentene, (Z)-	Olefin	79.16	13,372,000	0.142	0.362
2-Pentene, (E)-	Olefin	80.20	16,757,000	0.178	0.330
1-Pentene, 4-methyl-	Olefin	87.28	18,750,000	0.200	0.628
Cyclopentane	Naphthene	89.00	35,683,000	0.380	1.029
Pentane, 2-methyl- (CAS)	Iso-Paraffin	90.08	13,858,000	0.147	0.620
Pentane, 3-methyl-	Iso-Paraffin	93.60	58,437,000	0.622	1.018
1-Hexene	Olefin	95.04	48,970,000	0.521	1.288
Hexane	Paraffin	98.28	117,060,000	1.246	1.809
2-Hexene, (E)-	Olefin	99.72	22,573,000	0.240	0.316
2-Pentene, 2-methyl-	Olefin	100.44	34,964,000	0.372	0.620
2-Hexene, (Z)-	Olefin	102.80	41,736,000	0.444	0.708
Pentane, 2,2-dimethyl-	Iso-Paraffin	106.68	24,553,000	0.261	0.335
Cyclopentane, methyl-	Naphthene	107.68	50,922,000	0.542	0.687
Pentane, 2,4-dimethyl-	Iso-Paraffin	109.00	35,760,000	0.381	0.699
Butane, 2,2,3-trimethyl-	Iso-Paraffin	111.36	54,777,000	0.583	0.742
Benzene	Aromatic	117.68	131,640,000	1.401	1.645

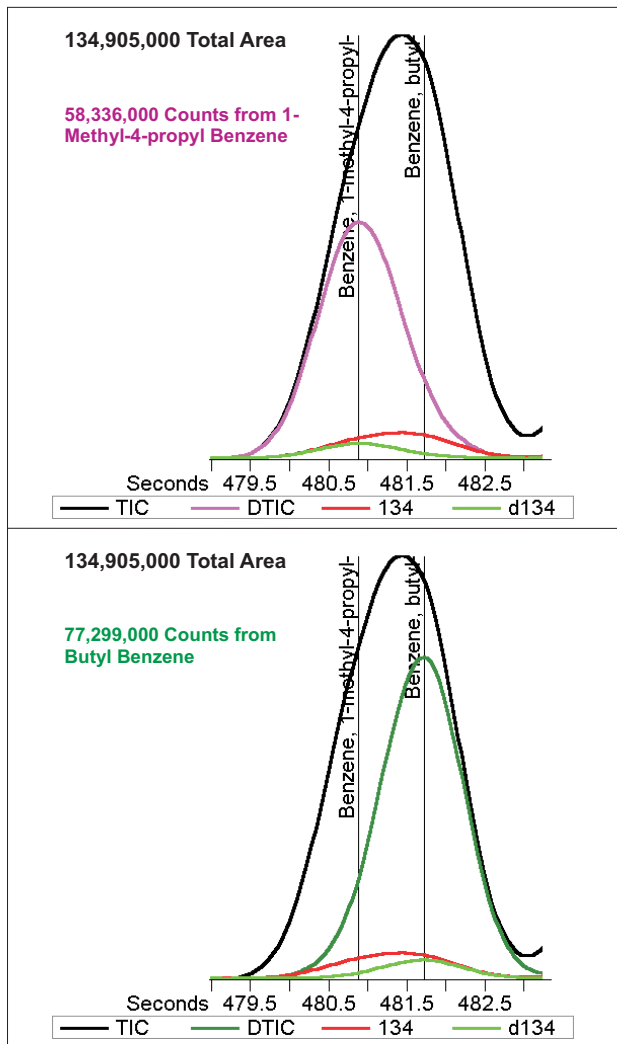


Figure 5. Calculated areas for coeluting peaks with shared masses.

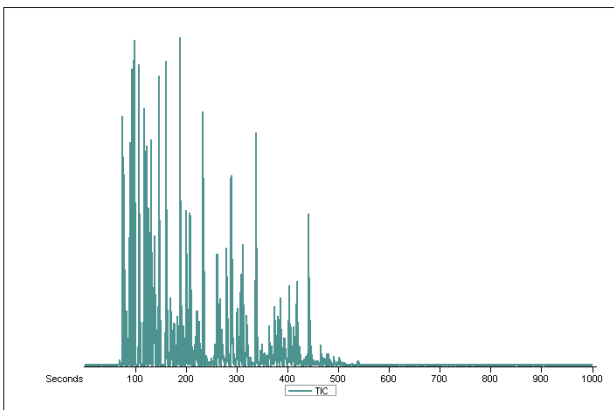


Figure 6. Chromatogram of a Naphtha Distillation Column Load process sample.

Figure 6 shows the chromatogram of a Naphtha Distillation Column Load process sample. This sample was analyzed using the conditions listed earlier and processed automatically at a signal-to-noise (S/N) level of 200:1. This means that the Processing algorithm will ignore components below a S/N level of 200. The Peak Find and Deconvolution algorithms identified 170 components. Area percentage and Retention Index were also calculated. Table 2 shows the results for this sample.

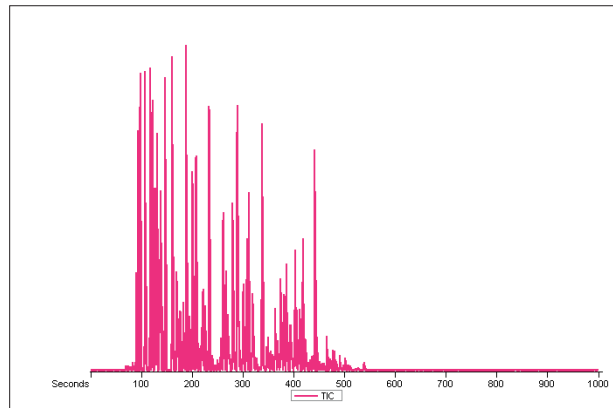


Figure 7. Chromatogram of a Naphtha Distillation Column Bottom process sample.

Figure 7 shows the chromatogram of a Naphtha Distillation Column Bottom process sample. This sample was also processed at a S/N level of 200:1. The Peak Find and Deconvolution algorithms identified a total of 152 components.

Table 2. Partial Table of Area percentage and Retention Index for Naphtha Distillation Column Load Process Sample.

Peak #	Name	R.T. (seconds)	Retention Index	Area	Area %
1	1-Butanol, 2-methyl-, (S)-	70.866	552.68	3147500	0.137
2	iso-Pentane	70.966	552.89	23682000	1.032
3	2-Buten-1-ol	73.646	558.47	17967000	0.783
4	Butane, 2,2-dimethyl-	78.786	569.17	3758400	0.164
5	Cyclopropane, methylmethylene-	81.886	575.62	246320	0.011
6	Cyclopentane	84.126	580.29	5596700	0.244
7	2,2-Dimethylbutane	85.126	582.37	27361000	1.193
8	3-Methylpentane	88.546	589.49	37074000	1.616
9	Hexane	93.126	599.02	55229000	2.408
10	2,2-Dimethylpentane	101.266	615.96	2930900	0.128
11	Methylcyclopentane	102.246	618	32080000	1.399
12	2,4-Dimethylpentane	103.506	620.63	4841800	0.211
13	Benzene	112.006	638.32	27612000	1.204
14	3,3-Dimethylpentane	114.586	643.69	2926700	0.128
15	Cyclohexane	116.446	647.56	25110000	1.095
16	2-Methylhexane	120.886	656.8	21948000	0.957
17	2,3-Dimethylpentane	121.866	658.84	19105000	0.833
18	1,1-Dimethylcyclopentane	123.526	662.3	4229800	0.184
19	3-Methylhexane	125.746	666.92	41389000	1.804
20	cis-1,3-Dimethylcyclopentane	129.606	674.96	10183000	0.444
21	trans-1,3-Dimethylcyclopentane	131.246	678.37	10283000	0.448
22	3-Ethylpentane	131.926	679.79	3160400	0.138
23	trans-1,2-Dimethylcyclopentane	132.886	681.78	20449000	0.891
24	Pentane, 2,2,4-trimethyl-	133.906	683.91	2372000	0.103
25	Heptane	141.006	698.69	74839000	3.263
26	Cyclopentane, 1,2-dimethyl-, cis-	154.586	714.94	6330000	0.276
27	Methylcyclohexane	154.866	715.27	58171000	2.536
28	1-Hexene, 3,5-dimethyl-	157.246	718.01	6043500	0.263
29	Ethylcyclopentane	163.866	725.65	11722000	0.511
30	2,5-Dimethylhexane	165.126	727.1	5667100	0.247
31	Hexane, 2,4-dimethyl-	166.626	728.84	8155500	0.356
32	Cyclopentane, 1,2,4-trimethyl-, (1à,2á,4à)-	170.966	733.84	9370900	0.409
33	Hexane, 3,3-dimethyl-	172.206	735.27	1168000	0.051
34	Cyclopentane, 1,2,3-trimethyl-, (1à,2à,3á)-	176.986	740.79	10708000	0.467
35	Pentane, 2,3,4-trimethyl-	179.446	743.63	2935600	0.128
36	Toluene	182.386	747.02	107090000	4.668
37	2,3-Dimethylhexane	189.266	754.96	8621700	0.376
38	Pentane, 3-ethyl-2-methyl-	190.126	755.95	6188100	0.270
39	2-Methylheptane	194.826	761.38	38509000	1.679
40	4-Methylheptane	196.126	762.88	14584000	0.636
41	Hexane, 3,4-dimethyl-	197.166	764.08	5570900	0.243
42	Heptane, 3-methylene-	199.426	766.68	596310	0.026
43	3-Methylheptane	201.666	769.27	33775000	1.472
44	cis-1,4-Dimethylcyclohexane	202.306	770.01	23708000	1.034
45	Unknown	202.666	770.42	5762000	0.251
46	trans-1,4-Dimethylcyclohexane	204.106	772.09	9522200	0.415
47	Cyclohexane, 1-ethyl-2-methyl-, cis-	209.146	777.9	3828200	0.167
48	Cyclopentane, 1-ethyl-3-methyl-, cis-	212.686	781.99	8080300	0.352
49	1-Ethyl-1-methylcyclopentane	216.006	785.82	19949000	0.870
50	trans-1,2-Dimethylcyclohexane	220.486	790.99	12077000	0.526

**Table 3. Partial Table of Area percentage and Retention Index for Naphtha Distillation Column Bottom Process Sample.**

Peak #	Name	R.T. (seconds)	Retention Index	Area	Area %
1	iso-Pentane	71.281	553.55	538070.000	0.023
2	Butane, 2-methyl-	73.961	559.13	469420.000	0.020
3	4-Methyl-1-pentene	82.201	576.28	507090.000	0.021
4	2,2-Dimethylbutane	85.481	583.11	11105000.000	0.468
5	3-Methylpentane	88.881	590.18	34694000.000	1.461
6	Hexane	93.461	599.72	79313000.000	3.340
7	2,2-Dimethylpentane	101.621	616.7	2818300.000	0.119
8	Methylcyclopentane	102.581	618.7	50061000.000	2.108
9	2,4-Dimethylpentane	103.901	621.45	6966300.000	0.293
10	2,2,3-Trimethylbutane	106.221	626.28	514300.000	0.022
11	Benzene	112.321	638.98	44367000.000	1.869
12	3,3-Dimethylpentane	114.961	644.47	1806500.000	0.076
13	Cyclohexane	116.761	648.22	50732000.000	2.137
14	2-Methylhexane	121.261	657.59	30828000.000	1.298
15	2,3-Dimethylpentane	122.221	659.58	27078000.000	1.140
16	1,1-Dimethylcyclopentane	123.881	663.04	9241900.000	0.389
17	3-Methylhexane	126.101	667.66	54972000.000	2.315
18	cis-1,3-Dimethylcyclopentane	129.941	675.65	16292000.000	0.686
19	trans-1,3-Dimethylcyclopentane	131.601	679.11	15729000.000	0.662
20	3-Ethylpentane	132.281	680.52	3924100.000	0.165
21	trans-1,2-Dimethylcyclopentane	133.221	682.48	31891000.000	1.343
22	Heptane	141.401	699.51	91772000.000	3.865
23	Unknown	154.881	715.28	10126000.000	0.426
24	Methylcyclohexane	155.201	715.65	84052000.000	3.540
25	Cyclopentane, 1,1,3-trimethyl-	157.741	718.58	7621300.000	0.321
26	Ethylcyclopentane	164.221	726.06	18094000.000	0.762
27	2,5-Dimethylhexane	165.501	727.54	6018100.000	0.253
28	2,4-Dimethylhexane	167.001	729.27	9645000.000	0.406
29	Cyclopentane, 1,2,4-trimethyl-, (1à,2á,4à)-	171.321	734.25	12449000.000	0.524
30	Hexane, 3,3-dimethyl-	172.581	735.71	2353400.000	0.099
31	Cyclopentane, 1,2,3-trimethyl-, (1à,2à,3á)-	177.321	741.18	13368000.000	0.563
32	Heptane, 3,3,4-trimethyl-	179.801	744.04	3330700.000	0.140
33	Toluene	182.721	747.41	129800000.000	5.467
34	2,3-Dimethylhexane	189.601	755.35	10109000.000	0.426
35	Hexane, 2,3,4-trimethyl-	190.501	756.39	6611500.000	0.278
36	2-Methylheptane	195.181	761.79	40207000.000	1.693
37	4-Methylheptane	196.461	763.26	16649000.000	0.701
38	Heptane, 3-methyl-	197.601	764.58	4957800.000	0.209
39	Heptane, 3-methylene-	199.761	767.07	1103000.000	0.046
40	3-Methylheptane	202.061	769.73	38490000.000	1.621
41	trans-1,4-Dimethylcyclohexane	202.641	770.39	31339000.000	1.320
42	Cyclohexane, 1,4-dimethyl-, cis-	204.421	772.45	11168000.000	0.470
43	Cyclohexane, 1,1-dimethyl-	209.501	778.31	4729100.000	0.199
44	1-Octene	213.041	782.4	8606800.000	0.362
45	1-Ethyl-1-methylcyclopentane	216.361	786.23	20618000.000	0.868
46	Unknown	218.241	788.4	946680.000	0.040
47	trans-1,2-Dimethylcyclohexane	220.861	791.42	14140000.000	0.596
48	Octane	228.001	799.66	96996000.000	4.085
49	Isopropylcyclopentane	234.701	806.06	2878200.000	0.121
50	cis-1-Methyl-2-ethylcyclopentane	245.161	815.95	2678600.000	0.113

#### 4. Conclusions

Using the Pegasus GC-TOFMS, it is possible to reduce the analysis time of Naphthas by taking advantage of the acquisition speed and spectral continuity generated by the mass spectrometer. Method ASTM D5143 was implemented in this platform, but was modified to take advantage of the hardware/software capabilities of the Pegasus.

It has been demonstrated that Area percentage and Retention Index calculations can be easily done even when chromatographic coelutions take place. The strength of the Pegasus GC-TOFMS for the analysis of these complex mixtures lies in its automated data handling capabilities. Peak finding, spectral determination, library searching, and area % determinations can be accomplished very rapidly, improving analytical results and productivity.



**LECO Corporation** • 3000 Lakeview Avenue • St. Joseph, MI 49085 • Phone: 800-292-6141 • Fax: 269-982-8977  
info@leco.com • www.leco.com • ISO-9001:2000 • No. FM 24045 • LECO is a registered trademark of LECO Corporation.