

Greetings from Houston! In addition to our routine use of *Nitric Oxide Ionization Spectrometry Evaluation (NOISE®)* for the quantitative analysis of hydrocarbon streams (B.P. 250 to 950°F) for hydrocarbon type by boiling point region, the technique of Nitric Oxide Chemical Ionization is also useful in the qualitative identification of hydrocarbons in the naphtha range. To demonstrate this capability (*see enclosed chromatogram*) the components of the Auto/Oil committee PONA IVb reference gasoline were identified by **NOISE** technique.

The analysis was performed on a research grade Finnigan chemical ionization mass spectrometer recently equipped with a new Varian Star 3400 chromatograph. The column is a 100 meter Supelco Petrocol DH using an oven temperature program optimized for gasoline analysis. The "*soft ionization*" reactions of NO⁺ with hydrocarbons enable us to unequivocally determine the hydrocarbon type and carbon number of over 300 components in the Auto/Oil mix.

The attached sixteen page chromatogram with hydrocarbon type followed by the carbon number, uses the following nomenclature for conciseness.

P	Paraffin (Normal)
I	Isoparaffin (Branched)
O	Olefin
OO	Diolefin
N	Naphthene (Cycloparaffin)
A	Aromatic
NO	Naphthenic Olefin (i.e. Methyl Cyclohexene)
NOO	Naphthenic Diolefin
NN	Dinaphthene (i.e. Decalin)
AN	Aromatic Naphthene (i.e. Indane)
ANO	Aromatic Naphthene Olefin (i.e. Indene)
AA	Diaromatic (i.e. Naphthalene)

Triton's *unique* identification capabilities for naphtha range hydrocarbons provides our customers with additional confidence for our more conventional (GC/FID) detailed quantitative analysis of naphthas. (see a portion of a typical tabulated report on the back of this page)

After you have made an evaluation of the data, feel free to discuss with us any aspect of the hydrocarbon analysis services available at TAC.

Detailed Hydrocarbon Analysis
Triton Analytics Corp.

File: 001R0201 Sample: PONA4B Analyzed: 15 May 92 06:44 AM
Method: DHA2.MTH Processed 320 Peaks Reported: 05-04-1992 22:03:20
DHA DBase File: RI-DATA.DBF Normalized to 100.00%

Analysis Performed at Triton Analytics Corp.
Sample: Auto/Oil Committee Gasoline Std PONA4

Composite Report

Totals by Group Type & Carbon Number
(in Weight Percent)

	Paraffins:	I-paraffins:	Aromatics:	Naphthenes:	Olefins:	Total:
C1:	0.000	0.000	0.000	0.000	0.000	0.000
C2:	0.046	0.000	0.000	0.000	0.000	0.046
C3:	0.531	0.000	0.000	0.000	0.000	0.531
C4:	0.502	0.184	0.000	0.000	0.326	1.012
C5:	0.703	3.701	0.000	0.069	3.066	7.539
C6:	0.864	3.536	0.478	1.454	2.080	8.413
C7:	2.326	4.035	2.891	4.689	1.819	15.760
C8:	4.004	5.143	6.315	5.906	0.389	21.756
C9:	3.453	5.977	7.026	4.679	0.219	21.354
C10:	2.263	4.629	5.919	1.654	0.210	14.675
C11:	0.976	1.208	1.321	0.438	0.000	3.943
C12:	0.274	0.421	0.413	0.000	0.000	1.108
C13:	0.213	0.000	0.000	0.000	0.000	0.213
C14:	0.188	0.000	0.000	0.000	0.000	0.188
Total:	16.343	28.834	24.363	18.889	8.110	96.539
Oxygenates:	1.885		Total C15+:	0.201	Total Unknowns:	1.376
					Grand Total:	100.000

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(in Volume Percent)

	Paraffins:	I-paraffins:	Aromatics:	Naphthenes:	Olefins:	Total:
C1:	0.000	0.000	0.000	0.000	0.000	0.000
C2:	0.100	0.000	0.000	0.000	0.000	0.100
C3:	0.792	0.000	0.000	0.000	0.000	0.792
C4:	0.648	0.247	0.000	0.000	0.399	1.293
C5:	0.839	4.460	0.000	0.069	3.498	8.865
C6:	0.976	4.013	0.405	1.435	2.218	9.051
C7:	2.540	4.403	2.489	4.614	1.918	15.965
C8:	4.255	5.457	5.432	5.722	0.401	21.266
C9:	3.592	6.191	5.989	4.468	0.240	20.481
C10:	2.314	4.711	4.996	1.545	0.218	13.785
C11:	0.980	1.219	1.115	0.409	0.000	3.722
C12:	0.272	0.417	0.346	0.000	0.000	1.036
C13:	0.210	0.000	0.000	0.000	0.000	0.210
C14:	0.184	0.000	0.000	0.000	0.000	0.184
Total:	17.705	31.117	20.775	18.262	8.893	96.752
Oxygenates:	1.782		Total C15+:	0.195	Total Unknowns:	1.271
					Grand Total:	100.000

(in Mole Percent)

	Paraffins:	I-paraffins:	Aromatics:	Naphthenes:	Olefins:	Total:
C1:	0.000	0.000	0.000	0.000	0.000	0.000
C2:	0.159	0.000	0.000	0.000	0.000	0.159
C3:	1.261	0.000	0.000	0.000	0.000	1.261
C4:	0.904	0.331	0.000	0.000	0.608	1.843
C5:	1.020	5.368	0.000	0.103	4.582	11.073
C6:	1.049	4.295	0.641	1.809	2.594	10.387
C7:	2.430	4.214	3.283	4.998	1.942	18.867
C8:	3.888	4.712	6.225	5.506	0.363	20.475
C9:	2.817	4.877	6.124	3.879	0.182	17.878
C10:	1.664	3.405	4.642	1.234	0.156	11.102
C11:	0.654	0.809	0.934	0.297	0.000	2.694
C12:	0.189	0.259	0.266	0.000	0.000	0.694
C13:	0.121	0.000	0.000	0.000	0.000	0.121
C14:	0.099	0.000	0.000	0.000	0.000	0.099
Total:	16.014	28.269	22.114	17.827	10.427	94.651
Oxygenates:	4.228		Total C15+:	0.099	Total Unknowns:	1.023
					Grand Total:	100.000

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Analysis Performed at Triton Analytics Corp.
Sample: Auto/Oil Committee Gasoline Std PONA4

Boiling Point Distribution Data

	Wt. Percent Off:	Vol. Percent Off:
deg.C.:	deg.F.:	deg.F.:
IBP (0.5%)	-42.04	-43.67
5.0%	27.84	82.11
10.0%	60.28	27.84
15.0%	68.73	155.71
20.0%	60.72	177.30
25.0%	91.85	197.33
30.0%	100.93	213.67
35.0%	110.63	231.13
40.0%	117.65	243.77
45.0%	123.30	253.94
50.0%	126.43	259.57
55.0%	136.20	277.16
60.0%	140.50	284.90
65.0%	144.43	291.97
70.0%	150.82	303.48
75.0%	161.20	322.16
80.0%	166.50	331.70
85.0%	174.15	345.47
90.0%	182.01	359.62
95.0%	195.90	384.62
FBP (99.5%)	235.40	455.72

Research Octane Number = 78.59
(Calculated from Individual Component Values)

Contribution to Total by:

Paraffins:	7.44
Iso-paraffins:	19.11
Aromatics:	25.83
Naphthenes:	15.32
Olefins:	7.56
Oxygenates:	1.90

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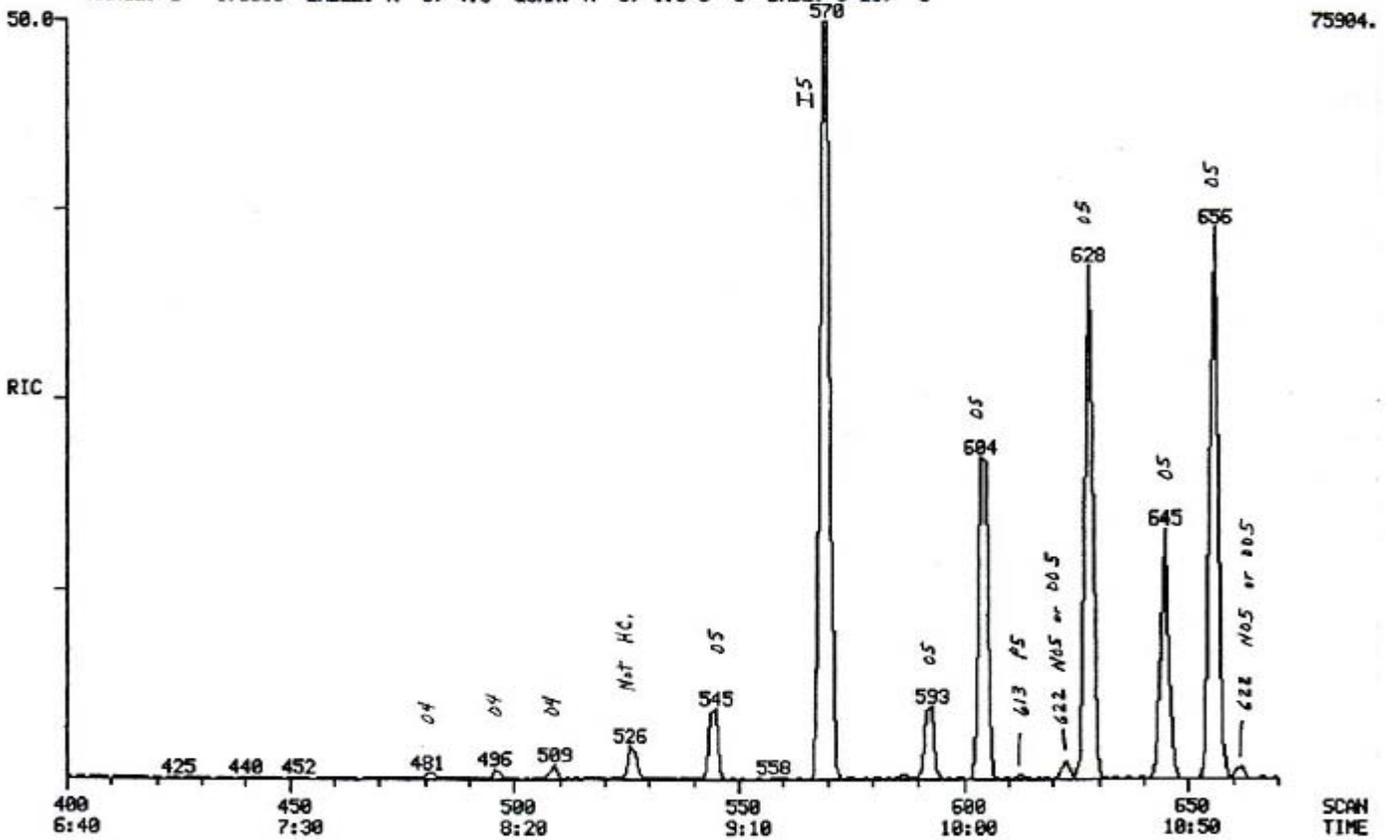
Analysis Performed at Triton Analytics Corp.
Sample: Auto/Oil Committee Gasoline Std PONA4

Components Listed in Chromatographic Order

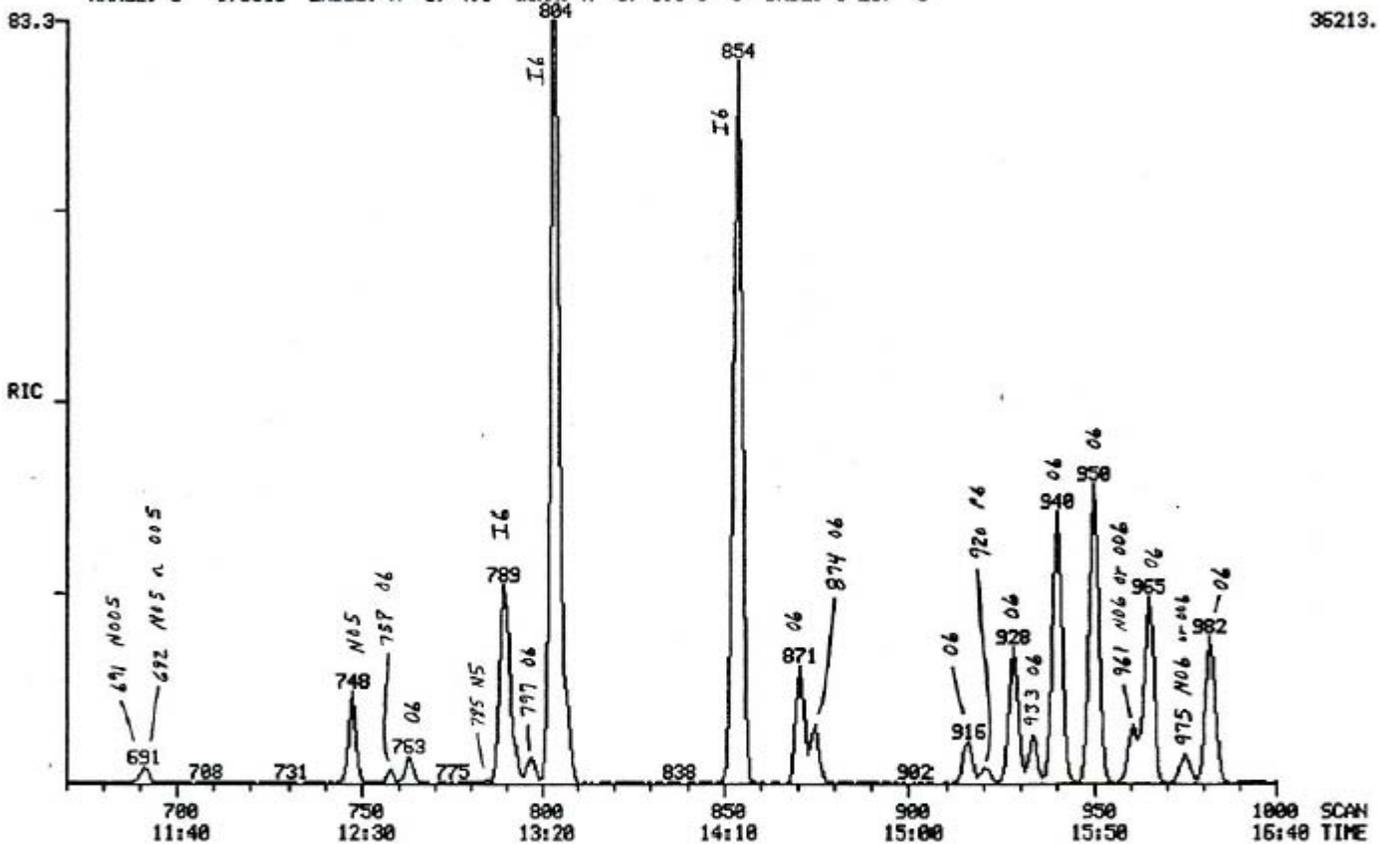
Min.	INDEX	Component	Wt%	Vol%	Mol%
7.125	203.3	Ethane	0.046	0.100	0.159
7.390	300.0	Propane	0.531	0.792	1.261
7.804	386.2	1-Butane/Methanol	0.184	0.247	0.331
8.043	390.3	Butene-1	0.056	0.070	0.104
8.157	400.0	n-Butane	0.502	0.648	0.904
8.279	410.0	t-Butene-2	0.120	0.149	0.224
8.481	424.5	c-Butene-2	0.150	0.180	0.280
8.731	440.1	Ethanol	1.784	1.688	4.053
9.052	457.1	3-Methylbutene-1	0.143	0.171	0.214
9.452	474.9	1-Pentane	3.701	4.460	5.368
9.719	485.2	1-Propanol	0.100	0.094	0.175
9.818	486.8	Pentene-1	0.367	0.428	0.548
10.007	495.3	2-Methylbutene-1	0.635	0.728	0.947
10.151	500.0	n-Pentane	0.703	0.839	1.020
10.302	505.0	Isoprene	0.023	0.025	0.035
10.379	507.4	t-Pentene-2	0.661	0.761	0.986
10.650	515.6	c-Pentene-2	0.364	0.415	0.544
10.825	520.6	2-Methylbutene-2	0.760	0.857	1.134
10.917	523.1	1t,3-Pentadiene	0.015	0.017	0.024
11.387	535.2	1c,3-Pentadiene	0.015	0.016	0.023
11.476	537.3	2,2-Dimethylbutane	0.023	0.026	0.028

12.291	555.1	Cyclopentene	0.083	0.080	0.127
12.446	558.2	4-Methylpentene-1	0.035	0.040	0.044
12.533	559.9	3-Methylpentene-1	0.052	0.058	0.065
12.678	566.4	Cyclopentane/MTBE	0.069	0.069	0.103
12.951	567.7	2,3-Dimethylbutane	0.420	0.474	0.510
13.064	569.7	2,3-Dimethylbutene-1	0.036	0.039	0.045
13.174	571.6	2-Methylpentane	1.873	2.142	2.275
14.008	585.1	3-Methylpentane	1.220	1.371	1.482
14.281	589.2	2-Methylpentene-1	0.189	0.206	0.235
14.341	590.0	Hexene-1	0.104	0.115	0.130
14.989	599.1	2-Ethylbutene-1	0.065	0.070	0.081
15.059	600.0	n-Hexane	0.864	0.978	1.049
15.179	601.6	t-Hexene-3	0.151	0.165	0.187
15.266	603.1	c-Hexene-3	0.061	0.066	0.075
15.369	604.6	t-Hexene-2	0.311	0.340	0.387
15.530	607.0	2-Methylpentene-2	0.306	0.331	0.381
15.720	609.6	3-Methylcyclopentene	0.052	0.051	0.067
15.774	610.4	3-Methyl-c-pentene-2	0.210	0.225	0.262
15.943	612.7	013	0.033	0.036	0.041
16.045	614.1	c-Hexene-2	0.179	0.193	0.222
16.512	620.3	3,3-Dimethylpentene-1	0.324	0.345	0.346
16.885	624.8	2,2-Dimethylpentane	0.022	0.025	0.023
17.073	627.3	Methylcyclopentane	1.048	1.045	1.303
17.370	630.9	2,4-Dimethylpentane	0.276	0.307	0.288
17.686	634.5	Cyclic Diolefin or Trioiefin	0.014	0.015	0.018
17.648	636.4	2,2,3-Trimethylbutane	0.015	0.016	0.015
18.615	646.8	4,4-Dimethyl-c-pentene-2	0.020	0.021	0.021
19.062	649.4	1-Methylcyclopentene	0.242	0.232	0.309
19.161	650.4	Benzene	0.478	0.406	0.641
19.629	655.0	3,3-Dimethylpentane	0.035	0.038	0.037
19.704	655.7	?	0.020	0.021	0.020
19.844	657.1	5-Methylhexene-1	0.015	0.016	0.016
20.096	659.5	Cyclohexane	0.406	0.390	0.505
20.223	660.6	2-Methyl-t-hexene-3	0.047	0.051	0.050
20.370	662.0	Diolefin (Hexadiene)	0.016	0.017	0.017
20.615	664.2	4-Methylhexene-1	0.035	0.037	0.037
20.864	666.4	4-Methyl-t/c-hexene-2	0.101	0.106	0.108
21.030	667.9	2-Methylhexane	1.495	1.645	1.562
21.228	669.6	2,3-Dimethylpentane	0.411	0.442	0.429
21.562	672.5	1,1-Dimethylcyclopentane	0.096	0.095	0.103
21.822	674.6	Cyclohexene	0.038	0.035	0.048
22.034	676.4	3-Methylhexane	1.571	1.707	1.641
22.447	679.7	3,4-Dimethyl-c-pentene-2	0.037	0.039	0.040
22.816	682.6	1c,3-Dimethylcyclopentane	0.557	0.559	0.594
23.165	685.3	1t,3-Dimethylcyclopentane	0.518	0.517	0.553
23.289	686.2	3-Ethylpentane	0.209	0.224	0.219
23.506	687.8	1t,2-Dimethylcyclopentane	0.683	0.679	0.728
23.626	688.7	2,2,4-Trimethylpentane	0.040	0.043	0.036
23.730	689.5	Heptene-1	0.062	0.066	0.066
24.463	694.7	3-Methyl-c-hexene-3	0.065	0.067	0.069
24.937	698.0	t-Heptene-3	0.222	0.236	0.237
25.232	700.0	n-Heptane	2.326	2.540	2.430
25.393	701.3	c-Heptene-3	0.048	0.050	0.051
25.503	702.1	2-Methyl-2-hexene	0.215	0.225	0.229
25.652	703.2	3-Methyl-t-hexene-3	0.095	0.102	0.101
25.912	705.2	t-Heptene-2	0.126	0.134	0.135
26.159	707.1	3-Ethylpentene-2	0.056	0.060	0.062
26.624	710.5	c-Heptene-2	0.186	0.195	0.198
27.159	714.3	2,3-Dimethylpentene-2	0.104	0.108	0.111
28.126	721.0	1c,2-Dimethylcyclopentane	0.269	0.274	0.287
28.270	722.0	Methylcyclohexane	2.168	2.104	2.311
28.790	725.4	1,1,3-Trimethylcyclopentane	0.342	0.341	0.319
30.250	734.7	Ethylcyclopentane	0.397	0.387	0.423
30.486	736.1	2,5-Dimethylhexane	0.220	0.237	0.202
30.660	737.2	2,2,3-Trimethylpentane	0.017	0.017	0.015
30.822	738.2	2,4-Dimethylhexane	0.334	0.356	0.306
31.809	744.0	1c,2t,4			

RIC DATA: LRI10724 #3999 SCANS 400 TO 670
 05/08/92 13:59:00 CALI: LRI10303B #6
 SAMPLE: AUTO/OIL PONA IUB STD NEIL JOHANSEN BY NITRIC OXIDE CI GC/MS.
 CONDS.: TRITON ANALYTICS CORP, HOUSTON, TX, DAN VILLALANTI 713-578-2289
 RANGE: G 1.8615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

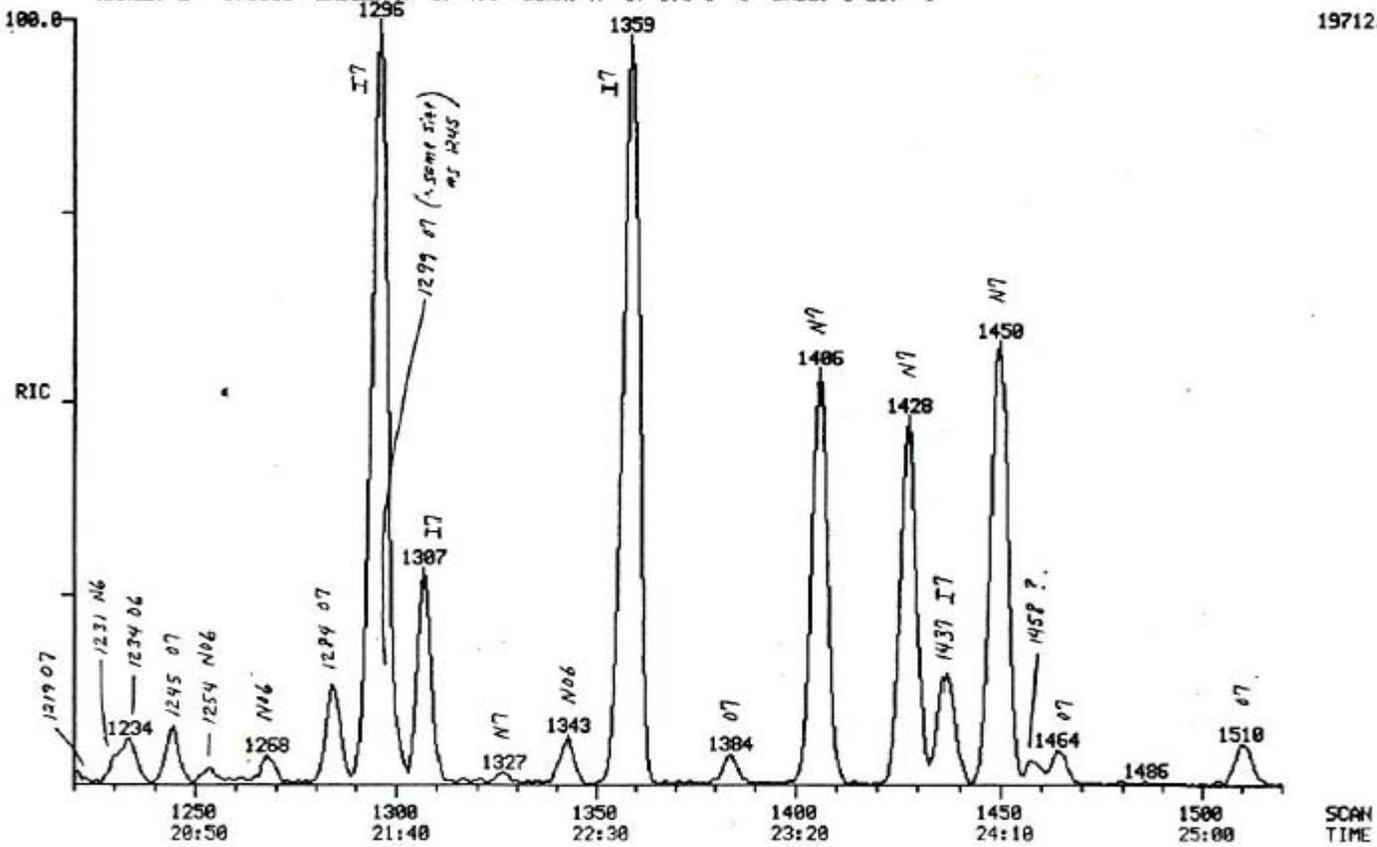


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 RANGE: G 1.8615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3



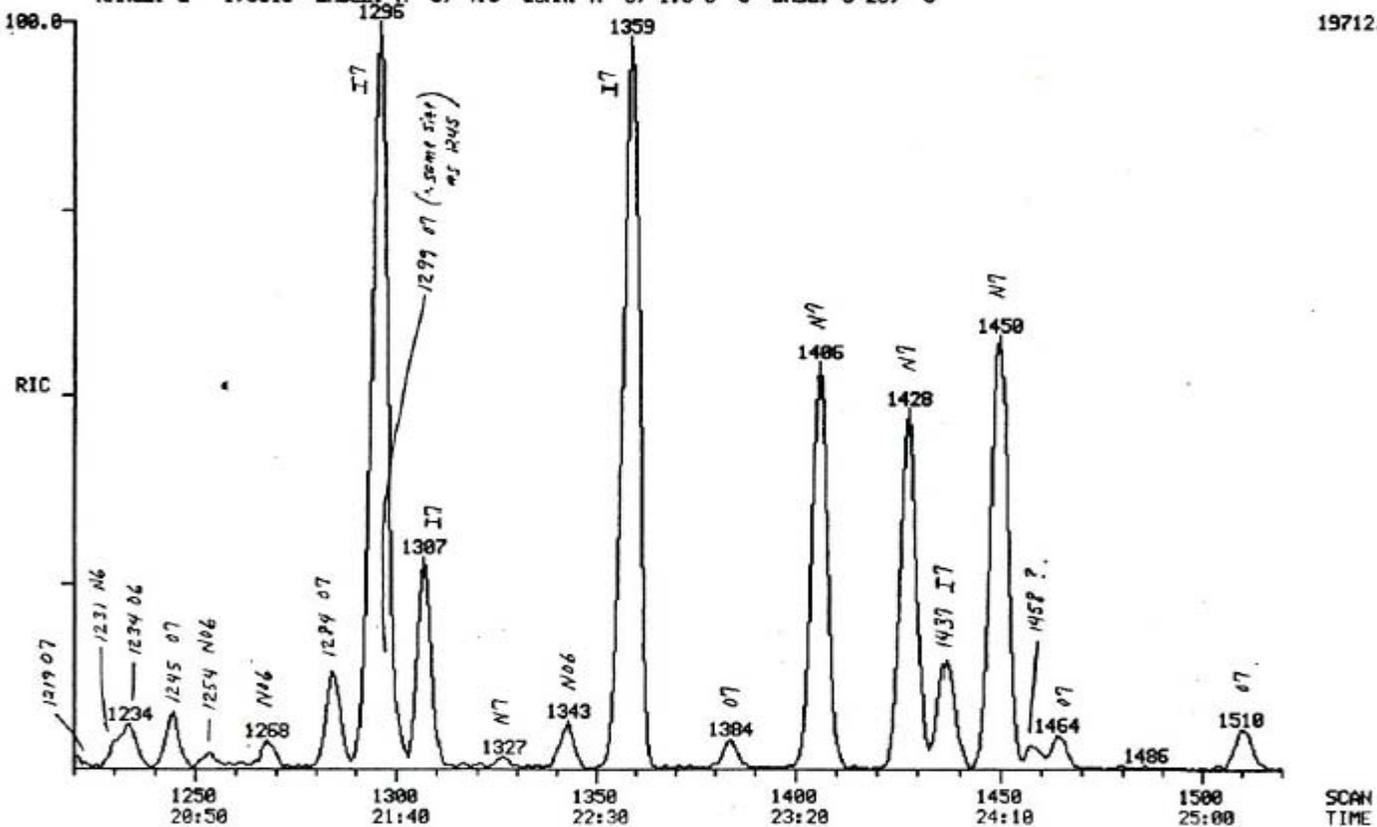
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05/08/92 13:59:00 CALI: LRI18383B #6
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CONDS.: TRITON ANALYTICS CORP, HOUSTON, TX. DAN VILLALANTI 713-578-2289
RANGE: G 1.8615 LABEL: H 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

19712.

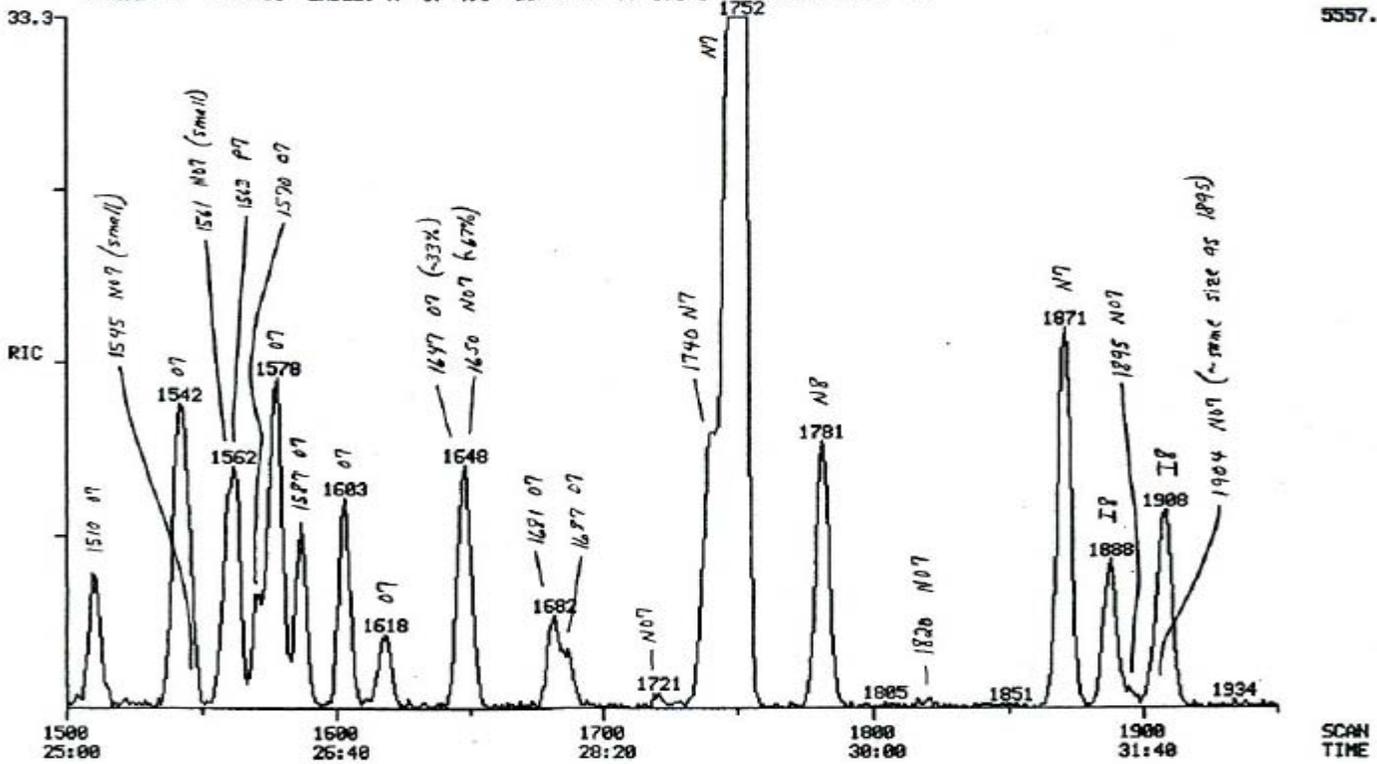


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CONDS.: TRITON ANALYTICS CORP, HOUSTON, TX. DAN VILLALANTI 713-578-2289
RANGE: G 1.8615 LABEL: H 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

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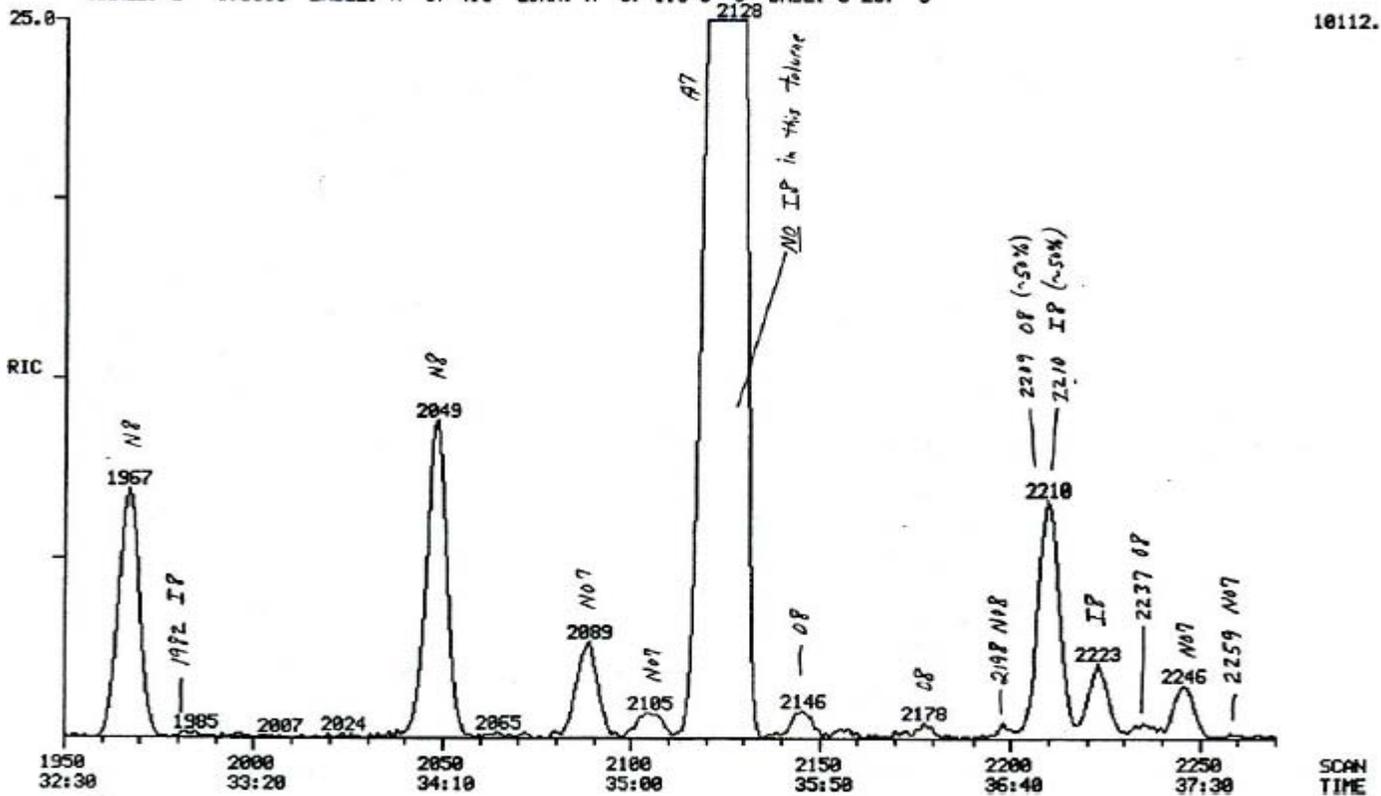


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 COND.: TRITON ANALYTICS CORP, HOUSTON, TX. DAN VILLALANTI 713-578-2289
 RANGE: G 1.8615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3



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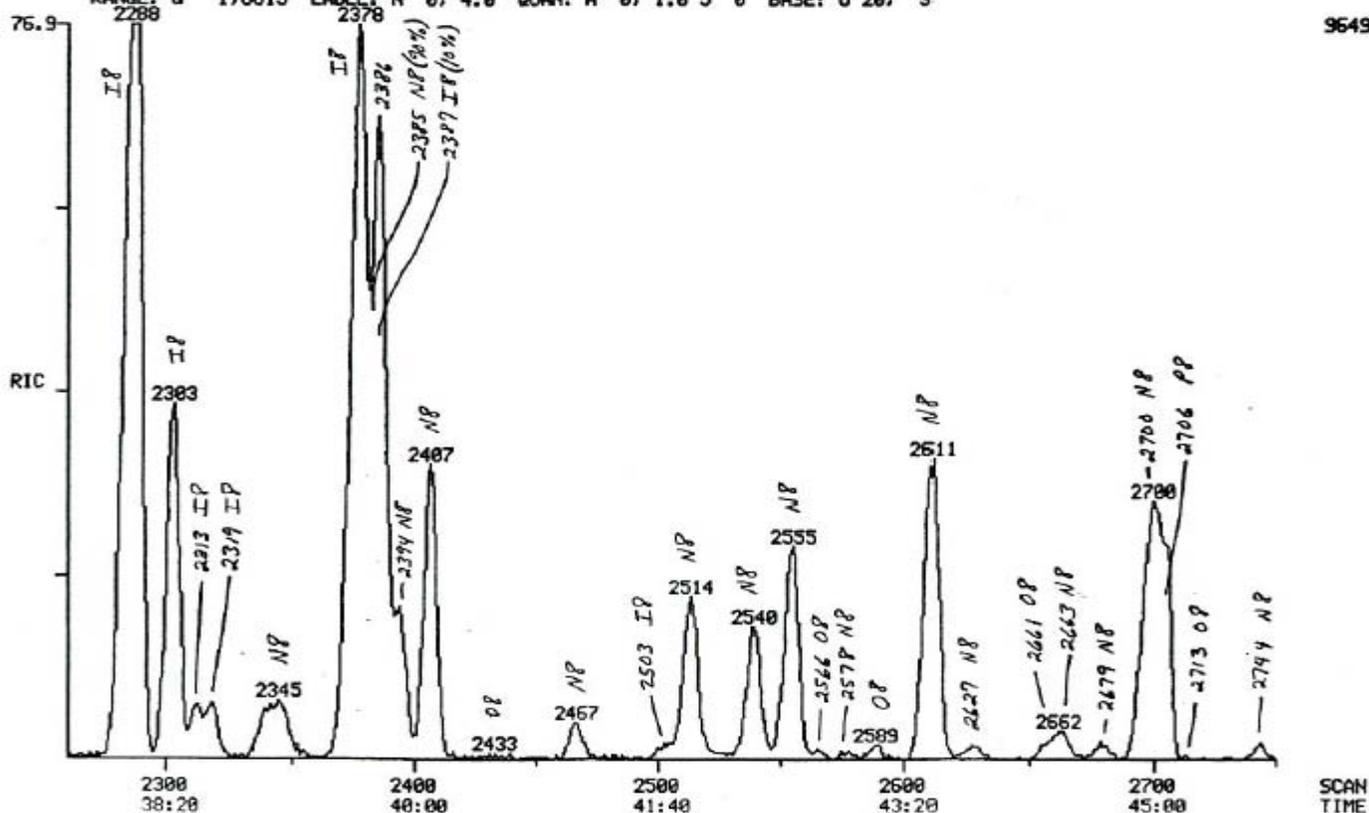
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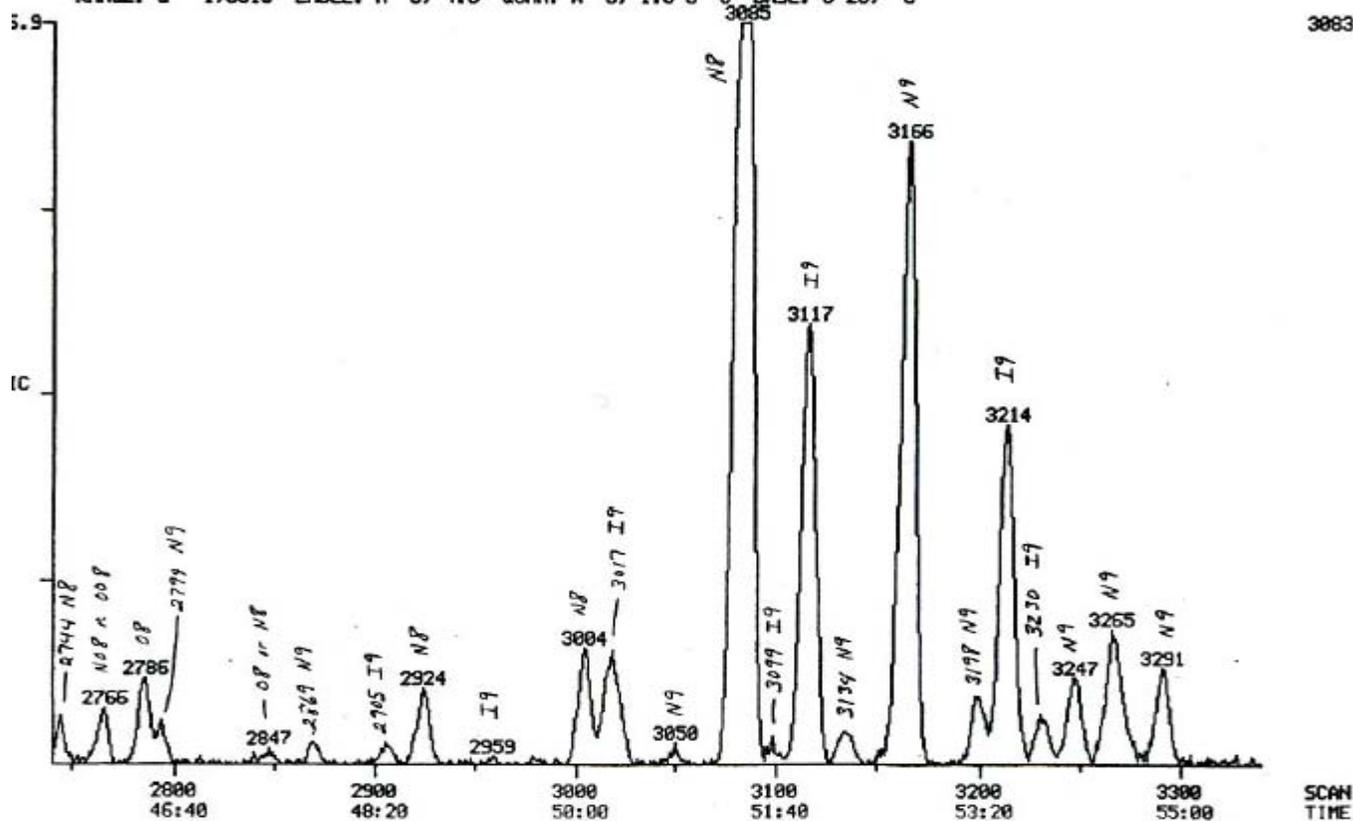
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 CONDS.: TRITON ANALYTICS CORP, HOUSTON, TX. DAN VILLALANTI 713-578-2289
 RANGE: G 1.8615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

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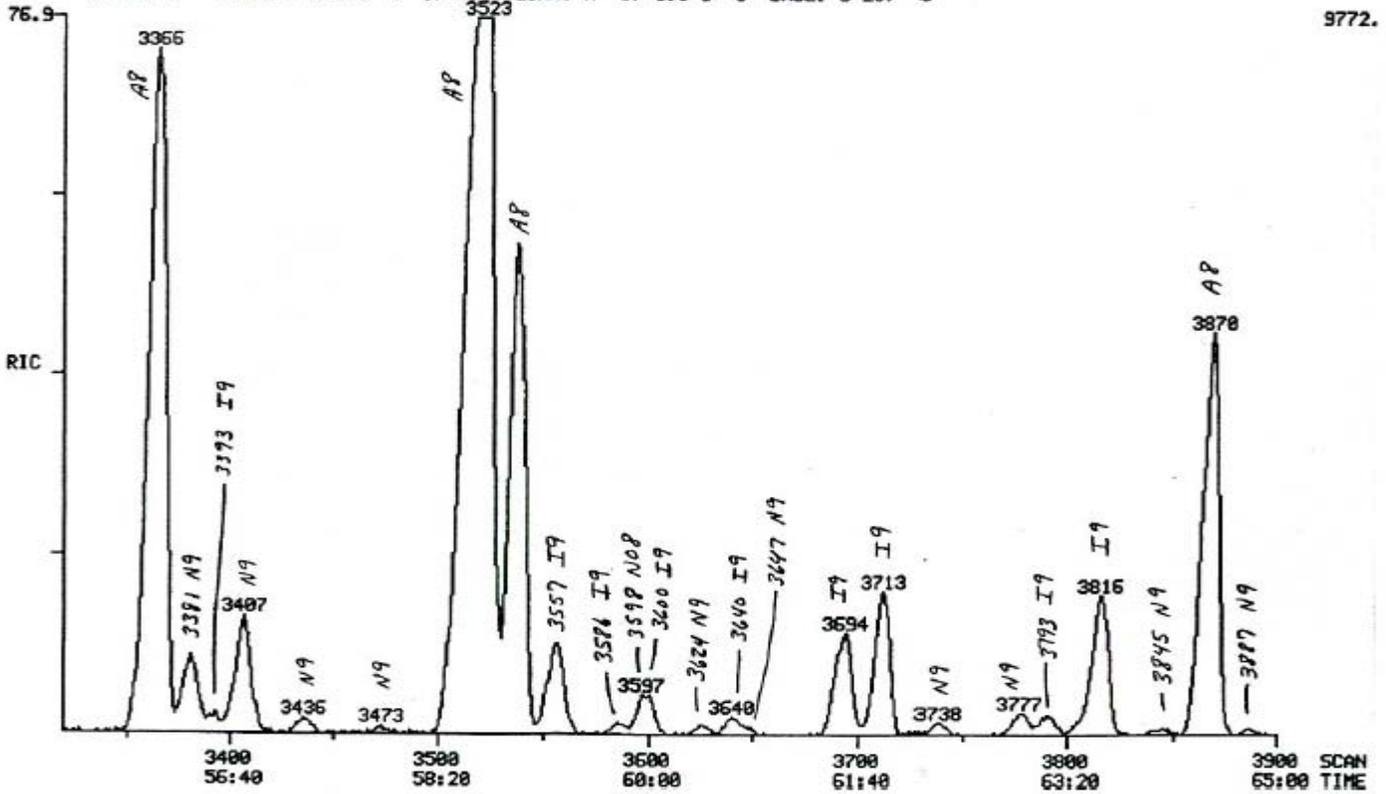


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3883.

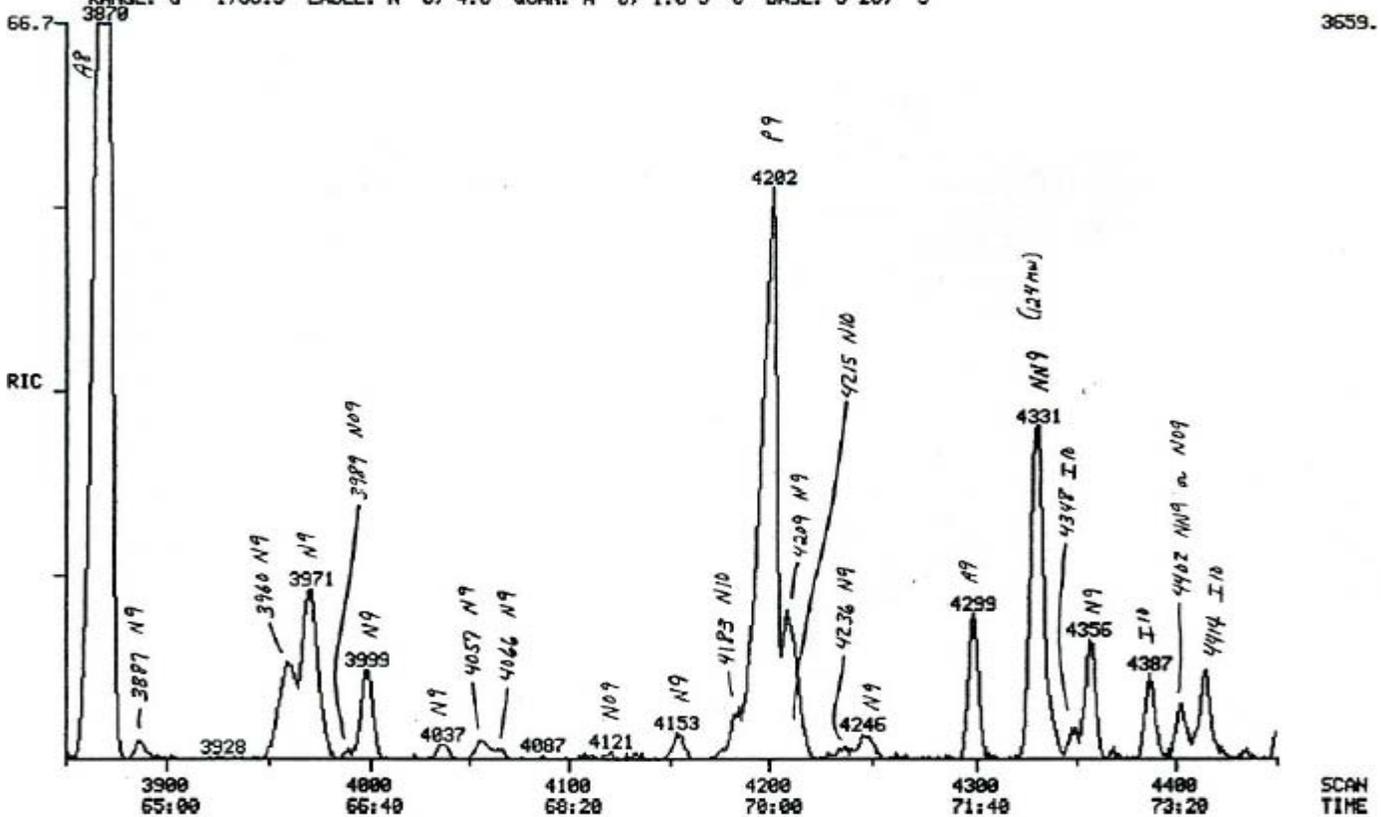


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 CONDS.: TRITON ANALYTICS CORP, HOUSTON, TX. DAN VILLALANTI 713-578-2289
 RANGE: G 1.8615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3



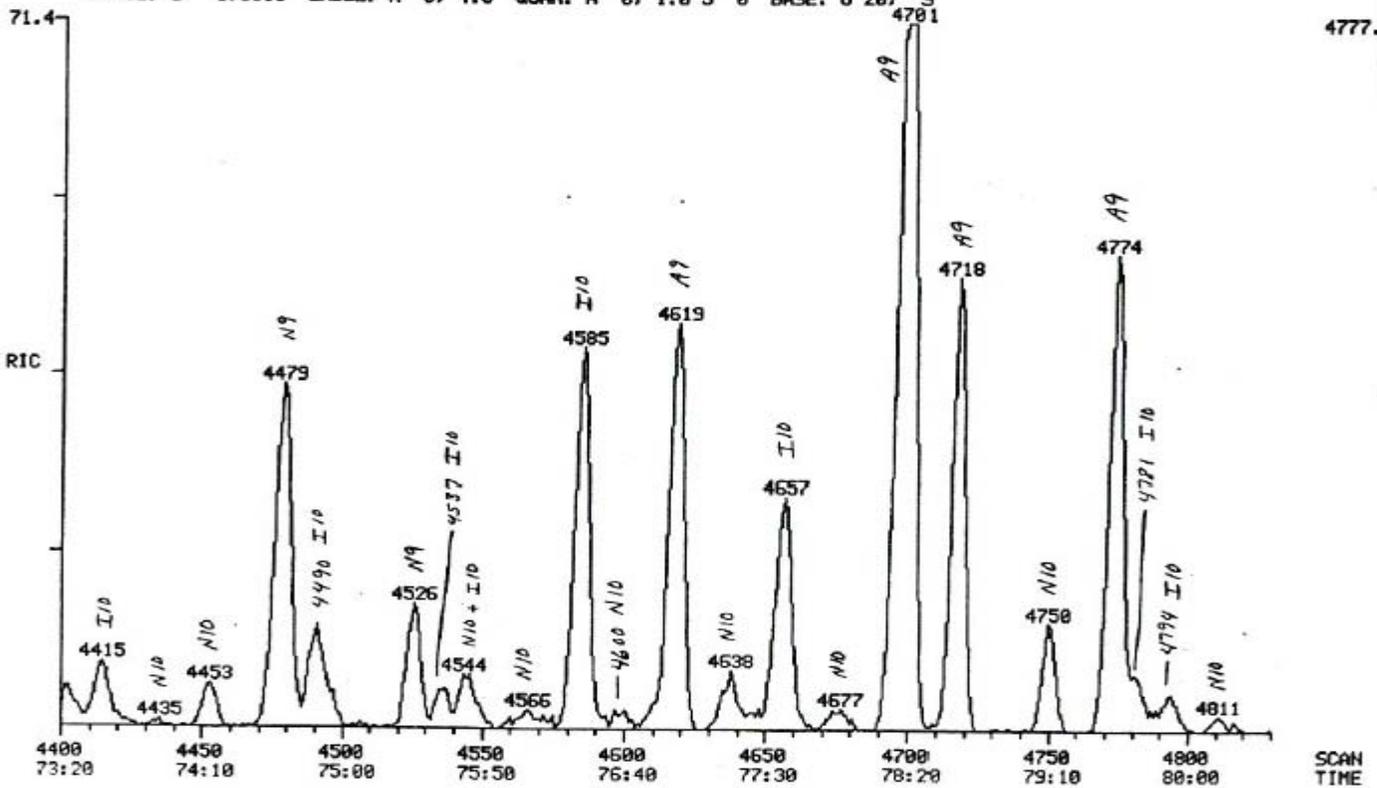
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 SAMPLE: AUTO/OIL PONA IUB STD NEIL JOHANSEN BY NITRIC OXIDE CI GC/MS.
 CONDS.: TRITON ANALYTICS CORP, HOUSTON, TX. DAN VILLALANTI 713-578-2289
 RANGE: G 1.8615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

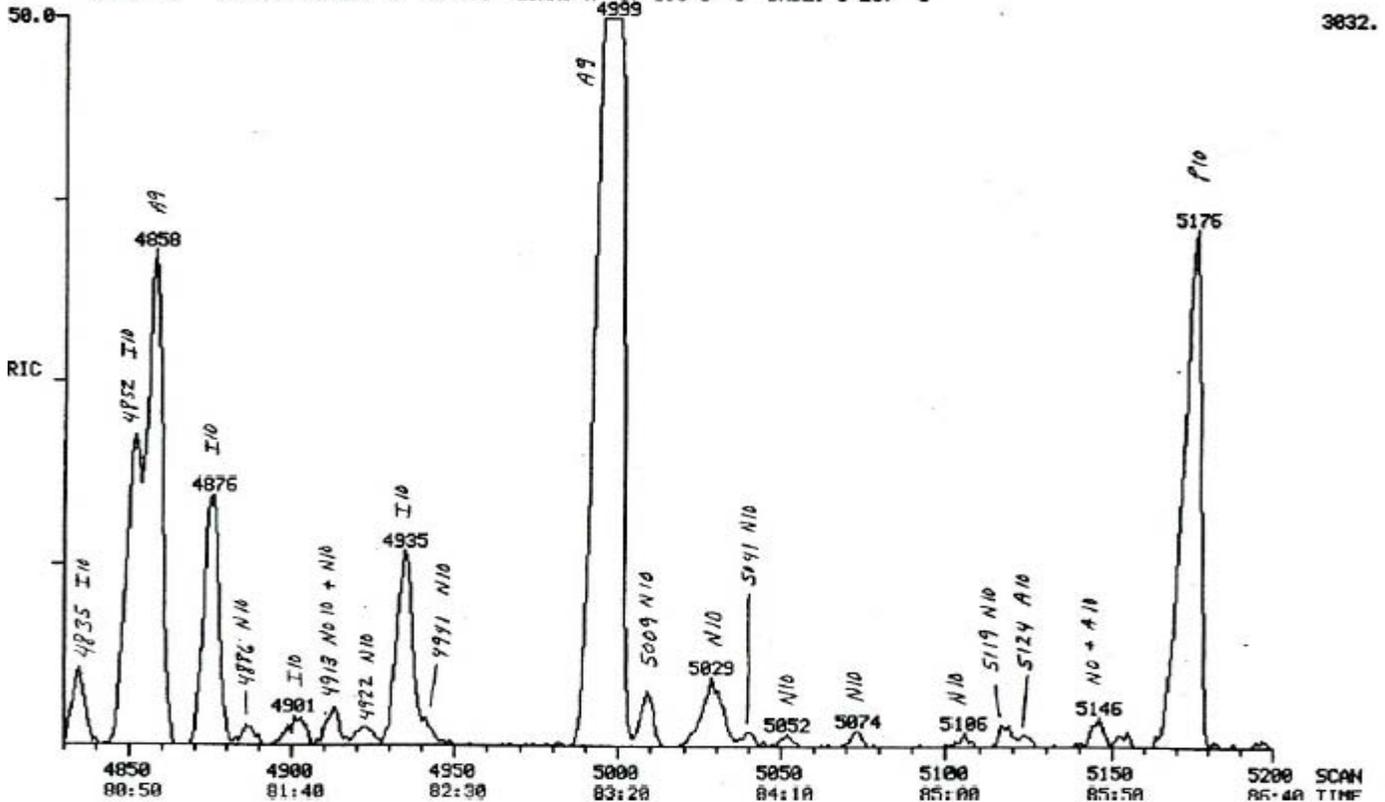


3659.

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 RANGE: G 1.0615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

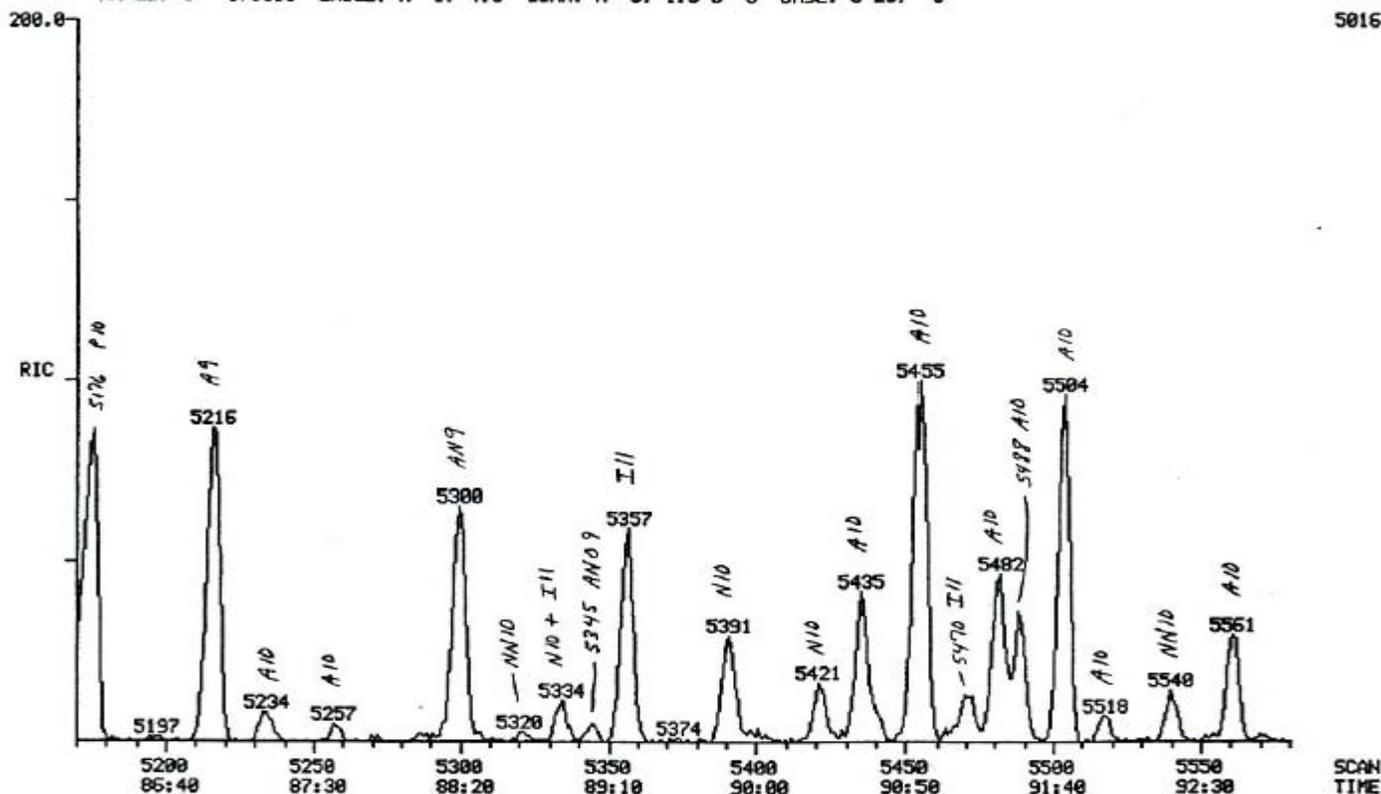


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 RANGE: G 1.0615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3



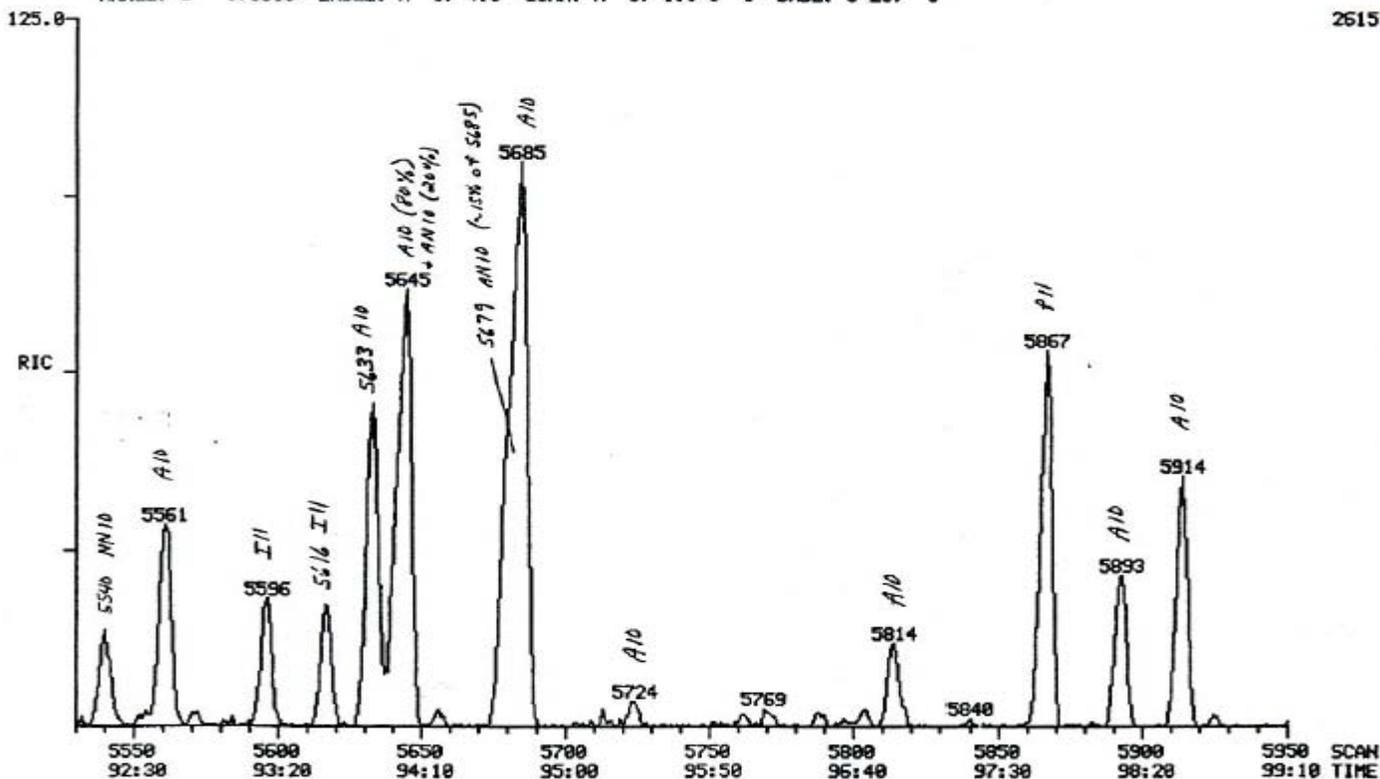
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 RANGE: G 1.0615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

5016.



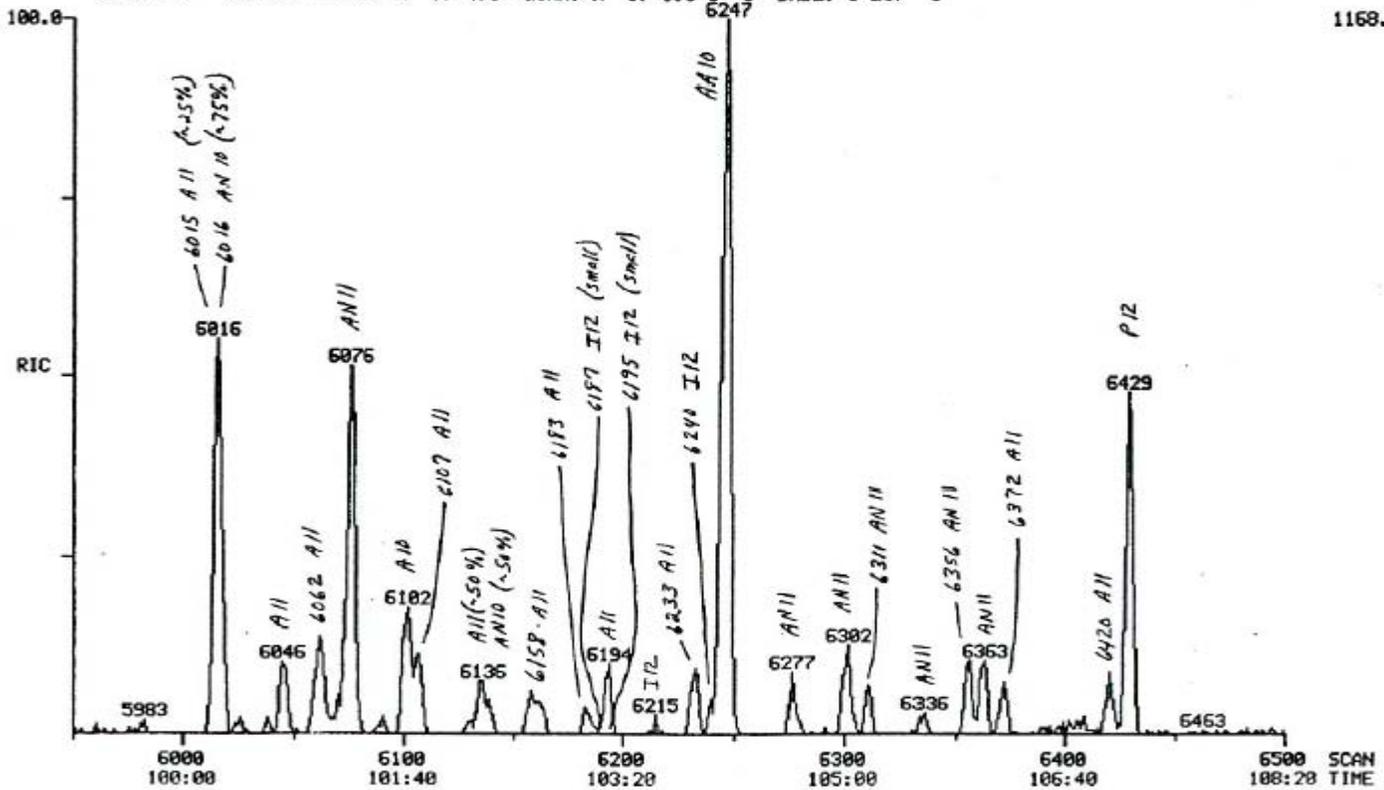
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 CONDS.: TRITON ANALYTICS CORP, HOUSTON, TX. DAN VILLALANTI 713-578-2289
 RANGE: G 1.0615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

2615.



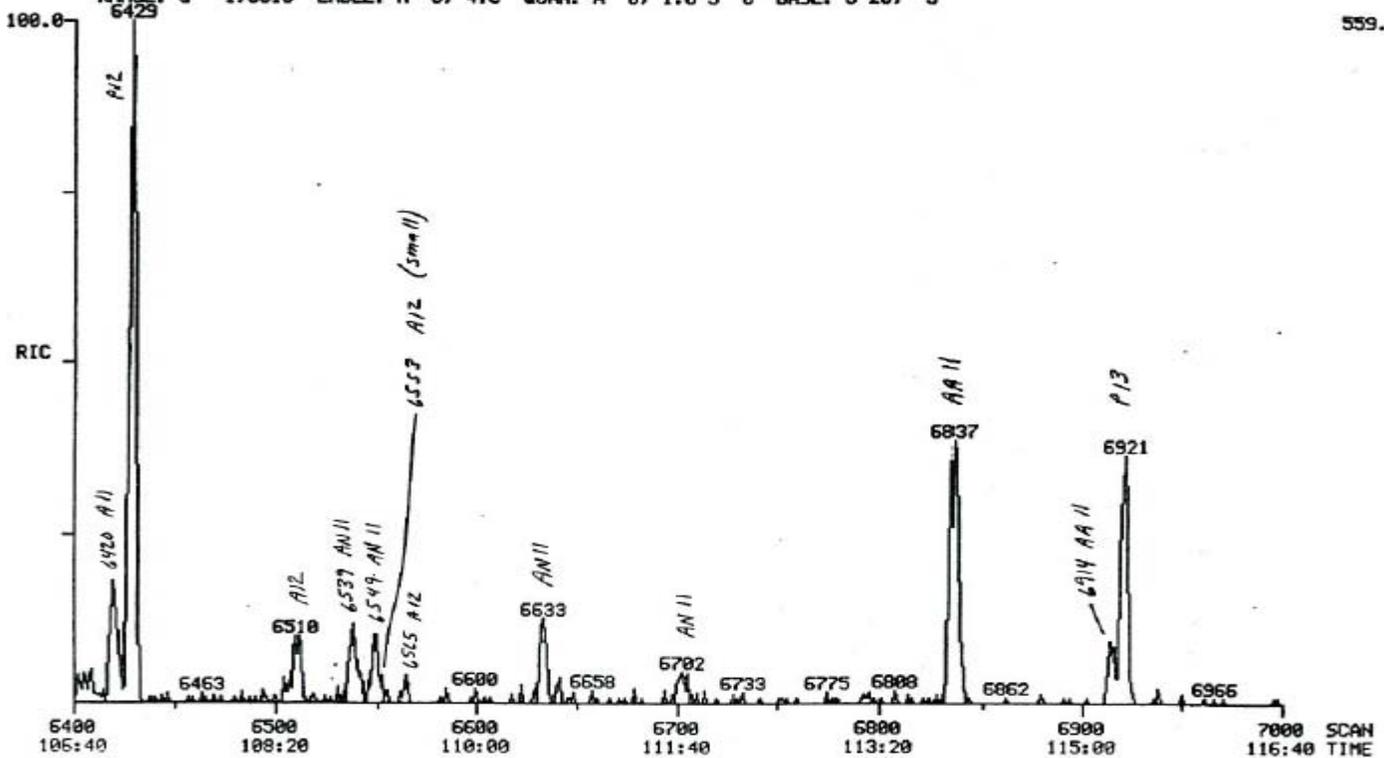
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 COND.: TRITON ANALYTICS CORP, HOUSTON, TX. DAN VILLALANTI 713-578-2289
 RANGE: G 1.8615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

1168.



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 RANGE: G 1.8615 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

559.



Pinpoint hydrocarbon types

New analytical method helps in processing clean fuels

P. A. Wadsworth and D. C. Villalanti,
Triton Analytics Corp., Houston

A fundamentally new method identifies components of hydrocarbon streams heavier than gasoline. It pinpoints structure and concentration. It's quick and cheap. The data now available will aid refinery and olefin plant operations, promote better fuels and save money. The nitric oxide ionization spectrometry evaluation (NOISE) has been called the first fundamentally new analysis method in 25 years which identifies hydrocarbons by quantity, and by carbon number (n) and hydrogen deficiency (Z). This information can be crucial in making clean fuels and in optimizing hydrotreater and refinery operation.

It is now being used to direct feedstocks to the most profitable process stream, set unit operating parameters and check results (Table 1). Exact composition of intermediate streams has never before been available without very rigorous and expensive analysis. No conventional method provides this knowledge. So processors have a new tool for optimizing.

Overview. The analysis consists of three advancements. It starts with a fundamentally new technique based on Townsend discharge nitric oxide chemical ionization. Next, specially built instruments apply the method to ordinary hydrocarbon streams. Finally, a special computer program manipulates the digital results to yield practical, usable information.

Nitric oxide ionization spectrometry evaluation works with petroleum distillates with a boiling range of 250°F to 950°F. It does not work with very light ends. Distillates below carbon number 6 or 7 usually are fairly simple. There are relatively few molecular permutations. And several alternate analysis methods do a fine job.

Gas chromatography first separates samples by boiling point. This segregates look-alike molecules and helps distinguish compounds within traditional reporting categories. In addition, gas chromatography separates sulfur-containing compounds from aromatics of the same molecular weight.

Boiling point fractions are then

bombarded with "soft" NO⁺ ions. Mass spectrometry identifies each component, and reports by carbon number and by degree of saturation. The instrument is a modified gas chromatograph/mass spectrometer¹ (GC/MS). Pure researchers have worked with similar devices for about 20 years. Instruments have been modified to automate thruput, handle samples across a broad boiling range and work specifically with hydrocarbons. The biggest modification was the implementation of Townsend discharge. It took several years and hundreds of runs to get the parameters just right to yield useful data on real-world problems.²

The analysis report represents another advance in practicality. Rather than list hundreds of substances, it organizes similar molecules into classes. Processors want to know the carbon chain lengths and the degree of saturation (or undersaturation). From this, they can develop answers on what to do with a specific stream or whether a specific process or catalyst is working adequately. NOISE report gives percentages by boiling range and by Z-number (for C_nH_{2n+Z}) where Z distinguishes between paraffins, cycloparaffins, mono-, di- and tri-aromatics. The latter represent a crucial step. Triton's technique helps refiners control aromatic content and meet changing product specifications. Streams that look alike to conventional analysis can be revealed as quite different with the new technique.

APPLICATIONS AND HISTORIES

Setting severity. Refinery operators use the ionization spectrometry analysis to set process severity for different streams. Checks after treating determine effectiveness. One company uses frequent analysis to characterize feed and product on CFH and FCC units for process and catalyst optimization. NOISE reports measure the depth of hydrotreating and help set working temperatures and pressures. This in turn optimizes production of naphtha, jet-A and diesel and maintains quality control.

Analysis of diesel fuels and fuel blends as well as ATFs have been carried out extensively. The results can predict cetane number with good precision on the basis of an extensive, proprietary, correlation effort. Analyses of hydrotreated, high-sulfur diesel fuels, which contain benzothiophenes and dibenzothiophenes suggest that these convert to alkylbenzenes and alkylbiphenyls under proper hydrotreating conditions.

We have analyzed hydrotreat-

Table 1. About NOISE analysis

Applicable to:

Boiling point 250°F to 950°F
Carbon number C₆ through about C₄₄
Naphtha through light bunker
Intermediate streams
Crude oil

Identifies:

Normal and isoparaffins
Rings
Double bonds
Di- and tricyclic compounds
Complex multinuclear compounds
Sulfur-containing rings

Useful in:

Optimizing hydrotreater operations
Directing incoming streams
Determining severity needed to meet diesel specs
Optimizing catalysts
Identifying spills or unknowns
Making the most out of a new crude
Conserving hydrogen
Scheduling maintenance or evaluating unit performance
Better understanding complex reactions and processes

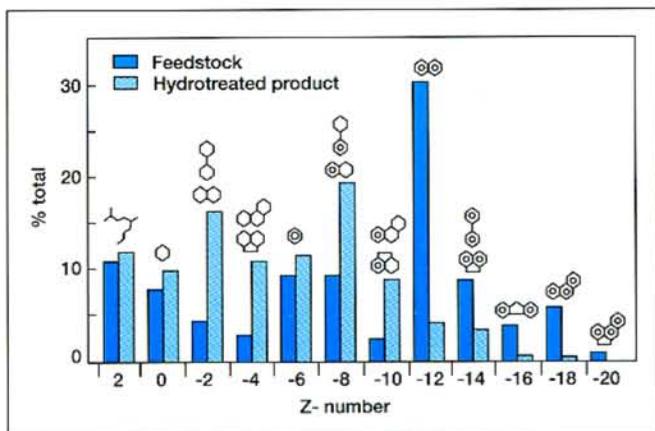


Fig. 1. Feed and product of a hydrotreater.

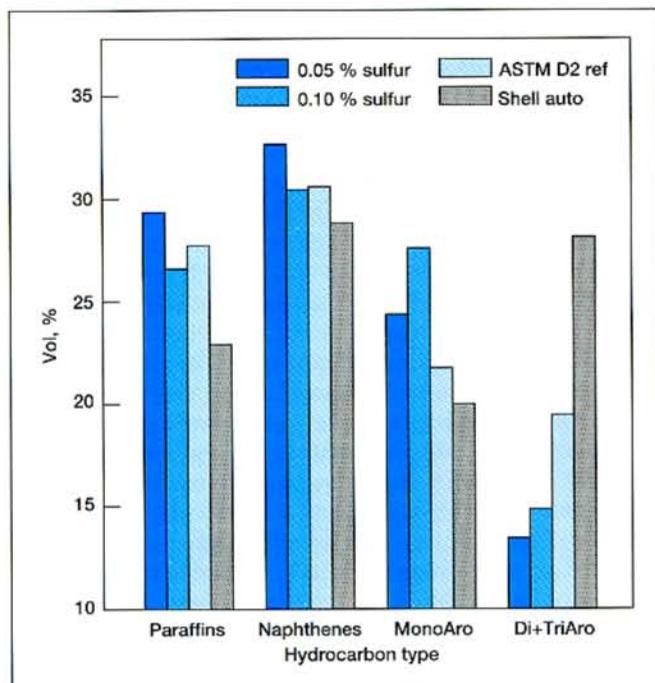


Fig. 2. Plot of NOISE analysis of four diesels.

ing/hydrocracking feed and product streams (Fig. 1) to study the effects of catalyst changes and process conditions. Fig. 1 shows Z number on the X-axis with typical structure above the bars. Note the dramatic change in hydrocarbon type, indicating the process effectiveness. Analysis of CCU feeds have also been made to establish the CC unit operating conditions and to predict yields. These jobs have enjoyed good in-plant success.

Directing streams. The new spectrometry technique also provides operators economic and logistical incentives for selecting olefin plant and reformer feeds. Without spectrometric analysis, the best use of a specific feed might not be known.

The mass spectrometer is an excellent comparator. It is particularly useful in "before and after" type studies. Analysis of crudes for hydrocarbon types by boiling range together with the determination of alkyl benzo- and dibenzothiophene types have been valuable in establishing how the crude may be best used as a feedstock. Several operators have evaluated crudes and distilled crudes using this GC/MS technique. Results give their potential as lubricating feedstocks based on their naphthene content.

One client identifies biomarkers as an indication of the source of crudes.

Long-term evaluation project. NOISE analysis results are typically a one or two page report. Table 2 shows work on an experimental, low sulfur (0.1%) diesel fuel from Phillips. The concentrations reported in this analysis are tabulated by three boiling point regions. The report gives Z number both for the individual boiling point fractions and normalized for each fraction. The last column shows sample totals.

Phillips reported the ASTM D-1319 hydrocarbon type analysis by FIA for this sample. Comparison of these FIA with the NOISE GC/MS results shows good agreement.

Component	FIA	NOISE
Aromatics	36.8	37.7
Saturates	61.9	62.4
Olefins	1.3	N/A

Results are in percent by volume. The analysis did not determine olefins in this sample. Olefins present could be distributed, depending on their chemical structure, between the aromatic and saturates classification.

Replicate analyses of this sample by this GC/MS method

Table 2. Typical NOISE report

Triton Analytics Corp. GC/MS results by noise method
Sample name: reference diesel ex Phillips lot R-309 0.1% S GC/MS
Run #: LRI02908

Bp range* (°F):	lbp-450	450 to 615	615+
Fraction, %	28.72	63.95	7.35

C _N H _{2N+2} Z number	Concentration by Vol% (normalized by fraction)		
	28.72	63.95	7.35
+2	31.04	24.40	26.67
+0	21.58	17.86	25.17
-2	16.94	9.05	8.84
-4	1.29	3.93	1.90
-6	19.81	5.48	5.31
-8	8.33	13.92	3.95
-10	0.00	5.44	7.35
-12	1.02	13.91	5.17
-14	0.00	5.20	8.03
-16	0.00	0.71	2.99
-18	0.00	0.10	4.49
-20	0.00	0.00	0.14
-22	0.00	0.00	0.00
-24	0.00	0.00	0.00
-26	0.00	0.00	0.00
-28	0.00	0.00	0.00
Sum	100.00	100.00	100.00

Z type	Percent of total sample				
	28.72	63.95	7.35	100.00	
+2	8.91	15.60	1.96	26.47	Paraffin
+0	6.20	11.42	1.85	19.47	Cyclopar
-2	4.86	5.79	0.65	11.30	"
-4	0.37	2.51	0.14	3.02	"
-6	5.69	3.50	0.39	9.58	Mono-arom
-8	2.39	8.90	0.29	11.58	"
-10	0.00	3.48	0.54	4.02	"
-12	0.29	8.90	0.38	9.57	Di-arom
-14	0.00	3.32	0.59	3.91	"
-16	0.00	0.45	0.22	0.67	"
-18	0.00	0.07	0.33	0.40	Tri-arom
-20	0.00	0.00	0.01	0.01	"
-22	0.00	0.00	0.00	0.00	"
-24	0.00	0.00	0.00	0.00	Tetra-arom
-26	0.00	0.00	0.00	0.00	"
-28	0.00	0.00	0.00	0.00	"
Sum	28.72	63.95	7.35	100.00	

Remarks:
* BP ranges correspond to emergence times of N-paraffins, BR 1: NC₁₂, BR 2: NC₁₃ to NC₁₈, and BR 3: NC₁₉



Fig. 3. Combination GC and MS first separates samples by boiling range, then determines molecular weights and saturations.

over a period of several months show for the saturates an average value of 61.7 vol% ($\pm 1.6\%$), and for the aromatics, 38.3 vol% ($\pm 1.6\%$). Results from the two entirely different methods of analysis show close concurrence.

We analyzed three other diesel fuels over a number of months for quality control. They show the same reproducibility. Two samples are reference fuels from Phillips (ASTM D-2 standard and a 0.05% sulfur). The other sample is an automotive diesel fuel, purchased at a service station (Fig. 2).

METHOD DETAILS

During the 1980s, there became available a new method of ionization of molecules. Chemical ionization uses a low molecular weight material. The charged species (reagent ion) serves to ionize the sample molecules. Energy levels distinguish chemical ionization (CI) from electron ionization (EI).

The resulting difference between the EI and CI mass spectra of various substances can be dramatic. CI can produce a simplified sample mass spectrum, often with enhanced sensitivity.

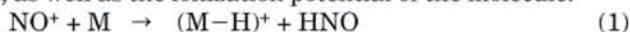
How NOISE works. The method uses GC followed by MS (Fig. 3) with a novel ionization method. NO^+ ions at relatively low energy replace ionization by the conventionally used electron impact mode. The combination of the separation power of the gas chromatographic techniques together with the unique ionization characteristics of nitric oxide provide unambiguous determination of certain hydrocarbon types.

A useful and much-used classification scheme for hydrocarbons is the equation $\text{C}_n\text{H}_{2n+Z}$ where Z is defined as the hydrogen deficiency. For example, a paraffin of any C number has a Z number of $+2$. An alkyl monoaromatic has a Z number of -6 . Benzene, C_6H_6 , the beginning of the alkyl monoaromatic series of compounds, is expressed as $\text{C}_n\text{H}_{2n-6}$. Mass spectrometric hydrocarbon type reports usually follow this format.

For example, the naphthalene, ($Z = -12$) and paraffin

($Z = +2$) types of hydrocarbons, which have the same nominal mass, resolve on the basis of their characteristic ionization using NO^+ ion. The naphthalene types produce an M^+ ion. The paraffin types produce an $\text{M}-1^+$ ion under these conditions. We observe this effect for other saturated aromatic hydrocarbon overlaps in EI-type mass spectra. Benzothiophenes and dibenzothiophenes separate by gas chromatographic technique from the alkyl aromatic and alkyl naphthalenes respectively.

The NO^+ reagent ions react with the analyte hydrocarbons through the three reactions: hydride ion abstraction (reaction 1), charge exchange (reaction 2) or addition reaction (reaction 3). The specific reaction or combinations of reactions seem to depend primarily on the carbon skeleton and the C-C bond configuration of the hydrocarbon molecule, M , as well as the ionization potential of the molecule.



Reaction 1 is most characteristic for saturated hydrocarbons. Reaction 2 predominates for aromatics with some minimal reaction 3 observed for the beginning members of each aromatic homologous series. Reaction 2 also occurs for the condensed polycyclic saturated hydrocarbons such as cholestane. Olefins show a mixed reaction depending on their structure for reactions 1, 2 and 3.

The most abundant reactions take place without cleaving carbon-carbon bonds in the parent molecule. The lower energy (compared to EI) allows structure to survive. Thus we can measure the original constituents directly rather than extrapolating from fragments.

Accuracy. Before offering the new method, we tested it with a wide variety of aggregates of hydrocarbon types, including model compounds and aromatic and saturate blends. The n -paraffin blends served to calibrate emergence times of the GC with temperature and recovery efficiency. For $n\text{-C}_{40}\text{H}_{82}$, bp at 977°F , recovery is 60%. But we do not detect $n\text{-C}_{44}\text{H}_{90}$, bp at $1,018^\circ\text{F}$.

Reproducibility is surprisingly good. Analysis of diesel

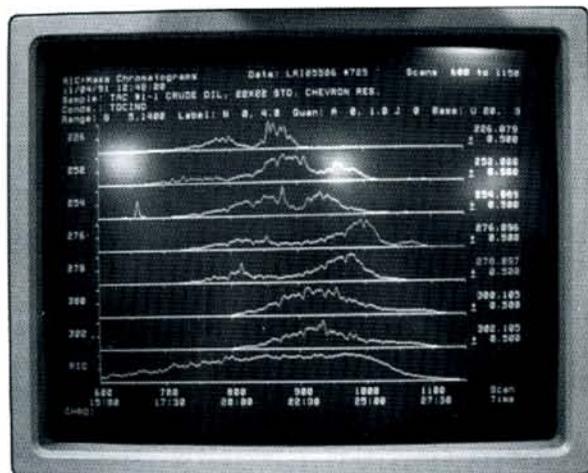


Fig. 4. NOISE gives real-time display. This screen establishes the presence of dibenzothiophenes at mass 226.

boiling range materials over a period of several months show a relative standard error of from 3% to 6% of the amount for those concentrations greater than 5% to 8% volume. Spiking experiments, using blends of model compounds, indicate that the accuracy and precision of the method are about the same, 3% to 7%. Comparison of the results with other methods of analysis, specifically C_{13} NMR, and UV also provide verification.

Analyzing and using data. Our GC/MS passes raw data to a computer. A set of simultaneous equations then apply to take into account the mass spectral characteristics for each class of compounds by the prespecified boiling ranges (Fig. 4). Results are expressed as liquid vol%. Estimates can be provided for the iso/normal paraffin distribution as well as certain of the aromatic thiophenic type sulfur compounds for some types of samples.

The new method provides the quantitative distribution of hydrocarbon types within specified boiling ranges. It can differentiate aromatic and saturated hydrocarbon compounds of the same nominal molecular weight as well as sulfur compounds from hydrocarbons of the same nominal molecular weight. The method can also provide an estimate of the normal/isoparaffin concentrations by either C number or boiling region.

Advantages over EI. With EI, most of the detected mass spectrum results from carbon-carbon bond fission. While one can guess the extent of fragmentation for any speculated type of hydrocarbon, nothing quantitative can be realized for the relative intensities of the observed ions. Under EI ionization, paraffin hydrocarbons of the general formula, C_nH_{2n+2} , the most abundant ions observed are ions of formula, C_nH_{2n+1} . This class is formed by the C-C bond fission.

For the analysis of gasoline range and higher boiling mixtures, any of the mass spectrometric methods of analysis have very little utility in determining individual compounds. However, for the analysis of very complex mixtures, type analysis has proven very useful. Type analysis determines component distribution by Z value, and, to a lesser degree of reliability, C number of these Z types. The utility of these type methods is that they provide a detailed and precise means of evaluating the mixture for value as a feedstock or effectiveness of a partic-

ular chemical or physical process.

Well established and tested mass spectrometric methods of type analysis apply to gasoline boiling range (<450°F) mixtures. Similar styles of mass spectrometric type analyses have been applied to kerosines and heavier fractions up to and including heavy lubricating oils. These methods provide a more approximate analysis than that determined for the gasoline boiling range. Mass spectral sensitivities used in these later methods were extrapolated from a very limited set of pure compounds and a limited number of separated hydrocarbon type aggregates.

For heavier materials, there are two kinds of hydrocarbon type analyses. The older method is the fragment peak method that estimates the distribution of substances by number of rings per molecule. It attempts to estimate the polyring molecules as condensed and noncondensed ring systems.

The other method, used with a high resolution mass spectrometer, is the parent peak method. This method depends on measurement of the intensities of what are believed to be the molecular ions in the sample. It applies appropriate sensitivity coefficients to determine a distribution of both N and Z of the mixture. The determination of Z number distribution is usually well-defined while the N distribution is, at best, an estimate. Various laboratories often use combinations of the fragment and parent peak methods combined in such ways as to suit their individual needs.

All the competing analytical methods, whether using a single focusing (low resolution), or a double focusing (high resolution) mass spectrometer, analyze the sample in the batch mode. Analysis time ranges from minutes to a few hours with the data reduction usually done in background. There is no means of fractionating the sample into specific boiling ranges except by prior separation into boiling point cuts from a distillation or some other sort of separation means.

LITERATURE CITED

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- Dzidic, I., Peterson, H. A., Wadsworth, P. A., and Hart, H. V., "Townsend discharge nitric oxide chemical ionization gas chromatography/mass spectrometry (TDCINO) for hydrocarbon type analysis of the middle distillates," *Anal. Chem.*, 1992 (in press).



The authors

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Dan C. Villalanti, president of Triton Analytics Corp., Houston, was a staff chemist with Shell Development Co., Houston. He specialized in hydrocarbon analysis with emphasis on refinery optimizations and environmental protection. Villalanti earned BS and PhD degrees in chemistry from the University of Arizona. Over 11 years with Shell, he made advances in chromatographic separations, octane number prediction and clean fuels. Villalanti serves as a referee for Journal of Chromatographic Science.

