

Appendix H

Naphthalene Analyses

Carlson, R. J., "Impurities In Naphthalene Samples From NYSEG Milliken Station," CONSOL R&D report to NYSEG, New York State Electric & Gas Corporation, Binghamton, New York, May 1995.

McCoy, Duane, "Follow-Up Analysis of Milliken Heat Pipe Naphthalene Samples," Letter to Dr. G. S. Janik (NYSEG), CO/NYSEG FGD 291, New York State Electric & Gas Corporation, Binghamton, New York, June 22, 1995.

IMPURITIES IN NAPHTHALENE SAMPLES FROM NYSEG MILLIKEN STATION

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The new heat pipe air heater at the NYSEG Milliken Station has not met design performance. Naphthalene is used in the heat pipes as the heat exchange working fluid. The equipment manufacturer, ABB API, indicated that non-condensable gases are building up inside some of the naphthalene-filled heat pipe tubes. Generation of this blanketing gas may be occurring due to the decomposition of naphthalene or a contaminant in the naphthalene. Three solid samples were received for analysis to determine if there are any impurities in the naphthalene that could cause a generation of gas in the heat pipe. The samples were "pure" unused naphthalene, naphthalene removed from a heat pipe at Milliken, and a sample of thianaphthene, the suspected impurity. It is not known if the unused naphthalene sample is from the same batch as that used to fill the heat pipe originally.

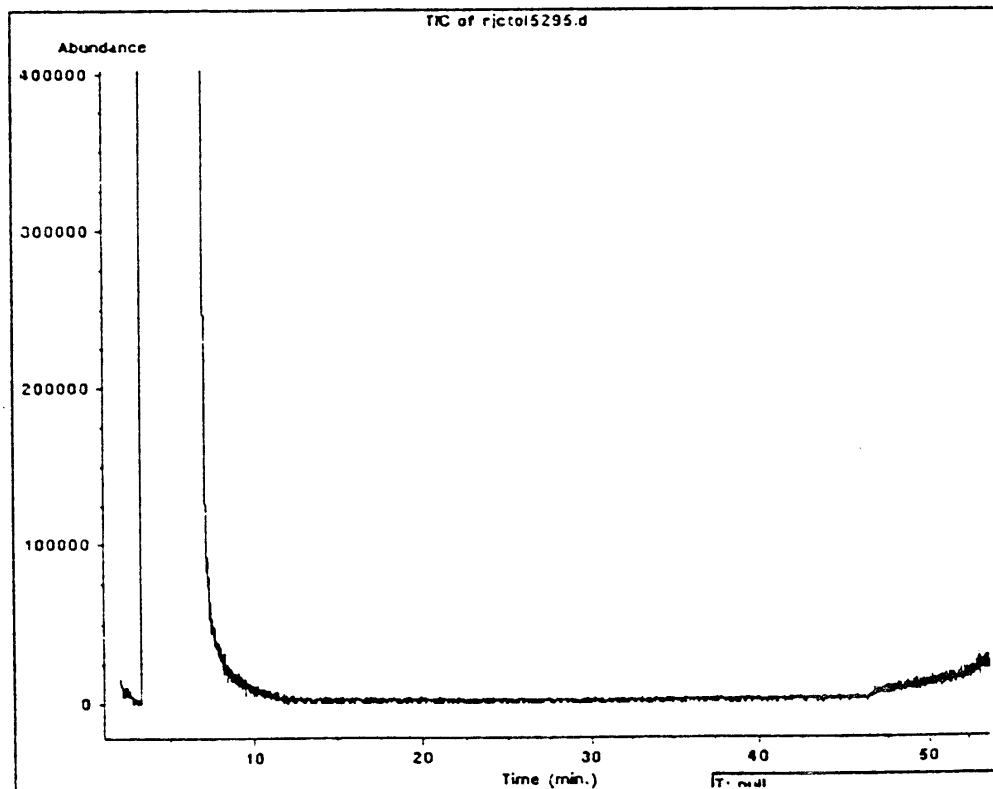
The two samples of naphthalene were analyzed by GC/MS. The ion chromatograms and mass spectral data are attached. Unfortunately, the suspected impurity, thianaphthene c1ccc2c(c1)sc2, elutes under the naphthalene peak at high concentrations of naphthalene. However, ion 134 is detected at the same retention time as naphthalene, indicating the possible presence of thianaphthene. Also present as impurities are indole c1ccc2c(c1)c[nH]2, quinoline c1ccc2c(c1)ncn2, and methyl naphthalenes.

The concentrations of indole, quinoline and methyl naphthalene were estimated from the total ion chromatogram. The thianaphthene concentration was estimated from an ion ratio of thianaphthene to methyl naphthalene and was based on the approximate concentration of methyl naphthalene. The estimated concentrations of these impurities are very approximate (-50% to +100%).

Impurities	Fresh Naphthalene	Naphthalene from Heat Pipe
Indole	200 ppm	100 ppm
Quinoline	10000 ppm	10000 ppm
Isoquinoline	400 ppm	400 ppm
Methyl naphthalenes	200 ppm	200 ppm
Thianaphthene	1000 ppm	800 ppm

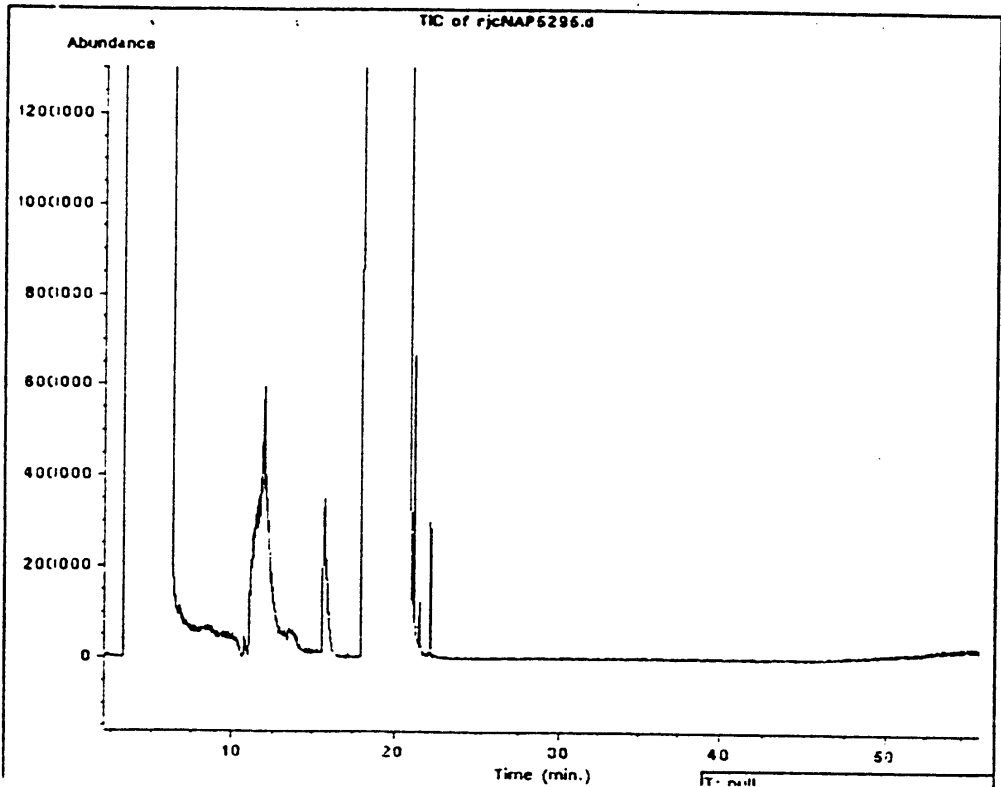
A sulfur determination also was run. Both naphthalene samples contained the same concentration of total sulfur (i.e. 400-450 ppm). Assuming all the sulfur is present as thianaphthene, the thianaphthene concentration is approximately 1800 ppm.

The fresh naphthalene total ion chromatogram has two additional peaks that were not identified. These peaks elute after the toluene but prior to the naphthalene peak and are very poorly formed, as an organic acid or ether peak would be. The best speculative identification from the mass spectrum is dimethoxymethane. However, this cannot be the parent compound. It is a fragment produced in the mass spectrometer. The parent compound must boil at a higher temperature than dimethoxymethane because it elutes between toluene and naphthalene. The concentrations of the unidentified components were not estimated because of the poor peak shapes. The absence of these components in the heat pipe samples suggests that the components that resulted in these two peaks either were not present in the naphthalene used to fill the heat pipe, or that these impurities decomposed in the heat pipe.

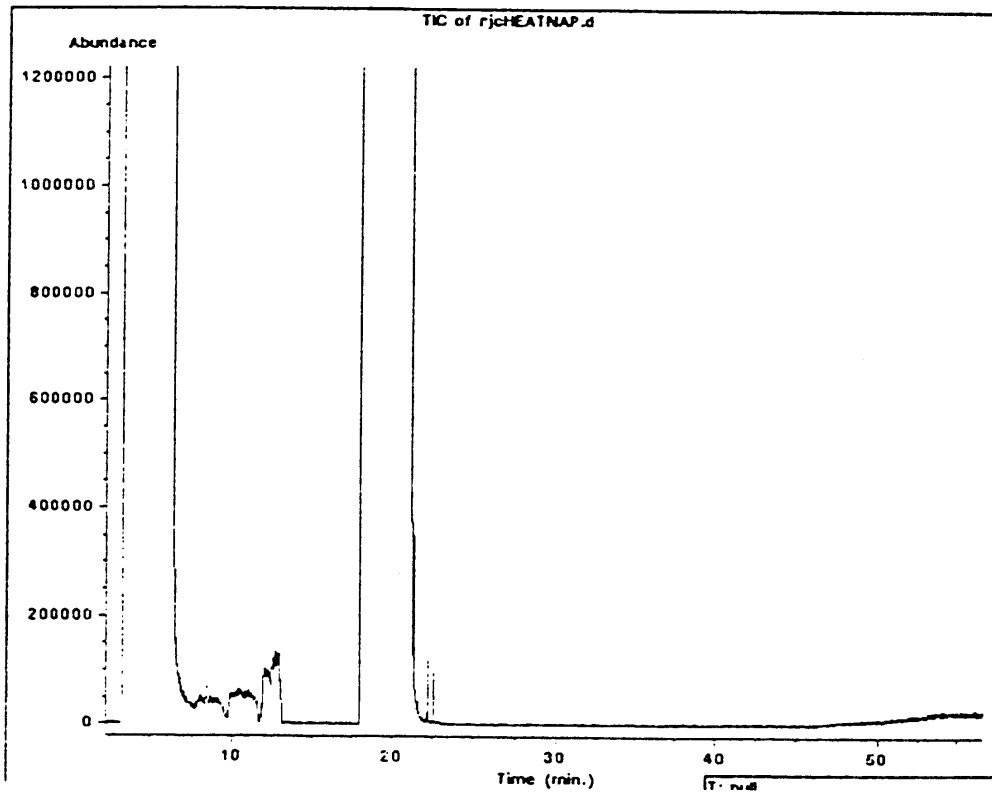


Total Ion Chromatogram of Toluene Run Prior to the Samples

1271

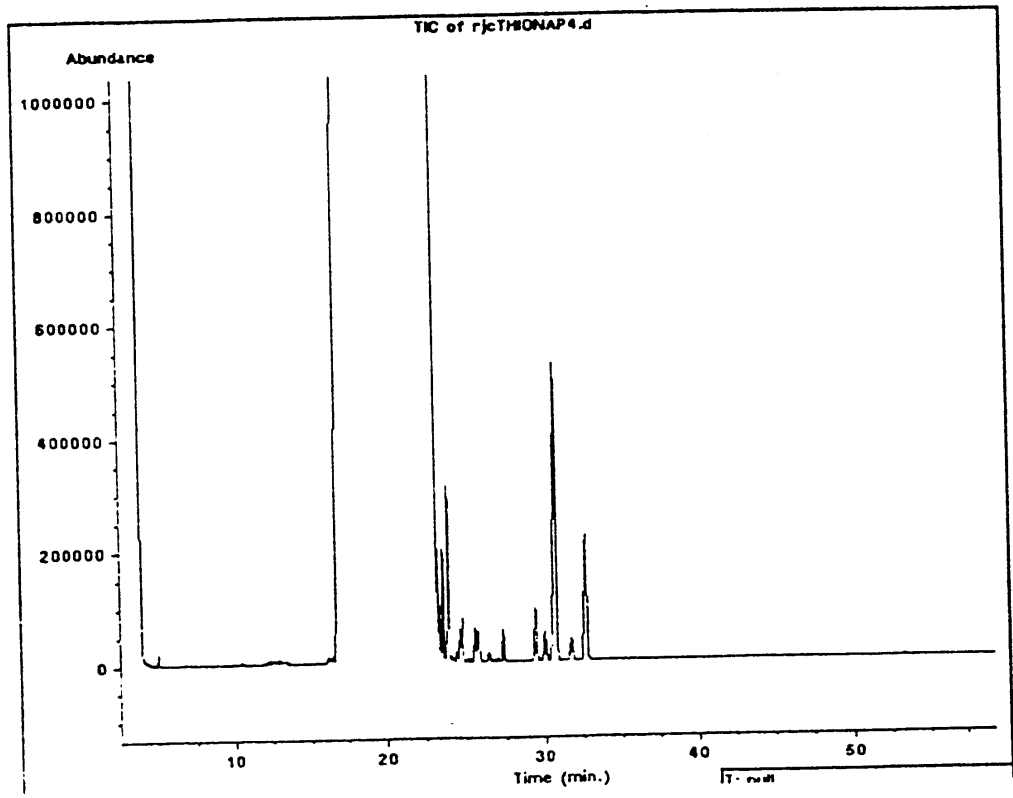


Total Ion Chromatogram of "Pure" Naphthalene.

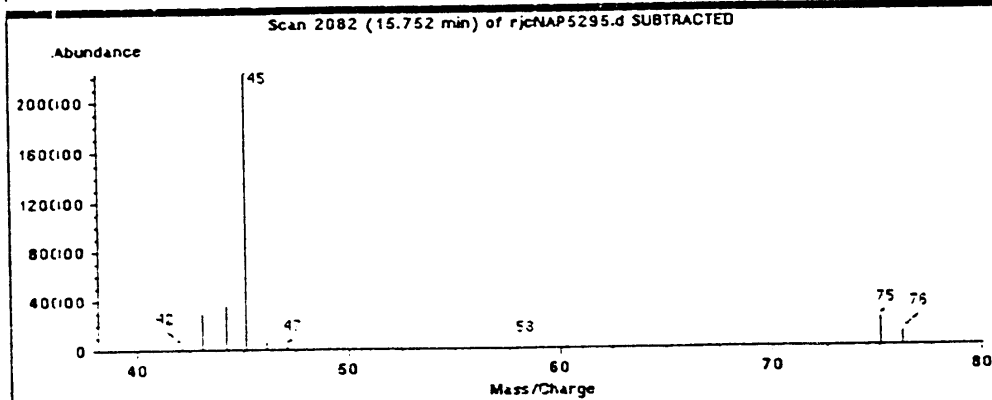
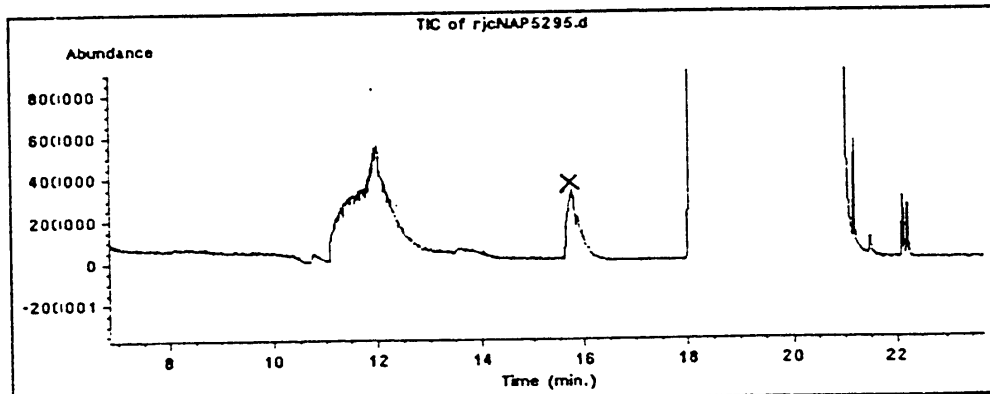
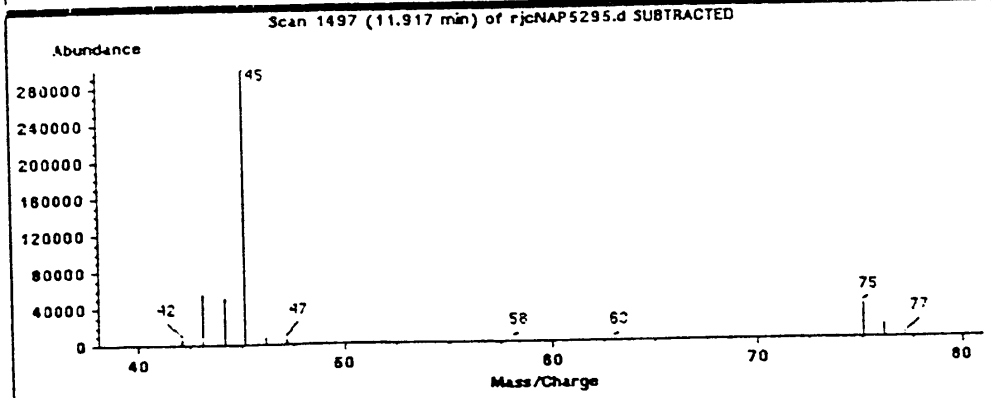
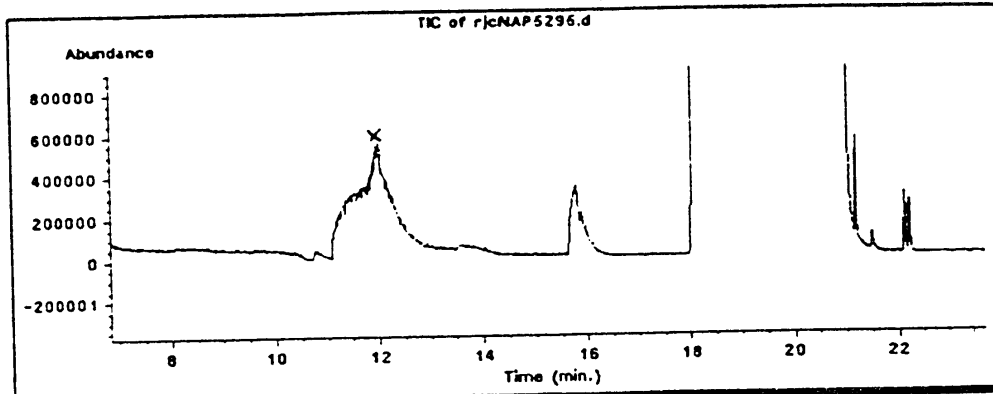


Total Ion Chromatogram of Naphthalene from Heat Pipe.

1272

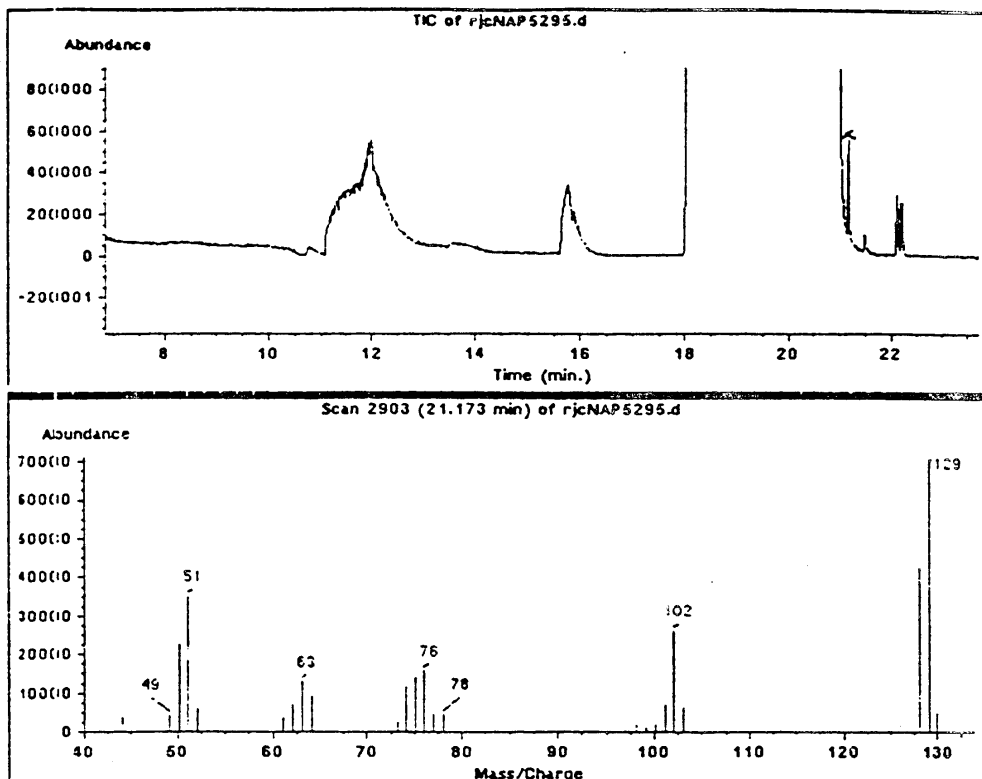


Total Ion Chromatogram of Thianaphthene.

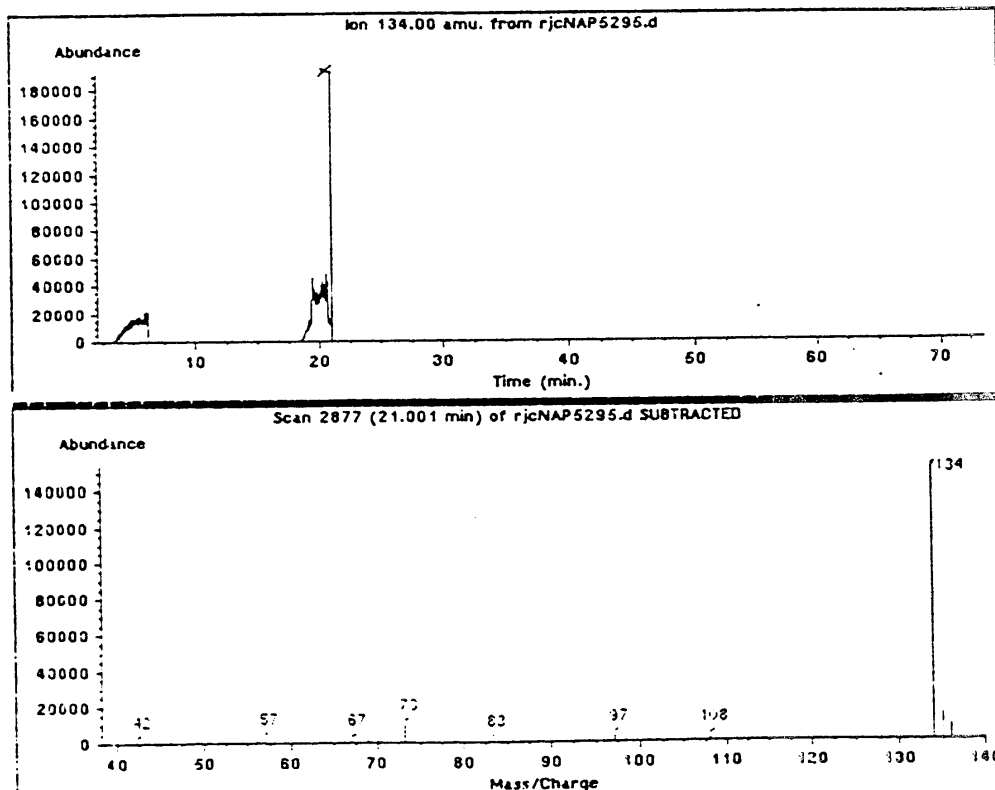


Spectra of the Two Peaks Eluting Prior to the Naphthalene in the Sample of "Pure" Naphthalene.

1274

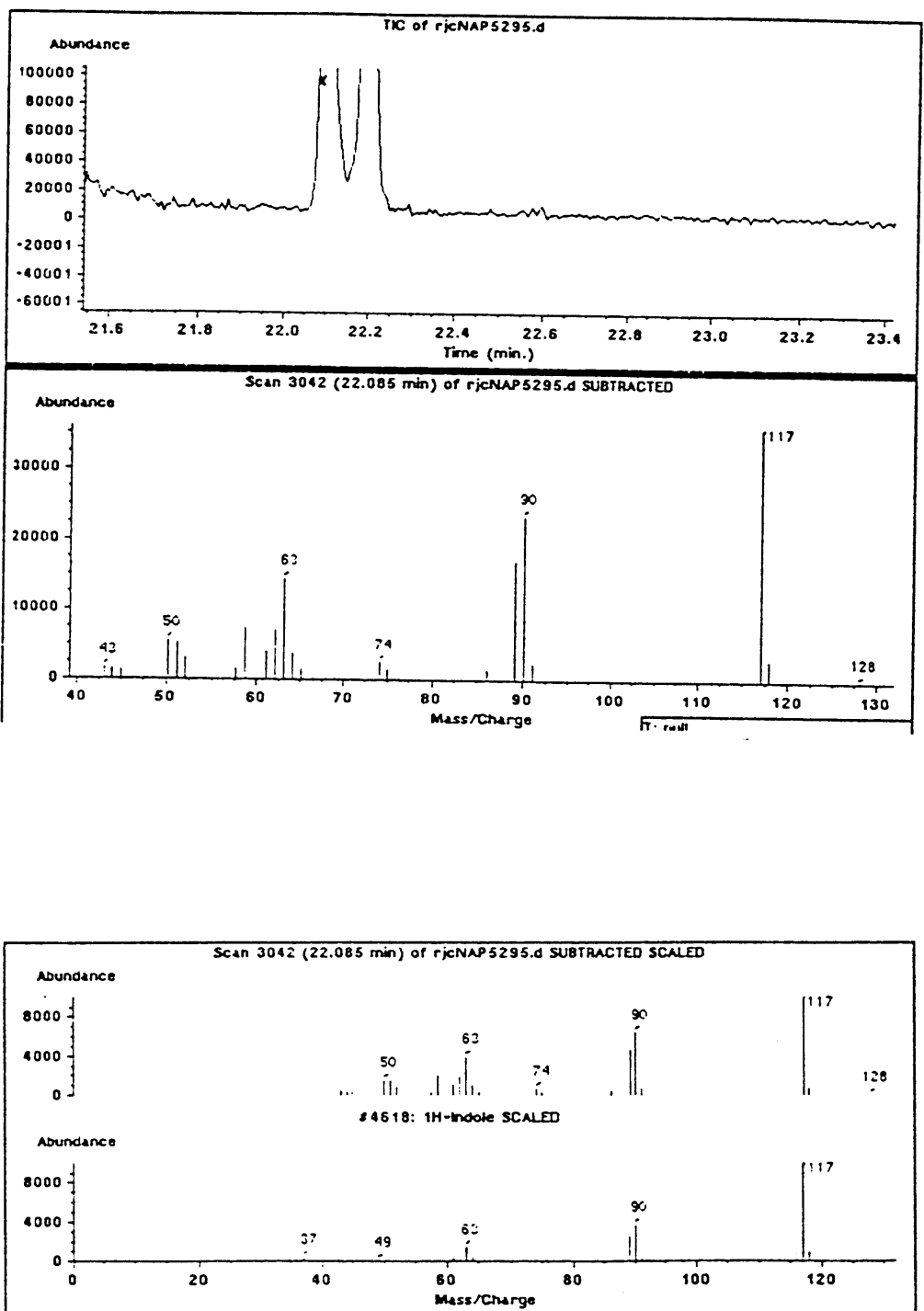


Spectrum of Peak Identified as Quinoline or Isoquinoline in the "Pure" Naphthalene.



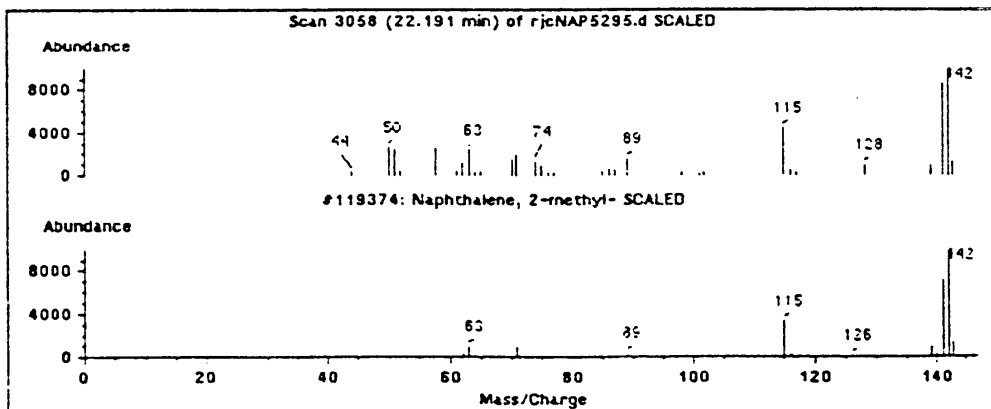
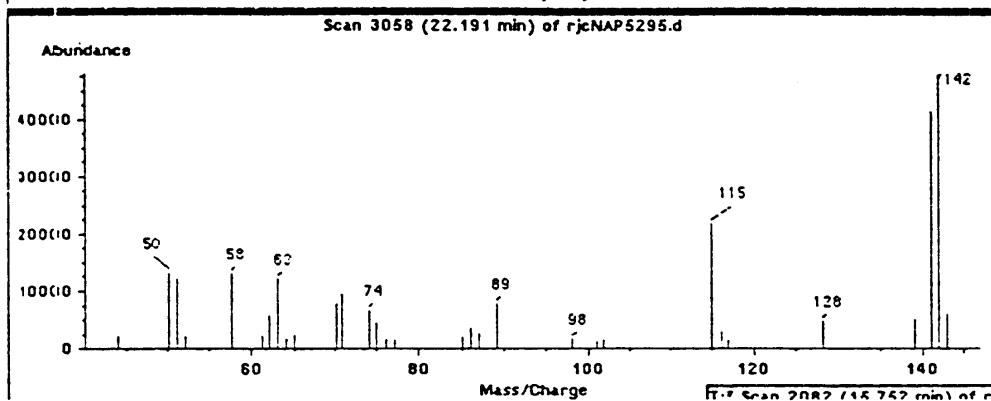
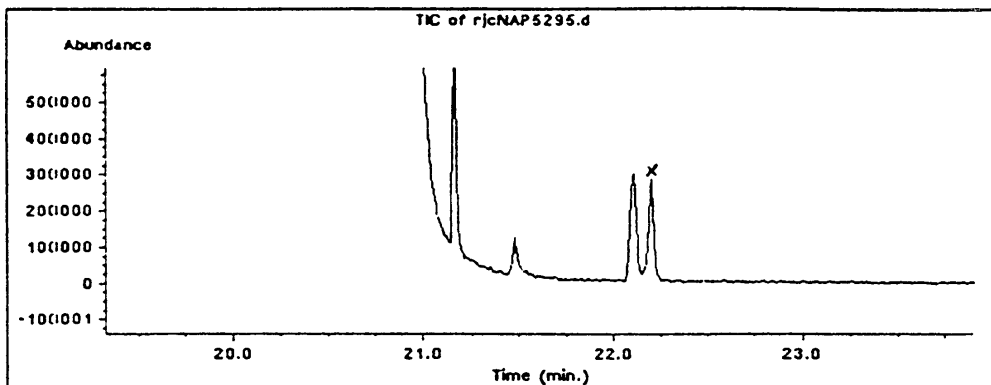
Subtracted Spectrum of Thianaphthene Found in the Naphthalene Peak.

1275



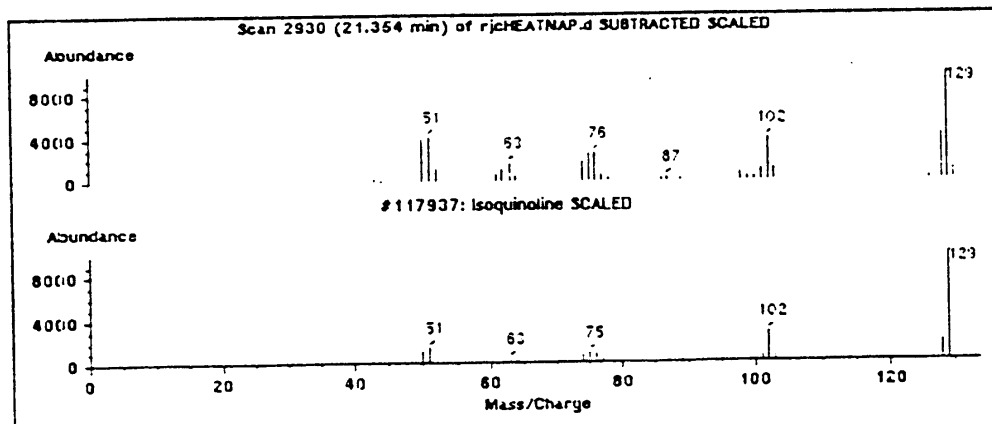
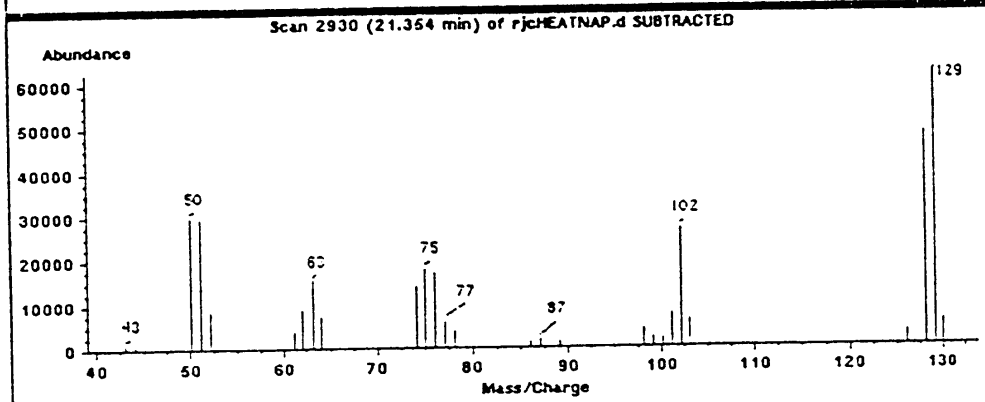
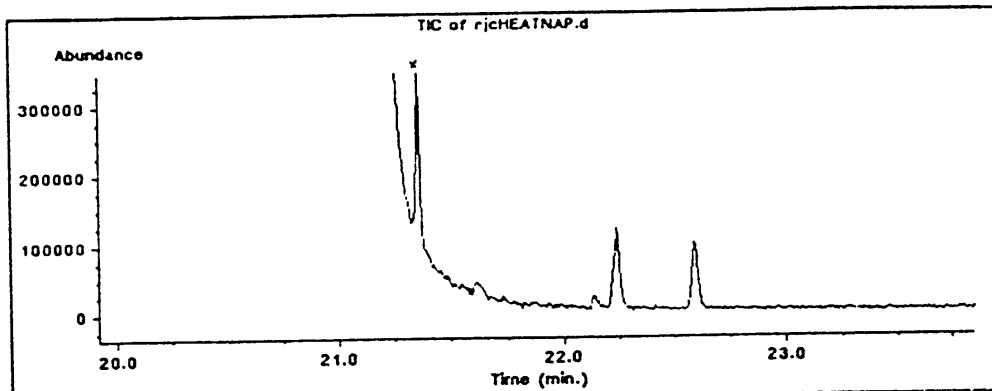
Spectrum of the Peak Identified as Indole in the "Pure" Naphthalene with the Library Identification Match.

1276



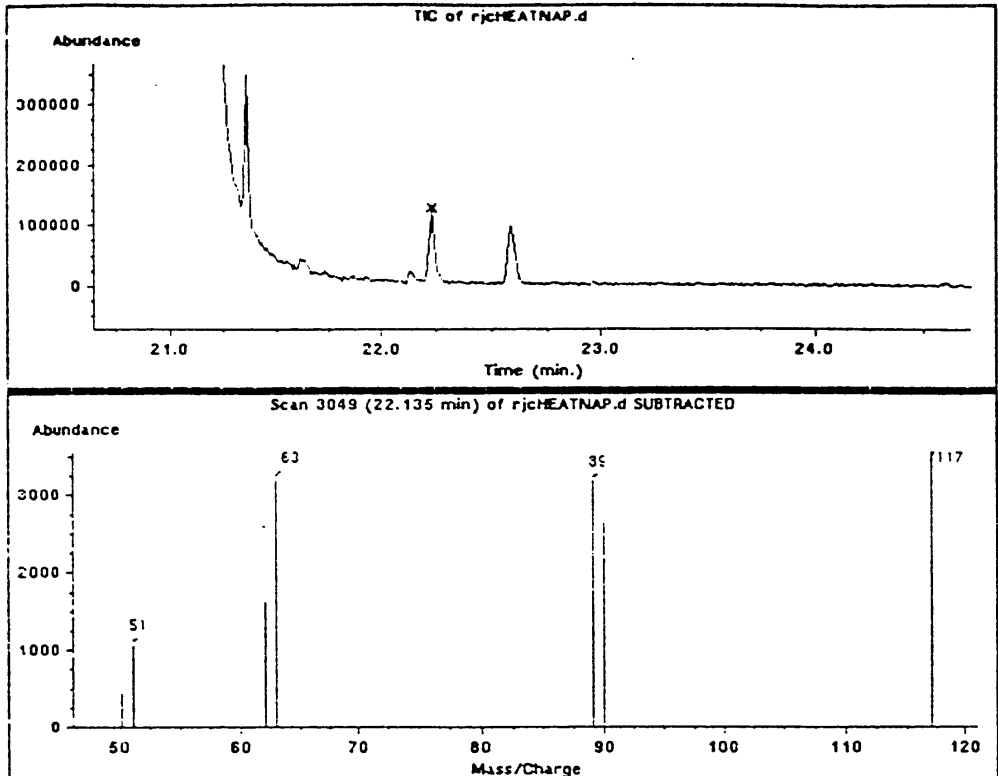
Spectrum of the Peak Identified as Methyl Naphthalene in the "Pure" Naphthalene with Library Identification.

1277

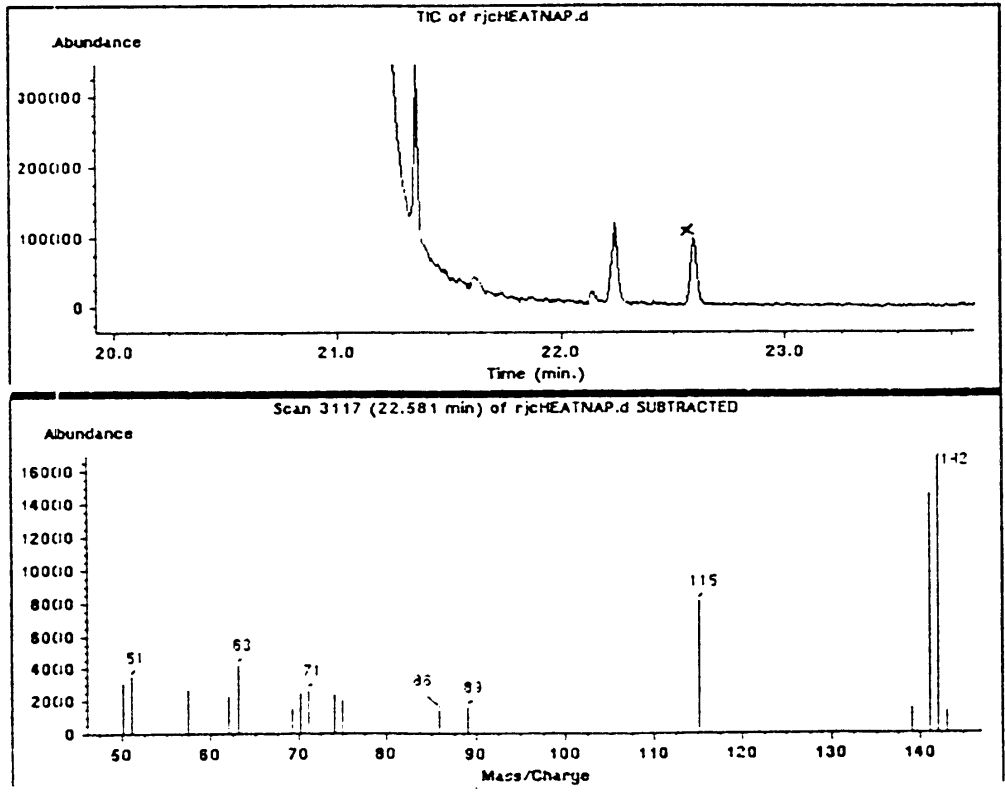


Spectrum of the Peak Identified as Quinoline or Isoquinoline in the Naphthalene Removed from the Heat Pipe.

1278

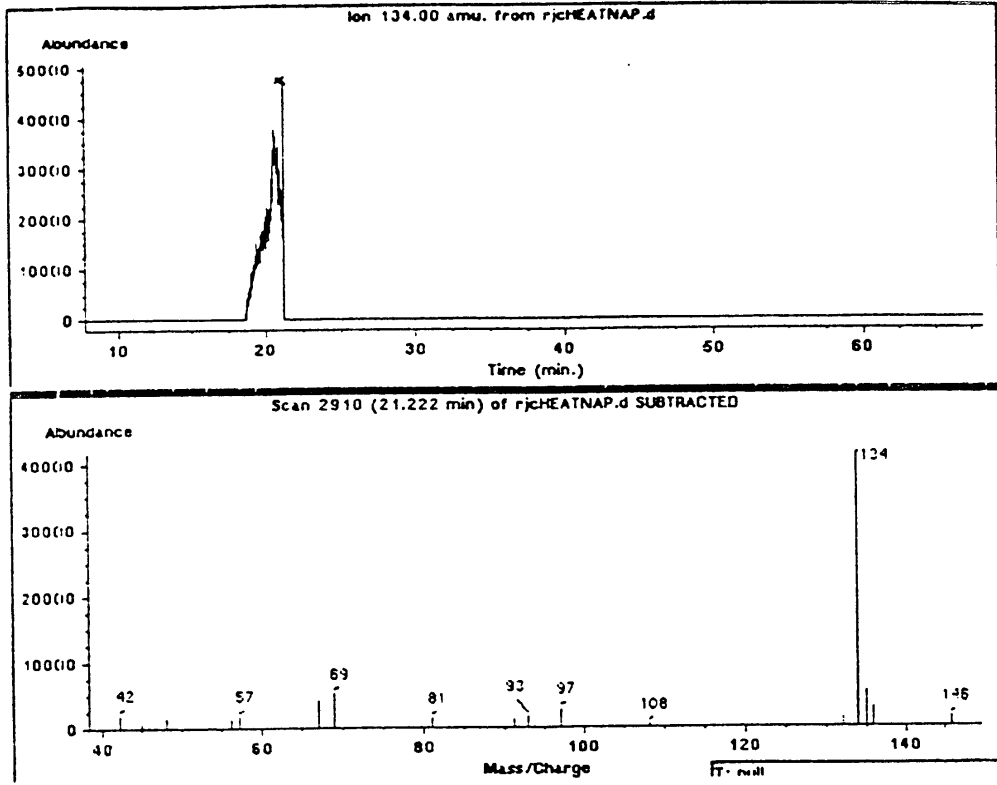


Spectrum of the Peak Identified as Indole in the Naphthalene Removed from the Heat Pipe.

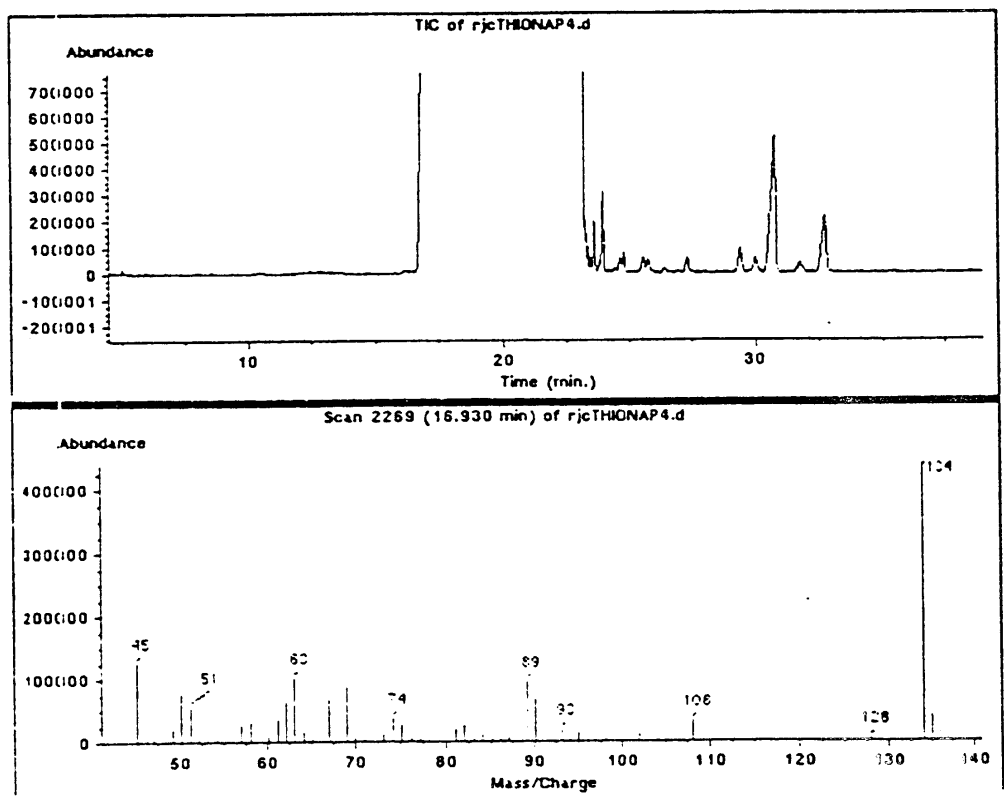


Spectrum of Peak Identified as Methyl Naphthalene in the Naphthalene Removed from the Heat Pipe.

1279



Subtracted Spectrum of Thianaphthene Found in the Naphthalene Removed from the Heat Pipe.



Spectrum of Thianaphthene.

June 22, 1995



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CO/NYSEG FGD 291

Subject: Follow-Up Analysis of Milliken Heat Pipe Naphthalene Samples

Dear Dr. Janik:

During May, CONSOL received "fresh" and "used" samples of heat pipe naphthalene for GC/MS analysis. Sample preparation included dissolving the naphthalene in deuterated toluene (mol wt 100). This results in a large 98 mol weight ion peak for the toluene component that overwhelms small peaks for lower boiling materials. Since reporting our original findings, we have attempted to determine if there are any compounds in the naphthalene which boil below toluene. This was done by injecting pure naphthalene into the GC/MS. To allow neat injection, the samples were melted by gentle heating. Assuming the heating did not evolve light ends, the tests failed to show the presence of any compounds other than first reported in my letter to you dated May 16, 1995. For completeness, the ion chromatograms are included here as Attachment 1.

Tests also were conducted to determine if strong inorganic acids were present in the naphthalenes. These tests involved placing a 1.00 gram naphthalene sample in a beaker containing 50 ml of water. The pH after several minutes of stirring was measured. The sample was then placed in an oven at 105°C for approximately 30 minutes and cooled for 10 minutes to melt the naphthalene and release any trapped acid. Again, the pH was measured. Since the heated samples were typically at about 60°C when the pH was measured, a temperature compensated probe was used to correct the pH to the 25°C standard temperature. Table 1 presents the data.

If we assume that the inorganic acid is HCl, we would need 0.001825 grams of HCl in 50 ml for a pH of 3.0. For a 1.00 gram naphthalene sample, this is equivalent to 1,825 ppm HCl. Table 2 shows the concentration of HCl in naphthalene needed to produce a given pH in 50 ml of water. The results indicate that if a strong inorganic acid is present in either naphthalene sample, it is probably at a level less than 1 ppm by weight.

This concludes our current work on analyzing the naphthalene samples.

Sincerely,

Duane C. McCoy
smd

Attachments: Ion Chromatograms

cc: B. Marker
W. Savichky

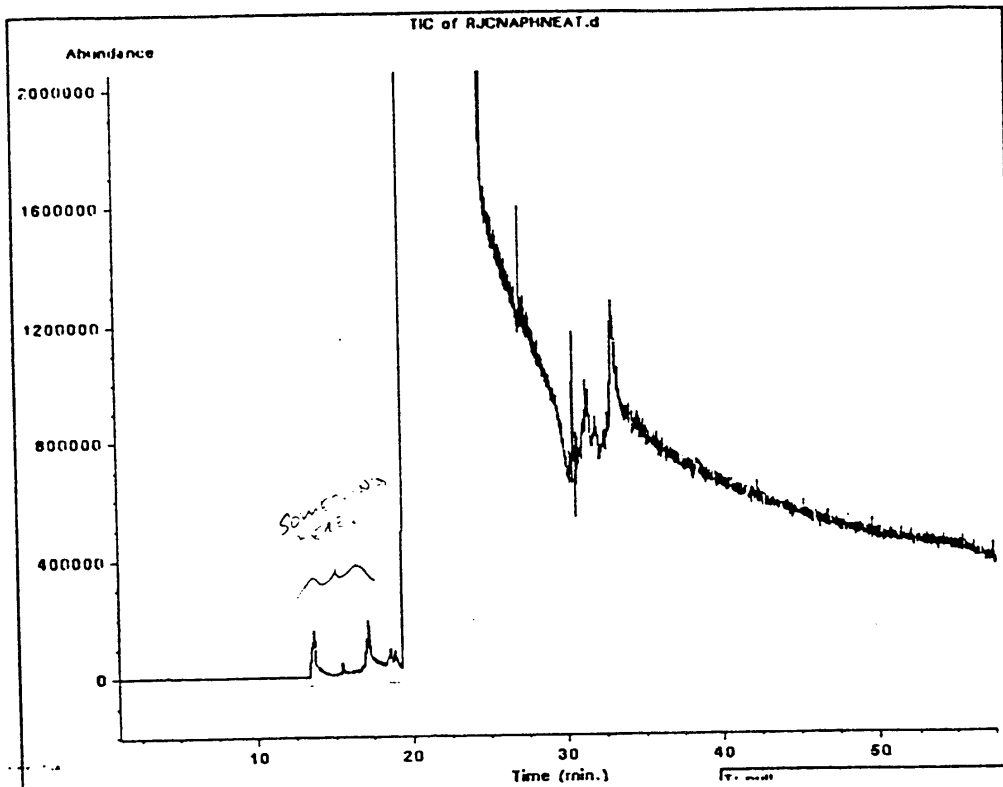
Table 1 Leach Water pH		
Sample	Naphthalene in Cold Water (1)	Naphthalene in Heated Water
Fresh Naphthalene	7.3	6.9
Used Naphthalene	6.5	6.8
(1) 1.00 g naphthalene in 50 ml of leach water		

Table 2 Required HCl Contaminant Levels	
If pH of 50 ml Wash Solution is:	HCl Level in Naphthalene Required, ppm wt
3.0	1,825
4.0	182
5.0	18
6.0	1.8

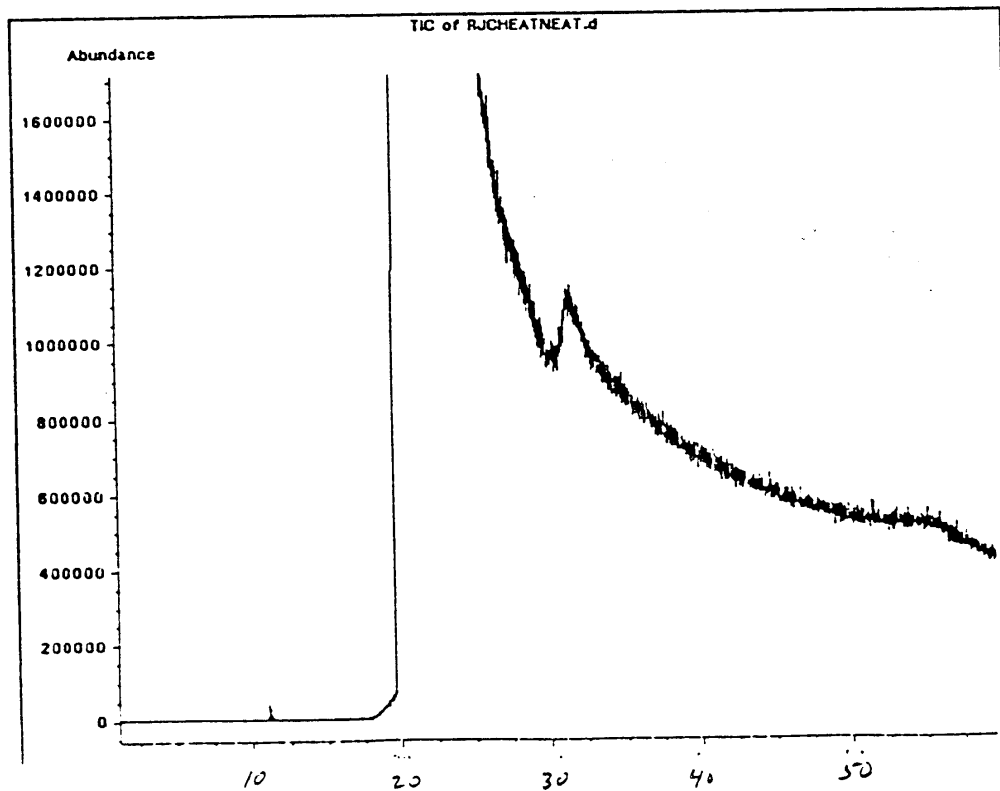
Attachment 1

Naphthalene Ion Chromatograms

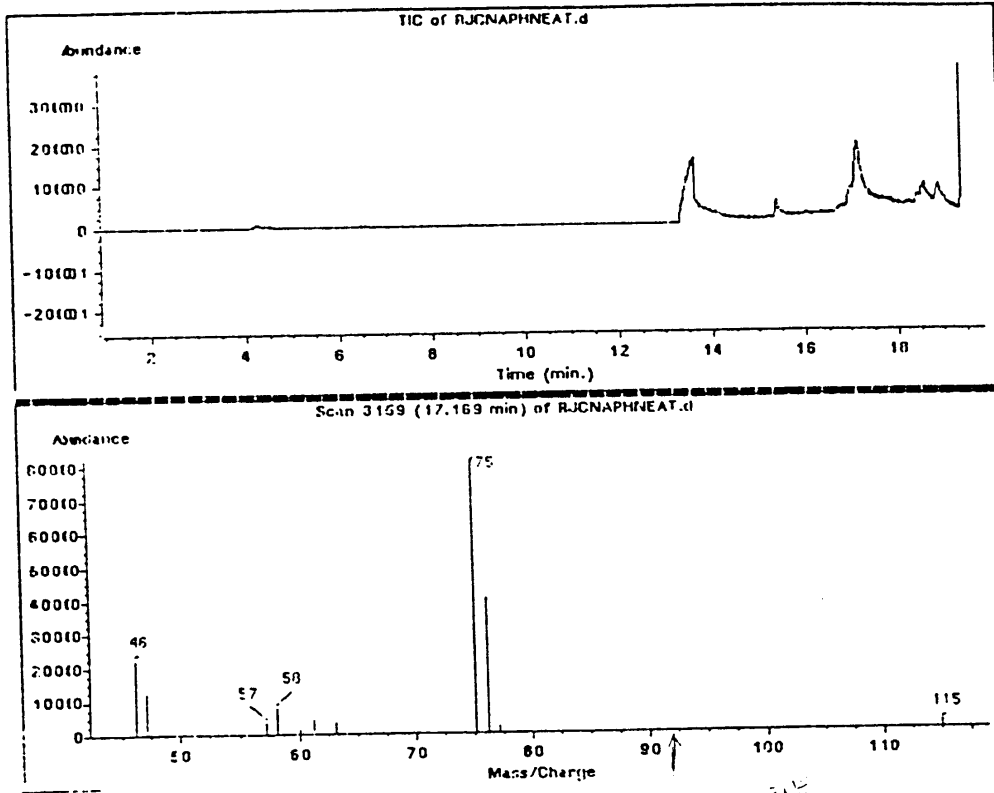
1283



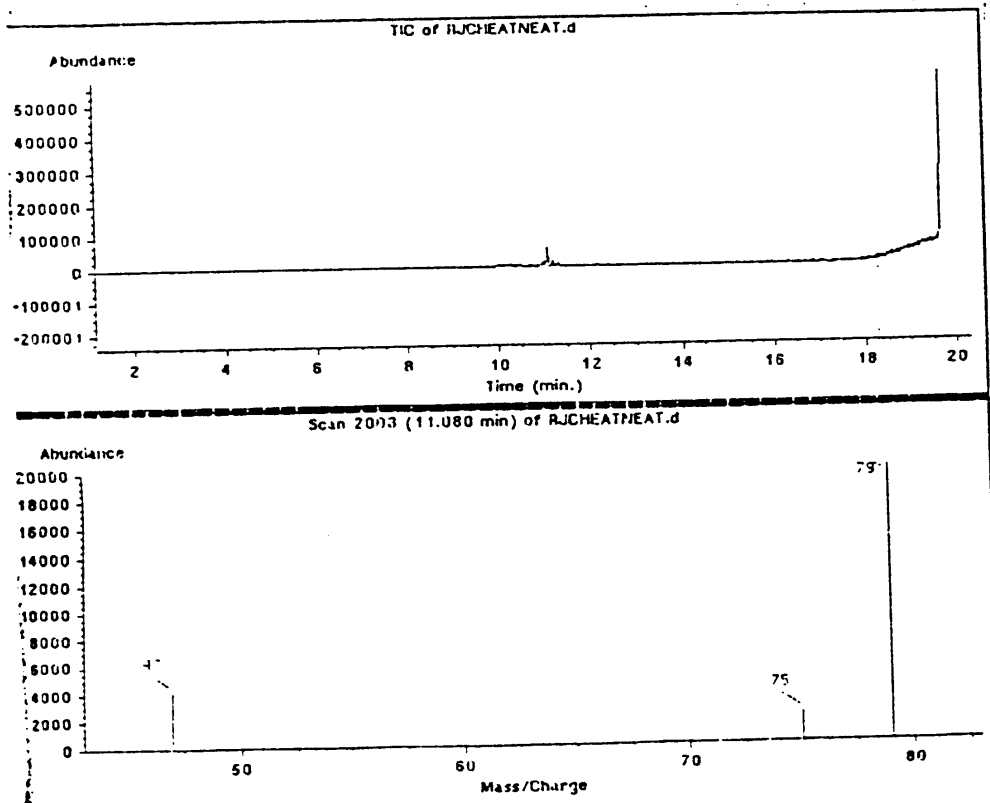
Total Ion Chromatogram of Fresh Naphthalene Analyzed NEAT



Total Ion Chromatogram of Naphthalene Removed from Heat Pipe Analyzed NEAT



No compounds eluting in the toluene region of Fresh Naphthalene



No compounds eluting in the toluene region of Naphthalene
Removed from the Heat Pipe