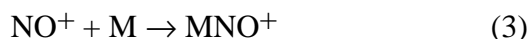
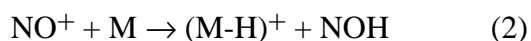


Hydrocarbon typing by nitric oxide chemical ionization mass spectrometry

The complexity of petroleum prevents the identification of its components except for light distillates such as gasoline. Various methods such as ASTM methods D2425 and D2786 use mass spectrometry to obtain a z-type analysis in which the components are sorted by z number according to the empirical formula C_nH_{2n+z} . Lumping all the isomers together within an empirical formula greatly reduces the apparent complexity of the petroleum. These methods require separation of the saturates from the aromatics prior to mass spectrometric analysis and do not provide detailed carbon number information.

Hunt and Harvey [1] investigated the use of nitric oxide as a chemical ionization reagent gas for hydrocarbons. Dzidic, *et. al.* [2] demonstrated its utility using gas chromatography-mass spectrometry to obtain carbon number distributions by z-type. The use of a soft chemical ionizing reagent to produce quasimolecular ions simplifies the data interpretation when compared to harder ionizing techniques that produce little or no molecular information. Typically, one sums the quasimolecular ion intensities over the elution range of the isotopes of each C_nH_{2n+z} group to obtain the carbon number versus z-type distribution.

Nitric oxide chemically ionizes hydrocarbons through three reactions, charge exchange (1), hydride abstraction (2), and addition (3):



Aromatics ionize by charge exchange with a small amount that ionizes by addition while saturates ionize by hydride abstraction. This difference permits one to use nitric oxide chemical ionization (NOCI) to differentiate between aromatics and saturates of equal mass. Olefins can ionize by any of the three reactions [3] making it difficult to differentiate them. Figure 1 illustrates the differentiation ability for saturates and aromatics. Figure 1(a) is the NOCI mass spectrum of decane and Figure 1(b) is the NOCI mass spectrum of 2-methyl naphthalene. Decane produces predominantly $(M-H)^+$ at m/z 141 whereas 2-methyl naphthalene produces M^+ at m/z 142. While the chromatograph can separate the isotopes of decane from the isotopes of methyl naphthalene, isotopic complexity at higher carbon number causes overlap.

Combining a chromatographic separation by boiling point with nitric oxide chemical ionization mass spectrometry allows one to type complex low olefinic hydrocarbon mixtures without prior sample preparation. A typical analysis of a heavy atmospheric gas oil is given in Table 1. The analysis sums the $(M-1)^+$ ions for z types +2 through -4 and the M^+ ions for z types -6 through -24. Table 2 gives the carbon number distribution for each z-type.

1. Donald F. Hunt and T. Michael Harvey, *Anal. Chem.*, **47**, 1965 (1975)
2. Ismet Dzidic, H. A. Petersen, P. A. Wadsworth, and H. V. Hart, *Anal. Chem.*, **64**, 2227 (1992)
3. Donald F. Hunt and T. Michael Harvey, *Anal. Chem.*, **47**, 2136 (1975)

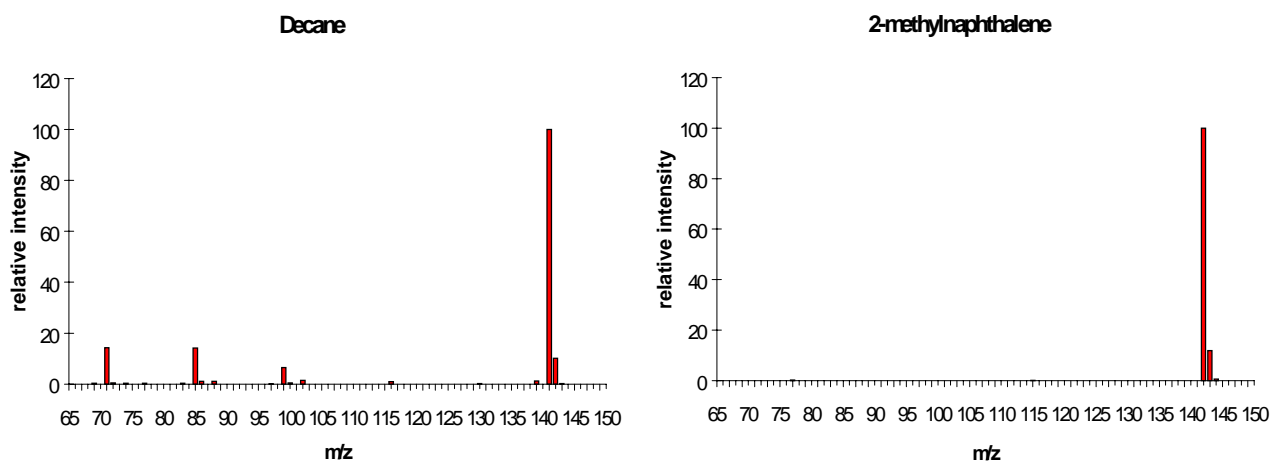


Figure 1. Nitric oxide chemical ionization mass spectra (a) decane spectrum shows the $(M-H)^+$ ion at m/z 141. (b) 2-methyl naphthalene spectrum shows the M^+ ion at m/z 142.

Table 1: Z type distribution for a heavy atmospheric gas oil measured by gas chromatography nitric oxide chemical ionization mass spectrometry.

data file 24030

z number	volume %
+2	32.06
0	24.67
-2	12.66
-4	5.54
-6	12.46
-8	6.40
-10	0.76
-12	2.34
-14	1.99
-16	0.49
-18	0.34
-20	0.08
-22	0.21
-24	0.02
	100.02

sample: **HAGO**

data file/run date: 24110 1/5/99

TAC ref: -

Note: values reported represent only a "best estimate"
 adjusted for HTSD recovery = 100% boiling below 1000F

LV %

Z number C#	+2(i+n)	+2(n)	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
6	0.45	0.01	0.62			0.02									
7	0.47	0.01	2.28	0.02		0.74									
8	0.48	0.02	3.25	0.04		1.46	0.00								
9	0.49	0.04	3.34	0.32		1.88	0.13	0.00							
10	0.56	0.08	2.39	0.94	0.00	1.61	0.87	0.01	0.16						
11	0.66	0.16	1.51	1.58	0.06	1.28	1.96	0.04	0.66	0.04					
12	0.82	0.26	1.02	1.56	0.15	1.61	1.79	0.06	0.77	0.20	0.00				
13	1.09	0.37	1.02	1.34	0.27	1.25	0.98	0.08	0.52	0.40	0.03				
14	1.19	0.48	0.89	1.06	0.30	0.78	0.53	0.09	0.26	0.40	0.05	0.00			
15	1.47	0.66	0.93	0.95	0.34	0.49	0.32	0.07	0.16	0.40	0.05	0.01			
16	1.73	0.79	0.99	0.76	0.38	0.42	0.19	0.04	0.09	0.25	0.05	0.02			
17	2.01	0.94	1.06	0.66	0.41	0.46	0.12	0.02	0.06	0.13	0.04	0.02	0.00		
18	2.28	1.01	1.08	0.62	0.39	0.36	0.11	0.02	0.04	0.06	0.03	0.01	0.01	0.01	0.00
19	2.37	1.00	1.07	0.58	0.35	0.32	0.09	0.01	0.04	0.04	0.02	0.01	0.01	0.02	0.00
20	2.35	1.01	1.00	0.49	0.28	0.31	0.09	0.01	0.03	0.03	0.01	0.01	0.01	0.00	0.00
21	2.15	0.94	0.93	0.43	0.24	0.28	0.09	0.01	0.03	0.02	0.02	0.01	0.00	0.00	0.00
22	1.95	0.86	0.78	0.32	0.18	0.26	0.08	0.01	0.03	0.02	0.00	0.01	0.00	0.00	0.00
23	1.81	0.72	0.68	0.26	0.15	0.22	0.07	0.01	0.02	0.02	0.01	0.01	0.00	0.00	0.00
24	1.45	0.60	0.51	0.20	0.10	0.19	0.06	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00
25	1.09	0.45	0.40	0.16	0.08	0.12	0.05	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00
26	0.85	0.36	0.28	0.10	0.05	0.10	0.04	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
27	0.57	0.24	0.20	0.07	0.04	0.09	0.03	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00
28	0.42	0.17	0.12	0.03	0.02	0.06	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
29	0.26	0.11	0.08	0.02	0.01	0.05	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
30	0.18	0.07	0.00	0.01	0.00	0.04	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
31	0.10	0.04	0.04	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
32	0.05	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
33	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
34	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
sum	29.33	11.45 (normal)	26.59	12.53	3.82	14.40	7.70	0.52	2.91	1.66	0.27	0.15	0.04	0.10	0.01
															100.03

Table 2: Carbon number versus z-type distribution for a heavy atmospheric gas oil measured by gas chromatography nitric oxide chemical ionization mass spectrometry.