IDENTIFICATION OF OIL SPILLS BY FIELD IONIZATION MASS SPECTROMETRY

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The U.S. Coast Guard provided SRI with a sample of an oil spill and seven other samples from the bilge of various ships suspected to be the source of the spill. Field Ionization Mass Spectrometric (FIMS) analysis of the samples links the unknown X with Sample B for following reasons.

Field ionization of most organic substances results in the formation of their molecular ions only, i.e., no fragmentation except in a few cases. The mass spectrum is therefore a molecular-weight profile of the sample. In the attached spectra, we can see that all samples contain a bimodal distribution of molecular weights. In all samples, there is some material in the mass range 120 to 350 amu showing a maximum around 170 amu, most likely the fuel. There is also some material of higher molecular-weight material and a broad mass distribution ranging from about 300 to 800 amu, probably some lubricant or wax.

All organic compounds containing carbon, hydrogen, and oxygen have even molecular weights, and therefore a FIMS of a fuel will have a preponderance of intensities of even over odd masses. Peaks at odd m/z arise due to (i) natural ^{13}C abundance, (ii) molecules containing odd number of nitrogen atoms, and (iii) fragmentation. In field ionization there is very little fragmentation, and the attached spectra have all been corrected for natural ^{13}C abundance. For these reasons, the spectra show peaks mainly at even masses, and the few odd mass peaks generally correspond to nitrogen-containing compounds.

FIMS of the unknown sample was obtained in duplicate to indicate the reproducibility of the technique for these samples. As can be seen, the technique displays remarkable reproducibility. For the purpose of identifying the oil spill, we make use of three spectral features.

1. Relative intensities of the lighter and heavier material, fuel, and lube. Of course, weathering will alter the ratio, and this criterion must be used with some care. It is, however, safe to assume that any weathering will only increase the relative amount of the heavier material and not vice-versa.

   Applying this criterion, we can rule out samples F and G as being the source of the spill.

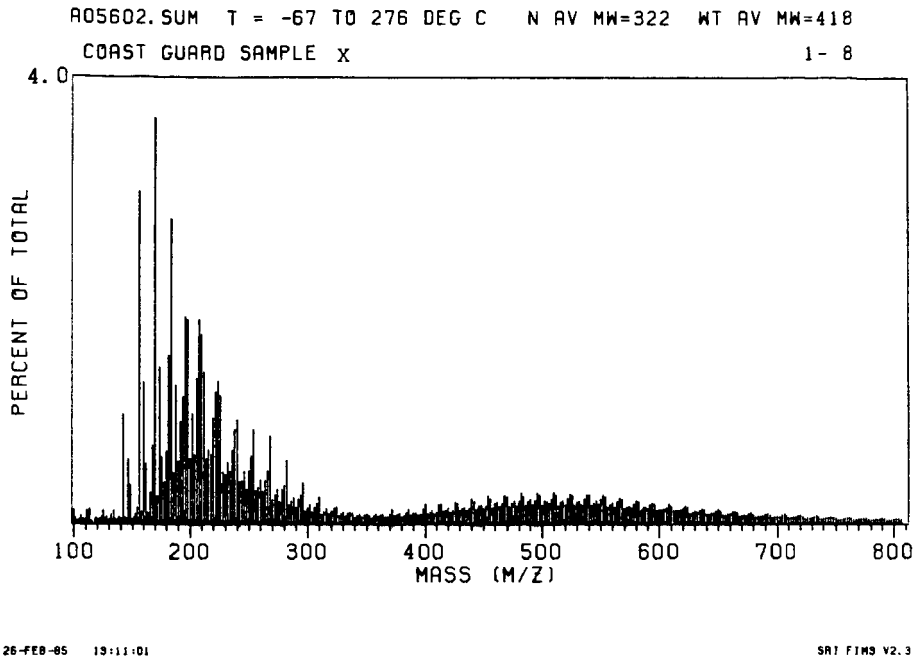
2. Pattern of intensities of some of the prominent peaks over a narrow mass range such that any weathering would alter the peaks to similar extents. Thus, examining the intensities of the peaks in the range 156 to 184 amu, paying particular attention to the pairs of peaks at m/z 156/160, 170/174, and 182/184, we can rule out samples A, D, E, and F. Samples F and G show a significantly more intense peak at m/z 146 relative to the one at m/z 142 than in other samples. This leaves samples B and C as possibly being linked to the spill.

3. Pattern of intensities of the odd mass peaks. These are the minor nitrogen-containing components that provide an additional fingerprint of the fuel. On the spectra, these peaks can be recognized as the dark stubs near the base line.

   On the basis of this criterion samples A, C, E, F, and G can be ruled out. The FI mass spectra of all the samples have also been plotted over the mass range 100 to 300 at much reduced full-scale intensity to better show the minor peaks and allow an easy comparison of the pattern of the odd mass peaks. Following this exercise, one arrives at the same conclusion.

The only sample not ruled out thus far is B.

5/85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1- 8
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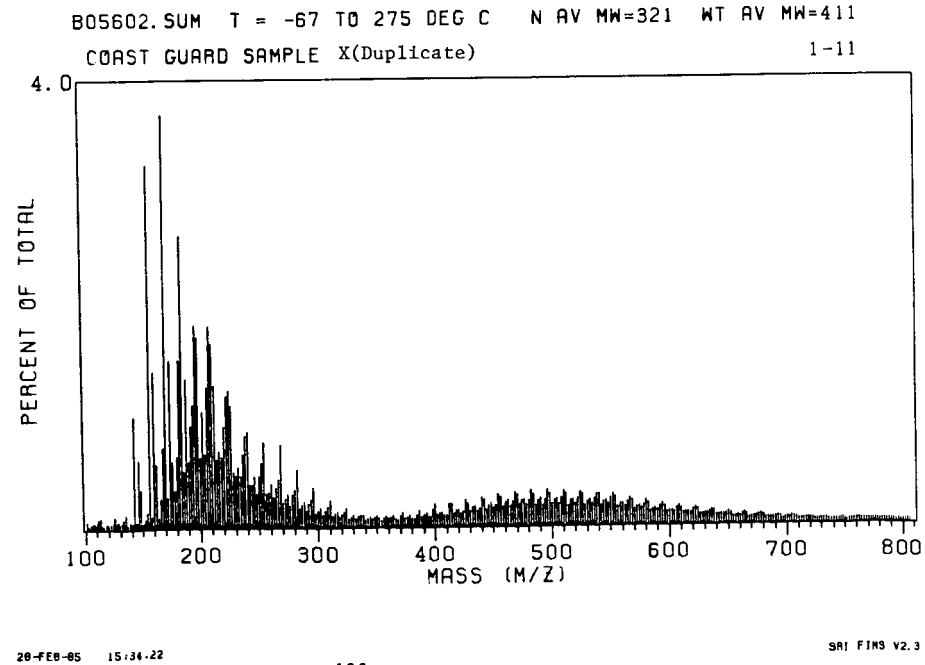
100
200
300
400
500
600
700
800
MASS (M/Z)
26-FEB-85 19:11:01
SRI FIMS V2.3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4.0
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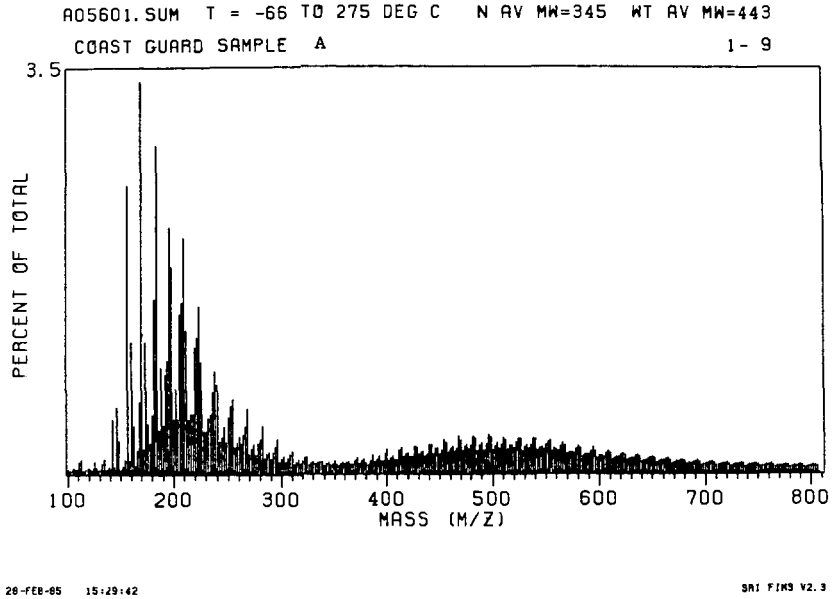
200
300
400
500
600
700
800
MASS (M/Z)
20-FEB-85 15:34.22
SRI FIMS V2.3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1- 9
3.5
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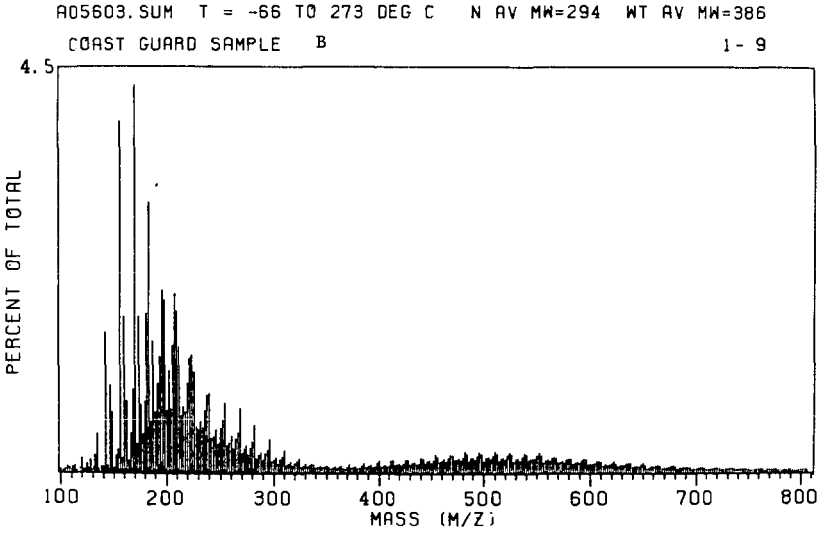
300
400
500
600
700
800
MASS (M/Z)
28-FEB-85 15:29:42
SRI FIMS V2.3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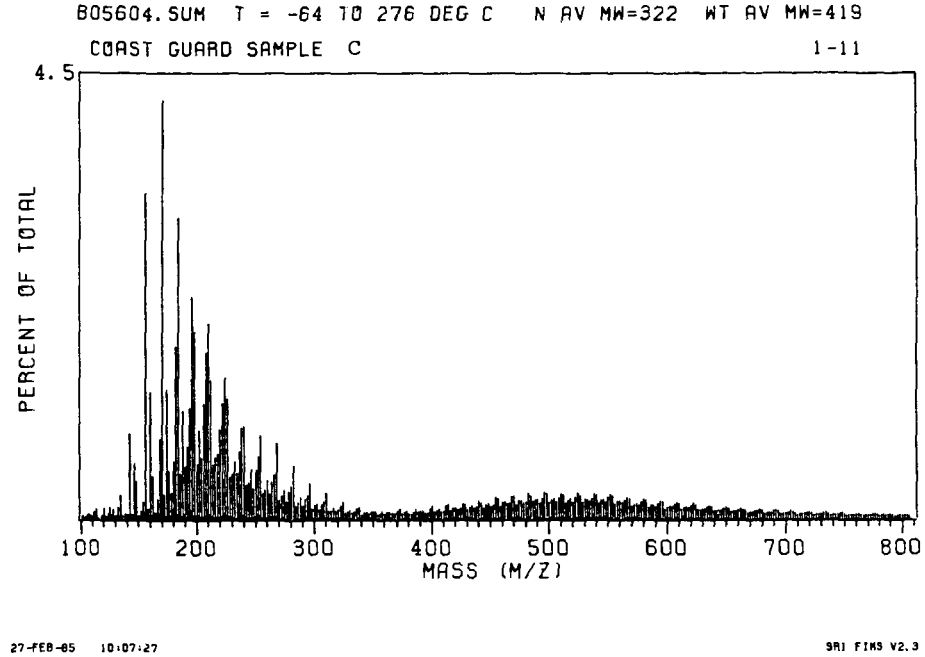
1- 9
4.5
PERCENT OF TOTAL
100
200
300
400
500
600
700
800
MASS (M/Z)
01-MAR-85 08:53:49
SRI FIMS V2.3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1-11
4.5
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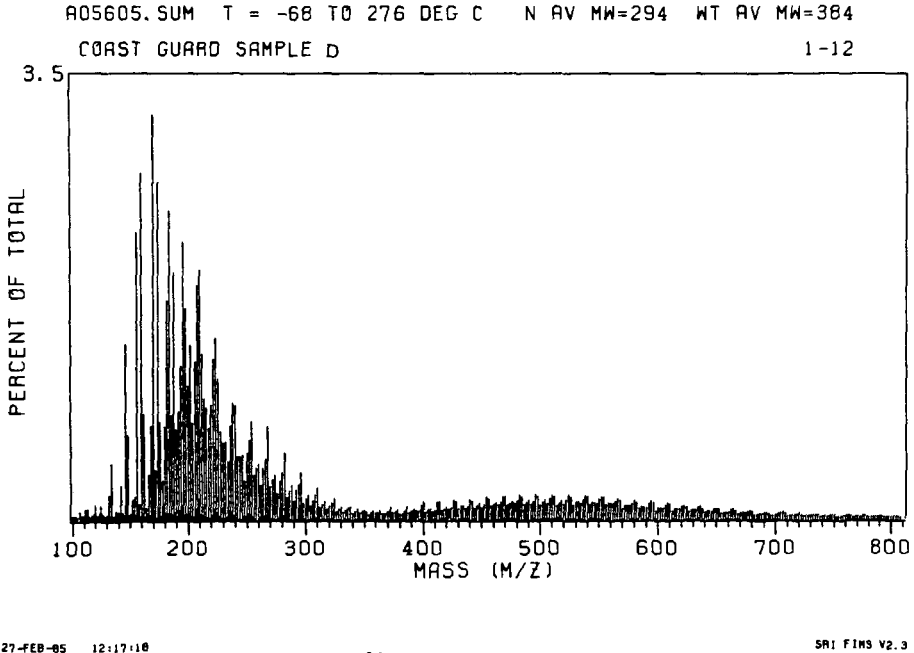
200
300
400
500
600
700
800
MASS (M/Z)
27-FEB-85 10:07:27
SRI FIMS V2.3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1-12
3.5
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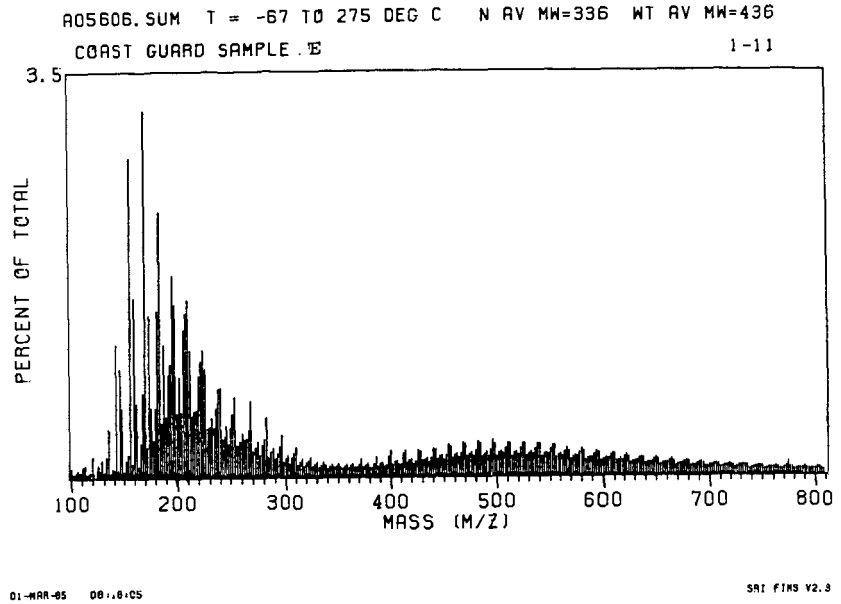
200
300
400
500
600
700
800
MASS (M/Z)
27-FEB-85 12:17:18
SRI FIMS V2.3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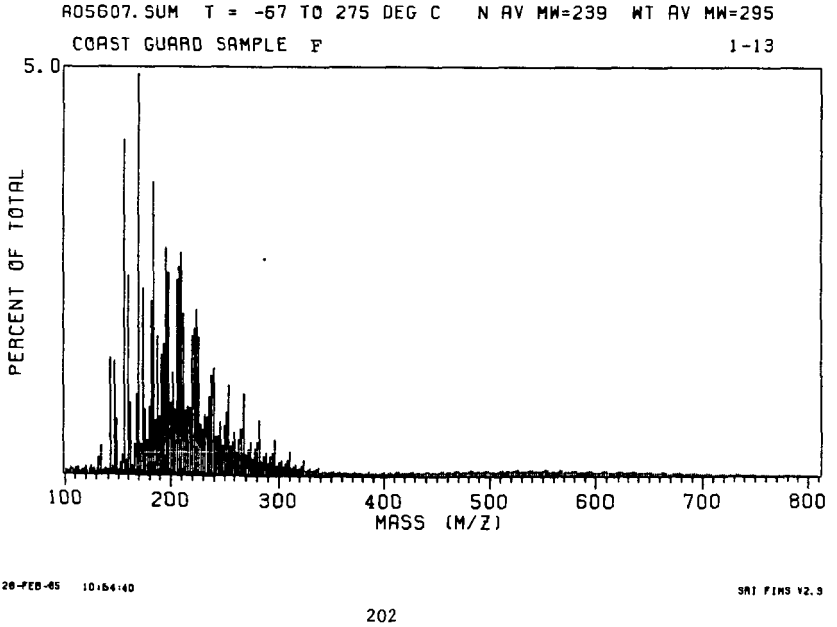
300
400
500
600
700
800
MASS (M/Z)
01-MAR-85 08:18:05
SRI FIMS V2.3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1-13
5.0
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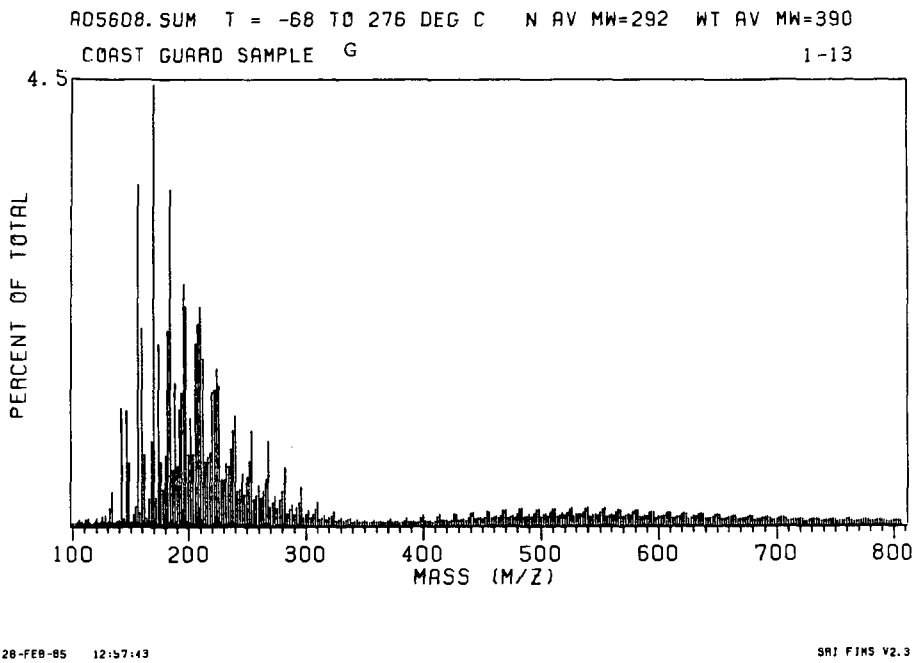
300
400
500
600
700
800
MASS (M/Z)
28-FEB-85 10:54:40
SRI FIMS V2.3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COAST GUARD SAMPLE G
1-13
4.5
PERCENT OF TOTAL
100
200
300
400
500
600
700
800
MASS (M/Z)
28-FEB-85 12:57:43
SRI FIMS V2.3