

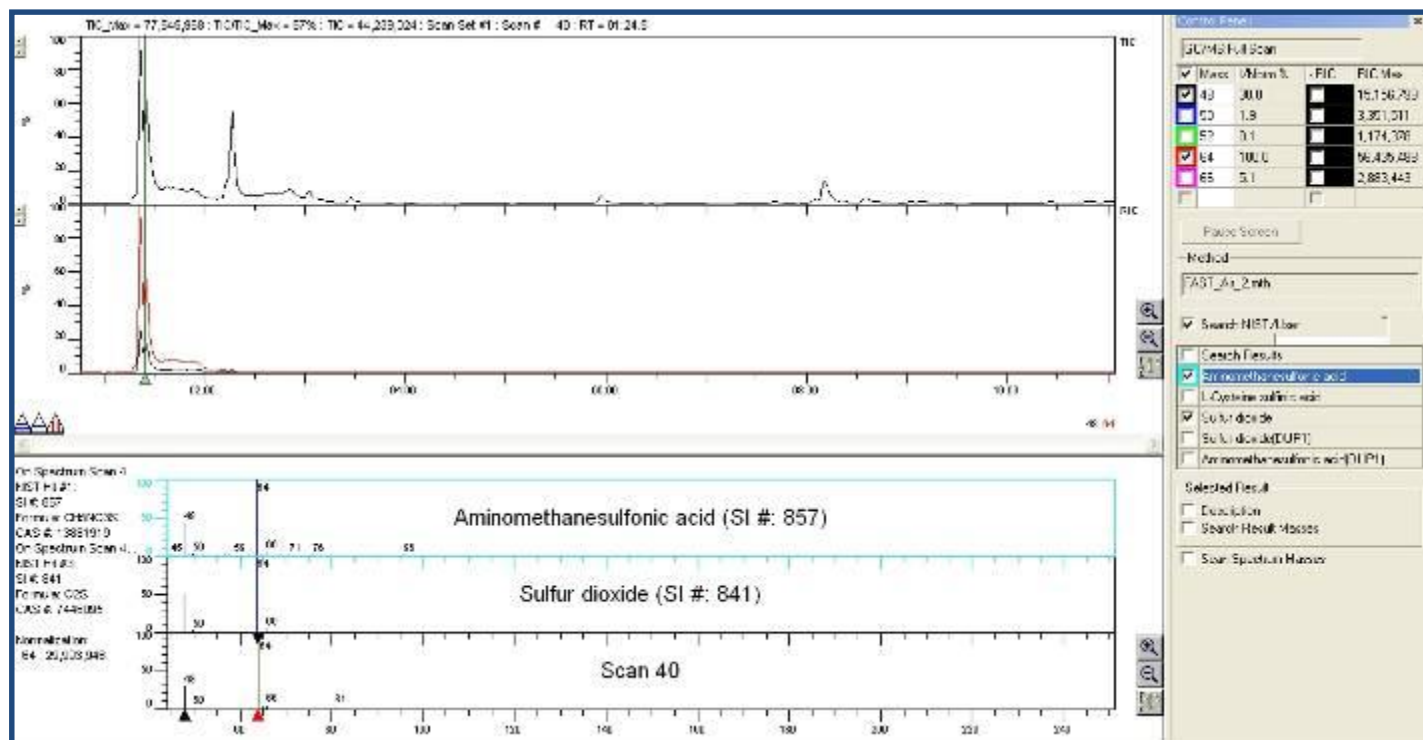
MassDEP Field Assessment and Support Team

After Incident Report

3-29,646

Lawrence – Unknown Chemical Cloud Incident

November 2010



A vapor cloud emanating from a scrap cylinder at a metal recycling facility on Medford Street in Lawrence was analyzed in the field by MassDEP personnel using a portable Gas Chromatograph/Mass Spectrometer.

- ☞ Chloromethane (also known as Freon 40);
- ☞ Sulfur Dioxide or Aminomethanesulfonic Acid; and
- ☞ 1, 1-Dichloroethane.

BACKGROUND

A map of Lawrence, MA, showing the location of the proposed site. A red arrow points from the word "Site" to a location on Haverhill St, near the intersection with Broadway. The map includes major roads like I-93, I-110, and I-28, and landmarks like St. Mary's Cemetery.

FAST MOBILIZATION

FAST arrived at the site at 12:10 AM on 11/14/10. The FAST vehicle was parked on Medford Street up-wind of the leaking cylinder, as shown in Figure 1. The 30 foot mast/weather station was immediately deployed to monitor wind direction and speed.

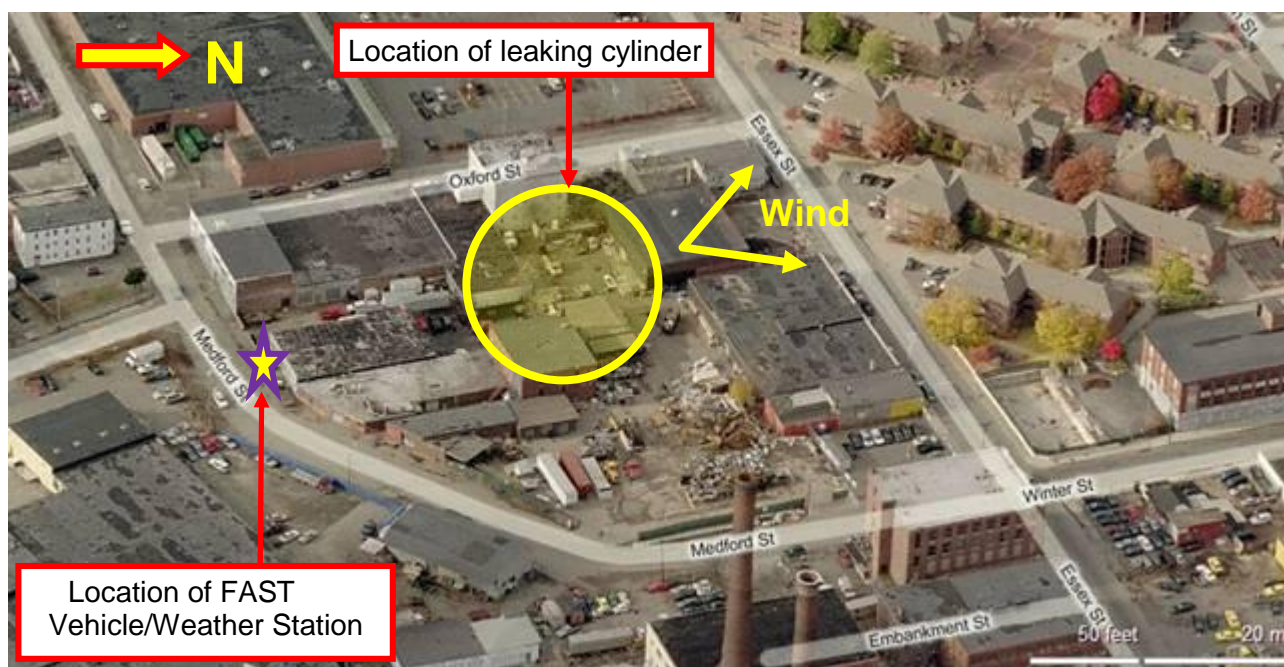


Figure 1: Site and Surrounding Area

Vapor Cloud Movement

Upon arrival at the site at 12:10 AM, FAST personnel observed the vapor cloud moving very slowly in a northerly direction (see photo on front page of report). Between 12:30 AM and 3:00 AM, the wind direction at the site was predominantly from the south and west (i.e., blowing towards the north and east), except for a brief period of northerly winds around 2:00 AM. Temperatures slowly fell from 41°F to 36°, with barometric pressure steady at about 30.05 inches of mercury. Fortunately, wind speed was minimal throughout this period (1-2 MPH). The vapor cloud hung low to the ground, dispersing to non-visible concentrations within a short distance from the leaking cylinder.

Downwind Analysis

Fires services personnel obtained two Tedlar bag air samples for analysis on a HAPSITE GC/MS unit located in the FAST vehicle. The first sample was downwind of the leaking cylinder, between the site and residential properties to the north. The Total Ion Chromatogram for this sample is displayed in Figure 2, and the data report is contained in Appendix 1

Basically, this sample contained very low-levels of petroleum hydrocarbons (< 20 ppbV), the highest being Toluene at 14 ppbV. The beginning peaks at 1 to 2 minutes contained sulfur compounds, including a peak identified as Aminomethanesulfonic Acid. The low levels detected suggested that there was not an immediate risk to the neighboring properties.

Source Analysis

In order to better identify the substance emanating from the cylinder, fire services personnel in protective equipment obtained a Tedlar bag air sample adjacent to the leaking valve. This sample was brought back to the FAST vehicle, where it was stored in the laboratory fume hood.

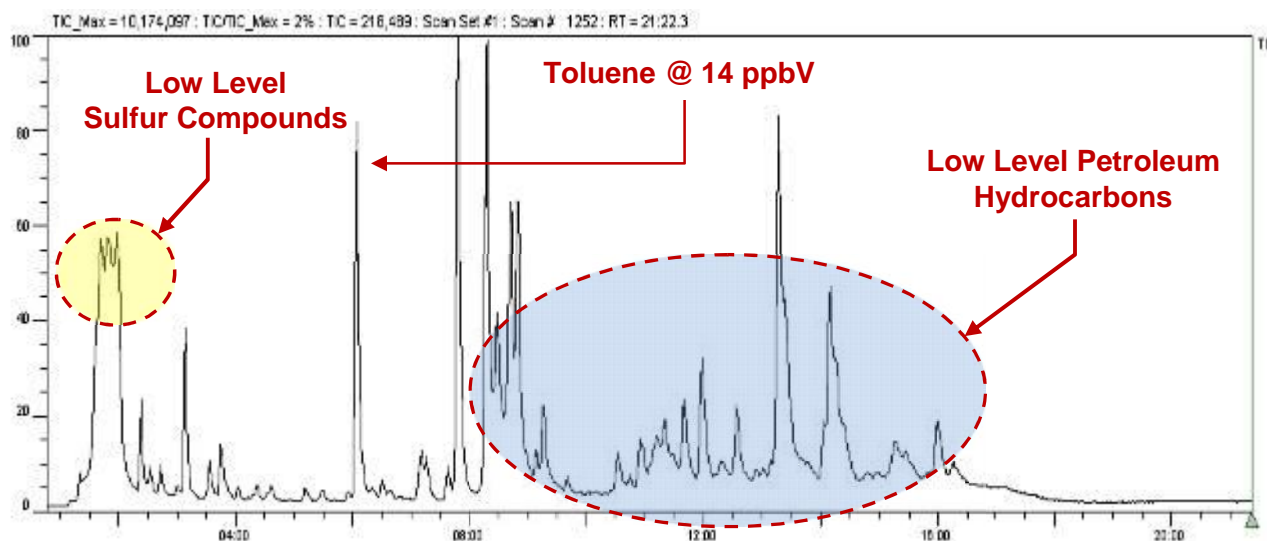


Figure 2: Downwind Air Sample

An approximately 10 cc sample was withdrawn from the Tedlar bag into the HAPSITE probe, while the bag remained in the fume hood. As an added safety measure, the column flow from the HAPSITE was directed into the fume hood using tubing.

Chromatographic details for this sample are displayed in Figure 3, and the data report is contained in Appendix 2. Note that the 10 cc sample represented about a 20 fold dilution from actual concentrations (necessary to prevent overloading the GC/MS).

While this sample also contained many of the same petroleum hydrocarbons seen in the downwind sample, it was comprised principally of several early eluting peaks, which represent the key components within the cylinder.

DISCUSSION

This second sample was much more concentrated than the “downwind” sample, and was useful in identifying the main components in the cylinder:

- The Total Ion Chromatogram (TIC) is dominated by several co-eluting peaks at around 1 minute, and a discrete peak eluting just after 2 minutes. This suggests that the contents of the cylinder were primarily comprised of 2 to 4 components.
- The second large peak at 2.16 minutes was 1,1-Dichloroethane (1,1-DCA). This can be confirmed because of the unambiguous spectra, and due to the fact this is a target analyte for which the HAPSITE has been calibrated for. Accounting for the 20X dilution, this constituent was present at a concentration of about 5 ppmV.
- The large early-eluting peaks are more complicated:
 - Instrument software identified the largest area within these peaks as Chloromethane, also known as Methyl Chloride and Freon 40.
 - The next largest area was identified as Aminomethanesulfonic Acid, based upon its mass spectra. However, as displayed in Figure 3, it is noted that this mass spectra is similar to the “fingerprint” for Sulfur Dioxide, which was also reported to be present (at a lower concentration).

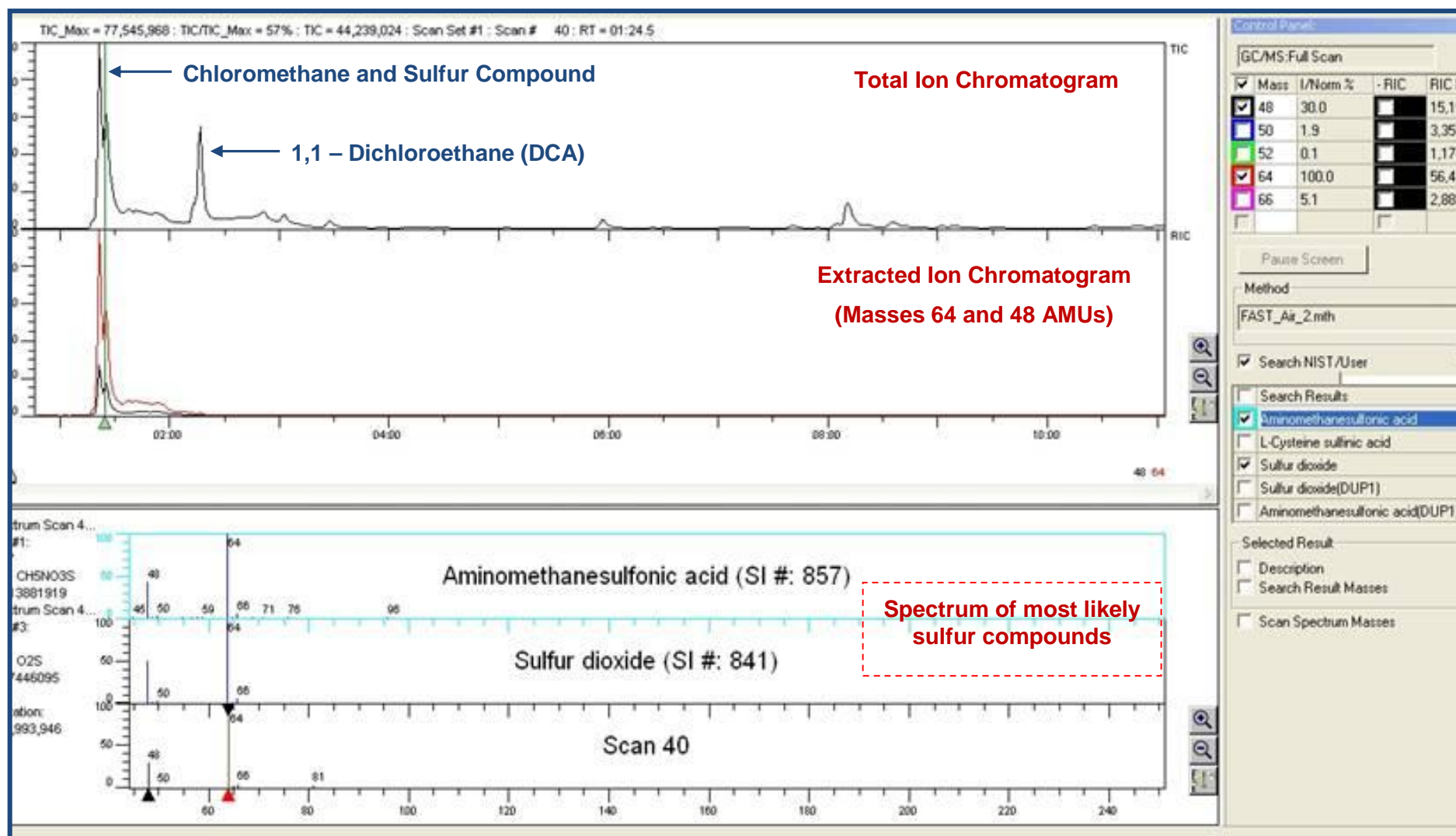


Figure 3: Air Sample from Discharge of Cylinder (approximately 20 fold dilution)

It is possible that the sulfur compound within the cylinder was Sulfur Dioxide, not Aminomethanesulfonic Acid:

- Chloromethane (Freon 40) and 1,1-DCA are both used as refrigerants, and it is not clear why Aminomethanesulfonic Acid would be mixed with them in the cylinder, unless as a stabilizer. However, based upon a limited Internet search, no such use was noted for this compound. Conversely, Sulfur Dioxide is also used as a refrigerant, which suggests a more likely nexus with the Chloromethane and 1,1-DCA.
- At typical environmental pressures and temperatures, Aminomethanesulfonic Acid is a white powder, while Sulfur Dioxide is a gas.
- Sulfur Dioxide has a vapor density greater than air (similar to Chloromethane and 1,1-DCA), which would be consistent with the observation of the “ground hugging” vapor cloud at the site.
- Sulfur Dioxide will elicit a response on common Hydrogen Sulfide (electrochemical) meters, which could explain the reported meter detection of Hydrogen Sulfide.

On a contrary note, the odor threshold of Sulfur Dioxide is listed as being in the range of 1 to 5 ppmV, which was probably exceeded in the vapor cloud near the cylinder. While no reports of a sulfur-odor were received by MassDEP personnel, it is possible that the use of respirators or self-contained breathing apparatus in the hot zone precluded this observation, together with plume dispersion in downwind areas.

While there is some uncertainty on the identity (and function) of the sulfur compound(s), it appears reasonably certain that the cylinder’s contents were pressurized gases/liquids meant to be used as refrigerants, and that the evaporative cooling (latent heat of vaporization) occurring as the contents “flashed” into the air produced the white, dense vapor cloud.

HEALTH RISKS

Relevant health metrics for Chloromethane, Sulfur Dioxide, and 1,1-DCA are presented in Table 1. No values are available for Aminomethanesulfonic Acid, which is generally described as being corrosive.

Table 1 – Health Metrics for Vapor Cloud Contaminants					
Contaminant	Concentration in Air in ppmV				
	Acute (IDLH)	Occupational (TLV-TWA)	General Public Exposure Guidelines		
			Mild/Reversible	Serious	Life Threatening
Chloromethane	2000	50	100 ³	380 ¹	1300 ¹
Sulfur Dioxide	100	2	0.2 ¹	0.75 ¹	9.6 ¹
1,1- DCA	3000	100	50 ²	200 ²	300 ²

¹ AEGLS - *Acute Exposure Guidelines* (EPA), 8 hour exposure

² ERPG - *Emergency Response Planning Guidelines*, (American Industrial Hygiene Assoc) – 1 hr

³ PAC – *Protective Action Criteria* (DOE)

Only 1,1,-DCA is a target analyte on the FAST HAPSITE unit, and it was not detected in the downwind sample, at a Reporting Limit of approximately 2.5 ppbV. (See Appendix 1)

Based upon peak height and the integration areas of the quantitation ion, the downwind concentration of Chloromethane is estimated to be very low; and well below 1 ppmV.

If Sulfur Dioxide was present, based upon peak height and integration areas, it would likely be at a concentration lower than the 0.2 ppmV (200 ppbV) "Mild/Reversible" health effects level.

On the basis of the above, it is unlikely that neighboring residents were exposed to significant concentrations of vapor cloud contaminants during the time of cylinder leakage (i.e., until about 1:00 AM, when fire services personnel were able to stop the discharge).

DEMOBILIZATION

FAST departed from the site at approximately 3:20 AM on 11/14/10. Prior to departure, the Lawrence Fire Department was provided with a one-page summary of analytical conclusions, which is provided as Appendix 3.

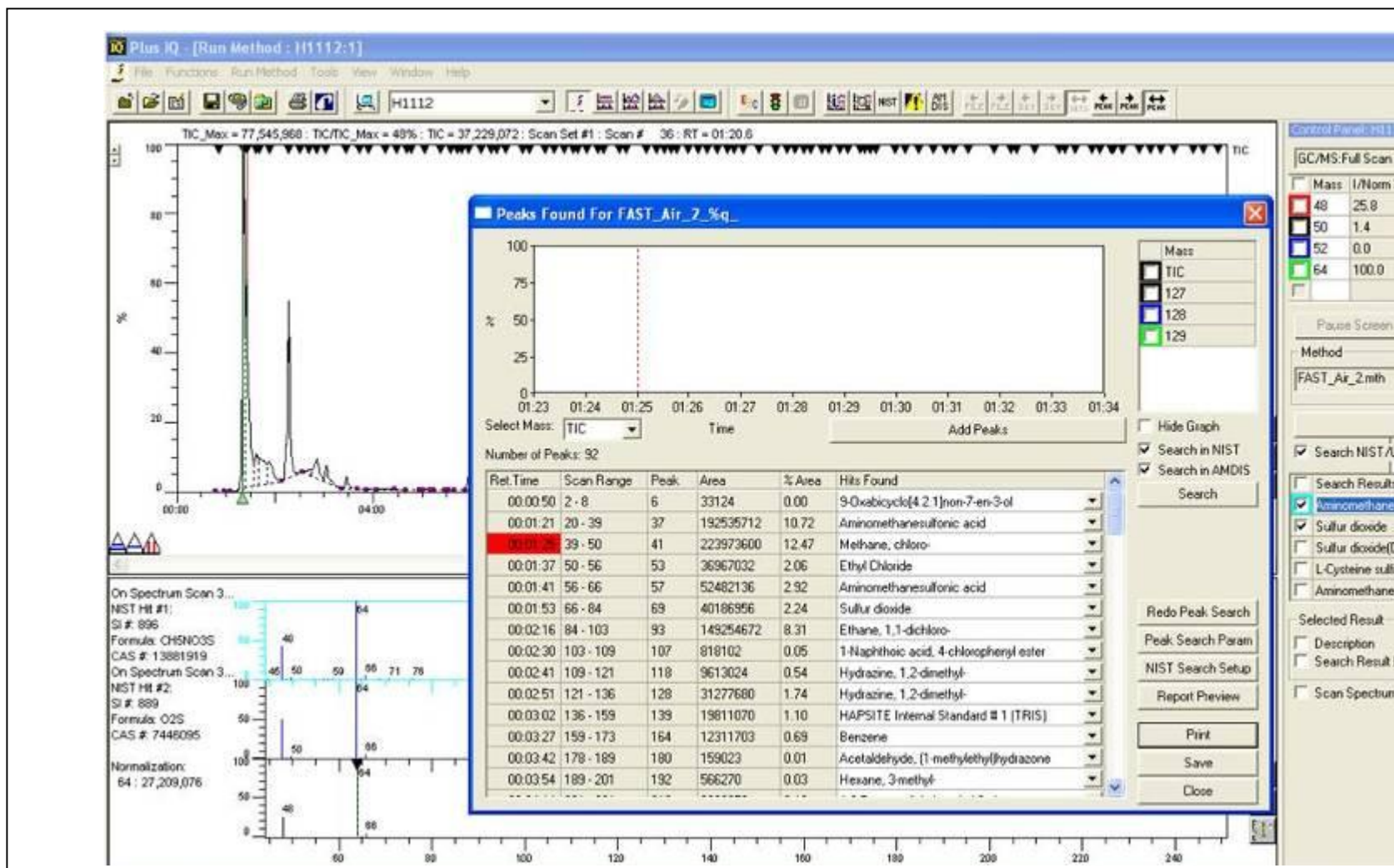
Appendix 1

MassDEP Field Assessment and Support Team (FAST)				Analytical Screening Data				Sample Field ID	Downwind
Town:	Lawrence		Address/Name:		Medford Street			RTN:	3-29,646
Sample Location:	Downwind of Vapor Cloud		Date:	11/14/2010	Time:	12:30 AM	Collector:	Lawrence Fire Department	
Date Analyzed:	11/14/10	Time:	1:10 AM	Lab ID:	Downwind	Method:	FAST_Air_2		
Analyte	Concentration		Reporting Limit		Retention	Quant	Peak	Comments	
	µg/M³	ppbV	µg/M³	ppbV	Time (min)	Ion	Fit		
1,1-Dichloroethane (1,1-DCA)	N.D.	N.D.	10	2.5	02:01.2	63	0.762		
MtBE	N.D.	N.D.	10	2.8	02:22.0	73	0.539		
1,1-Dichloroethylene (1,1-DCE)	N.D.	N.D.	10	2.5	02:25.9	96	0.894		
1,1,1-Trichloroethane	N.D.	N.D.	10	1.9	02:47.7	97	0.805		
Benzene	11.6	3.6	10	3.1	03:33.1	78	0.978		
Trichloroethylene (TCE)	N.D.	N.D.	10	1.9	04:21.6	130	0.996		
Toluene	51.5	13.7	10	2.7	06:04.2	91	1		
Tetrachloroethylene (PCE)	12.0	1.8	10	1.5	07:15.4	166	0.993		
Ethylbenzene	13.1	3.0	10	2.3	08:29.5	91	0.999		
p/m - Xylenes	16.5	3.8	10	2.3	08:29.5	91	0.944		
o-Xylene	38.4	8.9	10	2.3	08:42.3	91	1		
1,2,4-Trimethylbenzene	15.2	3.1	10	2.0	11:40.3	105	1		
Naphthalene	15.7	3.0	10	1.9	15:33.6	128	0.996		
Instrument:	HAPSITE GC/MS		Analyst:		Fitzgerald		Instrument Location:	On-Site/FAST vehicle	
Quality Assurance:	Daily Blank		QC Calibration Check Standard		✓ Internal Standards				
Comments: Reporting Limit is estimated									
Quant Ion = compound fragment used to quantify compound									

Appendix 2

MassDEP Field Assessment and Support Team (FAST)				Analytical Screening Data				Sample Field ID	Source (cylinder)
Town:	Lawrence		Address/Name:		15 Medford Street			RTN:	3-29,646
Sample Location:	At leaking cylinder		Date:	11/14/2010	Time:	1:15 AM	Collector:	Lawrence Fire Department	
Date Analyzed:	11/14/10	Time:	1:45 AM		Lab ID:	Source		Method:	FAST_Air_2
Analyte		Concentration		Reporting Limit		Retention	Quant	Peak	Comments
		µg/M³	ppbV	µg/M³	ppbV	Time (min)	Ion	Fit	
1,1-Dichloroethane (1,1-DCA)		976.5	241.11	10	2.5	02:16.9	63	0.979	
MtBE		N.D.	N.D.	10	2.8	02:08.0	73	0.483	
1,1-Dichloroethylene (1,1-DCE)		N.D.	N.D.	10	2.5	02:16.9	96	0.338	
1,1,1-Trichloroethane		N.D.	N.D.	10	1.9	03:18.2	97	0.808	
Benzene		47.97	15.04	10	3.1	03:27.1	78	0.97	
Trichloroethylene (TCE)		N.D.	N.D.	10	1.9	04:15.4	130	0.985	
Toluene		24.1	6.41	10	2.7	05:57.4	91	1	
Tetrachloroethylene (PCE)		2.666	0.39	10	1.5	07:08.5	166	0.987	
Ethylbenzene		5.618	1.29	10	2.3	08:22.6	91	0.999	
p/m - Xylenes		7.097	1.64	10	2.3	08:22.6	91	0.917	
o-Xylene		6.917	1.59	10	2.3	09:09.2	91	0.998	
1,2,4-Trimethylbenzene		3.928	0.80	10	2.0	11:12.6	105	0.981	
Naphthalene		20.15	3.85	10	1.9	15:25.7	128	1	
Instrument:	HAPSITE GC/MS		Analyst:	Fitzgerald			Instrument Location:	On-Site/FAST Vehicle	
Quality Assurance:	Daily Blank		QC Calibration Check Standard		✓ Internal Standards				
Comments: Reporting Limit is estimated									
Quant Ion = compound fragment used to quantify Compound									

MassDEP – Field Assessment and Support Team



Lawrence – Windfield Alloys – Medford Street Leaking cylinder Incident 11/13/10

Sample from cylinder – analyzed on HAPSITE GC/MS, 2:09 AM, 11/14/10

Major components – Chloromethane (Freon 40), Aminomethanesulfonic acid (or could be sulfur dioxide), and 1,1, Dichloroethane