



ANALYSIS OF SULFUR MUSTARD (HD) IN AIR BY GAS CHROMATOGRAPHY /TIME-OF-FLIGHT MASS SPECTROMETRY/ THERMAL DESORPTION



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INTRODUCTION

BACKGROUND:

A common technique for the analysis of the chemical warfare agent (CWA) mustard (HD) is by GC-FPD (flame photometric detector - in sulfur mode). While the FPD in sulfur mode eliminates much of the background detected in a typical atmospheric air sample, in terms of sensitivity for HD, it cannot compete with GC-TOFMS; nor does it provide the qualitative confirmation inherent to analysis by GC-TOFMS. Thus, analysis of HD by GC-TOFMS provides an additional level of confirmation (retention time and mass spectrum) as opposed to a retention time only, as seen with the FPD, and increased sensitivity.

OBJECTIVE:

The purpose of this study was to develop a method for the deposition of HD, in atmospheric samples, onto thermal desorption tubes and the subsequent analysis using Gas Chromatography/ Mass Spectrometry – Time – of – Flight (GCMS-TOF).

METHODS:

Analysis performed via GCMS-TOF interfaced with a thermal desorption unit. Samples collected on Markes thermal desorption tubes (3.5"(89mm) x 0.25"(6.4mm)o.d.).

RESULTS:

Able to achieve GPL¹ (general population limit – 0.00002mg/m³) sensitivity by analyzing 10L of sample.

CONCLUSIONS:

The analysis of HD in atmospheric samples by GC-TOFMS/ Thermal desorption provides qualitative (with confirmation) and quantitative (with increased sensitivity) data.

REFERENCES:

CSS.2018. SOP L-A-602 Analysis of CWAs in Air, Rev. 0.
Department of the Army, 2012. "Toxic Chemical Agent Safety Standards". Pamphlet 385-61. November 13.

Footnotes:

- 1.) Department of the Army, 2012. "Toxic Chemical Agent Safety Standards". Pamphlet 385-61. November 13. (table 2-1, Airborne exposure Limits).
- 2.) 40CFR part 136, Appendix B.
- 3.) CSS. 2018. SOP L-A-602 Analysis of CWAs in Air, Sect. 12.1, Rev. 0.

METHOD

Equipment

- Gas Chromatograph: Agilent 6890
- Thermal Desorption System: Markes Unity Xr
- Mass Spectrometer: LECO Pegasus III (upgraded to Pegasus IV)
- Desorption Tube: Markes #C2-CAXX-5138 (PAH)
- Cold Trap: Markes #U-T10CW-2S (Chemical Weapons)
- Auto Sampler: Markes Ultra Xr

METHOD

GC Parameters

GC program	Primary Column: Restek Rxi-5Sil 30m x 250um x 0.25um Secondary Column: Restek Rxi – 1 30m x 250um x 0.25um Temperature Program (both columns): 60 °C for 4.25 min; 5C/min, to 64 °C; 40C/min, to 300 °C. Flow: 1.2 mL/min.
Thermal Desorption Parameters	Trap Low: 5°C Trap High: 300°C Flow Path Temp: 180°C Tube Desorb Time: 8 minutes Tube Desorb Temp: 300°C Trap Desorb Time: 2.5 minutes Trap Desorb Temp: 300°C. Trap Split: 3:1
Sampling Program	CSLR™ (Calibration Solution Loading Rig) Temp: Ambient CSLR™ Time: 2 min. CSLR™ Flow: 400mL/min. Manifold Temp: Ambient Manifold Time: 100 min. Manifold Flow: 100mL/min.

Method Highlights

- Time – of – Flight MS
- GC run time of 11 minutes (3 analyses per hour)
- Thermal desorption tubes
- 100 minute sampling time

Method development

- Optimization of split at cold trap to achieve optimum sensitivity and chromatography.
- Optimization of gas chromatography parameters to achieve maximum sensitivity, optimum chromatographic resolution and minimum run time.
- Optimization of the thermal desorption parameters to achieve maximum sensitivity and minimum analysis time.

Procedure

- Six and seven point calibrations were performed by spiking 1uL aliquots of liquid HD standards onto thermal desorption tubes via a Markes CSLR™ at a flow (N₂) of 400mL/min. for 2 minutes.
- Samples for MDL² and Precision and Accuracy³ studies were prepared by spiking HD at various concentrations onto tubes with a flow of N₂ at 400mL/min. for 2 minutes via CSLR™. The tubes were then transferred to a manifold where the flow was set at 100mL/min. for 100 minutes (10L of N₂ pushed across tubes). An NOX Teflon/HD pre – filter was placed in – line prior to the N₂ entering the manifold. After 10L of N₂ was pushed through the tubes, the tubes were immediately capped and placed on the Markes autosampler for analysis by GC – TOFMS/TDU. Tubes at six different concentrations were analyzed, in duplicate, each day, for four consecutive business days. This equates to 12 tubes analyzed per day or 48 tubes analyzed over the four day study period. This procedure was performed by two different chemists on two different gas chromatography columns for a total of 192 samples analyzed.

Safety

- Gases that are vented through the Markes split vent are passed through a carbon filter before they are released to the environment.

RESULTS

Highlights

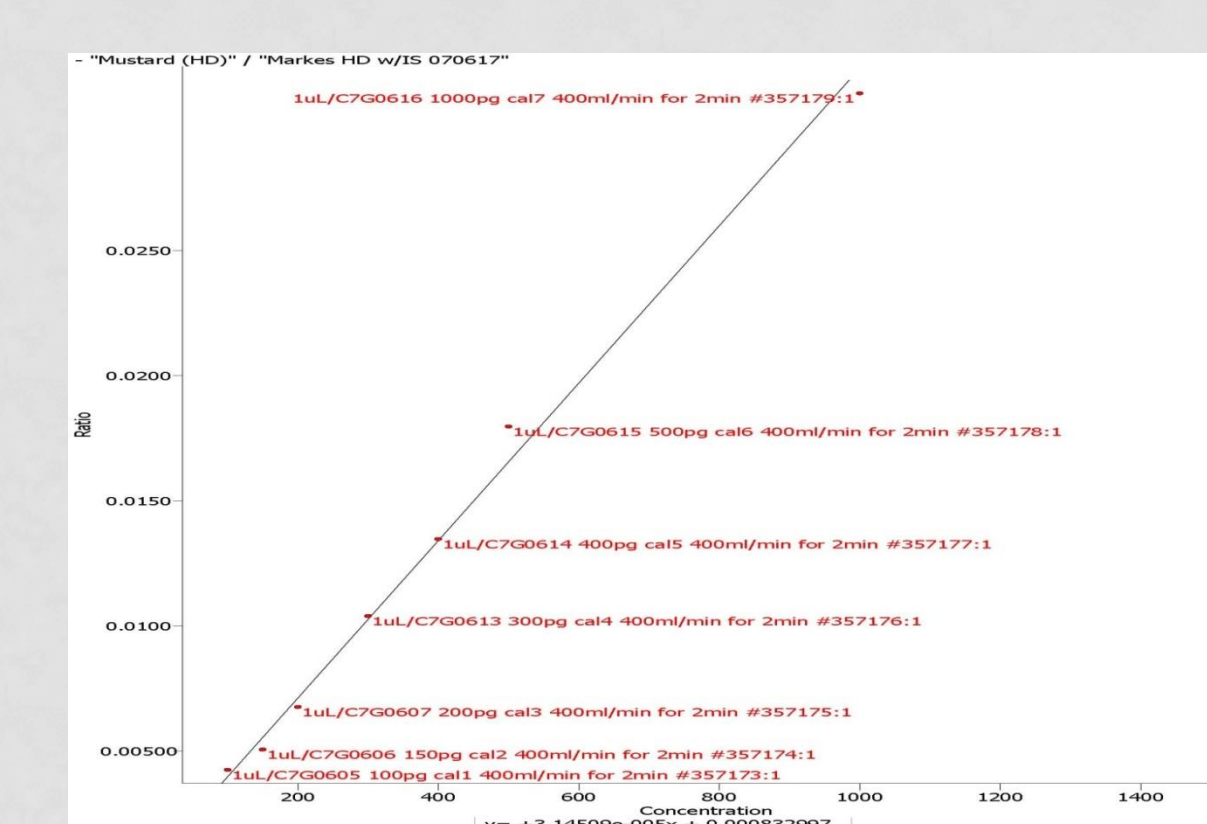
- ~100 picogram sensitivity (0.00001mg/m³ with a 10L sample)
- MDL studies verify picogram sensitivity
- Calibration satisfies common method acceptance criteria
- GCMS TOF sensitivity ~ 20x greater than GC-FPD

DATA

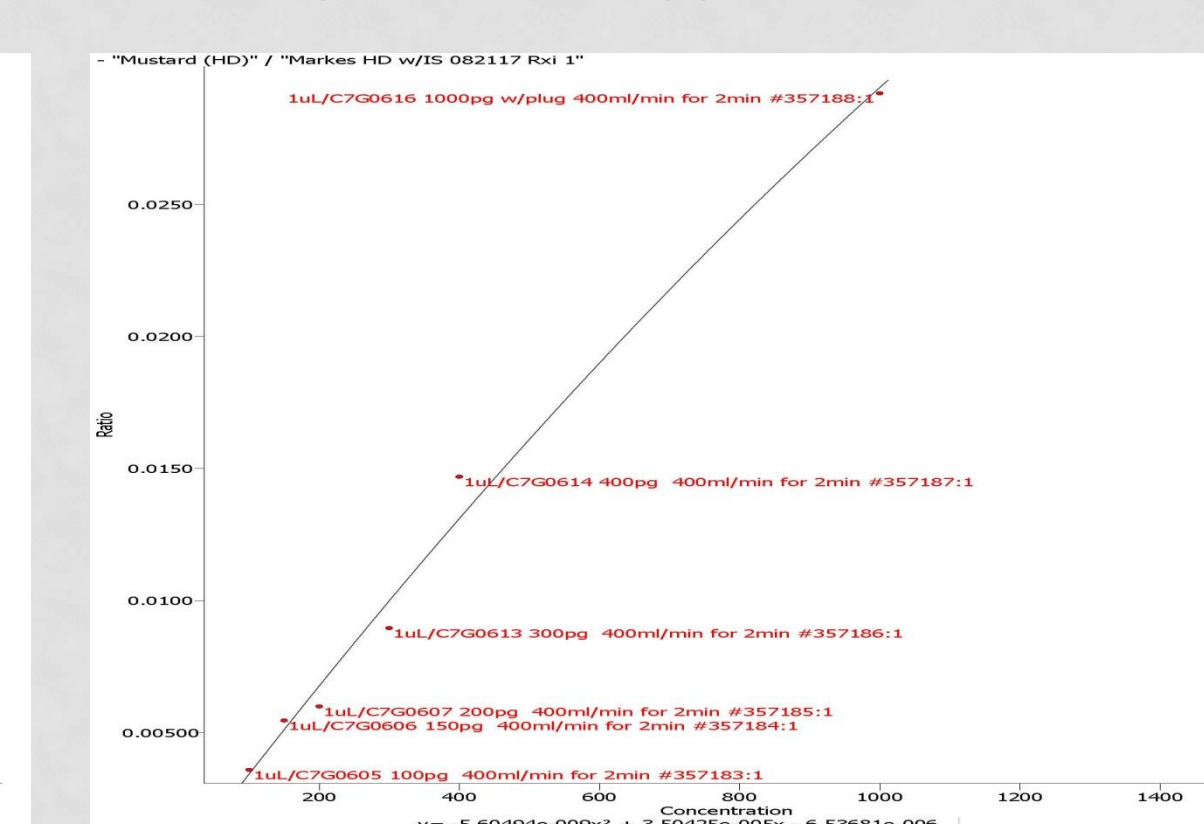
Calibrations

Compound/ Calibration Level	Correlation Coefficient (r)	%RSD RF	True Concentration (pg)	Calculated Concentration (pg)	% Drift
Mustard (HD) 070617 CAL 1	0.996	10.123	100	109	8.6
CAL 2			150	134	10.4
CAL 3			200	188	5.8
CAL 4			300	304	1.4
CAL 5			400	402	0.43
CAL 6			500	545	8.9
CAL 7			1000	968	3.2
Mustard (HD) 082117 CAL 1	0.991	11.1	100	104	4.4
CAL 2			150	160	6.7
CAL 3			200	176	12.0
CAL 4			300	267	10.9
CAL 5			400	452	13.0
CAL 6			1000	991	0.94

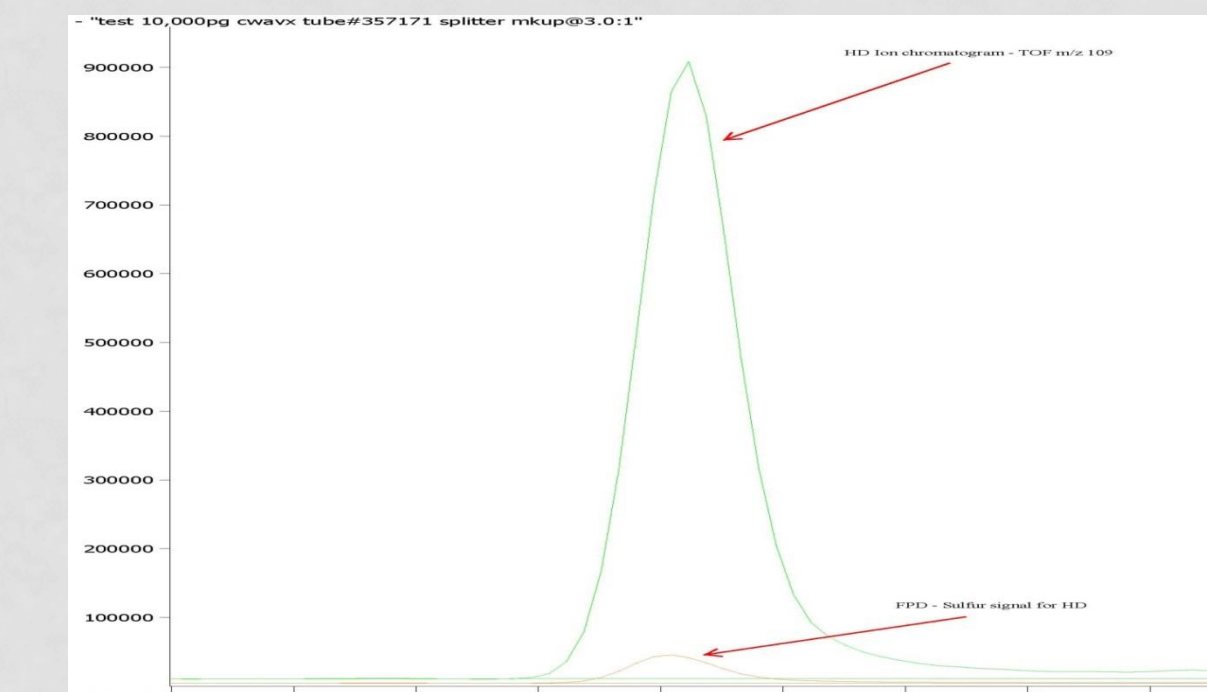
Calibration 070617 Rxi – 5Sil



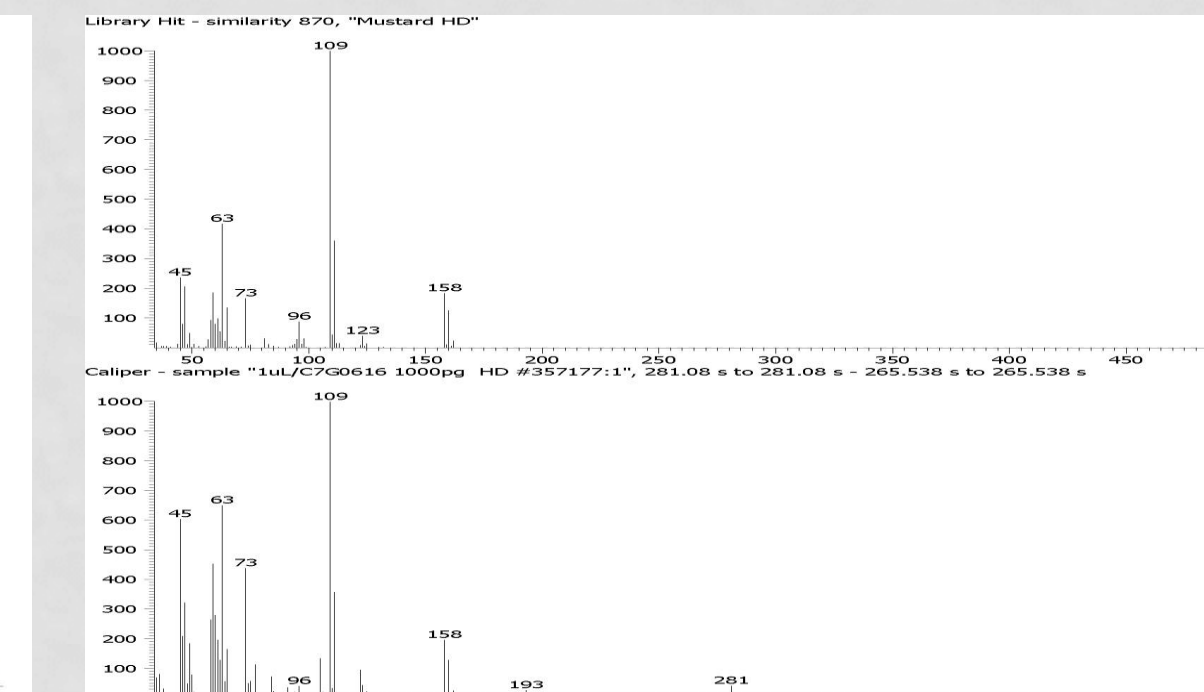
Calibration 082117 Rxi - 1



Sensitivity Comparison TOF vs FPD



HD Mass Spectrum



DATA

Precision and Accuracy Study

Concentration	% Recovery	% Recovery	% Recovery	% Recovery	Average % Recovery	%RSD
0.000000mg/m ³	Non-detect	Non-detect	Non-detect	Non-detect	-	-
0.000010mg/m ³	89.1	90.1	87.8	100.3	91.8	5.0
0.000015mg/m ³	99.2	105.9	104.1	135.9	111.3	14.4
0.000020mg/m ³	85.9	66.9	109.7	80.1	85.7	15.5
0.000030mg/m ³	88.4	88.3	101.3	90.5	92.1	5.4
0.000040mg/m ³	84.9	77.1	62.1	80.4	76.1	8.6
0.000050mg/m ³	98.2	96.2	88.5	94.7	94.4	3.6
0.000100mg/m ³	119.1	100.4	102.3	70.8	98.1	17.4
0.000200mg/m ³	121.3	115.9	118.1	60.2	103.9	25.3
0.000300mg/m ³	100.2	95.8	92.0	107.1	98.8	5.6
0.000400mg/m ³	90.9	97.8	94.4	111.5	98.7	7.8
0.000500mg/m ³	81.0	72.2	79.5	81.1	78.4	3.6
0.000600mg/m ³	91.8	84.0	104.2	86.3	91.6	7.8
0.000700mg/m ³	76.4	89.6	71.5	96.3	83.5	9.9
0.000800mg/m ³	92.9	85.2	80.1	92.9	87.8	5.4
0.000900mg/m ³	122.1	117.8	102.2	75.1	104.3	18.4
0.001000mg/m ³	126.4	127.5	113.5	98.2	116.4	11.9
0.000020mg/m ³	95.6	87.1	90.4	106.0	99.4	14.8
0.000030mg/m ³	104.7	100.0	82.5	102.9	98.3	9.4
0.000040mg/m ³	110.1	89.3	99.1	97.7	99.1	7.4
0.000050mg/m ³	111.8	80.8	110.3	103.9	101.7	12.4
0.000060mg/m ³	96.9	80.8	74.9	99.1	87.9	10.3
0.000070mg/m ³	100.9	86.8	85.1	99.1	92.9	7.1
0.000080mg/m ³	95.5	105.6	97.2	62.4	90.2	16.5
0.000090mg/m ³	120.2	123.4	110.2	83.7	109.4	15.6
0.000100mg/m ³	100.9	102.8	84.6	102.9	97.8	7.7
0.000110mg/m ³	107.9	106.0	92.7	112.1	104.7	7.2
0.000120mg/m ³	133.5	90.5	116.5	98.9	109.8	16.5
0.000130mg/m ³	113.6	80.0	128.2	104.0	106.5	17.5
0.000140mg/m ³	87.1	87.3	97.7	89.5	90.4	4.3
0.000150mg/m ³	77.9	84.6	93.4	99.7	88.9	8.3
0.000160mg/m ³	114.6	97.9	92.1	102.3	101.7	8.3
0.000170mg/m ³	134.3	134.3	99.4	120.1	122.0	14.3
0.000040mg/m ³	117.4	104.0	80.5	112.4	103.6	14.1
0.000050mg/m ³	124.6	111.9	108.1	116.6	115.3	6.2
0.000060mg/m ³	92.3	78.9	113.0	90.1	93.6	12.3
0.000070mg/m ³	105.8	89.6	116.8	106.0	104.6	9.7
0.000080mg/m ³	96.0	94.8	99.0	80.7	92.6	7.1
0.000090mg/m ³	107.1	81.6	99.4	94.6	95.7	9.3
0.000100mg/m ³	116.3	110.2	98.2	92.0	104.2	9.6
0.000110mg/m ³	127.9	126.9	106.9	104.6	116.6	10.8

Method Detection Limit Study

MDL Study	080717A	080817A	080917A	081017A	080717B	080817B	080917B	STDEV	MDL
Sulfur Mustard (HD) in pg (per 10L of sample)	84.85	77.14	62.07	80.37	98.15	96.19	88.53	12.32	38.73
Sulfur Mustard (HD) in mg/m ³	0.00000849	0.00000771	0.00000621	0.00000804	0.00000982	0.00000962	0.00000885	0.00000123	0.00000387

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